THE DEVELOPMENT OF CATIONIC ZINC COMPLEXES AS A NEW CLASS OF LACTIDE POLYMERIZATION CATALYST

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"Well, I try my best To be just like I am,
But everybody wants you To be just like them.
They say sing while you slave and I just get bored.
I ain't gonna work on Maggie's farm no more."

— Bob Dylan
(as recorded on the album "Bringing it All Back Home", 1964)

In memory of Earl Rutledge

Abstract

The thesis outlines the development of novel cationic zinc complexes for application in lactide polymerization catalysis. These complexes were characterized spectroscopically and crystallographically, and where appropriate their efficacy as catalysts for the polymerization of lactide was evaluated.

The strongly donating, neutral chelating ligands employed in this study were prepared by installation of either one or two phosphinimine donors on a dibenzofuran backbone. An efficient synthetic methodology was then developed for the synthesis of cationic complexes of the formula $[LZnE^{+}][BAr_4^{-}]$, wherein E = C_2H_5, CH_3, Ph, C_6F_5, OAc, OC_6F_5, or methyl-(D,L)-lactate, and Ar = Ph, C_6F_5, or *m*-$(CF_3)_2$-C_6H_3. Only the cationic zinc-lactate species were found to be highly active polymerization catalysts.

Tuning of the steric and electronic properties of the ligand resulted in the discovery of zinc-lactate systems that promote the rapid and well-controlled polymerization of lactide under mild conditions, marking the first well-defined cationic metal catalysts to do so.

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First and foremost, I would like to thank my supervisor, Prof. Paul Hayes, whose guidance and mentorship has been vital to my growth as a scientist. His energy and enthusiasm have been an inspiration, and his natural ability to foster a positive, intellectually stimulating work environment has made these years of graduate studies enjoyable and rewarding. Additionally, I would like to thank the past and present members of the Hayes group, whom I have enjoyed the opportunity of working with: Kevin Johnson, Benjamin Ireland, Prof. Jamie Ritch, Dr. Hudson Sun, Dr. Delphine Julienne, Breanne Kamenz, Andrea Glover, Sophia Vathracoulis, and Shayne Rybchinski. I am also grateful to the members of my PhD committee, Prof. René Boeré, Prof. Michael Gerken, and Prof. David Siminovitch, as well as the external examiner Prof. Philip Mountford.

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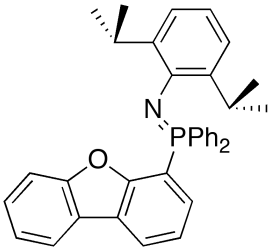
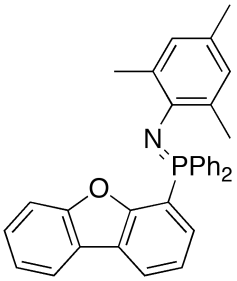
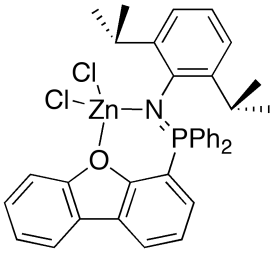
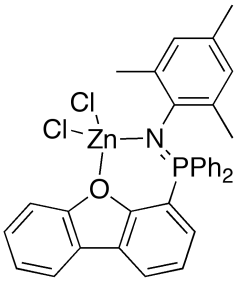
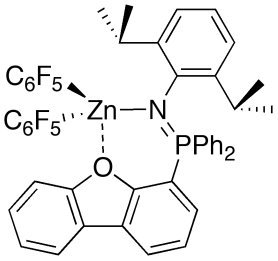
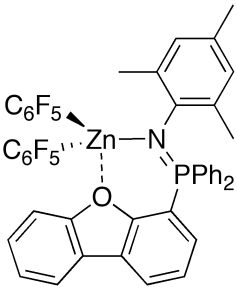
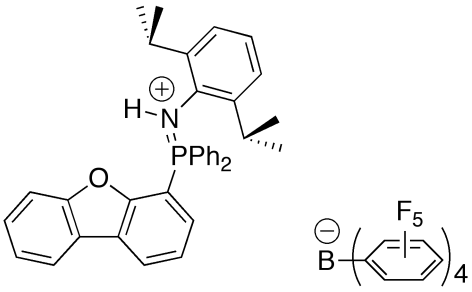
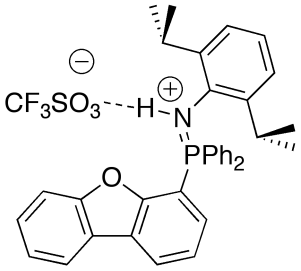
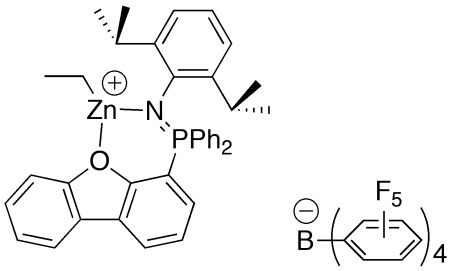
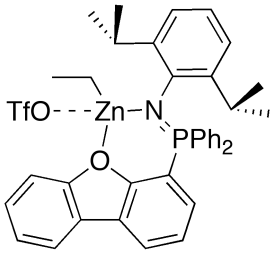
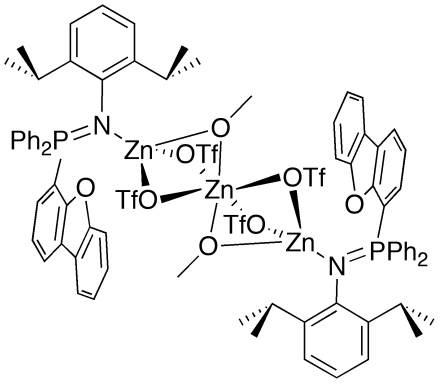
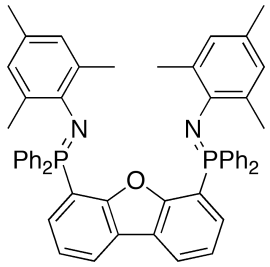
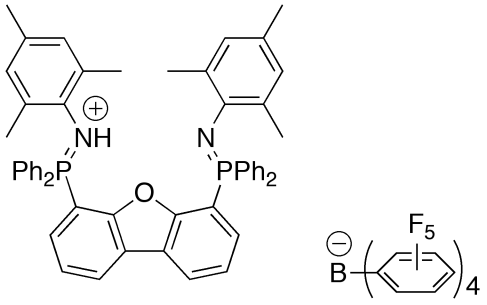
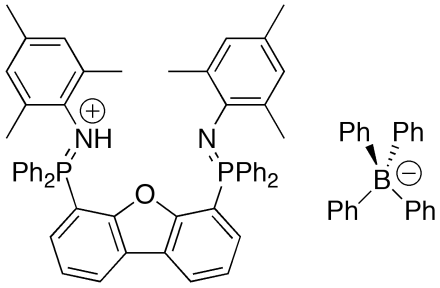
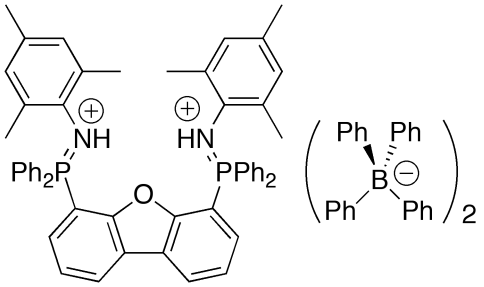
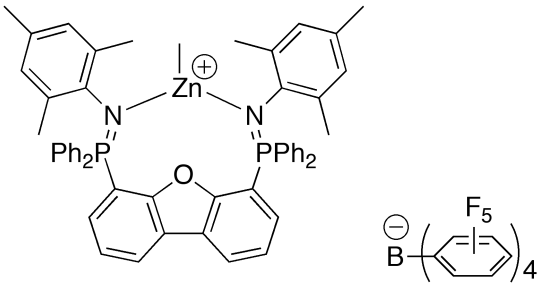
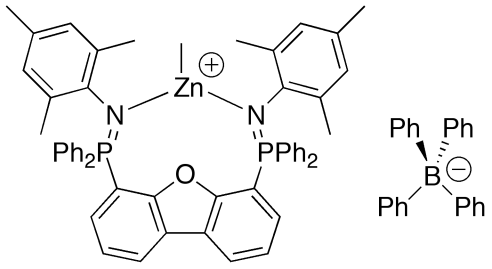
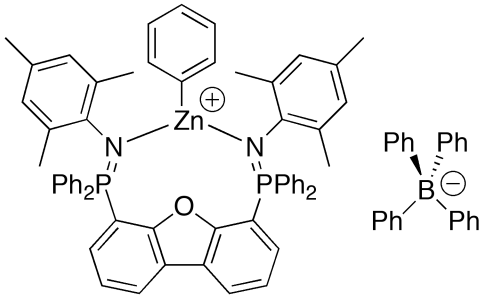
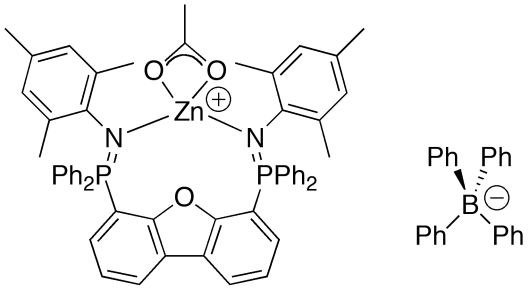
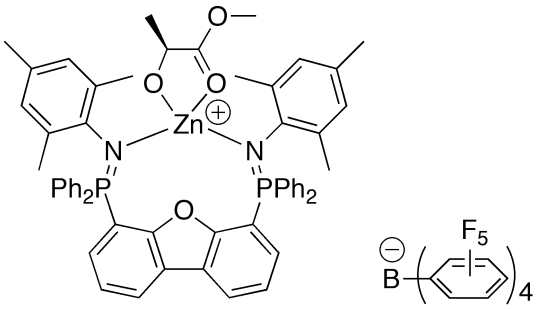
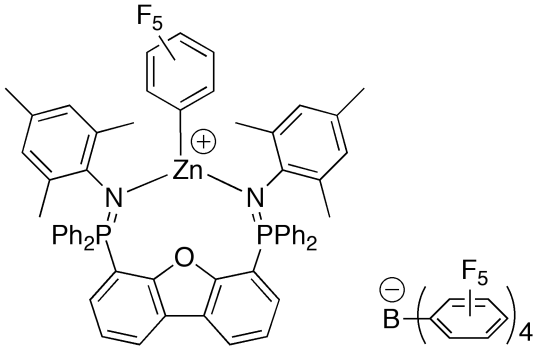
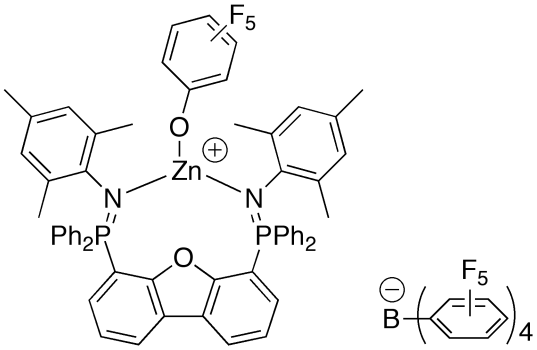
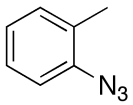
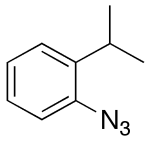
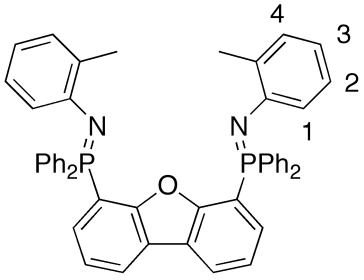
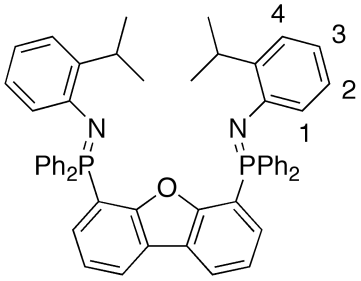
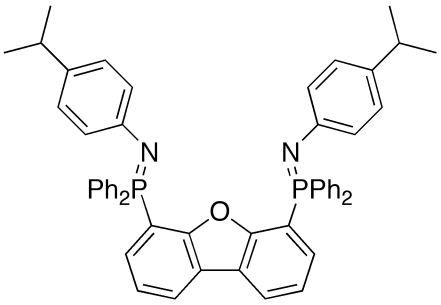
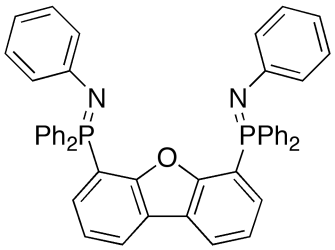
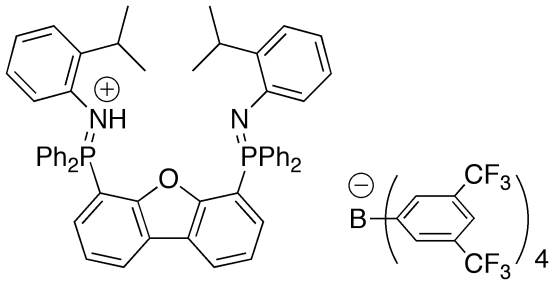
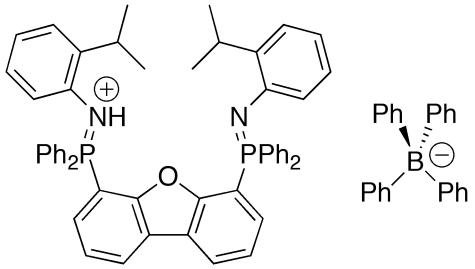
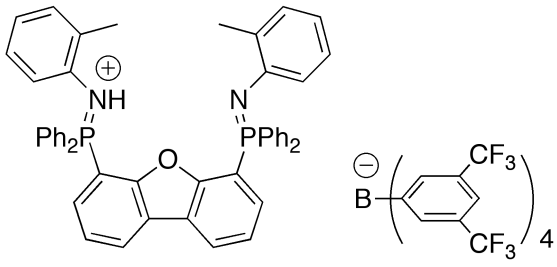
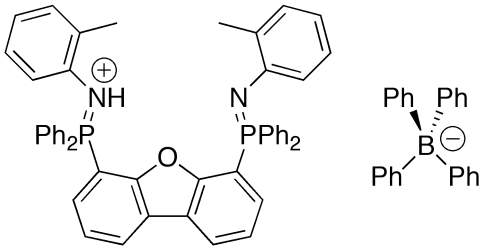
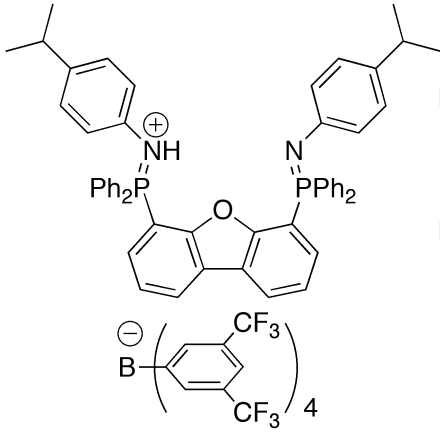
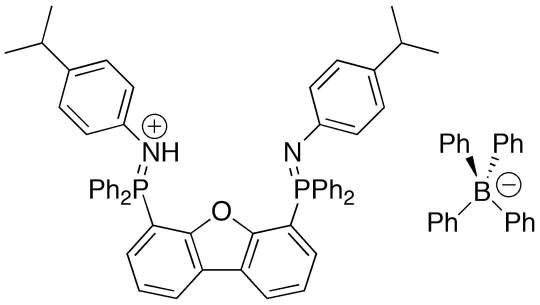
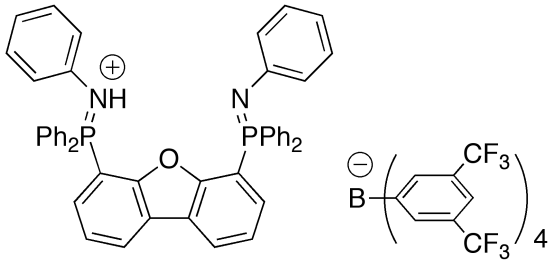
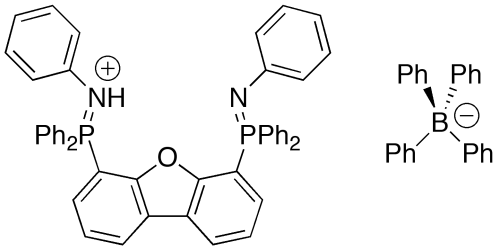
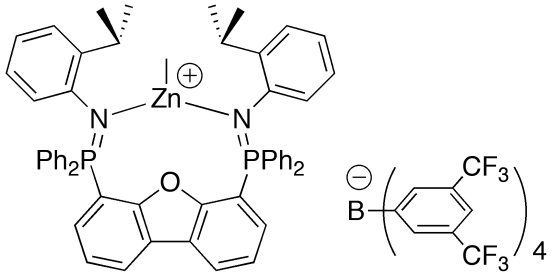
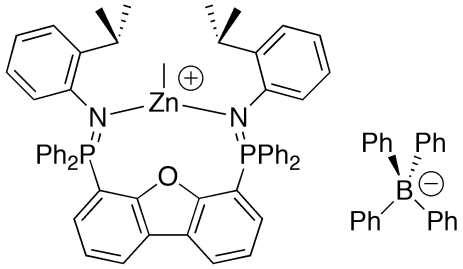
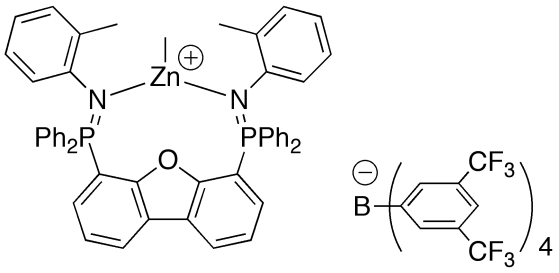
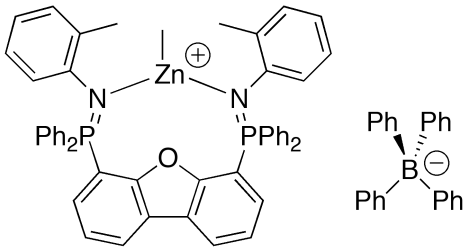
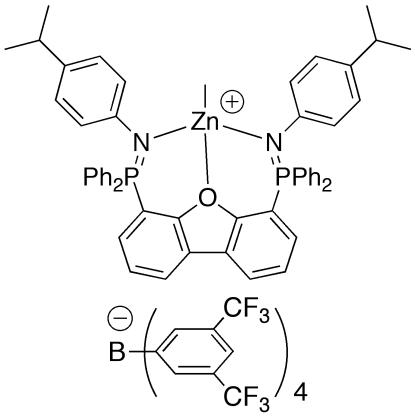
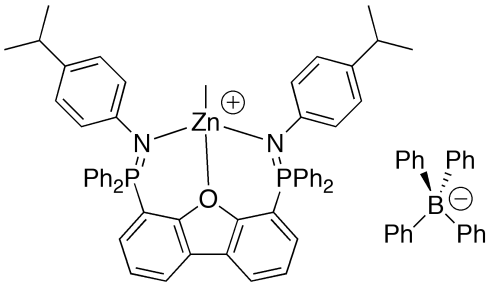
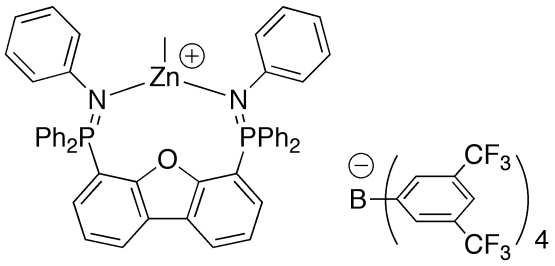
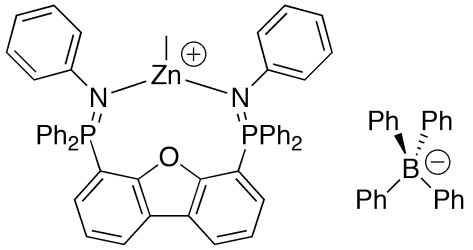
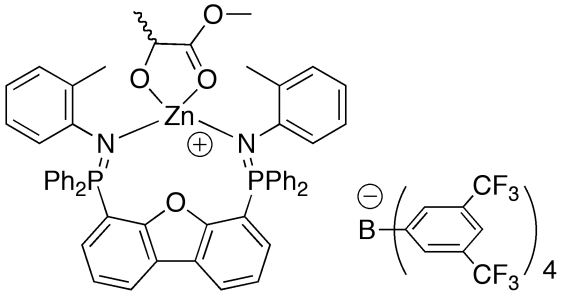
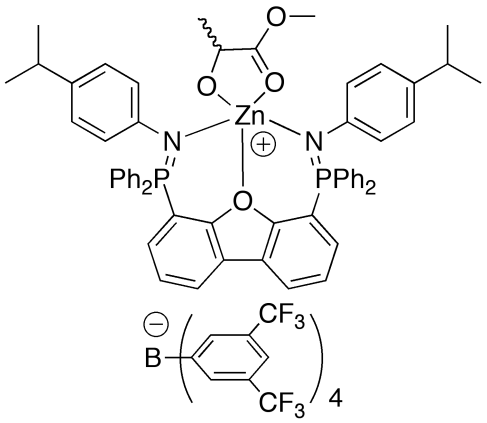
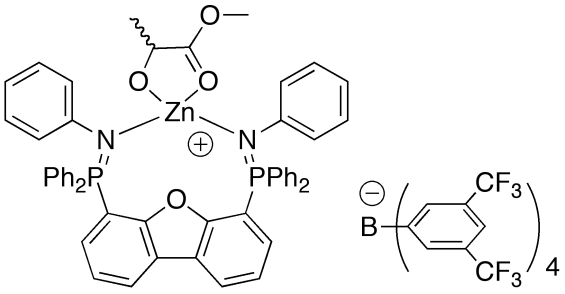
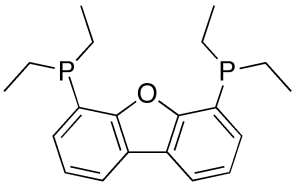
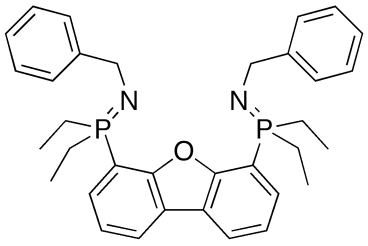
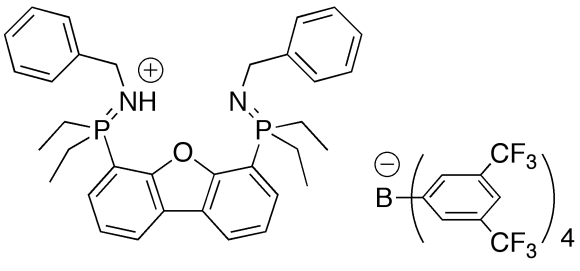
 **L_1^{Dipp}**	 **L_1^{Mes}**
 **1**	 **2**
 **3**	 **4**
 **5a**	 **5b**

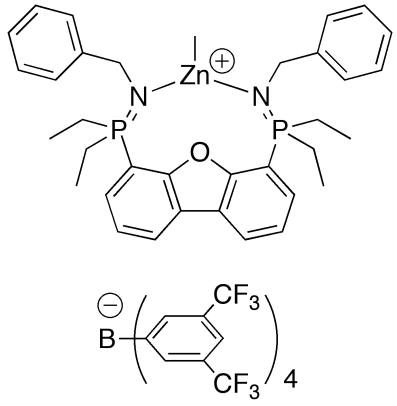
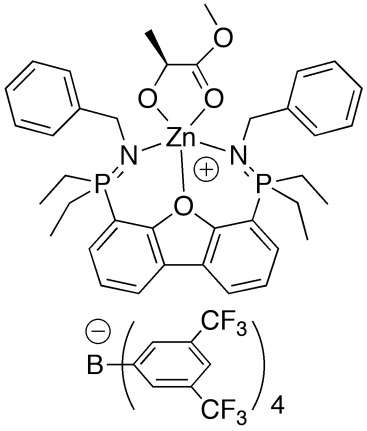
 **6a**	 **6b**
 **7**	 **L_2^{Mes}**
 **8a**	 **8b**
 **9**	 **10a**

 **10b**	 **11**
 **12**	 **13**
 **14**	 **15a**
 *o*-Tolyl-azide	 2-*i*PrPh-azide
 **L_2^{Tol}**	 **L_2^{Mipp}**

 **L_2^{Pipp}**	 **L_2^{Ph}**
 **16a**	 **16b**
 **17a**	 **17b**
 **18a**	 **18b**

 **19a**	 **19b**
 **20a**	 **20b**
 **21a**	 **21b**
 **22a**	 **22b**

 **23a**	 **23b**
 **24**	 **25**
 **26**	 **27**
 **L_3**	 **28**

 **29**	 **30**

List of Abbreviations and Symbols

a, *b*, *c*, *α*, *β*, *γ*	X-ray crystallographic unit cell parameters
Anal. Calcd.	analysis (elemental) calculated
Ar	aryl group
Å	angstrom, 10^{-10} meters
BDI	β-diiminate ligand
BGE	bis(guanidine)ethyl ligand
Bn	benzyl
BPA	bis(pyrazolyl)amide ligand
BPM	bis(phosphinimino)methanide ligand
br	broad
COSY	Correlation spectroscopy
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
d	doublet
D-	dextrorotatory
dbf	dibenzofuran
DCM	dichloromethane
dd	doublet of doublets
DEPT	distortionless enhancement by polarization transfer
Dipp	2,6-di*iso*propylphenyl
DMSO	dimethylsulfoxide
dn/dc	differential index of refraction
dt	doublet of triplets
Et	ethyl
g	gram(s)
GPC	gel-permeation chromatography
h	hour(s)
HSC	heteroscorpionate ligand
HSQC	Heteronuclear Single Quantum Coherence
Hz	hertz
^{i}Pr	*iso*propyl
J	joules
K	kelvin
k	rate constant
kJ	kilojoules
k_{obs}	observed rate constant
L	any generic ligand
L-	levorotatory
LA	lactide
lb(s)	pound(s)
m	multiplet
M	Molarity (mol/L)
m-	*meta*

m/z	mass to charge ratio
M:I	monomer to initiator ratio
MALDI	matrix-assisted laser desorption ionization
MAO	methylaluminoxane
Me	methyl
Mes	mesityl; 2,4,6-trimethylphenyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
Mipp	2-*iso*propylphenyl
mmol	millimole(s)
M_n	number average molecular weight
mol	mole(s)
MS	Mass Spectrum
MW	molecular weight
M_w	weight-average molecular weight
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
o-	*ortho*
o-tol	*ortho*-tolyl
OTf	triflate, trifluoromethanesulfonate
ov	overlapping
p-	*para*
PDI	polydispersity index (M_w/M_n)
PGSE	pulsed gradient spin-echo
Ph	phenyl
Pipp	4-*iso*propylphenyl
pK_a	acid dissociation constant
PLA	polylactide
ppm	parts per million
P_r	probability of racemic linkage in PLA
q	quartet
qq	quartet of quartets
R	alkyl group
rac-	racemic
ROP	ring-opening polymerization
s	singlet
S-EPP	(S)-*N*-ethyl-*N*-phenyl-2-pyrrolidinemethanamine ligand
sp	septet
SPS	solvent purification system
t	triplet
t	time
^{t}Bu	*tertiary* butyl
td	triplet of doublets
tert-	tertiary
THF	tetrahydrofuran

TIB	tris(indazolyl)borate
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMS	$SiMe_3$, tetramethylsilyl
TOF	time-of-flight
TPB	tris(pyrazolyl)borate ligand
VT	variable temperature
WCA	weakly coordinating anion
Z	number of formula units per unit cell
$^{z}J_{XY}$	coupling constant between x and y, separated by z bonds
$\{^1H\}$	proton decoupled
°	degree(s)
°C	degrees Celsius
δ	chemical shift (in ppm units) relative to reference signal
$\Delta\nu_{max}$	peak separation (Hz)
λ	wavelength
µL	microlitre(s)
µm	micrometer

Chapter 1. Introduction and Literature Review

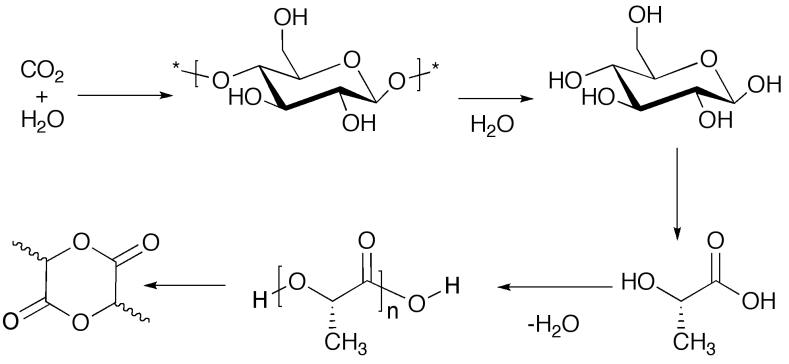
1.1. Introduction – Polylactide

In the present era of depleting petrochemical feedstocks and increasing environmental awareness, polylactide (PLA) has become an attractive alternative to conventional polyolefins.[1] PLA is produced *via* ring-opening polymerization (ROP) of lactide (LA), which in turn may be generated from renewable resources, such as beets and corn (Scheme 1.1). Its production can thus help to reduce the consumption of non-renewable petrochemical resources, of which 150 million tonnes are consumed annually as raw material for plastic production.[2] In addition, PLA-based plastics maintain many of the desirable properties of traditional plastics with the added bonus that they are also biocompatible, readily biodegradable, and easily recycled.

While PLA has found use as a specialty polymer for medical applications such as slow release drug delivery and biodegradable sutures,[3] its use as a commodity polymer has remained limited because of high production cost compared with conventional plastics, as well as poor activity and stereochemical control of available catalyst systems.

PLA is becoming increasingly economically viable as reduced production costs arising from technological advances have been magnified by concomitant increases in the price of petrochemical feedstocks. In 2002, Natureworks LLC, presently a joint venture between Cargill and Teijen Limited, opened a 300 million

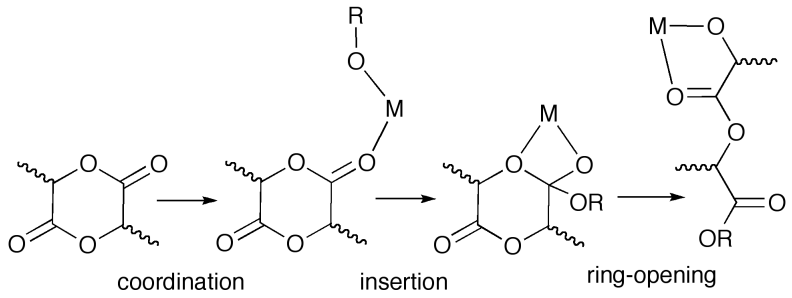
lb per year PLA production plant, marking the first commodity polymer to be derived from corn instead of fossil fuels. This industrially produced PLA, fabricated in isotactic form, has physical properties similar to polyolefins and polystyrene, and has found use in materials applications such as bulk packaging and fibers (trade name Ingeo™). By purchasing sufficient wind energy certificates, Natureworks LLC has demonstrated that this process can be carbon neutral.[4]



Scheme 1.1. Synthesis of LA monomer from natural resources.

1.1.1. PLA Production Process

The production of PLA starts from a starch or sugar feedstock which is processed to yield D-glucose. Optically pure L-lactic acid is then generated by a fermentation process using bacteria of the genera *Lactobacillus*, *Streptococcus* and *Pediococcus*.[5] Poly(L-lactic acid) can be produced as a low molecular weight pre-polymer (MW = 1000–5000) directly from lactic acid through condensation polymerization. The synthesis of LA is achieved by a depolymerization process to afford the LA monomer (Scheme 1.1). Generation of higher molecular weight PLA can then be accomplished by ring-opening polymerization using a suitable homogeneous metal catalyst (Scheme 1.2).



Scheme 1.2. General coordination–insertion mechanism for the metal-catalysed ring-opening polymerization of LA.

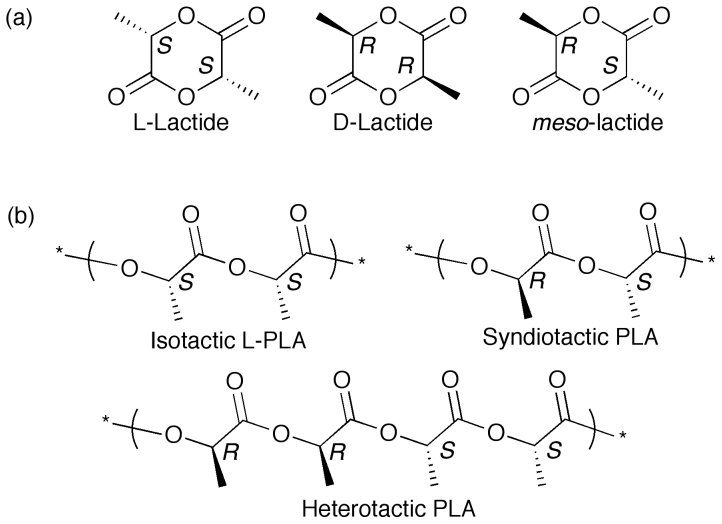


Figure 1.1. (a) LA monomer stereoisomers. (b) Microstructures of PLA which can be achieved either through polymerization of optically pure L-LA (L-PLA) or by stereochemically selective polymerization of *rac*-LA or *meso*-LA (heterotactic and syndiotactic PLA, respectively).

The depolymerization process used in the commercial synthesis of LA results in loss of optical purity,[6] generating a mixture of isomers which must be separated prior to polymerization. LA possesses two stereocenters, and thus there exist three stereoisomers; L-LA, its enantiomer D-LA, and the diastereomer *meso*-LA (Figure 1.1a). As such, there are a plethora of ordered polymer microstructures, the most

simple of which are depicted in Figure 1.1b. Isotactic L-PLA is the most easily prepared, requiring no polymerization stereocontrol when pure L-LA is utilized as the monomer. Syndiotactic PLA, however, can only be synthesized from *meso*-LA and requires that the catalyst selectively inserts at only one stereocenter of the monomer. Meanwhile, heterotactic PLA is produced from *rac*-LA by selective insertion of the LA isomer with opposite configuration to the previously inserted monomer. Catalysts which generate isotactic PLA from *rac*-LA are also an important target, as a mixture of isotactic L-PLA and D-PLA has bulk properties much different than that of pure L-PLA.[7]

The most desirable features for LA polymerization catalysts are high activity, ability to controllably produce high molecular weight, low polydispersity polymers and stereochemical control. In addition to these qualities, low toxicity, low cost, and minimal colour and odour are also desirable features. A number of single-site homogeneous catalyst systems incorporating many of these features have been reported over the past decade, and several excellent reviews are available.[8] Single-site homogeneous catalysts are particularly useful because rational fine-tuning of their steric and electronic properties is possible. A wide array of ligand frameworks have been employed, generating a library of catalysts with substantial variation in both steric environment and Lewis acidity. The effect of Lewis acidity on the activity of cyclic ester polymerization, however, is still not well understood,[9] and is further complicated by the potentially chelating nature of the growing polymer chain.[10] While there has been significant progress with stereoselective Group 3 and 13 initiators,[11,12] the literature review in this chapter aims to demonstrate that calcium,

magnesium, and zinc hold the most promise for industrial application owing to their low cost, remarkably high activities and minimal toxicity.

1.1.2. Stereospecific Polymerization

Several catalyst systems that exhibit good stereochemical control have revealed two unique and possibly competing mechanisms: chain-end control and enantiomorphic site-control.[12f] A chain-end control mechanism occurs when the stereochemistry of the most recently inserted monomer influences the stereochemistry of the subsequent insertion. Such control is typically observed in systems that exploit sterically bulky ligands to crowd the active site. Alternatively, the enantiomorphic site-control mechanism relies on the chirality of the ancillary ligand, and hence, the catalyst itself is the source of stereochemical selectivity due to steric interactions between the incoming monomer and the catalyst framework. When a chiral catalyst is used, stereochemical control may arise from a complicated interplay between these two mechanisms.[12f]

1.2. Literature Review – Ca, Mg, and Zn Catalysts

Herein, progress in the development of lactide polymerization catalysts based on the divalent metals calcium, magnesium, and zinc is presented. The following is not meant to be a comprehensive review, but rather is intended to highlight the most important and interesting contributions to the field from the perspective of the author. Furthermore, to assist in the clarity of presentation, catalyst systems discussed in this section have been assigned compound numbers.

These should not be confused with the numbers assigned to novel compounds prepared and characterized during the course of the thesis work, which will be discussed in Chapters 2–6.

The first portion of this section will focus on important metal complexes featuring monoanionic ligands while the latter discussions will address systems supported by neutral ligand frameworks. The reader will see that the chemistry of divalent metals supported by monoanionic ancillary ligands has been well studied, while the development of LA polymerization catalysts stabilized by neutral ancillary ligands is in its infancy.

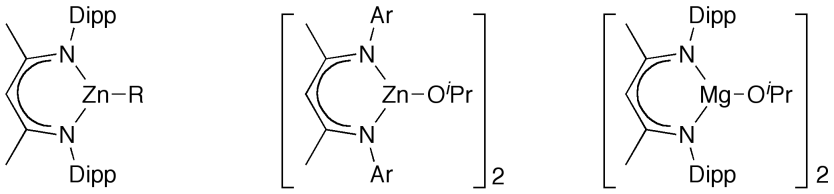
1.2.1. Anionic Ligands

While single-site metal catalysts have been successfully exploited for olefin polymerization,[13] prior to the turn of the 21st century very few such catalysts were applied to the polymerization of lactones. The pioneering work of Coates and co-workers in the development of *β*-diiminate (BDI) supported catalysts, and of Chisholm in the preparation of tris(pyrazolyl)borate (TPB) systems was largely responsible for breaking the field wide open.

1.2.1.1. β-diiminate complexes

An initial report by Coates and co-workers utilized the bulky 2,6-di*iso*propylphenyl (Dipp) substituted *β*-diiminate ligand (BDI-1), which they proposed may be capable of stereocontrol in the polymerization of *rac*-LA *via* a chain-end control mechanism.[14] Zinc complex **1** was readily generated in quantitative yield by reaction of $Zn(N(SiMe_3)_2)_2$ with the requisite proteo ligand.

This complex features a single amide initiating group and was found to slowly polymerize LA. The alkoxide bridged dimer [(BDI-1)Zn(O^{i}Pr)]$_2$ (**2**), which has an initiating group that is a closer mimic of the propagating alkoxide polymer chain, was generated by reaction of **1** with *iso*propanol. Reactivity studies revealed **2** to be a highly active catalyst for polymerization of *rac*-LA at 20 °C, giving high conversion to polymer after only 20 minutes (Table 1.1, entry 2). Notably, polymerization with this complex is highly controlled, affording a narrow molecular weight distribution (PDI = 1.10). Most interestingly, however, is the degree of stereocontrol incurred by this catalyst, yielding a highly heterotactic polymer (P_r = 0.90).[15] The stereoregularity could be even further enhanced by conducting the polymerization at lower temperature, yielding almost exclusively heterotactic polymers (P_r = 0.94) at 0 °C (Table 1.1, entry 3). Complex **2** represents the first Group 12 metal complex to initiate LA polymerization with substantial stereochemical control. β-diiminate systems have since been studied with great enthusiasm.



1 R = N(SiMe$_3$)$_2$
3 R = OCHMeCO$_2$Me
4 R = Et
5 R = OAc

2 Ar = Dipp
6 Ar = 2,6-diethylphenyl
7 Ar = 2,6-di-^{n}propylphenyl

8

Figure 1.2. General structure of single–site catalysts prepared from the BDI ligand framework.

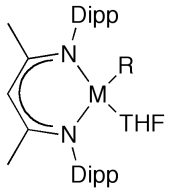
Table 1.1. Polymerization of *rac*-LA or L-LA by BDI and related catalysts (T_{rxn} = 20 °C and CH_2Cl_2 is the solvent, except where noted).

Entry	Catalyst	$[LA]_o$ (mol L^{-1})	Loading (mol%)	*t* (min)	% conv.[a]	PDI	P_r
1	**1**	0.4	0.5	600	97	2.95	-
2	**2**	0.4	0.5	20	95	1.1	0.9
3[b]	**2**	0.4	0.5	120	95	1.09	0.94
4	**3**	0.4	0.5	20	97	1.14	-
5	**4**	0.4	0.5	1200	97	1.83	-
6	**5**	0.4	0.5	4200	92	2.07	-
7	**6**	0.4	0.5	480	97	1.1	0.79
8	**7**	0.4	0.5	1140	97	1.09	0.76
9	**8**	0.4	0.5	2	> 99	1.59	atactic
10	**9**	0.46	1	4200	91	1.45	-
11	**10**	0.46	1	2	97	1.49	-
12[c]	**11**	0.46	1	5	94	1.6	-
13[c]	**12**	0.46	0.5	120	90	-	atactic
14[d,e]	**13**	N.R.	1	300	78	1.5	atactic
15[e]	**14**	2.8	1	8	81	1.78	atactic
16[f]	**15**	2.8	1	10	85	1.1	-
17[f]	**16**	2.8	1	30	90	1.15	-
18[c]	**17**	0.46	1	10	91	1.19	0.67
19[c]	**18**	0.46	1	90	90	1.7	0.85
20[f]	**19**	N.R.	1	150	61	1.44	-
21[f]	**20**	N.R.	1	120	> 99	1.74	-
22[d]	**21**	1.25	0.33	100	98	1.06	-
23[d]	**22**	1.25	0.33	90	97	1.06	-

[a]Determined by ^{1}H NMR spectroscopy. [b]T_{rxn} = 0 °C. [c]THF solvent. [d]T_{rxn} = 50 °C. [e]Benzene solvent. [f]Chloroform solvent.

A subsequent report by Coates and co-workers considered the same ligand framework in more detail, studying a greater breadth of initiating groups (R = $OCH(Me)CO_2Me$ (**3**), Et (**4**), OAc (**5**)), and reduced steric bulk on the ligand (BDI-2, Ar = 2,6-diethylphenyl; BDI-3, Ar = 2,6-di-*n*propylphenyl) (Table 1.1, entries 4–8).[16] Initiating group effects were systematically inspected through the preparation of complexes **3**–**5**, which confirmed the utility of alkoxide functionalities as initiators (as seen with **2**). Utilization of a methyl-lactate initiator (**3**) gave little change in

activity, while amide (**1**) and alkyl (**4**) initiators were significantly less active, and acetate (**5**) initiators were even worse. This report also established that the reduced steric bulk of the ancillary ligand (demonstrated by **6** and **7**, complexes of BDI-2 and BDI-3, respectively) caused diminished stereocontrol, thereby supporting the proposed chain-end control mechanism. A dimeric magnesium alkoxide complex (**8**) of BDI-1 was also reported in the same study (Table 1.1, entry 9). While this complex is more active than the zinc analogue, giving complete conversion of *rac*-LA to PLA under similar conditions in only 2 minutes, the resulting microstructure is atactic and the molecular weight distribution is broad (PDI = 1.59). Thus, the increase in activity comes at the expense of both molecular weight and stereocontrol.



9 M = Zn, R = $OSiPh_3$
10 M = Mg, R = O^tBu
11 M = Mg, R = N^iPr
12 M = Ca, R = $N(SiMe_3)_2$
13 M = Mg, R = $CH_2CH{=}CH_2$

Figure 1.3. Solvated magnesium, calcium, and zinc complexes of the BDI ligand.

The labour of Chisholm et al. has produced an analogous series of BDI-1 complexes, which are monomeric THF adducts rather than dimers (Figure 1.3).[17] Polymerizations were carried out in methylene chloride solvent, and the overall trends reported are similar to those previously discussed by Coates et al. (Table 1.1, entries 10–13). Magnesium complex **9** shows much higher activity than the zinc analogue **10** while exhibiting poor molecular weight control and no stereoselectivity whatsoever. Further studies by Chisholm explored a range of initiating groups, including amide derivative **11** (polymerization rates: O^tBu > N^iPr > $N(SiMe_3)_2$ >

$OSiPh_3$). Most interesting, however, is the report of solvent dependence on stereoselectivity, whereby **10** was found to generate 90% heterotactic PLA from *rac*-LA if the polymerization was carried out in THF rather than methylene chloride. In separate accounts, Chisholm and co-workers have recounted the synthesis and reactivity of the related calcium complex [(BDI-1)CaN$(SiMe_3)_2$] (**12**).[18] Notably, NMR studies indicated that **12** exists in a complex equilibrium between a variety of species in solution, and polymerization of *rac*-LA with this complex afforded atactic PLA exclusively.

An additional solvated magnesium complex of BDI-1 was prepared by Bochmann et al. using a different synthetic route.[19] The magnesium allyl complex **13** was generated by reaction of mixed-metal lanthanide/magnesium allyl complexes with proteo BDI-1. For example, reaction of $[Mg(THF)_6][Ln(\eta^3\text{-allyl})_4]_2 \cdot 2THF$ (Ln = Nd or Sm) with proteo BDI-1 yielded **13**, with propene and neutral tris-allyl lanthanide afforded as by-products. The rate of catalysis achieved using this complex was slower than that observed for either complexes **10** or **11**, requiring an elevated temperature of 50 °C to reach 78% conversion in 5 hours (Table 1.1, entry 14). The resulting polymer had a rather broad molecular weight distribution (PDI = 1.5), and analysis of the polymer microstructure revealed no stereochemical control. Overall, the results suggest that the allyl functionality is not a desirable initiating group.

There have been several attempts to improve the BDI catalyst system by substantial modification to the ligand framework. One prominent strategy has involved the installation of one or two ether appendages to generate the second

generation tridentate (BDI-4) and tetradentate (BDI-5) ancillary ligands, respectively. Magnesium and zinc complexes have been examined by Gibson and co-workers for BDI-4,[20] and by Chisholm in the case of BDI-5 (Figure 1.4).[21] It was anticipated that these hemilabile ether sites would serve to moderate the reactivity of magnesium complexes, thereby potentially improving molecular weight and stereochemical control.

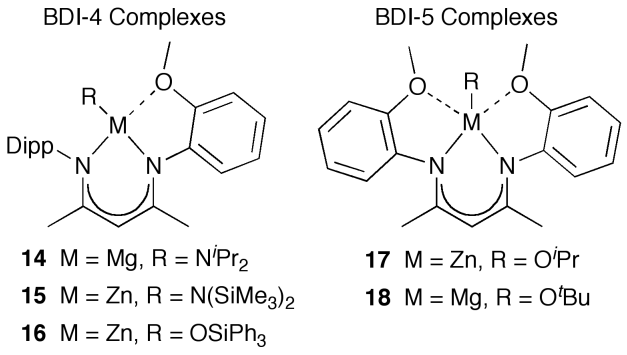
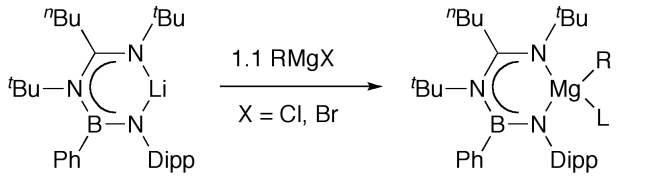


Figure 1.4. Magnesium and zinc complexes prepared from modified BDI ligands bearing ether substituents.

While the solid-state structure of **14** revealed a distinct, albeit relatively long M–O interaction (Mg–O = 2.486(5) Å), no such coordination was found in zinc complexes **15** or **16**. As a general trend, it was established that the BDI-4 complexes of zinc were significantly more active catalysts for LA polymerization than their first generation counterparts, but they suffered from limited stereo- and polydispersity control (Table 1.1, entries 16–17).[20] These findings are likely due to the reduced steric protection offered by this scaffold. Similarly, magnesium complex **14** maintained high activity with 81% conversion of *rac*-LA to PLA in 8 minutes at ambient temperature. As with zinc, no improvement in molecular weight or stereochemical control was achieved. It has been suggested that the ether

functionality dissociates from the metal in solution, and is thereby unable to assist in moderating the reactivity.

For the investigation of the potentially tetradentate BDI-5 ligand, Chisholm et al. synthesized zinc alkoxide **17** and the similar magnesium alkoxide **18**.[21] While an X-ray crystal structure was not obtained for the zinc complex, the magnesium species was established to be a dimer in the solid state with no coordination of the pendent ether groups. LA polymerization studies were performed under ambient conditions in THF with a 1% catalyst loading (Table 1.1, entries 18–19). As with the analogous BDI-4 species, **17** exhibits higher polymerization activity than its first generation counterpart, while maintaining polymerization control (PDI = 1.19). Unfortunately, stereochemical control is substantially diminished (P_r = 0.67). Conversely, magnesium complex **18** is plagued with severely hampered activity and broad polydispersity (PDI = 1.70), but exhibits notable stereoselectivity (P_r = 0.85). As with homogeneous olefin polymerization catalysis, overcoming the intricate inverse relationship between activity and selectivity remains a significant challenge.[22]



19 R = Me, L = OEt_2
20 R = Ph, L = THF

Scheme 1.3. Preparation of magnesium complexes of the "bamam" ligand.

A more substantial modification of the BDI backbone was recently detailed by Chivers and colleagues.[23] The general ligand architecture deviates from those

previously discussed by the placement of an electron accepting boron atom in the backbone of a boraamidinate/amidinate (bamam) framework. Magnesium alkyl and aryl complexes **19** and **20** were synthesized by reaction of the appropriate Grignard reagents with the proteo bamam ligand (Scheme 1.3).[23b] The solid-state structures of a variety of these complexes were obtained, and all were found to be monomeric, with a single THF or ether solvent molecule coordinated to the metal. Complexes bearing alkoxide or amide functionalities were not developed and only preliminary polymerization data were reported for the alkyl and aryl complexes. Unfortunately, these studies demonstrated poor molecular weight and stereochemical control, as well as lower activity than the comparable BDI complexes (Table 1.1, entries 20–21).

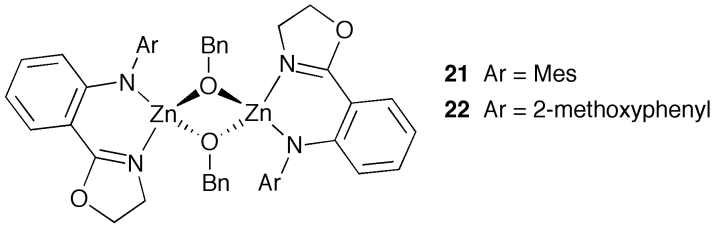


Figure 1.5. Dimeric zinc alkoxide complexes of an anilido-oxazolinate ligand framework.

Zinc complexes of an anilido-oxazolinate ligand framework, which is structurally and electronically similar to the BDI ligand, have been the subject of investigation by Chen et al.[24] Sequential reaction of the proteo ligand with diethylzinc followed by benzyl alcohol gave rise to the alkoxy bridged dimers **21** and **22** (Figure 1.5). These complexes differ only in the nature of the amide substituent, which for **22** is a potentially donating alkoxy group. Both complexes exhibited similar polymerization activity, requiring a temperature of 50 °C to reach

near complete conversion in a period of 100 and 90 minutes, respectively (Table 1.1, entries 22–23). The molecular weights of the resultant polymers were nearly monodisperse (PDI = 1.06) and correspond well to the monomer to initiator ratio, suggesting living character in the polymerization. No studies were undertaken to determine if the catalysts are able to impart stereochemical control.

1.2.1.2. Tris(pyrazolyl)borate and related ligands

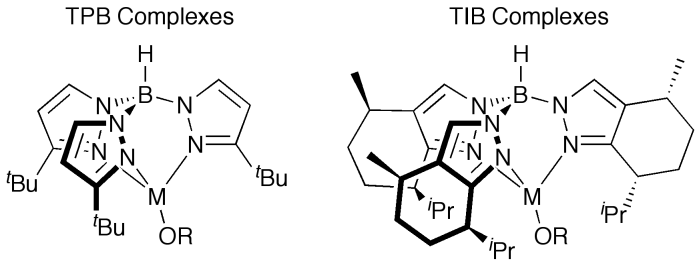
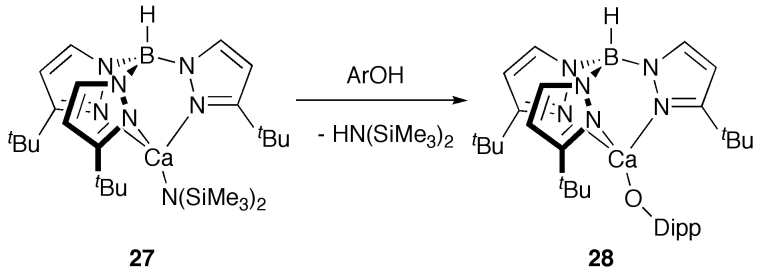


Figure 1.6. Complexes featuring tris(pyrazolyl)borate (TPB) and tris(indazolyl)borate (TIB) ligands.

Bulky tripodal ligands based on a substituted tris(pyrazolyl)borate (TPB) skeleton were shown by Parkin in the early 1990's to be useful ligands for stabilizing magnesium and zinc alkyl and hydroxide species;[25] however, it was not until Chisholm's ground-breaking work that these were considered as useful ligands for LA polymerization catalysts.[26] The initial report was quite comprehensive and detailed both zinc and magnesium complexes, chiral and achiral derivatives of the ligand, and variation of the sterically bulky substituents. As catalysts, the TPB complexes **23** and **24**, and the TIB complexes **25** and **26** (Figure 1.6) exhibited good molecular weight control (PDI = 1.1–1.25). Magnesium analogues **24** and **26** once

again displayed notably higher reactivity than their respective zinc analogues. This was attributed by the authors to be a result of the significant polarization of the M–OR bond by the more electropositive Mg centre.



27 **28**

Scheme 1.4. Synthesis of a calcium aryloxide complex of the TPB ligand.

While none of these catalyst systems demonstrated high enantioselectivity, their diastereoselectivities were tested in the polymerization of 1:1 mixtures of *meso*- and *rac*-LA. All of the tested complexes exhibited some preference for polymerization of *meso*-LA, with the selectivity of the chiral magnesium complex **26** being the most notable. Impressively, when the polymerization was catalysed by **26** and conducted at –40 °C in methylene chloride, complete and selective consumption of *meso*-LA was observed, leaving the *rac*-LA unconsumed. Examination of the resulting polymer also indicated a modest preference for a syndiotactic microstructure.

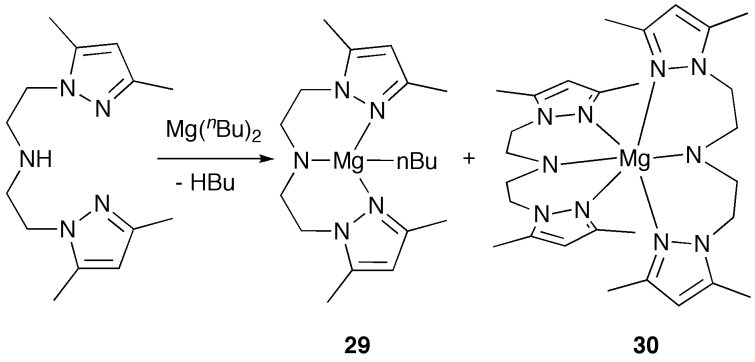
Table 1.2. Polymerization of *rac*-LA by TPB, BPA and HSC catalysts (T_{rxn} = 20 °C and THF was the solvent except where noted).

Entry	Catalyst	$[LA]_o$ (mol L^{-1})	Loading (mol%)	t (min)	% conv.	PDI	P_r
1	**27**	-	0.5	1	90	1.74	> 0.9
2	**28**	-	0.5	1	90	1.68	> 0.9
3	**30**	0.8	0.5	60	97	1.33	atactic
4	**31**	0.4	1	1800	93	1.71	atactic
5	**32**	0.4	1	1800	95	1.23	atactic
6[a]	**32**	1.6	0.25	1800	>99	1.4	atactic
7[b]	**33**	-	1	4320	31	1.09	atactic
8[b]	**34**	-	1	4320	42	1.09	atactic
9[c]	**35**	-	1	2880	71	1.13	atactic
10[c]	**36**	-	1	2880	63	1.11	0.68
11[c,d]	**36**	-	1	2880	89	1.23	0.6

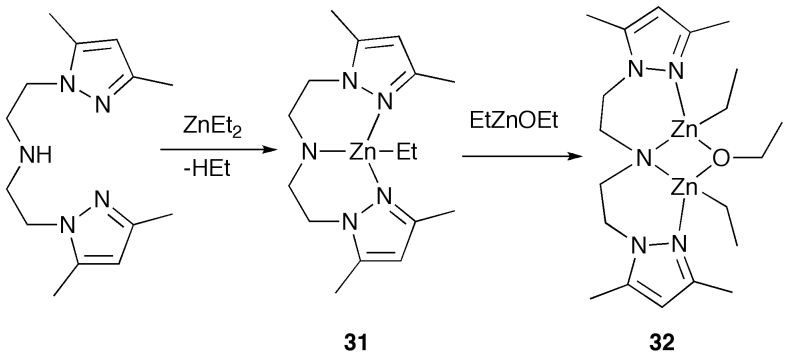
[a]CH_2Cl_2 solvent. [b]T_{rxn} = 70 °C, Toluene solvent. [c]T_{rxn} = 110 °C, Toluene solvent. [d]Addition of 1 equivalent of *iso*propanol to the precatalyst.

The excellent properties of magnesium and zinc TPB based catalysts prompted an investigation of their analogous calcium chemistry.[18b] Chisholm et al. prepared and structurally characterized both amide (**27**) and aryloxide derivatives (**28**) of the calcium TPB compounds (Scheme 1.4). As was the case for the BDI derivatives, these species exhibited a marked improvement in polymerization activity over zinc and magnesium counterparts (Table 1.2, entries 1 and 2). A 0.5% catalyst loading resulted in 90% monomer conversion within 1 minute under ambient conditions. While these catalysts afforded only modest control over molecular weight (PDI = 1.74 and 1.68, for **27** and **28**, respectively), they showed remarkable stereoselectivity, producing heterotactic PLA almost exclusively (P_r > 90%). It has been proposed that the improved stereocontrol of these calcium complexes relative to analogous BDI species (*vide supra*) is a result of increased steric protection.

The success of this early work by Chisholm has prompted a number of other researchers to study related tripodal frameworks bearing pyrazole donor groups. One example is a bis(pyrazolyl)amide (BPA) ligand which has been investigated by Carpentier and colleagues.[27] Reaction of BPA with one equivalent of di^{n}butylmagnesium led to concomitant production of the targeted heteroleptic complex **29** and the homoleptic sandwich species **30** (Scheme 1.5). Adjustment of the reaction parameters failed to generate the heteroleptic species selectively, and attempts to separate the two components were unsuccessful. However, pure **30** could be obtained by reaction of di^{n}butylmagnesium with two equivalents of BPA. Intriguingly, even though **30** lacks a traditional initiating group, it is highly active for the polymerization of *rac*-LA, giving 97% monomer conversion in 60 minutes at a catalyst loading of 0.5% (Table 1.2, entry 3). Under these conditions, a relatively narrow polydispersity of 1.33 was observed. It is important to note that in this situation it is probable that the ligands themselves act as initiating groups, and thus, the complex does not represent a single–site catalyst in the usual sense.



Scheme 1.5. Reaction of BPA with 1 equivalent of dibutylmagnesium yielding a mixture of target heteroleptic complex **29** and the homoleptic sandwich by-product **30**.

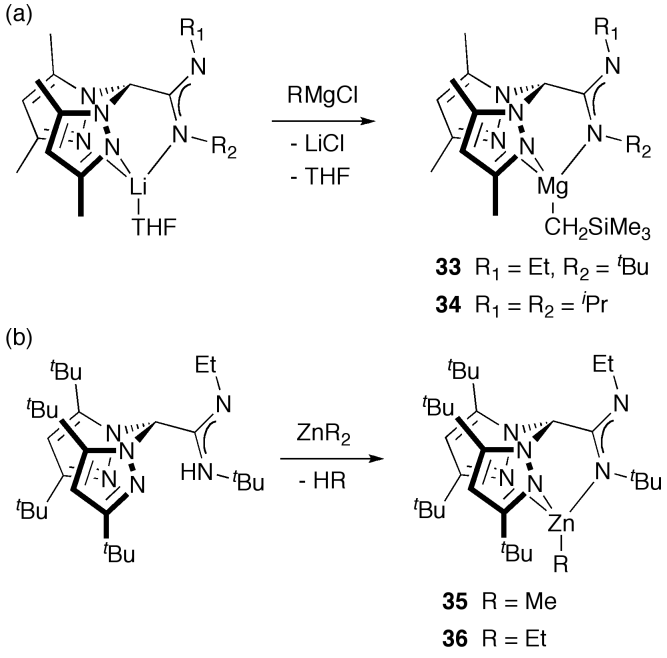


Scheme 1.6. Synthesis of the BPA supported mononuclear zinc ethyl complex **31** and the binuclear zinc alkoxide **32**.

Further efforts by Carpentier et al. have resulted in the isolation of several zinc complexes of the same ligand (Scheme 1.6).[27b] The ethylzinc complex **31** was generated simply by reaction of one equivalent of diethylzinc with the proteo BPA ligand. Reaction of this complex with one equivalent of [(EtO)ZnEt] yielded the corresponding binuclear complex **32** which bears a bridging ethoxide initiating group. Polymerization data were obtained for both complexes, with **32** consistently demonstrating superior activity and polydispersity (Table 1.2, entries 4–6). Even at an extremely low catalyst loading of 0.25%, complex **32** achieved complete conversion in 30 hours at ambient temperature, while **31** reached only 93% conversion in the same timeframe with 1% catalyst loading.

A family of ligands more closely resembling the tris(pyrazolyl)borate framework has been developed by Sànchez-Barba and colleagues. These so-called "heteroscorpionate" (HSC) ligands are based on a bis(pyrazolyl)methane system, but feature a third donor arm which can incorporate one of a variety of monoanionic functionalities. The HSC system used for LA polymerization catalysis bears an

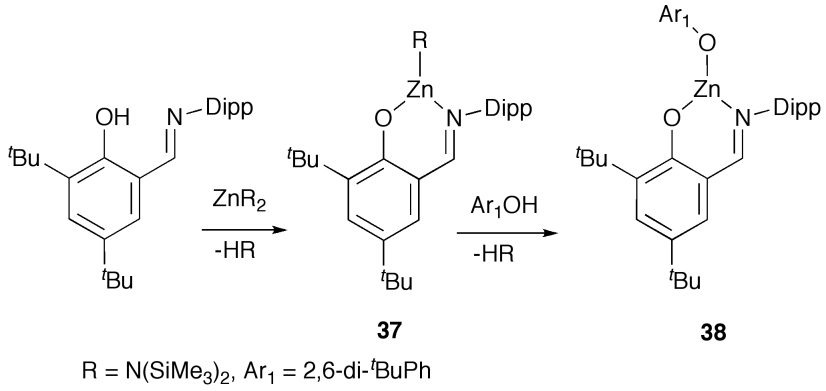
amidinate donor arm.[28] Sànchez-Barba et al. have successfully isolated a wide array of magnesium alkyl complexes supported by this heteroscorpionate framework *via* reaction of LiL with the appropriate Grignard reagent (Scheme 1.7). Complexes **33** and **34** differ in steric bulk at the amidinate arm (HSC-1: R_1 = Et, R_2 = ^{t}Bu; HSC-2: R_1 = R_2 = ^{i}Pr), and only those bearing a hefty alkyl initiating group were investigated as LA polymerization catalysts. Polymerization experiments were carried out at an elevated temperature of 70 °C in toluene with a catalyst loading of 1%, and it was determined that consumption of *rac*-LA proceeded at a relatively slow rate (Table 1.2, entries 7 and 8). Specifically, the more sterically encumbered complex **33** required 72 hours to reach 31% conversion, while **34** achieved 42% conversion in the same timeframe. It was established that despite their poor activity, the catalysts yielded polymer with a narrow molecular weight distribution (PDI = 1.09), though no stereocontrol was noted.



Scheme 1.7. Preparation of (a) magnesium and (b) zinc complexes of HSC scaffolds.

Heteroscorpionate zinc alkyl complexes of HSC-1 (**35** and **36**) have more recently been investigated (Scheme 1.7b).[28b] As with their magnesium analogues **33** and **34**, these complexes exhibited poor activity and stereochemical control. Complexes **35** and **36** required long reaction times and elevated temperatures to produce high conversion to polymer (Table 1.2, entries 9–11), though excellent polydispersities were obtained under these conditions. Slightly better activity was noted when one equivalent of *iso*propanol was added to the precatalyst. Polymerization of *rac*-LA using these catalysts gave a slight heterotactic bias. A less bulky analogue of **35**, in which the *tert*-butyl groups on the pyrazole rings were replaced with methyl groups, was also studied. This did not have substantially improved activity, and not surprisingly, resulted in complete loss of stereochemical control.

1.2.1.3. Phenolate and analogous ligands



Scheme 1.8. Synthesis of zinc amide (**37**) and aryloxide (**38**) complexes of a Schiff base ligand.

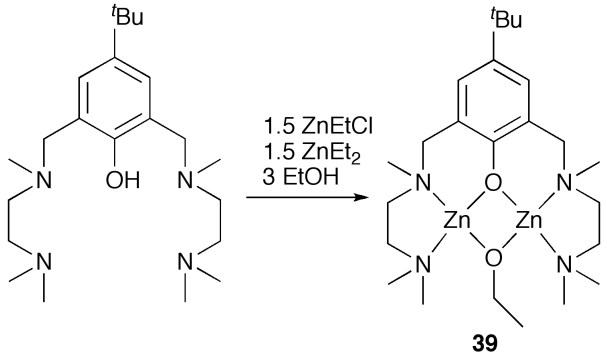
Table 1.3. Polymerization of *rac*-LA or L-LA by complexes supported by phenolate and related ancillary ligands (T_{rxn} = 25 °C, CH_2Cl_2 solvent, except where noted).

Entry	Catalyst	$[LA]_o$ (mol L^{-1})	Loading (mol%)	*t* (min)	% conv.	PDI	P_r
1[a,b]	**37**	0.83	5	180	90	N.R.	atactic
2[a]	**38**	0.83	5	4320	90	N.R.	atactic
3	**39**	1	0.33	30	90	1.19	-
4	**40**	1	0.15	5	96	1.42	-
5	**40**	1	0.1	13	96	1.4	-
6	**40**	1	0.067	18	93	1.34	-
7	**41**	2.5	1	120	98	1.09	N.A.[d]
8	**42**-BnOH	2.5	1	60	99	1.16	N.A.[d]
9[b,c]	**43**	1–2	1	15	>99	3.6	atactic
10[b,c]	**44**	1–2	1	1440	>99	1.9	atactic
11[b,c]	**45**	1–2	1	180	>99	1.7	atactic
12[b]	**46**	0.5	0.5	240	97	1.26	0.59
13[b]	**47**	0.5	0.5	240	98	1.14	0.65
14[b]	**49**	0.5	0.5	240	95	1.07	0.65
15[b]	**50**	0.5	0.5	360	98	1.13	0.74
16[e]	**51**	0.25	1	4	93	1.15	N.A.[d]
17[e]	**52**	0.25	1	4	87	1.13	N.A.[d]
18[e]	**53**	0.25	1	4	90	1.07	N.A.[d]
19[e]	**54**	0.25	1	4	92	1.16	N.A.[d]
20[e]	**55**	0.25	1	4	>99	1.12	N.A.[d]
21[e]	**56**	0.25	1	4	88	1.08	N.A.[d]
22[c]	**57**	-	0.5	90	>99	1.31	N.A.[d]
23[c]	**58**	-	0.5	120	>99	1.33	N.A.[d]
24[e]	**59**	0.5	0.5	4	98	1.08	N.A.[d]
25[e]	**60**	0.5	0.5	5	97	1.08	N.A.[d]
26[e]	**61**	0.5	0.5	5	94	1.06	N.A.[d]
27[e]	**62**	0.5	0.5	5	97	1.05	N.A.[d]
28[e]	**63**	0.5	0.5	5	92	1.05	N.A.[d]
29[e]	**64**	0.5	0.5	5	93	1.09	N.A.[d]
30[c]	**65**	0.5	0.5	8	97	1.13	N.A.[d]
31[c,e]	**66**	0.5	0.5	2	>99	1.46	N.A.[d]
32[c]	**67**	0.5	0.5	4	89	1.08	N.A.[d]
33[f]	**68**	-	0.14	30	69	1.04	N.A.[d]
34[c,g]	**69**	0.49	1.67	400	92	1.03	atactic

[a]Benzene solvent. [b]T_{rxn} = 20 °C. [c]Toluene solvent. [d]Not applicable. [e]T_{rxn} = 0 °C. [f]Melt polymerization, 110 °C. [g]T_{rxn} = 80 °C.

Phenolate ligands bearing a variety of pendant nitrogen-donor groups have recently garnered interest for their ability to stabilize magnesium and zinc amides and alkoxides. Early zinc complexes of a Schiff base ligand bearing

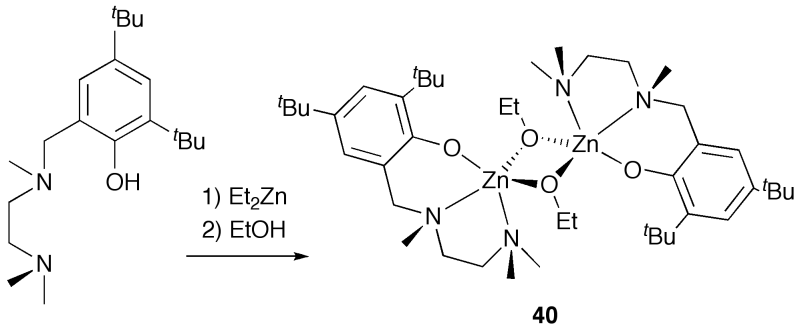
bis(trimethylsilyl)amide (**37**) and 2,6-*tert*-butylphenoxide (**38**) initiating groups (Scheme 1.8) have been described.[29] These species were reportedly catalytically active for the polymerization of both L-LA and *rac*-LA (Table 1.2, entries 1 and 2). At a relatively high catalyst loading of 5 mol% both **37** and **38** lacked remarkable activity at 25 °C (**37** resulted in 90% conversion to polymer after 3 hours while **38** required approximately 72 hours to reach the same point). The lower rate of polymerization observed with **38** was attributed to the large steric demands associated with the initiating group. Neither catalyst displayed any appreciable stereoselectivity.



Scheme 1.9. Preparation of the highly active dinuclear zinc alkoxide **39**.

Within the past 9 years Hillmyer and Tolman have demonstrated a notably more successful use of a phenoxy based ancillary which possesses two ethylenediamine tethers installed at the *ortho* sites of the phenoxy ring.[30] Highly active zinc alkoxide catalysts were prepared by reaction of the proteo ligand with a mixture of EtZnCl and $ZnCl_2$, followed by treatment with ethanol, to ultimately afford the binuclear monoalkoxide complex (**39**) in good yield (Scheme 1.9). At a catalyst loading of 0.33%, complex **39** controllably polymerized *rac*-LA to 90%

conversion in only 30 minutes (Table 1.3, entry 3). This highly active catalyst also generated approximately monodisperse polymer (PDI = 1.19) and exhibited living catalyst behaviour.



Scheme 1.10. Preparation of zinc alkoxide **40**.

The aforementioned promising results prompted further studies by the same researchers. Particularly noteworthy are the family of mononuclear zinc complexes supported by a phenoxy ligand bearing a single ethylenediamine tether at the *ortho* position (Scheme 1.10).[31] Such complexes were produced by reaction of the substituted phenol with diethylzinc and subsequent derivatization to the corresponding alkoxide by treatment with ethanol. Complex **40** was established to exist as an alkoxy bridged dimer in the solid state. In addition, pulsed gradient spin-echo (PGSE) NMR measurements demonstrated that the complex is monomeric in solution. It was reported that **40** has an incredibly high catalytic activity for the polymerization of *rac*-LA and exhibits narrow polydispersities (PDI = 1.34–1.42) even with very low quantities of catalyst (Table 1.3, entries 4–6). At 0.15% catalyst loading, 96% conversion was obtained in 5 minutes. High molecular weight PLA was yielded (130 kg mol^{-1}) at 0.067% catalyst loading, with 93% conversion to polymer in a mere 18 minutes. Indeed, at the time of publication, **40** represented the most

active zinc based LA polymerization catalyst known to date, with the most effective activity at the lowest known concentration of any zinc catalyst, and still remains one of the most active known catalysts. The only drawback of this remarkable system appears to be its lack of stereochemical control.

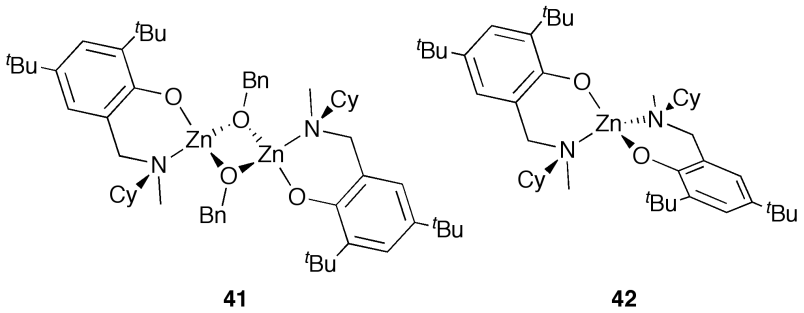


Figure 1.7. Heteroleptic (**41**) and homoleptic (**42**) zinc complexes of an aminophenolate ligand.

Both the hetero- and homoleptic zinc complexes of a simple bidentate aminophenolate ligand have been the subject of study by Sobota and co-workers.[32] Reaction of one equivalent of the ligand with diethylzinc, followed by one equivalent of benzyl alcohol yielded the corresponding heteroleptic alkoxy bridged dimer **41**, while reaction of diethylzinc with two equivalents of the ligand afforded complex **42**. Both species were found to effectively initiate the polymerization of L-LA at ambient temperature (Table 1.3, entries 7 and 8). Complex **41** achieved 98% polymerization in two hours, while complex **42**, upon addition of one equivalent of benzyl alcohol as a cocatalyst, required only one hour for near quantitative conversion. The molecular weight distributions were narrow for both (PDI = 1.09, 1.16), and neither catalyst has been employed for stereoselective polymerization.

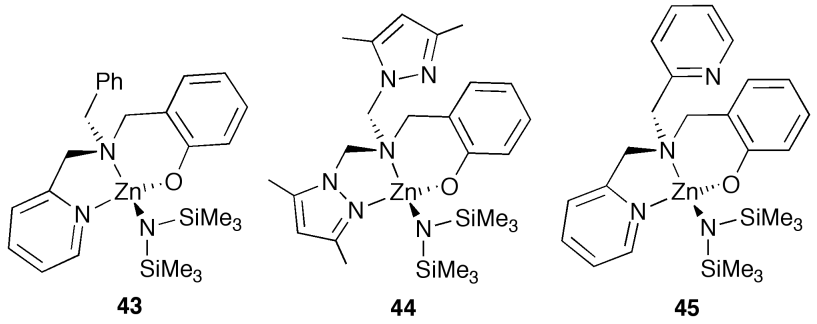
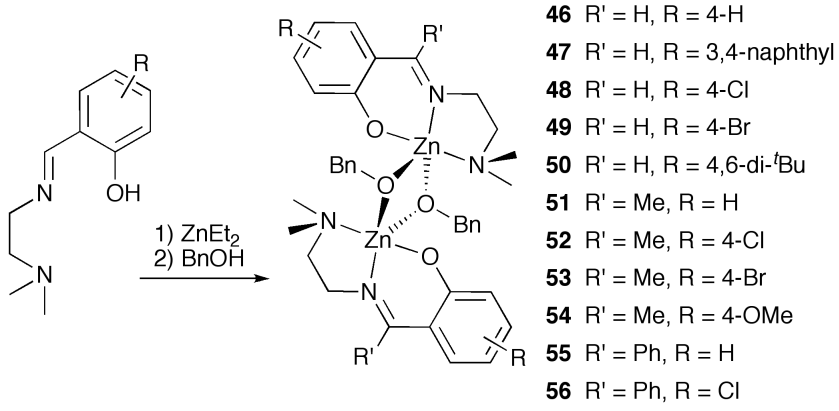


Figure 1.8. Zinc amide complexes of multidentate aminophenolate ligands.

A similar series of aminophenolate ligands bearing one or two additional nitrogen donor functionalities (pyridyl or pyrazolyl) have been used to synthesize the monomeric zinc amide species **43**, **44**, and **45** (Figure 1.8).[33] These complexes were generated through an amine elimination route *via* reaction of the proteo ligand with the requisite zinc precursor. While all three complexes were determined to be reactive toward *rac*-LA at ambient temperature, their activities varied dramatically (Table 1.3, entries 9–11). Catalyst **43** is by far the most active of this set, giving complete conversion within 15 minutes at 1% catalyst loading. However, analysis of the polymer revealed a very broad molecular weight distribution (PDI = 3.6), suggesting a poorly controlled polymerization process. Complex **44** gave an improvement in the molecular weight distribution (PDI = 1.9), but at the price of significantly lower activity (24 hours was required for total monomer consumption). Finally, complex **45** demonstrated the most desirable catalytic properties of the group, generating polymer with moderately narrow polydispersity (PDI = 1.7), while retaining notable activity. Unfortunately, no evidence for stereochemical control was observed with any of these catalysts.

The incredible catalytic activity associated with zinc alkoxide complexes of phenolate ancillary ligands has prompted further investigation by several groups. Among these, Lin and co-workers[34] have attempted to combine the best features of Chisholm's bidentate Schiff base framework and Tolman's tridentate phenoxy(diamine) ligand (Scheme 1.11). Although a range of ligand variants have been explored (**46**–**50**), a zinc alkoxide complex (**46**) of the most simple derivative, which contains an unsubstituted backbone ring, has been most thoroughly studied. Data for the polymerization of *rac*-LA were obtained for all derivatives, and under the conditions chosen, the catalysts gave between 95% and 98% conversion to polymer after 4 or 6 hours (Table 1.3, entries 12–15), with the exception of **48**, which was found to be completely inactive. The polymerization was well controlled (PDI = 1.07–1.26) and a modest selectivity for heterotactic microstructure was observed (P_r = 0.59–0.74). The bulkier derivative bearing *tert*-butyl substituents (**50**) showed superior molecular weight and stereochemical control (PDI = 1.13; P_r = 0.74) but reduced activity, requiring 6 hours to achieve 98% conversion under identical conditions.

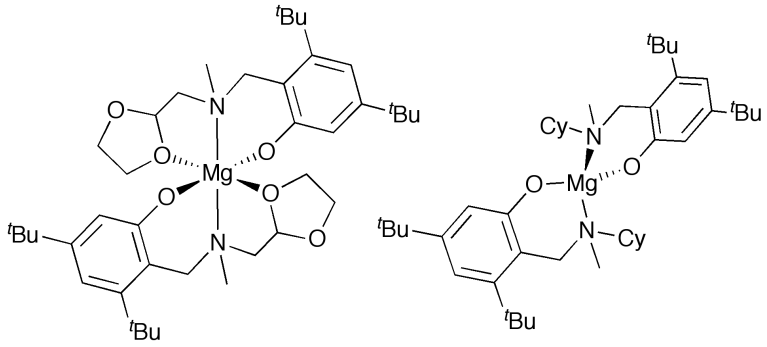


Scheme 1.11. Preparation of zinc alkoxide complexes of a tridentate Schiff base ligand.

Further modifications of this Schiff base catalyst system have been undertaken by Lin and co-workers, differing only in the placement of substituents at the imine carbon.[35] Specifically, compounds **51**–**54** (Scheme 1.11) all incorporate a methyl group at this position, while **55** and **56** instead bear a phenyl ring. This modification of the ligand backbone proved to be very successful in improving the activity of the resulting zinc alkoxide catalysts. All are extremely active at a reduced temperature of 0 °C, giving between 87% and 100% conversion in only 4 minutes (Table 1.3, entries 16 to 21). As previously described for **46**–**50**, those complexes which have an unsubstituted phenyl ring in the ligand backbone are most active, while those bearing electron withdrawing substituents exhibit reduced activity. In addition, these catalysts produced nearly monodisperse polymer (PDI = 1.07–1.16), suggesting a living polymerization. The authors did not probe the stereochemical control of these catalysts; however, this exciting study clearly indicates that modification of the imine carbon substituent can significantly enhance the catalytic competence of Schiff base supported catalysts.

The homoleptic magnesium complexes **57** and **58** (Figure 1.9) were prepared by reaction of two equivalents of the appropriate aminophenolate ligand with $MgBu_2$. The two ligands differ in the nature of the amine substituent, which is the potentially coordinating oxolane in **57** and the non-coordinating cyclohexyl group in **58**. As with the homoleptic magnesium complex **30**, **57** and **58** lack a traditional initiating group, and thus it is expected that the first turnover will require insertion of LA into the metal-oxygen bond, thereby incorporating one ligand from each complex as the terminal group in each polymer chain. Regardless,

these complexes do exhibit reasonable polymerization activity at ambient temperature (Table 1.3, entries 22 and 23). Intriguingly, the molecular weight distributions of the corresponding polymers are only slightly broad (1.31–1.33).



57 **58**

Figure 1.9. Homoleptic magnesium complexes of related tridentate (**57**) and bidentate (**58**) aminophenolate ligands.

While important work is being performed by several research groups with bis(phenolate) frameworks, ligands of this type are generally dianionic and thus outside the scope of this discussion.[36] One study, however, has changed this divalent ancillary into a monovalent analogue by conversion of the alkoxide group into a sulfonate functionality.[37] These alkoxide-bridged magnesium dimers **59**–**64** (Figure 1.10) differ only in the benzenesulfonate substituent. All of the complexes are remarkably active at 0 °C; after only 5 minutes complete consumption of monomer was observed when 0.5 mol% catalyst was added (Table 1.3, entries 24–29). Excellent molecular weight control was also achieved (PDI = 1.05–1.08), though no substantial stereochemical control was found.

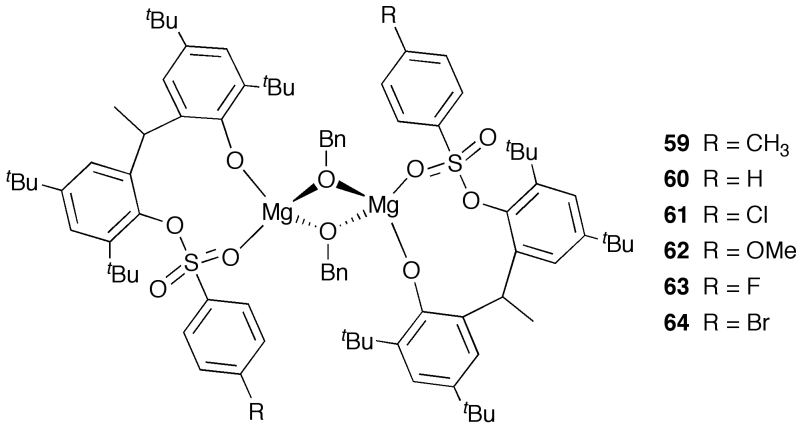
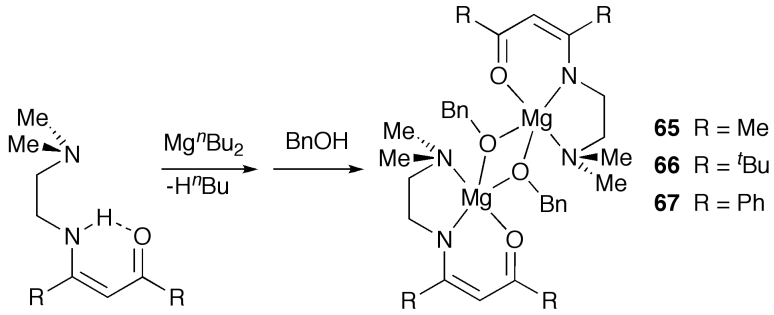


Figure 1.10. Dimeric magnesium alkoxide complexes of a monoanionic bis(phenolate) ligand.

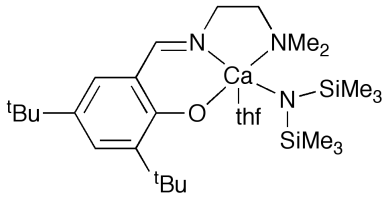
While few phenolate-supported magnesium complexes have been reported as catalysts for the polymerization of LA, magnesium complexes of the structurally analogous ketiminate ligand are known.[38] These species were constructed *via* a standard alkane elimination protocol followed by reaction of the resulting complexes with benzyl alcohol to afford the alkoxy bridged dimers (Scheme 1.12). Complexes **65**, **66**, and **67** differ only in the degree of steric bulk in the ligand backbone. Their activity toward L-LA polymerization was studied (Table 1.3, entries 30–32), and it was determined that complex **66** is by far the most active, generating complete conversion to PLA in two minutes at 0 °C. It should be noted, however, that the molecular weight distribution was relatively broad (PDI = 1.46). Complexes **65** and **67** are highly active at ambient temperature, completely consuming LA monomer in under 10 minutes (PDI = 1.13 and 1.08, respectively). Variable temperature ^{1}H NMR studies suggested that these complexes exist in solution as an equilibrium between dimeric and monomeric species; the dramatically higher activity of **66** is attributed to greater steric bulk which enhances the tendency of this complex to dissociate to a monomer in solution. On the basis of these observations,

it was proposed that the monomeric complexes possess substantially greater activities than their respective dimers.



Scheme 1.12. Synthesis of magnesium alkoxide complexes supported by a ketiminate ancillary ligand.

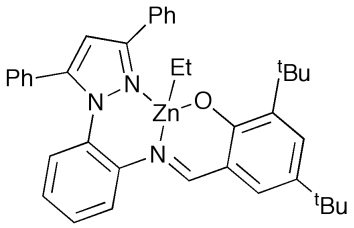
A single example of Schiff base supported heteroleptic calcium LA polymerization catalysts has been described.[39] Reaction of the Schiff base ligand with calcium iodide in THF in the presence of two equivalents of $NaN(SiMe_3)_2$ yielded the solvated calcium amide complex **68** (Figure 1.11). Melt polymerization experiments were conducted at 110 °C and even with a catalyst loading as low as 0.14%, 69% conversion was achieved within 30 minutes. (Table 1.3, entry 33) Furthermore, the polymer polydispersity approached unity (PDI = 1.04). While no significant stereochemical control was achieved with this calcium complex, it is notable for such low catalyst loading to display such excellent molecular weight control.



68

Figure 1.11. Monomeric calcium amide complex of a simple Schiff base ligand.

The standard Schiff base framework has been incorporated into the ligand design of Wang and co-workers, such that a pendant pyrazole ring is incorporated into the system.[40] A zinc complex of this ligand bearing an ethyl initiating group has been isolated (**69**, Figure 1.12), but the authors were unable to prepare an alkoxide analogue. Nonetheless, complex **69** demonstrated catalytic competence for LA polymerization at 80 °C in toluene, although a relatively high catalyst loading and long reaction times were required to achieve high conversion of *rac*-LA to polymer (Table 1.3, entry 34). No stereochemical control was realized; however, the resulting polymer has an extremely narrow molecular weight distribution (PDI = 1.03).



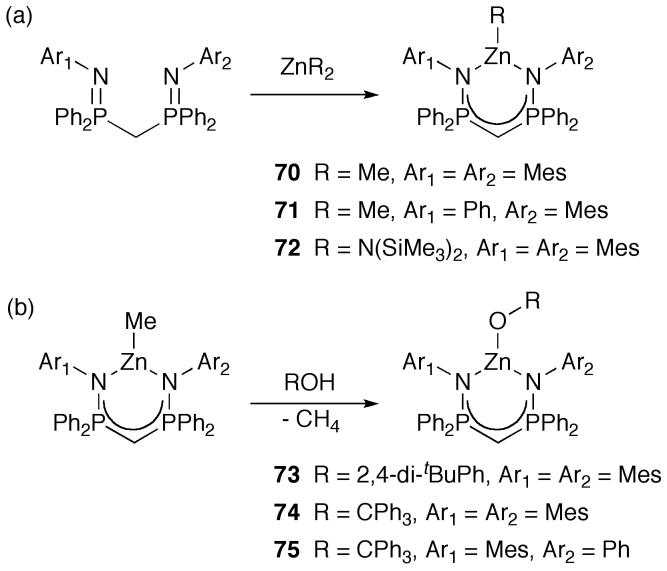
69

Figure 1.12. Zinc complex of a Schiff base ligand with a pendant pyrazole arm.

1.2.1.4. Bis(phosphinimino)methanide complexes

The bis(phosphinimino)methanide (BPM) scaffold, which is extremely electronically versatile and bears a significant structural resemblance to the BDI ligands (*vide supra*), has recently demonstrated promise for supporting a plethora of metal complexes. Upon deprotonation of the methylene backbone this ligand serves as a bidentate monoanionc ancillary. Initial attempts to prepare LA polymerization catalysts from this ligand focused on the preparation of zinc alkoxides analogous to

the most successful BDI species.[41] The authors targeted three-coordinate zinc complexes with C_2 (BPM-1) or C_s (BPM-2) symmetric ligands. The corresponding zinc alkyl compounds **70** and **71**, and the amido compound **72** were prepared by reaction of bis(alkyl) or bis(amido) zinc precursors with the appropriate neutral ligand (Scheme 1.13a). Zinc alkoxide derivatives were subsequently generated by reaction of **70** or **71** with a suitable alcohol (Scheme 1.13b). Unlike the BDI alkoxides, all of these species are monomeric in the solid state. This may be attributed to the enhanced steric bulk of the alkoxide initiating groups.



Scheme 1.13. Synthesis of zinc complexes supported by the BPM ligand.

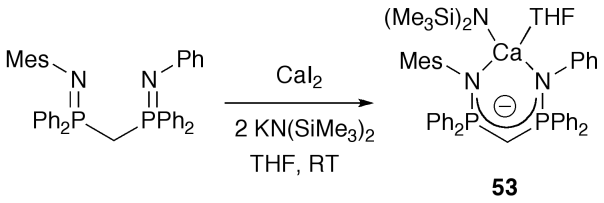
Unfortunately, none of the BPM complexes were found to be catalytically active for LA polymerization at ambient temperature; however, the alkoxide derivatives **73**, **74**, and **75** exhibited varying degrees of activity at 60 °C (Table 1.4, entries 1–3). Not surprisingly, higher polymerization activities were observed for the less sterically encumbered **75**. Polydispersities of the resulting polymers were broad and somewhat erratic, suggesting a poorly controlled polymerization.

Likewise, polymer molecular weights are much higher than the theoretical value calculated from the monomer to initiator ratio. It has been suggested by the authors that the large initiating groups may be effectively inhibiting monomer coordination, and that the carbanionic character of the ligand backbone may be modifying the behaviour of the system in unpredictable ways. This illustrates the need for further study to better understand the fundamental chemistry inherent to this type of catalyst.

Table 1.4. Polymerization of LA by BPM supported catalysts.

Entry	Catalyst	$[LA]_o$ (mol L^{-1})	Loading (mol%)	*t* (min)	% conv.[a]
1[b]	**73**	0.29	1	240	> 95
2[b]	**74**	0.29	1	300	> 95
3[b]	**75**	0.29	1	120	> 95
4[c]	**76**	N.R.	0.5	< 1	> 99

[a]Determined by ^{1}H NMR Spectroscopy. [b]T_{rxn} = 60 °C, toluene solvent [c]T_{rxn} = ambient temperature, THF solvent



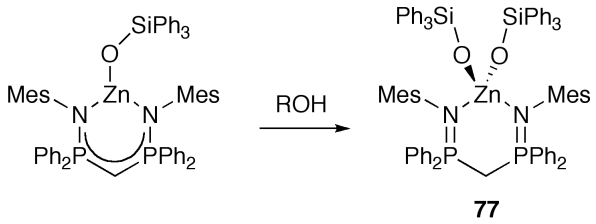
Scheme 1.14. Preparation of calcium complex **76**.

Details regarding a calcium complex of the symmetric BPM ligand (**76**) were recounted separately by Hill et al. (Scheme 1.14).[42] A single THF molecule is bound to the calcium centre and the complex is monomeric in the solid state. While only preliminary polymerization studies were undertaken, the complex is dramatically more reactive than the analogous zinc complexes, reportedly giving quantitative polymerization under the same conditions in less than a minute (Table 1.4, entry 4).

1.2.2. Neutral Ligands

While the majority of LA polymerization catalysts involve monoanionic ligands, several researchers have recently been exploring the use of neutral ligands for stabilization of divalent metals. The exploration of neutral ligands has the potential to generate novel chemical reactivity which may differ from that achieved through the use of anionic ligands. The following section will highlight examples of neutral ligands employed for stabilizing LA polymerization catalysts.

1.2.2.1. Neutral bis(phosphinimine)methane



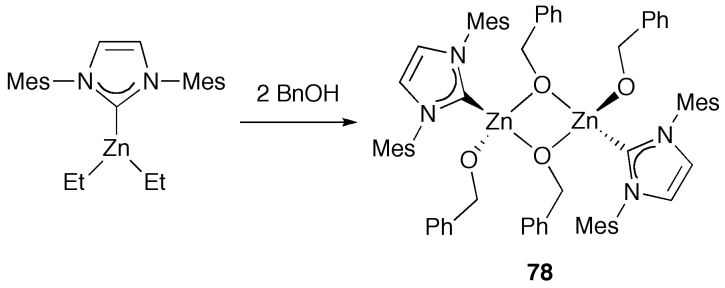
77

Scheme 1.15. Preparation of a zinc bis(alkoxide) bound to a neutral bis(phosphinimine) ligand (**77**).

It has been shown that alkoxy-zinc complexes featuring neutral BPM supports may be prepared from analogous species supported by anionic BPM ligands when the bulky triphenylsiloxide group is utilized.[41] Reaction of one equivalent of the silanol with **70** yielded the expected three-coordinate zinc complex of the anionic BPM ligand. However, addition of a second equivalent resulted in ligand protonolysis, affording the corresponding disiloxyzinc complex **77** (Scheme 1.15). Complex **77** was not catalytically active for the polymerization of LA, even at 60 °C. This inactivity is likely due to excessive steric bulk of the triphenylsiloxide initiating group, which has been shown by Chisholm et al. to dramatically decrease activity.[17]

1.2.2.2. N-heterocyclic carbenes

While N-heterocyclic carbene (NHC) complexes of zinc have been known for a considerable time, their first described use as LA polymerization catalysts appeared only 7 years ago.[43] Alkoxy bridged dimer **78** was synthesized *via* the straightforward reaction between a previously known diethylzinc complex[44] and two equivalents of benzyl alcohol (Scheme 1.16).



78

Scheme 1.16. Preparation of an NHC supported zinc alkoxide (**78**)

Complex **78** is an effective catalyst for the polymerization of *rac*-LA, with an impressive rate only marginally less than the highly active zinc complex previously reported by the same group (Table 1.5, entry 1).[31] At 25 °C, 96% monomer consumption occurred after only 20 minutes, and the resultant polymer had a relatively narrow polydispersity of 1.25.

Table 1.5. Polymerization of *rac*-LA by NHC complex **78** and the free parent carbene (T_{rxn} = 25 °C, 0.77 mol% catalyst, [LA] = 1 M, CH_2Cl_2).

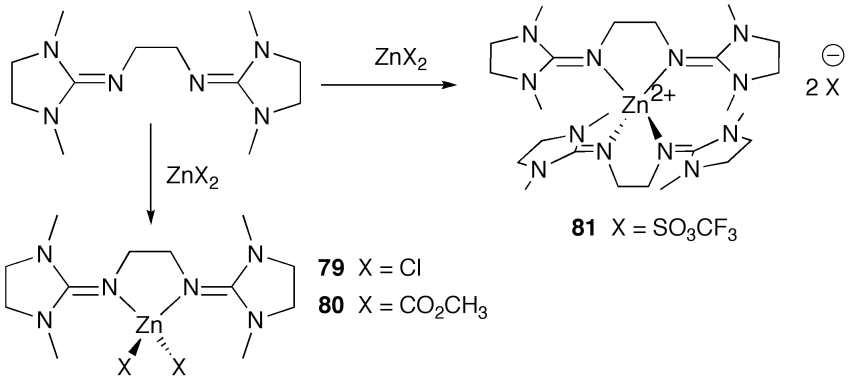
Catalyst	*t* (min)	% conv.	PDI	P_r
78	20	96	1.25	0.6
Carbene[a]	30	98	1.23	0.41

[a]In the presence of benzyl alcohol.

Free carbenes are known to be excellent organocatalysts for the ring-opening polymerization of LA,[45] and though these ligands are generally considered to be non-labile, the possibility exists that ligand dissociation may occur, and that the free ligand may be responsible for the observed activity of **78**. This concern was addressed by the authors, but never fully disproven. Zinc complex **78** is only slightly more active than the free carbene (Table 1.5); however, notably different polymer microstructures were obtained from each, as the zinc complex generated heterotactic enriched PLA (P_r = 0.60), while the free carbene generated isotactic enriched PLA (P_r = 0.41) (Table 1.5). This would suggest that at least a substantial portion of the catalytic activity of **78** is due to polymerization by the intended complex.

1.2.2.3. Bis(guanidine) complexes of zinc

While relatively few guanidine complexes of the group 2 and 12 metals are known, the use of neutral bidentate bis(guanidine) ligands to stabilize other transition metals has been well established.[46] An interesting family of bis(guanidine) ligands has been explored in detail by Herres-Pawlis and co-workers.[47] Specifically, several zinc complexes of the bis(guanidine)ethyl (BGE) ligand have been prepared and tested as catalysts for the bulk polymerization of LA.[48] The production of heteroleptic complexes **79** and **80** was achieved by reaction of BGE with zinc dichloride and zinc acetate, respectively, while reaction with zinc triflate selectively afforded homoleptic complex **81** (Scheme 1.17).



Scheme 1.17. Complexes prepared from the BGE ligand.

Table 1.6. Selected data for melt polymerization of *rac*-LA by BGE complexes of zinc (t = 24 h).

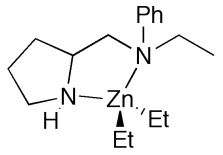
Catalyst	Loading (mol%)	T_{rxn} (°C)	% conv.	PDI
79	0.2	135	82	1.74
79	0.1	150	70	1.55
79	0.2	165	61	1.62
80	0.2	135	63	1.63
80	0.1	150	86	1.77
80	0.2	165	46	1.54
81	0.2	135	82	1.74
81	0.1	150	93	1.88
81	0.2	165	51	1.58

Though none of these complexes contained an alkoxide initiating group, all were moderately active in the neat polymerization of *rac*-LA. At temperatures ranging from 135 to 165 °C, and with catalyst loadings of 0.1% and 0.2%, moderate to high yields of polymer (46% to 93%) with relatively broad polydispersities (PDI = 1.54–1.88) were achieved within a 24 hour period (Table 1.6). While these results appear promising, the nature of the active catalyst and the mechanism of polymerization remains unclear. The possibility of dissociation of zinc from BDE, as for NHC complex **78** was not addressed. Several studies of similar complexes have

been more recently undertaken by the same group, with quite similar results being reported.[49]

1.2.2.4. Zinc complexes of other neutral ligands

A noteworthy account by Jeong et al. describes the use of the chiral (S)-N-ethyl-N-phenyl-2-pyrrolidinemethanamine (S-EPP) ligand (Figure 1.13).[50] The pyrrolidine N–H has an exceptionally high pK_a value (~44 in DMSO)[51] which will not easily undergo protonolysis, thereby rendering S-EPP a neutral donor. Although only the zinc dichloride complex of S-EPP was isolated, polymerization of *rac*-LA was investigated using the *in situ* generated diethylzinc species (**82**). Unfortunately, the desired stereochemical control was not imparted by the system. This may be due to ligand dissociation, which would necessarily render the catalyst achiral. Additional work is required to unambiguously identify the active catalyst.



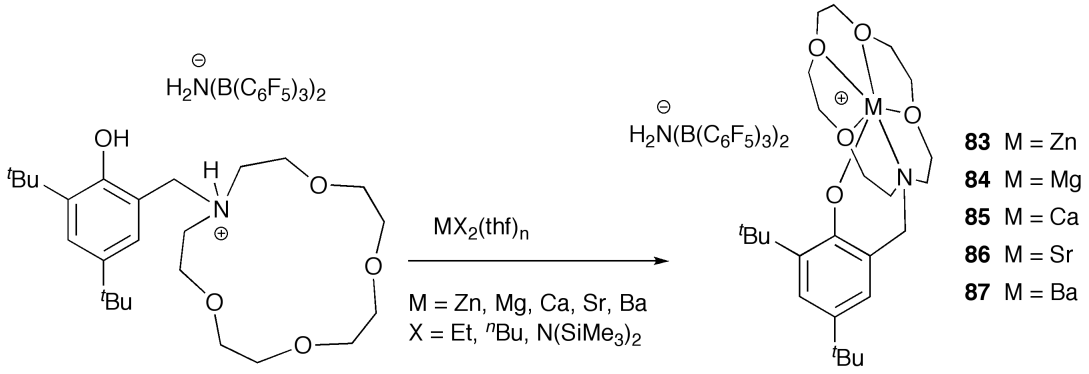
82

Figure 1.13. Proposed structure of a diethylzinc complex (**82**) of the neutral pyrrolidine ligand.

1.2.3. Cationic Complexes

When this project was first initiated, there had been very few reports of the use of cationic metal complexes as catalysts for the ring-opening polymerization of lactide. Herres-Pawlis and co-workers have studied a cationic zinc complex coordinated by two bis(guanidine) ligands, but this homoleptic complex did not bear a suitable initiating group and was only tested for melt-polymerization at very high temperature.[48] Also, Dagorne et al. had reported a cationic aluminium complex,

but when exposed to lactide the complex was found to be completely unreactive after a single insertion.[52] Additionally, Bochmann has examined a cationic zinc-amide species, but this too was inactive for polymerization of lactide.[53]

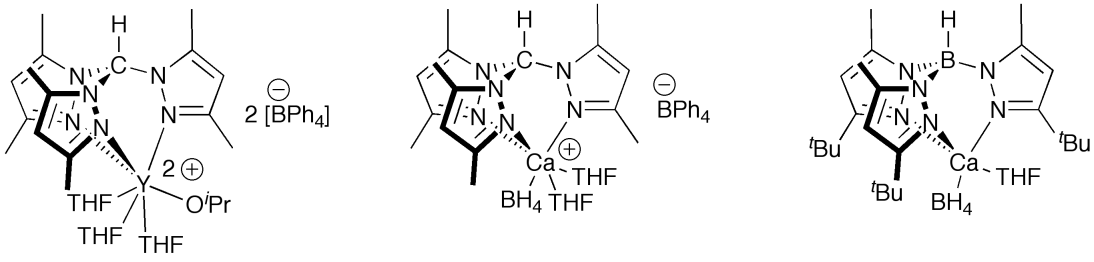


Scheme 1.18. Preparation of cationic Zn and alkaline-earth metal complexes of a phenolate ligand.

There have been several more successful reports of cationic catalysts since the initiation of this thesis work. For example, Carpentier et al. reported a series of cationic complexes of a phenolate ligand bearing a pendant crown-ether functionality (Scheme 1.18). Complexes of Zn (**83**) and the alkaline-earth metals from Mg to Ba (**84**–**87**) were prepared and their efficacy for the polymerization of lactide was examined. Unfortunately, these complexes were not highly active even in the presence of *iso*propanol cocatalyst. The most active of the series was the calcium complex **85**, which required heating to 60 °C for several hours for high conversion to be achieved. [54] Moreover, the active catalyst species is ill-defined, and the metal may not necessarily retain its cationic nature upon exposure to the ^{i}PrOH cocatalyst.

Mountford et al. have recently reported the dicationic yttrium complex **88**, which features a tris(pyrazolyl)methanide ancillary ligand (Figure 1.14).[55] The

complex displays excellent molecular weight control and a well-defined mechanism, but unfortunately it is only active at an elevated temperature of 70 °C, requiring 12 hours to achieve high conversion.



88 **89** **90**

Figure 1.14. Cationic yttrium and calcium complexes of a tris(pyrazolyl)methane ligand, and an analogous neutral Ca complex of a TPB ligand.

More recently, however, the same group has reported the cationic calcium tetrahydroborate complex **89**, which does display excellent activity at ambient temperature, giving reasonable conversion after 2 hours (Figure 1.14). In addition, the system was shown to exhibit excellent molecular weight control, and the polymerization was clearly demonstrated to occur *via* a coordination-insertion mechanism.[56] Interestingly, the directly related neutral calcium complex **90** was much more active and exhibited better stereocontrol, which suggests that rendering a calcium system cationic may actually have a detrimental effect on activity.

1.3. Thesis Goals and Summary

A quick examination of the above literature review reveals that there have been very few studies of cationic metal complexes or the use of neutral ligands for the polymerization of lactide. This is despite the fact that cationic, or "activated",

metal compounds are such an important class of catalysts for the polymerization of olefins.[13] In light of some of the recent promising reports of cationic systems mentioned above, the goal of the thesis was to design a new class of well-defined single-site zinc catalysts that bear a positive charge. The targeted complexes also incorporate an appropriate initiating group such that they catalyse the polymerization *via* a controlled ring-opening mechanism, rather than simply initiating a cationic polymerization. It was expected that such species would be highly active, as the electronic and coordinative unsaturation of the metal should promote rapid monomer insertion.

Chapter 2 discusses preliminary investigations of a potentially bidentate neutral monophosphinimine ligand system, which incorporates a neutral dibenzofuran (dbf) backbone. Complexation studies resulted in the isolation and characterization of the neutral $ZnCl_2$ and $Zn(C_6F_5)_2$ complexes. It was then demonstrated that cationic complexes are most efficiently prepared by first protonating the ligand, followed by reaction of the protonated ligand with diethylzinc. The efficacy of the resulting cationic species as catalysts for lactide polymerization was briefly investigated.

A related, potentially tridentate, bis(phosphinimine) pincer ligand was investigated in Chapter 3, and it was found to be more suitable for preparation of stable heteroleptic cationic zinc complexes. A series of complexes bearing different initiating groups was prepared and structurally characterized, but unfortunately simple alkoxide derivatives could not be made. Installation of a lactate initiating

group was achieved, however, and this proved to be the only compound in the series capable of promoting efficient coordination-insertion polymerization of lactide.

In Chapter 4, modification of the bis(phosphinimine) ligand framework gave four derivatives that differed in the steric bulk of the N-aryl groups. Simple cationic methylzinc complexes of each ligand derivative were prepared and structurally characterized. The steric bulk of the ligand was found to have a dramatic effect on the structure, whereby the ligand was bound to the metal centre in either a bidentate or tridentate mode.

Chapter 5 describes a series of cationic zinc-lactate complexes of these same ligand derivatives. Three different zinc-lactate complexes were prepared and structurally characterized. The two least sterically encumbered systems were discovered to be highly active, living lactide polymerization catalysts at ambient temperature.

In Chapter 6, a significant modification of the ligand placed alkyl groups on both the phosphinimine nitrogen and phosphorus atoms in place of aryl groups. A zinc-lactate complex was prepared and structurally characterized, and this complex was found to be significantly more active than the most active catalysts studied in Chapter 5. The system is capable of polymerizing a batch of *rac*-lactide in less than 30 minutes at ambient temperature, which is comparable in rate to the highly successful zinc complexes of the BDI and TPB ligands.

Chapter 2. Neutral and Cationic Zinc Complexes of a Monophosphinimine Ligand

2.1. Introduction

The original work presented in this thesis is focused on the preparation of zinc complexes and their application for the polymerization of lactide. Zinc has been chosen for these initial studies because the chemistry of neutral zinc complexes and their polymerization of lactide has been well established, thereby laying the appropriate groundwork for the study of novel cationic zinc species for this same application. Furthermore, zinc has especially high potential for applicability in an industrial setting because it is inexpensive and non-toxic. A brief overview of zinc chemistry has been included such that this thesis may be placed in appropriate context. Additionally, the preparation of cationic (or "activated") zinc complexes is a central theme of the thesis, as is the use of phosphinimine-based ancillary ligands, and as such, overviews of these topics are also included in this section. Finally, the introduction concludes with a discussion of the targeted ancillary ligand and a proposed synthetic route to cationic zinc complexes.

2.1.1. Organometallic Chemistry of Zinc

Elemental zinc does not occur naturally, but rather, exists only in the form of its compounds. The most common ore is ZnS, which is found in cubic (*zinc blende*) or hexagonal (*wurtzite*) form. Metallic zinc is then obtained by reduction of zinc

oxide, which is prepared by "roasting" the sulfide ore. Metallic zinc is a bluish-white metal that has a density of 7.14 g cm^{-3}, a melting point of 419.6 °C, and a boiling point of 908.5 °C. Although it is quite brittle at ambient temperature it is ductile between 100 and 200 °C and can be formed into sheets or wires. It is stable in air due to the formation of a thin ZnO layer that adheres strongly to the surface.

The first organozinc compounds were discovered in 1849 by Sir Edward Frankland, when he combined finely granulated zinc with ethyliodide, resulting in formation of the compounds ethylzinc iodide and diethylzinc.[57] While these were not the first known organometallic compounds, their discovery has widely been credited as the beginning of the modern era of organometallic chemistry.[58] This is because they were at the time the only available source of nucleophilic alkyl groups. This manner of application has since been superseded by the more nucleophilic Grignard reagents, but interest in the chemistry of organozinc compounds has been maintained for a variety of reasons. These include low toxicity (including products of decomposition), high functional group tolerance, and the high chemoselectivity and stereoselectivity they can impart on certain reactions (*vide infra*).

2.1.1.1. Synthesis and Structure of Simple Organozinc Compounds

As mentioned in the preceding section, compounds of the general formula ZnR_2 and RZnX, where R is a simple alkyl group and X is a halide, are some of the earliest known examples of organometallic compounds. Organozinc halides can be prepared by direct reaction of zinc metal with the corresponding alkyl halide under an inert atmosphere. The dialkylzinc can then be prepared by a thermal disproportionation process, whereby heating the organozinc halide gives both ZnR_2

and ZnX_2. Diorganozinc compounds are weaker Lewis acids than related organomagnesium compounds and are always monomeric with a linear geometry. On the contrary, organozinc halides exhibit a significant degree of aggregation, due to bridging of the halide atoms. These aggregates were originally proposed to exist as tetramers, whereby four tetrahedral zinc atoms and four halide atoms make up the vertices of a cube (Figure 2.1).[59] However, the crystal structure of EtZnCl was later determined by Bochmann et al., and it was shown that a complicated polymeric sheet structure is formed in the solid state.[60]

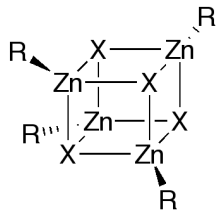


Figure 2.1. Proposed solution-state structure of alkylzinc halides.

Organozinc alkoxides (or aryloxides) are easily prepared by reaction of the diorganozinc species with one equivalent of an alcohol (or phenol), which results in replacement of one alkyl group through an alkane elimination pathway. Like the organozinc halides, these compounds tend to aggregate due to bridging of the alkoxide functionality. However, the degree of association can vary considerably depending on the steric bulk of the alkyl and alkoxide groups and also on the nucleophilicity of the oxygen bridge.[61] In the typical case, where neither the alkyl nor the alkoxide is overly bulky or electron withdrawing, a tetrameric cube structure is formed (Figure 2.2a). For example, the tetrameric structure of $[MeZnOMe]_4$ has been confirmed crystallographically.[62] The bulkier ^{t}BuZnO^{t}Bu was

determined in 1968 to be trimeric from molecular weight calculations.[61] However, the solid-state structure of the trimer was not determined until very recently, where it was shown that one of the three zinc centres is coordinatively unsaturated (Figure 2.2b).[63] When the alkoxide or aryloxide group bears electron-withdrawing substituents, the degree of aggregation can be reduced significantly. For example, the dimeric structure of $[EtZnOC_6F_5]_2$ in solution is well established (Figure 2.2c). A dimeric structure can also be obtained by employing a very bulky aryloxide, as is the case for $[EtZnO(2,6\text{-}(^tBu)_2\text{-}Ph)]_2$, whose structure has been confirmed crystallographically.[64]

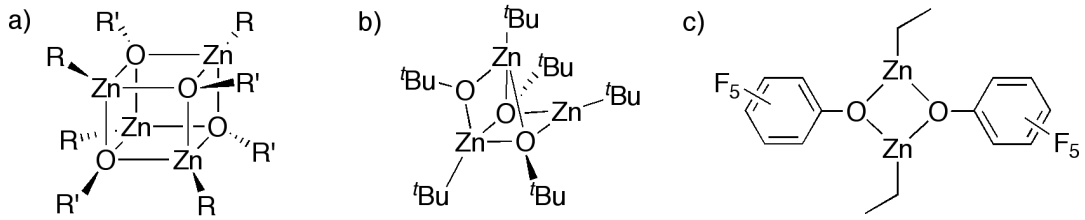


Figure 2.2. Tetramer (a), trimer (b), and dimer (c) structures of some heteroleptic zinc alkoxide compounds.

Organozinc amides are typically prepared in a manner similar to organozinc alkoxides, with reaction between a diorganozinc compound and one equivalent of a secondary amine giving single substitution under controlled conditions. However, such complexes are less common due to the tendency of the reaction to give double substitution, resulting in poorly soluble diamide compounds. While the degree of aggregation depends on the precise nature of the amide, the most common structural motif is the dimer, in which the amide groups bridge two zinc centres.

The best known example is $[MeZnNPh_2]_2$, whose structure was first proposed in 1965,[65] and has more recently been confirmed by X-ray crystallography.[66]

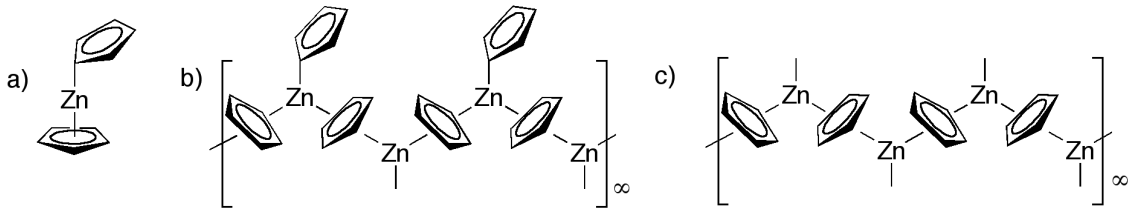
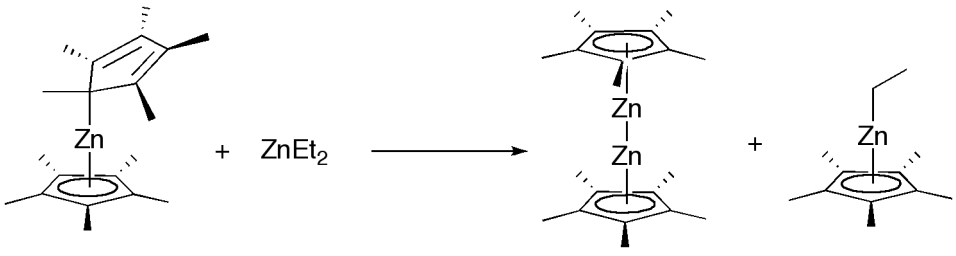


Figure 2.3. Monomeric (a) and polymeric (b) structures of zincocene and the polymeric structure of CpZnMe (c).

Cyclopentadienyl (Cp) complexes of zinc are rather rare compared with many of the transition metals. While zincocene is a known compound, it is not isostructural with ferrocene, but rather, has a slipped sandwich structure, whereby one Cp group is η^5-π-bonded and the other is η^1-σ-bonded (Figure 2.3a).[67] The complex is monomeric in solution but is polymeric in the solid state as a result of bridging of the π-bonded Cp group (Figure 2.3b). The heteroleptic compound CpZnMe is also known and exists as a polymer in both solution and solid states due to bridging of the π-bonded Cp group (Figure 2.3c).[68]



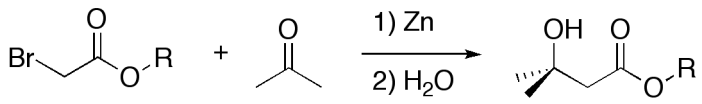
Scheme 2.1. Synthesis of decamethyldizincocene from decamethylzincocene and diethylzinc.

The organometallic chemistry of zinc has been dominated by the +2 oxidation state, and until recently there were no known stable Zn(I) compounds. The earliest detected Zn(I) compound was Zn_2Cl_2, which was thought to be formed

when zinc metal was heated to 285–350 °C in the presence of $ZnCl_2$, as evidenced by a detectable increase in volatility. However, the real breakthrough in Zn(I) chemistry came in 2004 when the synthesis and structure of decamethyldizincocene was reported.[69] Reaction of decamethylzincocene with diethylzinc afforded the Zn(I) compound $Zn_2Cp^*_2$ as a by-product along with the expected Zn(II) compound Cp*ZnEt (Scheme 2.1), and the Zn(I) compound was isolated from the mixture by crystallization. The most interesting feature of this novel compound, besides the unusual low-valent oxidation state, is the presence of a Zn(I)–Zn(I) bonding interaction. The chemistry of Zn(I) has since been expanded significantly through the use other ligand frameworks, including *β*-diketiminate[70,71] and trispyrazolylborate,[72] and all of these examples retain a similar dimeric structure with a robust Zn(I)–Zn(I) bonding interaction.

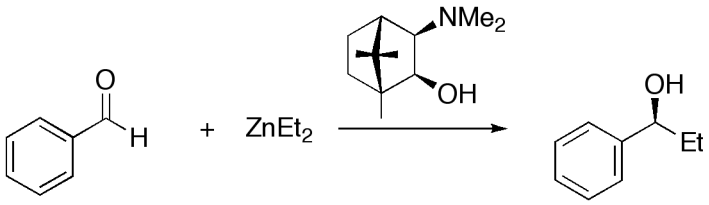
2.1.1.2. Reactivity of Organozinc Compounds

In general, organozinc compounds are not thermally sensitive or photosensitive, but they do react violently with water and are pyrophoric in air. Additionally, they readily form complexes with electron donating species, such as ethers, amines, and pyridines, due to their electron deficient character. Indeed, the design of even more complicated ligands for the preparation of such complexes is an active area of research, and is a major component of the original research presented in this thesis. Simple organozinc reagents have found application in a plethora of chemical reactions,[73] and several of their more important uses are briefly highlighted below. In particular, zinc compounds have played an important role in many carbon–carbon bond forming reactions.



Scheme 2.2. The Zn mediated Reformatsky reaction.

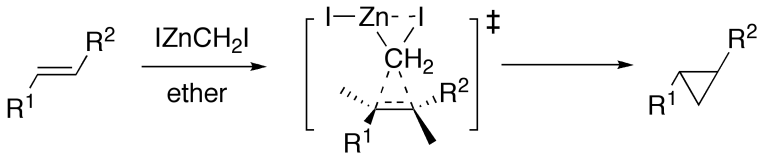
A classic C–C bond forming reaction involving Zn is the Reformatsky reaction, which was first described more than a century ago,[74] and several reviews have been published over the years.[75] In this reaction, an α-haloester and a carbonyl-containing compound combine in the presence of zinc metal to give a *β*-hydroxyester (Scheme 2.2). In practice, the reaction typically involves a single step, which combines both reagents together in ethereal solvent in the presence of a suspension of zinc. The first step of the reaction mechanism is oxidative addition of the α-haloester to zinc, giving the organozinc halide, which is known as the Reformatsky reagent. Addition of this reagent across the C=O bond of a ketone, followed by quenching with water, gives the *β*-hydroxyester product.



Scheme 2.3. Asymmetric addition of dimethylzinc to benzaldehyde.

Organozinc reagents have been particularly useful for asymmetric addition to aldehydes.[76,77] Due to the importance of this process, an abundance of examples are known, but these usually employ a stoichiometric amount of a simple dialkylzinc, such as diethylzinc, and a catalytic amount of a chiral ligand. For

example, the addition of diethylzinc to benzaldehyde, using a camphor-derived amino alcohol as catalyst, is shown in Scheme 2.3. A similar process has also been applied to the asymmetric addition to ketones[78] and imines.[79]

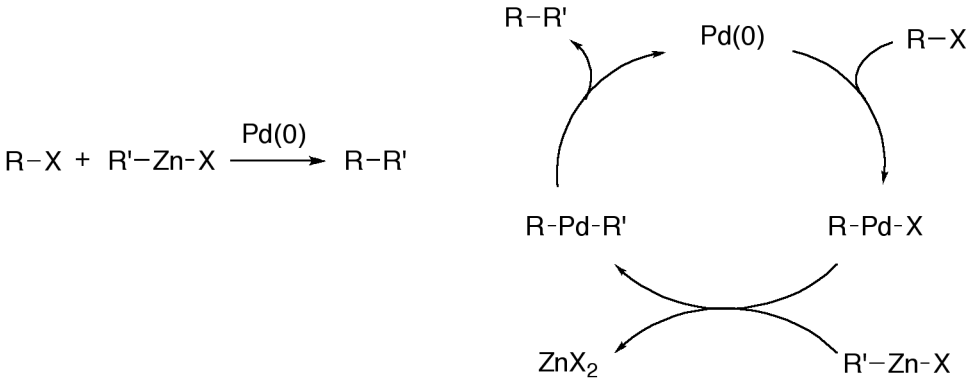


Scheme 2.4. A general Simmons-Smith reaction scheme.

It was discovered in 1929 that elemental zinc reacts with diiodomethane to give the unique organozinc halide compound $IZnCH_2I$.[80] However, it was not until 30 years later that the applicability of this compound for the stereoselective cyclopropanation of alkenes was discovered by Simmons and Smith.[81] The so-called Simmons-Smith reaction has seen extensive use, and the efficiency has been improved through the discovery of better methods for the *in situ* formation of $IZnCH_2I$.[82] The general cyclopropanation reaction may be seen in Scheme 2.4, including the proposed transition state, which accounts for the inherent stereoselectivity of the reaction.

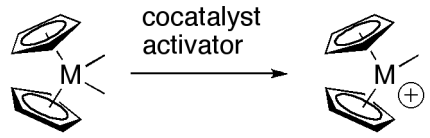
Perhaps the best-known C–C bond forming reaction in which zinc plays a central role is Negishi coupling,[83] the discoverer of which was awarded a share of the Nobel Prize for Chemistry in 2010. The process involves reaction of an organic halide with an organozinc halide in the presence of a Pd(0) catalyst and results in direct combination of both organic groups (Scheme 2.5). The mechanism involves oxidative addition of the organic halide to Pd(0), transmetalation between the Pd and Zn compounds, followed by reductive elimination of the resulting diorganopalladium species. The use of an organozinc compound in the reaction

provides superior yields, higher functional group tolerance, and improved selectivity relative to previous related methods employing Grignard reagents or organolithium compounds.



Scheme 2.5. The palladium-catalysed Negishi coupling.

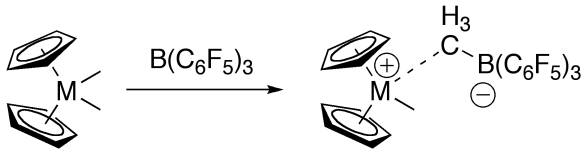
2.1.2. Activation Chemistry



Scheme 2.6. Activation of a metallocene to generate a cationic metal-alkyl species.

A major historical theme of organometallic chemistry over the last several decades has been the development of single-site olefin polymerization catalysts, with early-metal metallocenes being of particularly high importance.[13] In order to enhance the activity of these metallocene precatalysts, they are generally transformed into the "active" species through the addition of an appropriate cocatalyst, which renders the metallocene system cationic (Scheme 2.6). One of the earliest and most commonly employed cocatalysts to serve this purpose is methylaluminoxane (MAO). This cocatalyst is prepared by the controlled hydrolysis

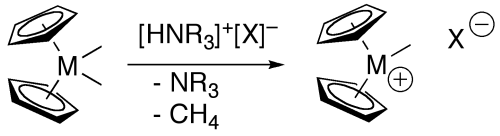
of trimethylaluminum and consists of –Al(R)–O– structural units.[22,84] It has been shown that MAO combined with metallocene dihalides results in excellent polymerization activity, although a large excess of MAO is typically required. Unfortunately, both the structure of MAO and the mechanism of activation are not well understood, but it has generally been accepted that MAO acts both as an alkylating agent and as a Lewis acid to generate catalytically active cationic species.[85]



Scheme 2.7. Alkide abstraction with a triarylborane activator.

Activation using triarylboranes represents a major step towards a well-understood and controlled activation process, and the highly Lewis acidic compound $B(C_6F_5)_3$ has been most important. Although first synthesized in 1963,[86] this borane was not exploited for activation of metallocenes until the early 90's.[87] As a cocatalyst, $B(C_6F_5)_3$ provided access to highly active systems, and also allowed for isolation and crystallographic characterization of the resulting well-defined cationic metallocene complexes. The activation occurs simply by transfer of an alkide group from the metallocene (or other organometallic complex) to the borane, generating a well-defined ion pair (Scheme 2.7). It has, however, been generally accepted that some contact exists between the ions, and that the resulting species may often be best regarded as a zwitterion. Since this breakthrough, borane activators have not been limited to early metal metallocenes, but have also been applied to catalyst

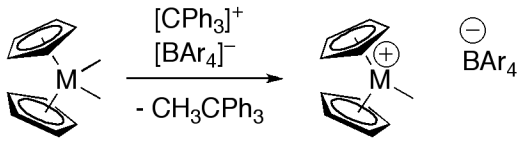
systems based on many other metals, including Ni,[88] Fe, Co,[89]and Zn,[90] to name just a few.



Scheme 2.8. Activation of a metallocene using a protic activator.

An alternative to borane abstraction is the installation of weakly coordinating anions through the use of Brønsted acids. Reaction of a metal-alkyl complex with a protic activator of the general formula $[HNR_3^+][X^-]$, where X^- is a weakly coordinating anion (WCA), results in removal of an alkide group by protonolysis and formation of an ion pair (Scheme 2.8). Traditional weakly coordinating anions, such as BF_4^- and PF_6^-, exhibit relatively low reactivity and nucleophilicity. However, these anions are susceptible to F^- abstraction by sufficiently electrophilic metals.[91] This led to the use of the more weakly coordinating BPh_4^-, which gave rise to longer lived catalysts.[92] However, such tetraarylborate counterions are also known to be prone to aryl abstraction by highly electrophilic metals. For this reason, the perfluoroarylborate analogue was eventually developed and was shown to be much less prone to these aryl transfers that ultimately result in catalyst death.[86b,93] In addition to the $B(C_6F_5)_4^-$ anion, the related tetraarylborate anion $B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-$ is similarly non-nucleophilic due to the presence of electron-withdrawing CF_3 groups. The sodium salt was first reported by Kobayashi in 1983,[94] and its popularity has grown in part due to its superior crystallization properties relative to the perfluoroarylborate analogue. Protonolysis of organometallic complexes using ammonium salts does have its

limitations, particularly in late-metal systems for which these salts are not sufficiently acidic. Additionally, the amine conjugate base may coordinate to the cationic metal centre and inhibit activity. For this reason, the oxonium acid $[H(OEt_2)_2^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$ was developed by Brookhart in 1992 and was shown to be sufficiently acidic to activate a cobalt system, due to its much higher Brønsted acidity.[95] Additionally, the analogous oxonium acid of the perfluoroarylborate anion was prepared and characterized by Jutzi in 2000,[96] and has since been commonly referred to as "Jutzi's acid".



Scheme 2.9. Activation of metallocenes using a trityl salt.

There are several alternatives to protonolysis for the generation of activated complexes supported by the aforementioned WCAs. The use of the trityl cation for alkide abstraction was first demonstrated by Chien and co-workers in 1991 using the perfluoroarylborate anion.[97] The synthesis of the trityl salt of $B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-$ followed shortly thereafter.[98] The highly Lewis acidic trityl cation causes abstraction of the alkyl group in a manner akin to borane activators, but the process is irreversible, thereby generating a solvent-separated ion pair (Scheme 2.9).

The development of new activators is an ongoing area of research, and this work has resulted in a variety of novel cocatalyst salts which vary both in the nature of the cation and the WCA. Unique cationic components have included Ag^+,[99] which can remove a halide by salt metathesis, and Cp_2Fe^+,[100] which has been shown

capable of generating cationic metal complexes *via* a redox process.[101] Novel WCAs include a diborate anion introduced by Bochmann,[102] which displayed excellent crystallization properties, and $B(C_6F_4\text{-}CF_3)_4$ reported by Herrmann et al.,[103] which is purported to be even less nucleophilic than $B(C_6F_5)_4$, as well as a variety of other examples.[104]

2.1.3. Phosphinimine Chemistry

Phosphinimine ligands have seen growing use in recent years, and there are many examples of complexes of a diverse range of metals.[105] These have included early[106] and late[107] transition metals, rare-earth metals,[108] main group metals,[109] and a variety of examples of zinc in particular.[110] The many applications of these complexes have included olefin polymerization,[106a] ring-opening polymerization of lactide,[108a–b, 110e] hydroamination,[108d] and stabilization of unusual metal–main-group multiple bonds.[111] The phosphinimine functional group can be elegantly prepared by reaction of the requisite phosphine with an aryl or alkyl azide in what is known as a Staudinger reaction.[112] This reaction is facile, does not generally suffer from unwanted side-reactions, and the only by-product is N_2 gas. The electronic properties of phosphinimine donors have been closely compared with the more extensively studied imine functionality, and this relationship has been carefully examined computationally by Budzelaar et al.[113] It was concluded in this study that these two systems are comparable in terms of their σ-donation strength, but that phosphinimines are much poorer π acceptors. However, in studies of phosphinimine

complexes of zinc, π–back-bonding is not likely to be a considerable factor due to the filled d-shell of Zn(II).[114]

2.1.4. Ligand Design and Approach to Complex Synthesis

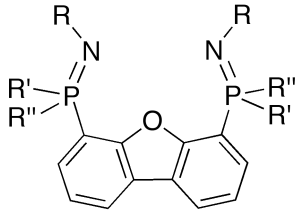
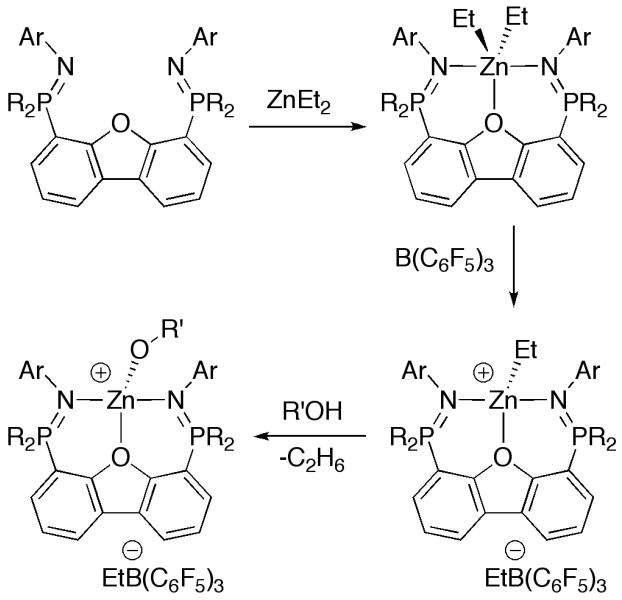


Figure 2.4. General structure of a bis(phosphinimine) pincer ligand.

An important consideration, when attempting to prepare stable cationic species, is the design of an appropriate ancillary ligand. The targeted ligand in the present work is based on a dibenzofuran (dbf) backbone (Figure 2.4). The dbf moiety should impart a high level of rigidity, which will allow greater control over the environment surrounding the bound metal centre. Also, the dbf oxygen can potentially coordinate to the metal, providing an additional degree of electronic stabilization. Another important consideration is the high resistance of this moiety to deprotonation, which will ensure that the ligand remains formally neutral even in the presence of a highly electrophilic metal centre. Installation of phosphinimine groups at the 4 and 6 positions then gives a potentially tridentate neutral pincer architecture. In addition to strong σ-donation, phosphinimine groups were chosen because they are highly modular, chemically robust, and the presence of ^{31}P (I = ½) expedites the study and identification of complexes by NMR spectroscopy.



Scheme 2.10. Proposed synthesis of cationic zinc alkoxides of a bis(phosphinimine) pincer ligand.

Initially it was expected that cationic complexes could be prepared by the route shown in Scheme 2.10, which begins with the synthesis of a neutral dialkylzinc complex. A cationic alkylzinc complex can presumably then be prepared by abstraction of an ethyl group using the borane activator $B(C_6F_5)_3$, or by protonolysis with a suitable Brønsted acid. It was expected that a cationic zinc alkoxide species could then be obtained by reaction with a simple alcohol. The current chapter details early progress toward this goal and some interesting discoveries that have been made along the way.

2.2. Synthesis and Characterization of Monophosphinimine Ligands

Upon initiation of this project, it was quickly determined that installation of only a single phosphinimine group on dbf can be performed much more readily, due

to the inherently low acidity of dibenzofuran. Furthermore, the monophosphinimine system is significantly simpler in structure, which has facilitated the study of the fundamental properties of the neutral ligand framework in initial scoping studies. Therefore, this chapter discusses the preparation and use of ancillary ligands containing only one phosphinimine donor group (**L_1**).

The ligand was easily synthesized by reaction of the monophosphine precursor, prepared according to a modified literature procedure, with an appropriate aryl azide under standard Staudinger conditions. Preparation of **L_1^{Dipp}** was achieved in this way using 2,6-di*iso*propylphenylazide, affording the ligand as an analytically pure, thermally stable white powder in 79% yield. **L_1^{Dipp}** gives rise to a single resonance at δ –13.4 in the $^{31}P\{^1H\}$ NMR spectrum (benzene-d_6), and overall C_s symmetry is observed in solution. The *iso*propyl groups are chemically equivalent on the NMR timescale, as evidenced by a single *iso*propyl methyl resonance at δ 1.06 and δ 24.4 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. **L_1^{Mes}** was similarly prepared by reaction of the precursor monophosphine with 2,4,6-trimethylphenylazide. This afforded the ligand in 69% yield, giving a material with equally high purity and stability. The diagnostic $^{31}P\{^1H\}$ NMR resonance appears at δ –15.3, which is upfield of the corresponding **L_1^{Dipp}** resonance by ~2 ppm. While the aromatic region of the ^1H NMR spectrum is complicated, the mesityl groups provide excellent spectroscopic handles, with singlets appearing at δ 2.30 and 2.21 for the *para*- and *ortho*-CH_3 groups, respectively.

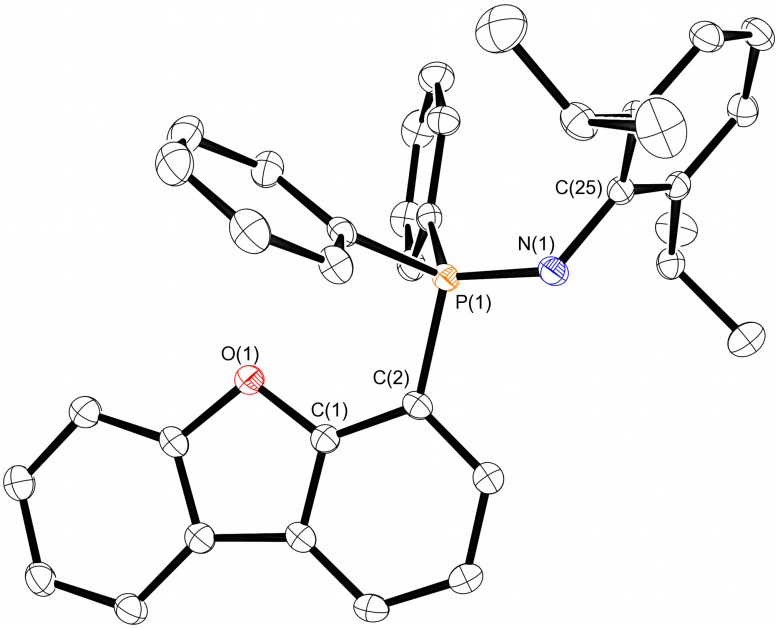


Figure 2.5. Displacement ellipsoid plot (30% probability) of $\mathbf{L_1^{Dipp}}$. Hydrogen atoms have been omitted for clarity.

X-ray quality single crystals of $\mathbf{L_1^{Dipp}}$ were readily obtained and its molecular structure was determined crystallographically (Figure 2). The ligand binding geometry can be roughly defined by measurement of two torsion angles, which measure the rotation about the P(1)–C(2) and P(1)–N(1) bonds. An ideal 6-membered chelate ring would have C(1)–C(2)–P(1)–N(1) and C(2)–P(1)–N(1)–C(25) torsion angles of 0° and 180°, respectively. The solid-state structure of the free ligand, however, exhibits corresponding torsion angles of 168.0(2)° and 155.7(2)°. The significant rotation about the C(2)–P(1) bond is likely a result of steric interactions between the dbf backbone and the bulky Dipp group of the phosphinimine functionality.

2.3. Reaction with Diethylzinc

Our initial motivation for preparing these ligands was to generate cationic heteroleptic zinc complexes by the route described in Scheme 2.10. To that end, the preparation of the neutral diethylzinc complex was attempted, which would then be converted to the cationic ethylzinc complex via alkide abstraction. However, reaction of $\mathbf{L_1^{Dipp}}$ with diethylzinc did not give the anticipated result, but rather it was discovered that exposure of the ligand to a single equivalent of diethylzinc in C_6D_6 solution caused little change in the observed NMR spectroscopic features of the ligand. Specifically, only a slight change in the $^{31}P\{^1H\}$ NMR resonance (δ 12.6) was observed, representing a shift of only 0.8 ppm relative to the free ligand. This small change does not suggest a tightly bound complex because the $^{31}P\{^1H\}$ NMR chemical shifts of phosphinimine moieties are well established to be much more sensitive to the presence of a metal centre. For example, a recent report by Mehrkhodavandi et al. examined a phosphinimine-imine ligand, which resonated at δ 0.9, and upon complexation of $ZnCl_2$ the resonance shifted to δ 29.9.[110b] It is thus not surprising that attempts to isolate a complex of $ZnEt_2$ in the present study resulted in loss of diethylzinc upon removal of the solvent *in vacuo*, giving only the free ligand after prolonged exposure to vacuum.

Exposure of $\mathbf{L_1^{Mes}}$ to diethylzinc in C_6D_6 caused a more perceptible change, resulting in a $^{31}P\{^1H\}$ NMR resonance at δ –8.7 when three equivalents of diethylzinc were used, which is 6.6 ppm downfield of the free ligand. However, this change is still much smaller than expected for a tightly bound complex, and attempts to isolate

a complex again resulted in regeneration of the free ligand. Furthermore, despite the fact that 3 equivalents of $ZnEt_2$ were employed, only one unique set of resonances for the ethyl groups was observed in the ^1H NMR spectrum (δ 1.19 and 0.14 for the CH_3 and CH_2 protons, respectively). This suggests an exchange process that is rapid on the NMR timescale due to labile metal-ligand bonding.

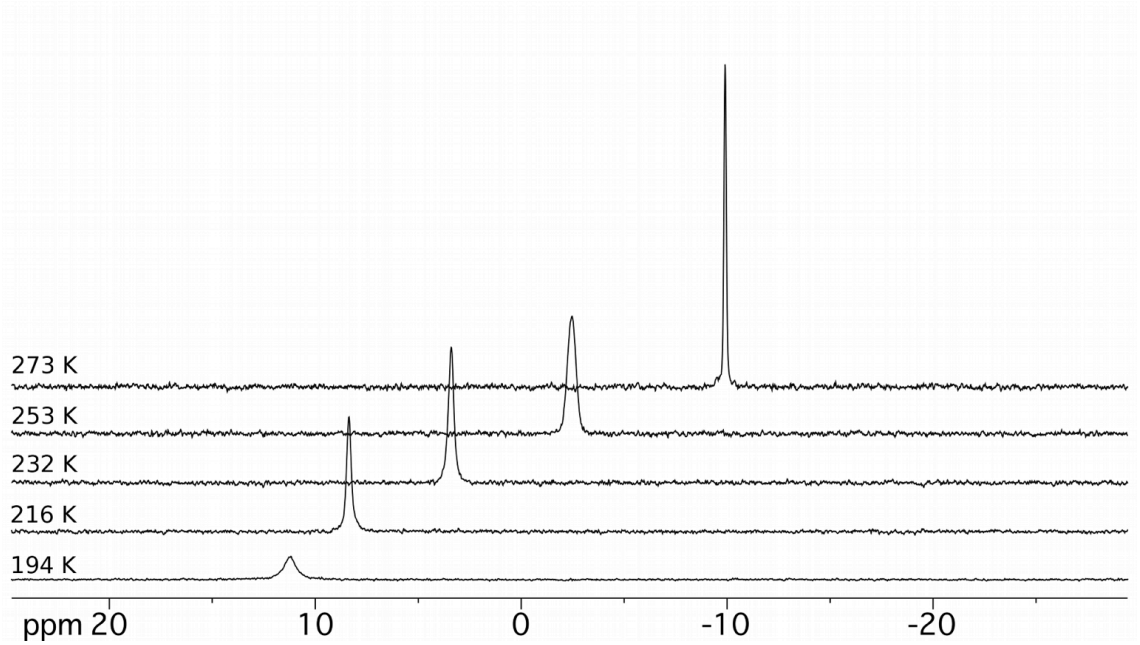


Figure 2.6. VT $^{31}P\{^1H\}$ NMR spectra of $\mathbf{L_1^{Mes}}$ and 3 equivalents of $ZnEt_2$ combined in C_6D_6 solvent.

Variable temperature (VT) NMR studies (toluene-d_8) were performed in an attempt to garner more information about the metal-ligand interaction (Figure 2.6). It was found that the chemical shift of the ^{31}P NMR signal is highly dependent on temperature, with more downfield chemical shifts observed at lower temperatures. At 194 K, the resonance appears at δ 11.2, which is 26.5 ppm downfield of the free ligand. This observation confirms that the system exists in equilibrium between the metal complex and the free starting materials. The fact that free $ZnEt_2$ and $\mathbf{L_1^{Dipp}}$ are greatly favoured at ambient temperature suggest very weak metal–ligand binding.

2.4. Reaction with Electron Deficient Zinc Species

2.4.1. Complexes of $ZnCl_2$

Due to the inability to make neutral dialkylzinc complexes, the preparation of zinc complexes using much more electron deficient zinc precursors was pursued. Despite the poor solubility of $ZnCl_2$, all reactions and solution NMR studies were performed in non-coordinating solvents (toluene, CD_2Cl_2) due to the likelihood of coordinating solvent efficiently competing with the ligand for complexation of zinc. Reaction of $\mathbf{L_1^{Dipp}}$ with $ZnCl_2$ required harsh conditions due to the poor solubility of $ZnCl_2$ in toluene solvent, but at 120 °C, slow and irreversible conversion to a new species was observed. After 48 hours, compound **1** was isolated as an analytically pure white powder in 65% yield. The complex exhibits a single peak in the $^{31}P\{^1H\}$ NMR spectrum at δ 30.5 ppm (CD_2Cl_2), which is indicative of tight binding of the ligand. Additionally, it was observed in the ^1H NMR spectrum that the *iso*propyl methyl groups become inequivalent, giving rise to doublets at δ 1.21 and 0.23. The complex is only sparingly soluble in aromatic solvents, and as a result some of the product crystallized on the walls of the reaction vessel during the course of the reaction. From this material, high quality single crystals were obtained, and the molecular structure of **1** was determined crystallographically. The structure is depicted in Figure 2.7, while selected metrical parameters may be found in Table 2.1. The molecular structure revealed that **1** is monomeric, with binding of the zinc centre to the ligand in a bidentate manner. The bond length between the phosphinimine nitrogen and zinc is in the expected range [Zn(1)–N(1) = 1.960(1)

Å], while the distance between zinc and the dbf oxygen donor is significantly longer [Zn(1)–O(1) = 2.381(1) Å], suggesting a much weaker interaction. Furthermore, examination of the bond angles leads to the conclusion that the coordination geometry at zinc is best described as distorted trigonal pyramidal. The nitrogen and chloride atoms occupy the equatorial sites with all bond angles close to 120°, and the sum of these angles about zinc is 356.63(5)°. Interestingly, the zinc centre lies significantly out of the plane of the dibenzofuran backbone (~1.67 Å).

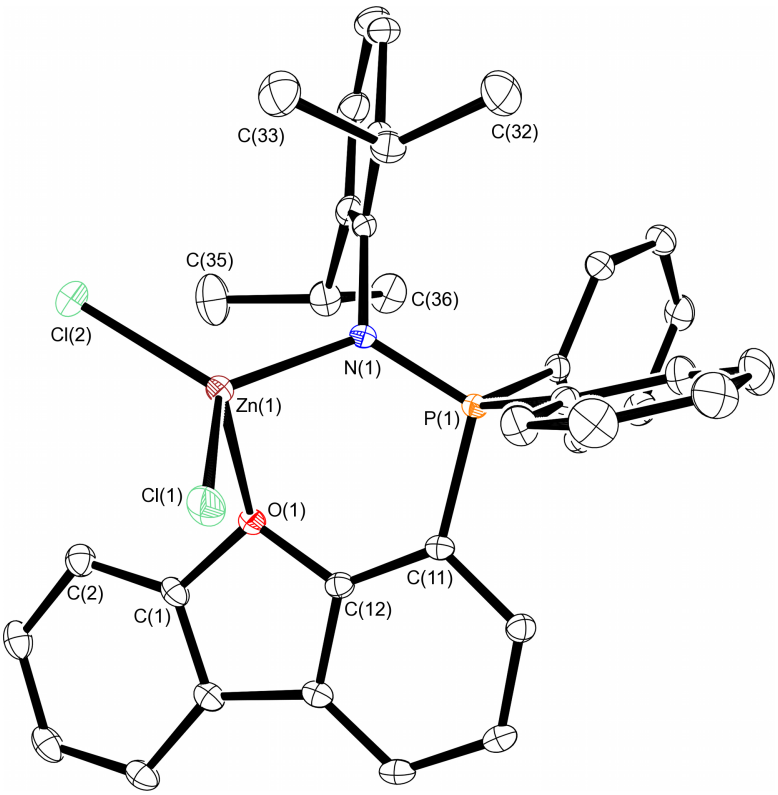


Figure 2.7. Displacement ellipsoid plot (30% probability) of compound **1**. Hydrogen atoms have been omitted for clarity.

$\mathbf{L_1^{Mes}}ZnCl_2$, **2**, was prepared under similar reaction conditions as **1**, giving an analytically pure white powder in approximately 89% yield. This complex is dramatically less soluble than **1** in common organic solvents, and consequently only

^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were obtained. A single resonance is noted in the $^{31}P\{^{1}H\}$ NMR spectrum at 28.0 ppm, while diagnostic mesityl peaks appear at δ 2.01 (*o*-CH_3) and δ 1.87 (*p*-CH_3). Elemental analysis indicated the same stoichiometry of one ligand per unit of $ZnCl_2$. However, the limited solubility of the compound implied some degree of aggregation.

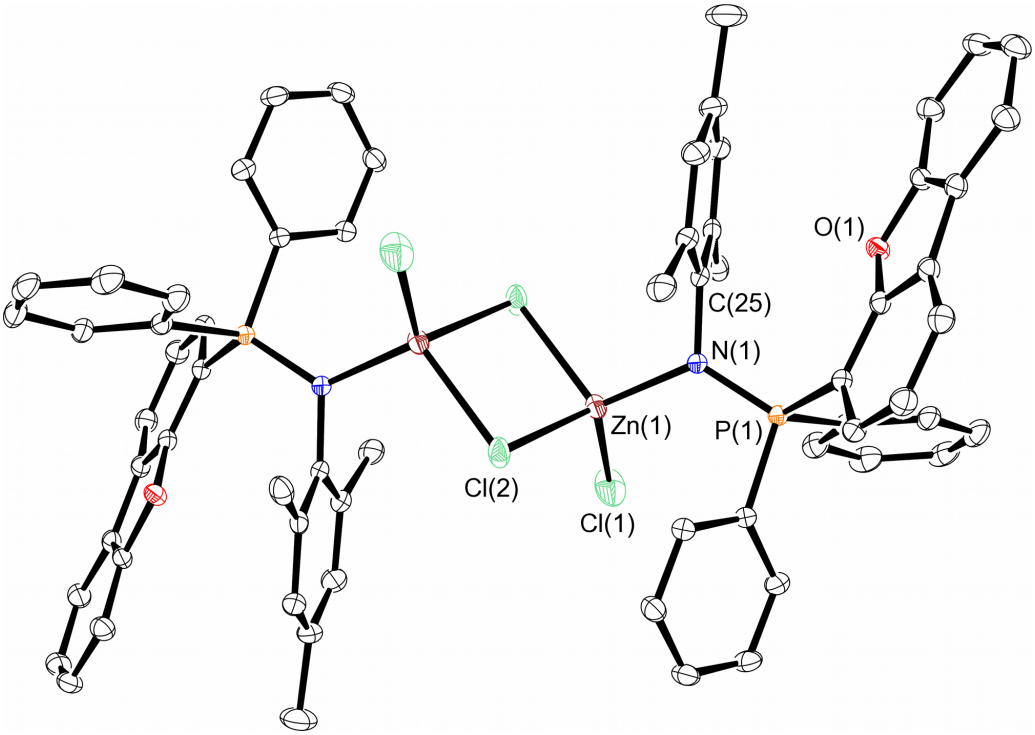


Figure 2.8. Displacement ellipsoid plot (30% probability) of compound **2**. Hydrogen atoms and a molecule of toluene have been omitted for clarity.

From material that had crystallized during the course of the reaction, a suitable single crystal of **2**·C_7H_8 was obtained and the X-ray crystal structure was determined (Figure 2.8, Table 2.1). The structure confirmed that aggregation does indeed occur, with the complex existing as a dimer in the solid state. The ligand does not adopt an orientation suitable for bidentate coordination, and no interaction was noted between the zinc centre and the dbf oxygen atom. Instead, the available

coordination site is occupied by a bridging chloride Cl(2), giving rise to the observed dimeric structure. The two bridging chlorides are virtually equidistant between the zinc atoms with a bond length of 2.34 Å and Zn(1)–Cl(2)–Zn(1b) angles approaching 90°. The terminal Zn–Cl distance is significantly shorter at 2.2048(8) Å, while the Zn–N bond is in the expected range (1.994(2) Å). In this case, the geometry is best described as four-coordinate tetrahedral.

The reason for the large difference in structure between complexes **1** and **2** is likely due primarily to steric effects. In the less crowded **2**, dimerization is favoured over the weak Zn–O bonding interaction. Conversely, the bulky *iso*propyl groups of complex **1** inhibit this dimerization, forcing the zinc centre to interact with the dbf oxygen instead.

Table 2.1. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Atoms	**1**	**2**
Zn(1)–N(1)	1.960(1)	1.994(2)
Zn(1)–O(1)	2.381(1)	N/A
Zn(1)–Cl(1)	2.2003(3)	2.2048(8)
Zn(1)–Cl(2)	2.1713(4)	2.3437(9), 2.3450(9)
P(1)–N(1)	1.609(1)	1.609(2)
N(1)–Zn(1)–Cl(1)	120.87(3)	115.86(7)
N(1)–Zn(1)–Cl(2)	118.95(3)	107.47(7), 115.41(7)
Cl(1)–Zn(1)–Cl(2)	116.81(2)	112.18(4), 112.42(4)
Cl(1)–Zn(1)–O(1)	98.59(3)	N/A
P(1)–N(1)–Zn(1)	125.05(6)	124.4(1)
Zn(1)–Cl(2)–Zn(1b)	N/A	89.37(3)

2.4.2. Complexes of $Zn(C_6F_5)_2$

Complexes of $Zn(C_6F_5)_2$ were much more straightforward to prepare than complexes **1** and **2** due to the high solubility of $Zn(C_6F_5)_2$ in toluene, and complexation occurred immediately upon mixing the reagents together in toluene solution. Reaction of $\mathbf{L_1^{Dipp}}$ with $Zn(C_6F_5)_2$ gave **3** as an analytically pure pale yellow crystalline material in 81% yield, while the corresponding reaction of $\mathbf{L_1^{Mes}}$ afforded **4** in similar form and 88% yield. Each complex exhibits a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, with chemical shifts approximately 2 ppm upfield of the corresponding $ZnCl_2$ complex. (**3**: δ 28.5; **4**: δ 25.7). The ^1H NMR spectra are also very similar to those observed for complexes **1** and **2**. For complex **3**, the *iso*propyl methyl resonances appear at δ 1.11 and 0.38, while the corresponding methine signal does not differ significantly from the free ligand (δ 3.84). The *p*-CH_3 ^1H NMR signal of complex **4** is observed at δ 1.87. Both complexes are highly soluble in aromatic solvents, suggesting no significant aggregation. Single crystals of both **3**·$1.5C_7H_8$ and **4**·C_5H_{12} suitable for X-ray diffraction were grown from toluene/pentane solutions at –35 °C. The molecular structures are depicted in Figure 2.9 and Figure 2.10 for **3** and **4**, respectively, and selected metrical parameters for both are located in Table 2.2.

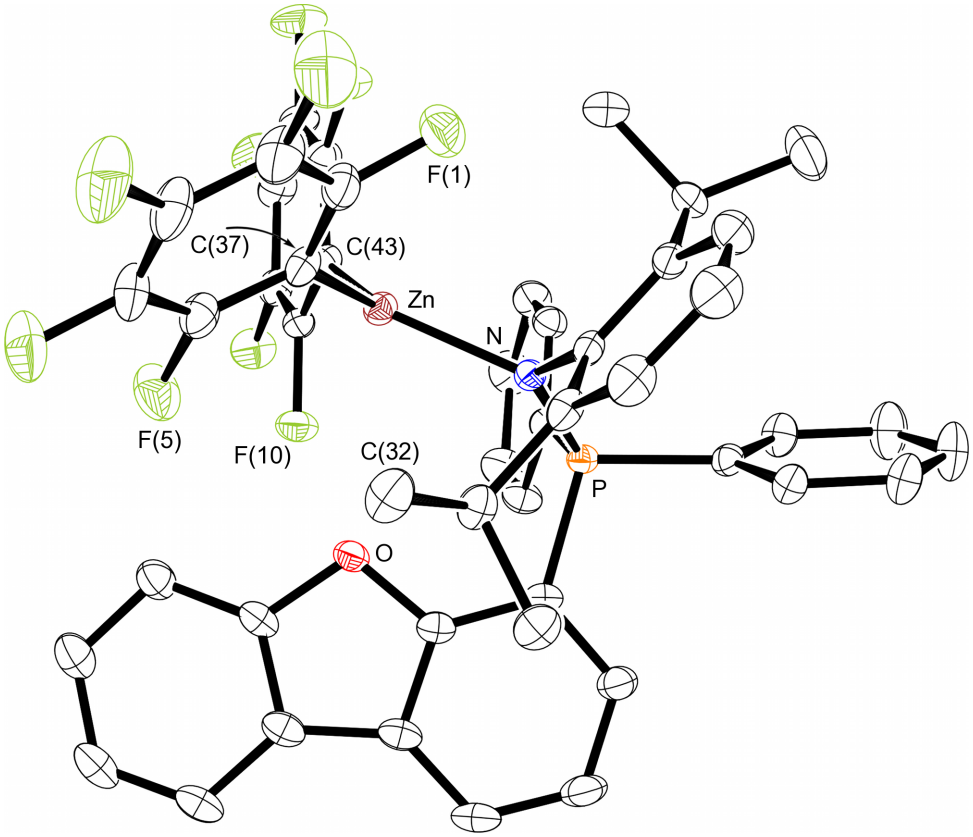


Figure 2.9. Displacement ellipsoid plot (30% probability) of compound **3**. Hydrogen atoms and a molecule of toluene have been omitted for clarity.

The molecular structure of complex **3** revealed monodentate coordination of the ligand, with no significant bonding interaction between zinc and the dbf oxygen (the two atoms are separated by a distance which is greater than 2.91 Å, the sum of their Van der Waals radii; Zn(1)–O(1) = 3.144(2) Å).[115] It is likely that the high steric demands of the C_6F_5 disfavour the κ^2 binding mode, and consequently the coordination geometry is trigonal planar and the metal is coordinatively unsaturated. The P–N distance is in the expected range [P(1)–N(1) = 1.614(2) Å],[116] as are the Zn–C bonds of the pentafluorophenyl substituents [Zn(1)–C(37) =

2.014(2)Å; Zn(1)–C(43) = 2.012(2) Å]. The bond angles about the zinc centre do not deviate significantly from 120°, and the sum of these angles is 358.9(1)°.

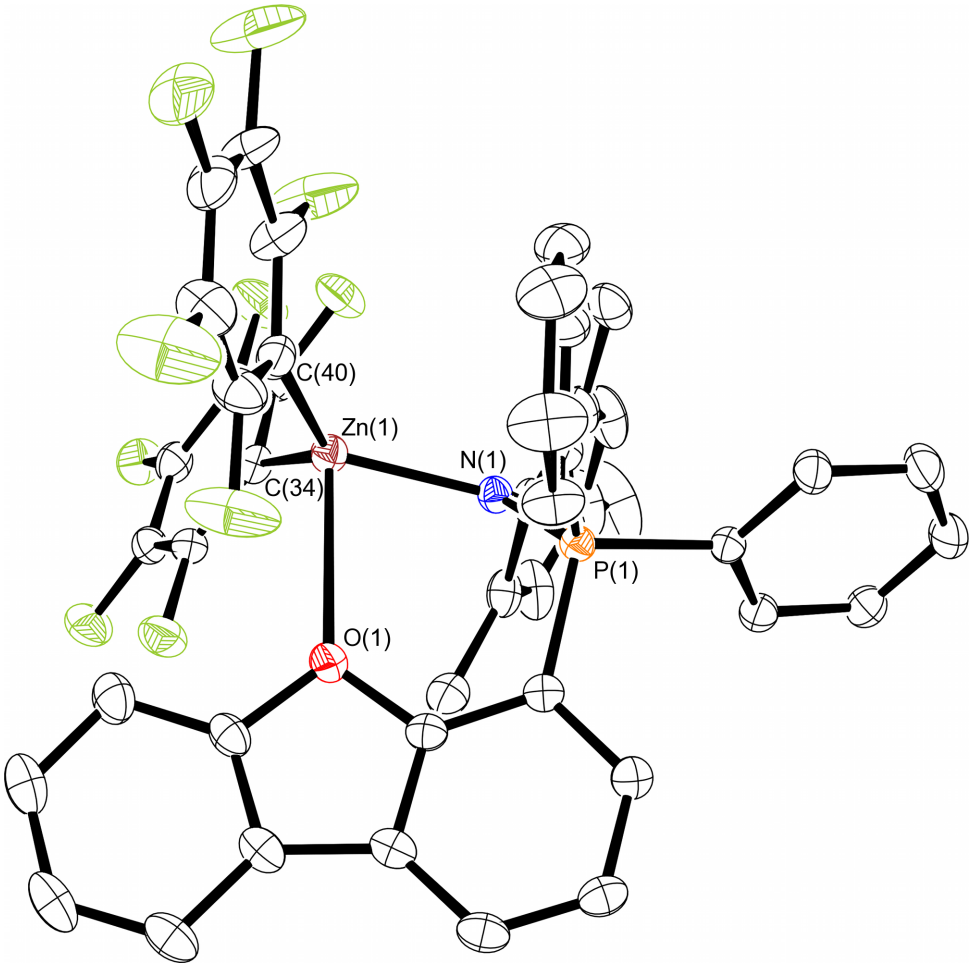


Figure 2.10. Displacement ellipsoid plot (30% probability) of compound **4**. Hydrogen atoms and a molecule of pentane have been omitted for clarity.

Complex **4** is essentially isostructural with **3**, with one notable exception being a significantly shorter Zn–O interaction [2.669(2) Å]. This is presumably due to the reduced steric bulk of the ligand, which allows a more suitable orientation for bidentate coordination. However, the steric demands of the system remain high, thereby preventing a close interaction. Nevertheless, there is significantly more deviation from trigonal planar geometry in this complex compared with **4**. In

particular, the sum of angles about the zinc atom is reduced to 355.8(2)°, while the zinc centre lies 0.24 Å out of the plane defined by these atoms (*cf.* 0.12 Å in **4** and 0.22 Å in **1**).

Table 2.2. Selected bond lengths (Å) and angles (°) for compounds **3** and **4**.

Atoms	**3**	**4**
Zn–N	2.016(2)	2.006(2)
Zn–O	3.144(2)	2.669(2)
Zn–C(x)[a]	2.014(2)	2.014(2)
Zn–C(y)[a]	2.012(2)	2.010(3)
P–N	1.614(2)	1.603(2)
P–N–Zn	125.6(1)	122.1(1)
N–Zn–C(x)[a]	113.22(8)	108.33(9)
N–Zn–C(y)[a]	123.53(8)	119.94(9)
C(x)–Zn–C(y)[a]	122.18(9)	127.5(1)
N–Zn–O	74.39(6)	81.08(7)

[a]**3**: x = 37, y = 43; **4**: x = 34, y = 40.

While these complexes represent interesting fundamental findings, they are charge neutral and thus not the direct target of the research project. Additionally, they are not useful catalysts for lactide polymerization due to the absence of a suitable initiating group. Attempts to functionalize complexes **1**–**4** have met with little success. In particular, attempted salt metathesis reactions of the $ZnCl_2$ complexes with alkali metal amide or alkoxide salts appeared to result in aggregation of the zinc species with concomitant loss of the free ligand. While the C_6F_5 groups of **3** and **4** are not particularly amenable to derivatization, attempts were made to remove a C_6F_5 group using the Brønsted acid activator

$[HNMe_2Ph^+][B(C_6F_5)_4^-]$, but this was also unsuccessful. Further work thus focused on exploring alternate strategies for the preparation of cationic alkylzinc complexes.

2.5. Cationic Zinc Complexes

2.5.1. Ligand Protonation

Bochmann et al. have previously reported the synthesis of cationic zinc complexes prepared from a protonated diazadiene ligand.[117,118] The work described herein utilizes a similar methodology, which, to the best of the author's knowledge, represents only the second example of such a synthetic route. Isolation of the protonated ligand prior to complexation is advantageous because diethylzinc does not bind tightly to the ligand to form the requisite neutral complex. Thus, a one-pot reaction between L, $ZnEt_2$ and a Brønsted acid activator does not afford the desired cationic species as cleanly as the stepwise procedure described herein. In addition, the one-pot reaction of the neutral ligand with EtZnCl and $K[B(C_6F_5)_4]$ does not generate cationic zinc species as a salt metathesis product.

It was found that reaction of $\mathbf{L_1^{Dipp}}$ with the Brønsted acid activator $[HNMe_2Ph^+][B(C_6F_5)_4^-]$ gives rise to complete transfer of the acidic proton to the phosphinimine N of the ligand, resulting in the protonated species $[\mathbf{L_1^{Dipp}}H^+][B(C_6F_5)_4^-]$, **5a**. Alternatively, the ligand can be protonated with triflic acid to install the more strongly coordinating triflate anion, giving $[\mathbf{L_1^{Dipp}}H^+][SO_3CF_3^-]$, **5b**. Both compounds were isolated as analytically pure, thermally stable white solids in excellent yield (97% and 85%, respectively). The conjugate base by-

product can either be removed, as in the case of **5a**, or is itself a weakly coordinating anion, as happens with **5b**.

Compound **5a** exhibits a $^{31}P\{^{1}H\}$ NMR resonance at δ 36.1 in a 1:1 benzene-d_6/bromobenzene-d_5 solvent mixture, which is shifted 49.4 ppm downfield relative to the neutral ligand. The acidic proton appears as a doublet at δ 4.96 in the ^{1}H NMR spectrum, with $^{2}J_{PH}$ = 9.3 Hz. This coupling constant is similar in magnitude to that reported for related aminophosphonium salts, and is thus indicative of a two-bond separation between the proton and phosphorus atoms.[119] The molecule retains C_s symmetry in solution, as evidenced by a single *iso*propyl methyl doublet at δ 0.56 in the ^{1}H NMR spectrum. The borate anion exhibits the expected ^{19}F NMR spectrum, with *ortho*, *para*, and *meta* fluorine environments resonating at δ –131.6, –162.4, and –166.2, respectively. These resonances do not differ significantly from those of the anilinium precursor and are consistent with a weakly coordinating anion.[120] Coordination of the anion would necessarily give rise to a distinct set of C_6F_5 resonances from the coordinated aryl group. While weak and transient Zn···F interactions cannot be completely ruled out, the system is still best regarded as a solvent-separated ion pair. Similar spectroscopic signatures were observed for triflate derivative **5b**, which gives rise to a single $^{31}P\{^{1}H\}$ NMR resonance at δ 33.5 (a 46.9 ppm downfield shift relative to the neutral ligand). Likewise, **5b** also retains C_s symmetry in solution.

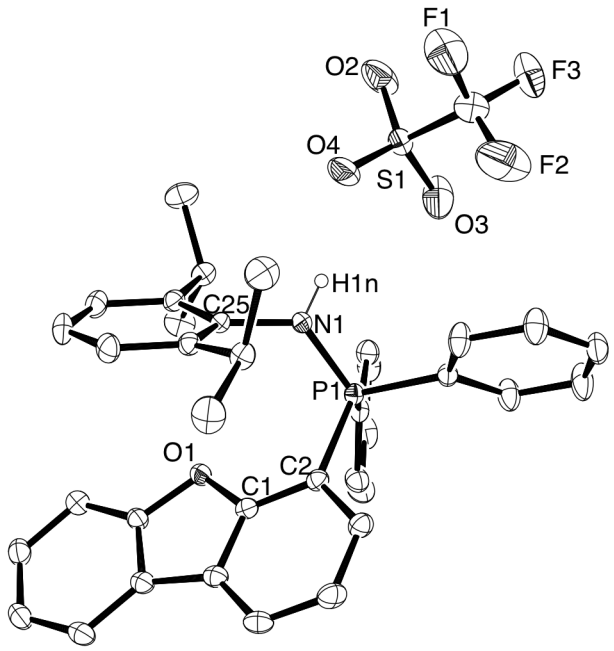


Figure 2.11. Displacement ellipsoid plot (30% probability) of compound **5b**. All hydrogen atoms except H1n, disordered atomic positions, and a molecule of benzene have been omitted for clarity.

In an effort to unambiguously locate the acidic proton, the solid-state structure of **5b** was determined (Figure 2.11). It was located on the electron density map [H(1n)] and refined freely. A significant hydrogen-bonding interaction between the triflate anion and H1n is noted [N(1)–O(4) = 2.789(2) Å]. Further evidence for the protonation of the phosphinimine nitrogen is provided by a P–N bond [P(1)–N(1) = 1.633(2) Å] elongation of 0.07 Å relative to that observed in the neutral structure. The torsion angles about the C–P [C(1)–C(2)–P(1)–N(1) = 64.9(2)°] and P–N bonds [C(2)–P(1)–N(1)–C(25) = –34.6(2)°] are both distorted from ideal chelate geometry. However, unlike the neutral analogue, the major distortion is rotation about the P–N bond, which is presumably due to the cation-anion hydrogen-bonding interaction.

2.5.2. Zinc Complexation

Reaction of **5a** or **5b** with diethylzinc occurs *via* an alkane elimination pathway with loss of ethane and concomitant generation of complexes [$\mathbf{L_1^{Dipp}}$ZnEt$^+$][B(C_6F_5)$_4^-$], **6a**, and $\mathbf{L_1^{Dipp}}$ZnEt(OSO_2CF_3), **6b**, respectively. The formation of ethane was corroborated by observation of effervescence and a resonance at δ 0.80 in the ^{1}H NMR spectra of both complexes when reaction progress was observed *in situ*. Complexes **6a** and **6b** were isolated as thermally stable white solids in good yield (87% and 83%, respectively) and were established to be indefinitely stable if stored under an inert atmosphere. Similar to **5a** and **5b**, complexes **6a** and **6b** exhibit downfield ^{31}P{^{1}H} NMR signals of δ 30.1 and 26.9, respectively, in 1:1 benzene-d_6/bromobenzene-d_5 solvent, indicative of tight phosphinimine binding to the zinc centre. Both complexes exhibit the anticipated methyl (**6a**, δ 1.00; **6b**, δ 1.36) and methylene (**6a**, δ 0.73; **6b**, δ 0.80) ^{1}H NMR resonances, which integrate as 3H and 2H, respectively, and are thus consistent with the presence of a single ethyl group. The ^{19}F NMR spectrum of **6a** changes very little compared with the protonated precursor (δ –131.6, –162.4, –166.2). Specifically, the ^{19}F NMR spectrum of **6a** is consistent with a weakly coordinating B(C_6F_5)$_4^-$ anion with no indication of fluorine or C_6F_5 transfer to the metal centre, even after prolonged periods in solution at elevated temperature (100 °C, 24 hours). Likewise, no evidence was observed for close Zn–F contacts in solution. Based on these observations, complex **6a** is best regarded as a solvent-separated ion pair in solution.

Although repeated attempts to grow X-ray quality crystals of **6a** were unsuccessful, the molecular structure of **6b** has been crystallographically established (Figure 2.12). Unsurprisingly, the crystal data revealed that the less weakly coordinating triflate anion is bound to the zinc centre. A high degree of disorder exists in the structure, necessitating the modelling of the zinc atom, the ethyl group, and the dbf portion of the ligand together as a 2:1 disorder over two sites. This disorder appears to result from interplay between the steric interaction of the ethyl group and ligand versus binding strength of the zinc centre and the oxygen atom of the dbf framework. The major component of the disorder has a geometry in which the ethyl group is rotated away from the Dipp group, resulting in a long Zn–O interaction [Zn–O(1) = 2.60(1) Å]. In the less abundant component, the ethyl group is rotated toward the Dipp group in a sterically less favoured position, but the Zn–O bond distance is substantially shorter [Znb–O(1b) = 2.08(2) Å]. Interestingly, there is a widening of the N–Zn–C_{ethyl} bond angle in the minor component [N(1)–Zn–C(37) = 131.6(2)°; N(1)–Znb–C(37b) = 138.8(5)°], rather than the opposite effect which would be expected from stronger coordination of the oxygen atom. This can be attributed to the enhanced steric repulsion between the ethyl and Dipp groups. These observations suggest that while the Zn–O interaction is not as strong as the Zn–N bonding, it is likely to play a key role in the chemistry of the system. For both components, torsion angles about the C–P [N(1)–P(1)–C(2)–C(1) = 20(2)°, 21(3)°] and P–N bonds [C(2)–P(1)–N(1)–C(25) = –156.1(6)°, –154(1)°] are close to ideal.

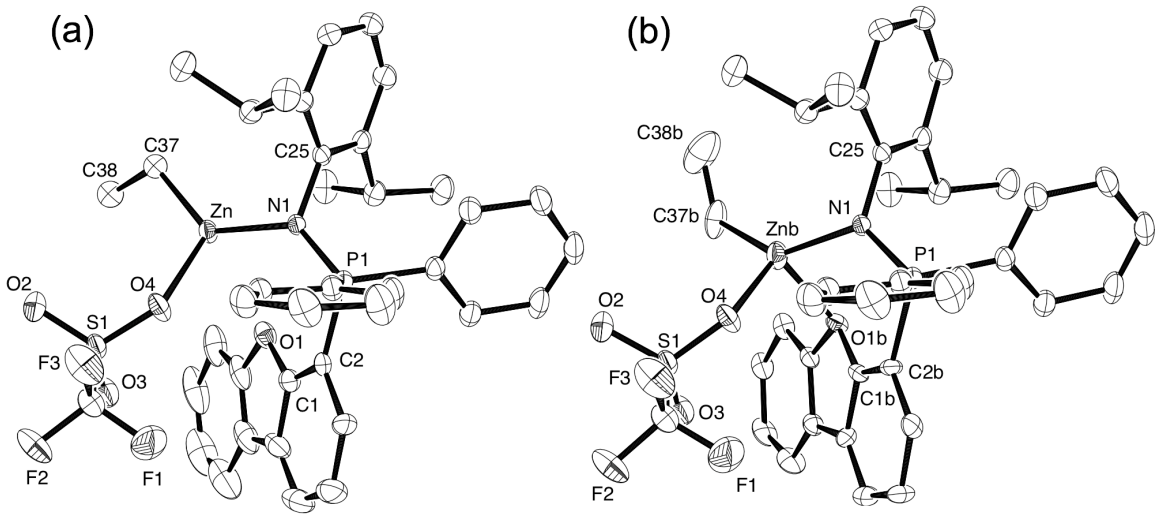


Figure 2.12. Displacement ellipsoid plot (30% probability) of complex **6b**, where (a) is the major component and (b) is the minor component of a disorder. Atoms that are not disordered are shown in the images of both components, including the entire phosphinimine subunit and the coordinated triflate anion. Hydrogen atoms are omitted for clarity.

Although the solid-state structure of **6b** indicates that the triflate anion is coordinated to zinc [Zn–O(4) = 2.069(4) Å], it is anticipated that it should be highly susceptible to displacement,[121] a phenomenon that has been successful for generating cationic supramolecular materials of late transition metals.[122] Thus, while the complex cannot be considered an ion pair, it can accurately be described as "activated".

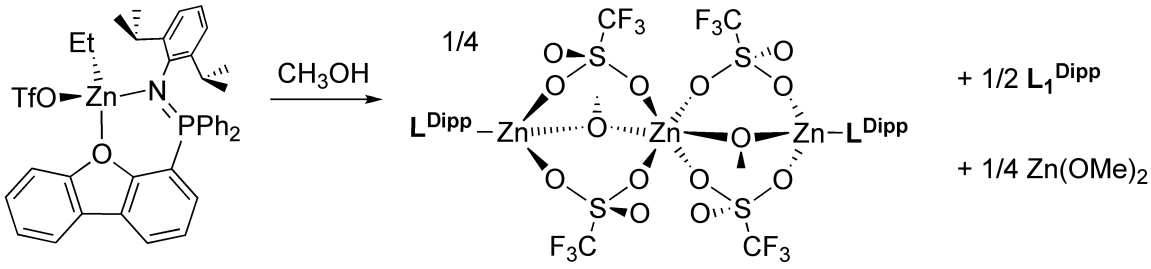
2.5.3. Polymerization of L-Lactide

Preliminary investigations of the reactivity of **6a** and **6b** towards the catalytic ring-opening polymerization of L-lactide have been undertaken. Polymerization experiments were performed on an NMR scale in 1:1 C_6D_6/C_6D_5Br

solvent and conversions were determined by integration of the lactide ^{1}H NMR methine resonance. With an initial 1 M concentration of L-lactide and a 1% catalyst loading, complex **6a** gave 90% conversion after 6 hours at 100 °C, while **6b** required 9 hours to reach 85% conversion under the same conditions, as determined by *in situ* NMR analysis. The reduced activity of **6b** compared with **6a** is likely a direct result of competitive coordination of the triflate anion, a conclusion that is consistent with the observed coordination of the anion in the solid-state structure of the complex. PLA samples isolated from these experiments were analysed by gel-permeation chromatography (GPC). The data obtained are similar for material isolated from both catalysts and show a bimodal molecular weight distribution. The molecular weights are lower than expected, ranging from an estimated 2500 to 5000 g mol^{-1} for the higher molecular weight components. Such results imply significant rates of transesterification and chain transfer side reactions; the bimodality suggests both inter- and intra-chain transesterification mechanisms may be operative.[123] Overall, the activities of these complexes are mediocre when compared with the well-known neutral zinc alkoxide catalyst systems discussed in Chapter 1, but are more active than some previously reported neutral alkylzinc species.[27,28,40] Additionally, **6a** and **6b** exhibit substantially better activity than previously reported cationic zinc amide[53] and cationic aluminium alkoxide[52] species, which are inactive toward the ROP of lactide.

2.6. Attempted Alkoxide Preparation

It is desirable to prepare zinc alkoxide species because such compounds are known to be superior catalysts for lactide polymerization compared with analogous alkylzinc species. However, since complexes **1**–**4** could not be successfully functionalized, the derivatization of compound **6b** was explored. It was anticipated that it would be possible to selectively replace the ethyl group by alkane elimination, while the presence of the weakly coordinating triflate group would maintain the high Lewis acidity of the metal centre necessary to prevent ligand dissociation. Thus, **6b** was reacted with one equivalent of dry methanol in C_6D_6 and the reaction mixture was examined *in situ* by NMR spectroscopy. No reaction occurred at ambient temperature, but after heating to 100 °C for 1 hour, ethane was observed in the ^{1}H NMR spectrum. However, the solution contained the free ligand and a new species, which resonated broadly at δ 31.7 in the ^{31}P{^{1}H} NMR spectrum, in approximately a 1:1 ratio. Within 1 day at ambient temperature, a significant amount of material had crystallized from the reaction mixture. This material proved too insoluble in non-coordinating organic solvents to characterize by NMR spectroscopy, but single crystals suitable for X-ray diffraction had formed. Therefore, the solid-state structure was determined, revealing it to be the linear trinuclear compound **7**. In order to give a balanced chemical equation, complex **7** must arise with concomitant formation of 0.25 equivalents of $Zn(OMe)_2$ and 0.5 equivalents of $\mathbf{L_1^{Dipp}}$ (Scheme 2.11), which is corroborated by the observation of free $\mathbf{L_1^{Dipp}}$ in the reaction mixture.



Scheme 2.11. Formation of complex **7** and by-products in the reaction of **6b** with 1 equivalent of methanol.

The solid-state molecular structure of complex **7** is depicted in Figure 2.13, and selected bond lengths and angles are shown in Table 2.3. Two crystallographically unique zinc atoms exist in the complex, and there are two symmetry related ligand moieties. Each ligand is bound only at the phosphinimine N to a four-coordinate, tetrahedral zinc centre [Zn(2)], of which there are two in the complex. Each of these zinc atoms is also bound to two bridging triflate groups and a bridging methoxide, which connect to the central, octahedrally coordinated Zn atom [Zn(1)]. This complex can be considered as two molecules of the targeted complex linked by a $Zn(OTf)_2$ moiety. While it is surprising that such a linear trinuclear zinc complex was formed in this case, the structural motif is known in zinc chemistry and was first reported by Clegg and co-workers in 1985.[124] There have been many such examples reported since and these typically incorporate bridging acetate ligands.[125] However, complex **7** is, to the best of our knowledge, the first example to incorporate either triflate or simple alkoxide bridges. Although formation of this complex was not the desired result, it does suggest excellent potential for derivatization of neutral alkylzinc complexes of this type in future work.

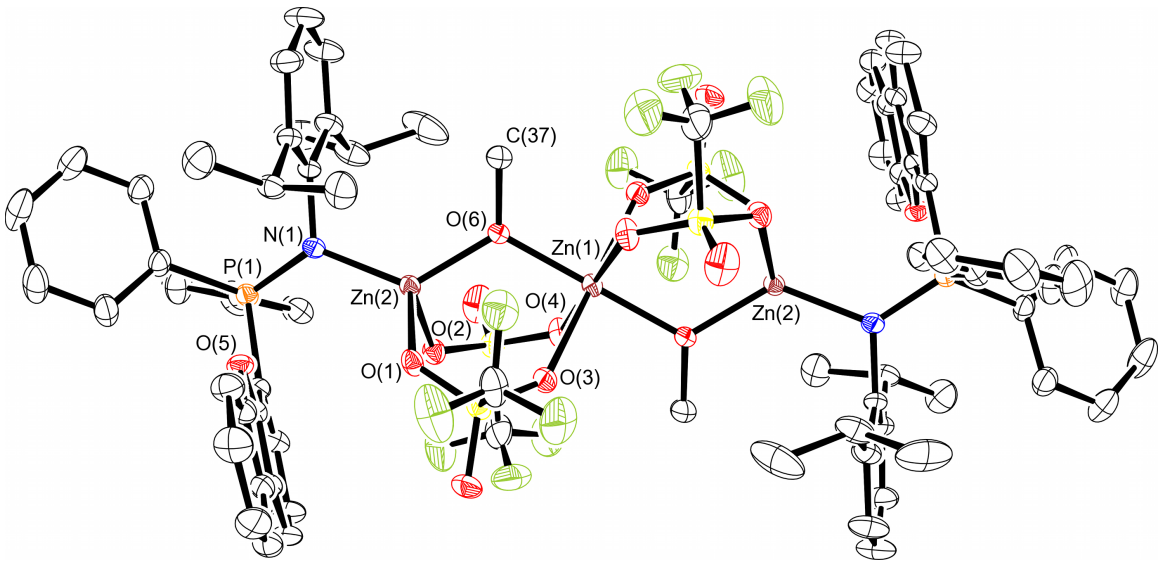


Figure 2.13. Displacement ellipsoid plot (30% probability) of compound **7**. Hydrogen atoms have been omitted for clarity.

Table 2.3. Selected bond lengths (Å) and angles (°) for compound **7**.

Bond		Angle	
P(1)–N(1)	1.618(3)	N(1)–Zn(2)–O(1)	114.1(1)
Zn(2)–N(1)	1.944(2)	O(1)–Zn(2)–O(6)	104.21(9)
Zn(2)–O(1)	2.015(2)	N(1)–Zn(2)–O(2)	106.4(1)
Zn(2)–O(2)	2.023(2)	O(2)–Zn(2)–O(6)	101.65(9)
Zn(2)–O(6)	1.902(2)	Zn(2)–O(6)–Zn(1)	120.0(1)
Zn(1)–O(3)	2.200(2)	O(6)–Zn(1)–O(4)	90.77(8)
Zn(1)–O(4)	2.212(2)	O(6)–Zn(1)–O(3)	90.14(8)
Zn(1)–O(6)	1.968(2)	O(6)–Zn(1)–O(6)′	180.00(8)

2.7. Conclusions

In summary, zinc complexation studies of two novel monophosphinimine ligands have been performed. It has been discovered that only highly electron deficient zinc species bind tightly to the ligand, while exposure of either ligand to diethylzinc results in a solution equilibrium that favours free ligand at ambient temperature. Structural characterization of neutral $ZnCl_2$ and $Zn(C_6F_5)_2$ complexes have been performed, and the results show that the binding mode of the ligand (bidentate versus monodentate) varies greatly depending on the steric bulk of the N-aryl group.

Protonation of the ligand prior to reaction with diethylzinc provides an efficient route to cationic organozinc complexes.[126] This is an underdeveloped synthetic route, and such a methodology likely holds significant promise for the development of many types of sterically and electronically unsaturated metal complexes. Most notably, this approach allows a divalent metal centre to be activated toward monomer insertion while still retaining an initiator group for the ring-opening polymerization of cyclic esters, such as lactide. In this way, two activated phosphinimine stabilized cationic/activated organozinc complexes were prepared from the requisite aminophosphonium salts. While both are catalytically active for the polymerization of L-lactide at elevated temperature, the perfluorophenylborate ion pair **6a** is substantially more active, suggesting that competitive coordination of the triflate anion reduces the activity of **6b**. This study

represents the first example of a cationic zinc complex to be employed as a single-site catalyst for the ring-opening polymerization of lactide.

Since alkylzinc compounds are generally known to be poor initiators compared with alkoxides, further derivatization was attempted. Functionalization of complexes **1**–**4** by salt metathesis or protonolysis was unsuccessful. However, attempts to functionalize complex **6b** by reaction with methanol gave rise to **7**, a novel linear trinuclear zinc complex with methoxy and triflate bridges, suggesting that this protonolysis route does have some potential.

Overall, the observed weak binding of the ligand, the difficulty in preparing zinc alkoxide derivatives, and the relatively poor catalytic performance of the cationic organozinc complexes suggest that the monophosphinimine ligand framework $\mathbf{L_1}$ does not provide a sufficiently high degree of stabilization for the electrophilic zinc centres. For that reason, all subsequent studies have focused on a bis(phosphinimine) ligand architecture ($\mathbf{L_2}$).

Chapter 3. Cationic Zinc Complexes of a Bis(phosphinimine) Ligand

3.1. Introduction

After finding in Chapter 2 that a more strongly donating ligand is likely to be essential for the success of this project, it was decided that focusing on a bis(phosphinimine) ligand would be most productive. Since it was determined that the dibenzofuran oxygen is a very weak donor, the presence of an additional phosphinimine group should substantially increase the overall electron donating capacity of the ligand. This was hoped to thereby circumvent many of the problems encountered in Chapter 2. A series of cationic, coordinatively unsaturated zinc complexes supported by a bis(phosphinimine) ligand have been prepared and structurally characterized, while attempts to synthesize simple zinc alkoxide analogues have continued. Through these studies, several complexes have been shown to exist as coordinatively and electronically unsaturated three-coordinate trigonal planar cations. This is a significant result given the rarity of such compounds, as only a handful of three-coordinate cationic zinc compounds were known prior to undertaking this work.[117,118]

3.2. Ligand Synthesis

The chelating bis(phosphinimine) architecture $\mathbf{L_2^{Mes}}$, which was employed in the studies presented in this chapter, was produced in high yield (94%) by reacting

4,6-bis(diphenylphosphino)dibenzofuran[127] with two equivalents of 2,4,6-trimethylphenylazide ($MesN_3$) under standard Staudinger conditions.[112] The $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{L_2^{Mes}}$ contains a single peak at –17.6 (C_6D_6) which indicates C_{2v} symmetry in solution. The mesityl groups also give diagnostic signals in the ^1H NMR spectrum, with *ortho*- and *para*-CH_3 groups appearing at δ 1.93 and 2.27, respectively.

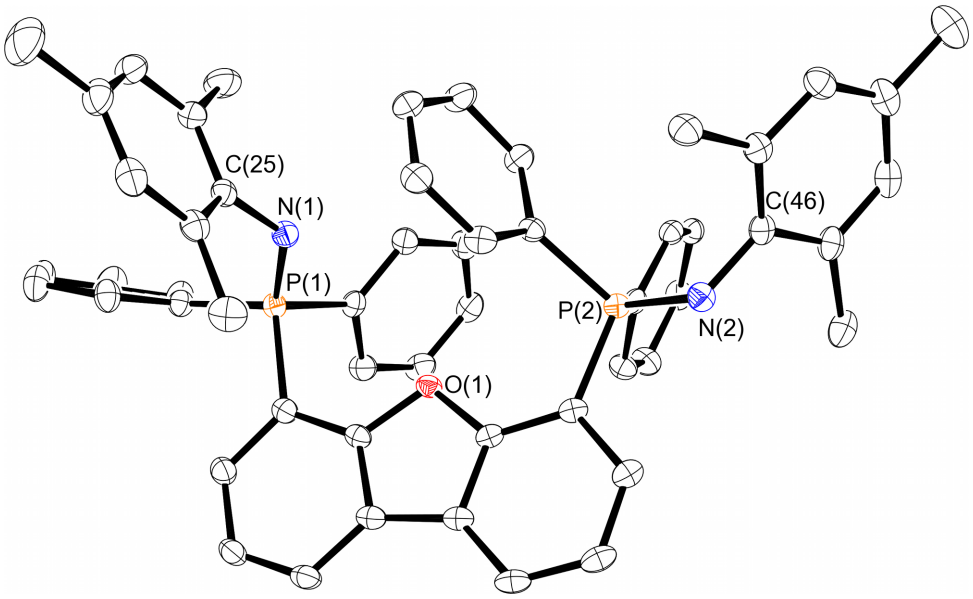


Figure 3.1. Displacement ellipsoid plot (30% probability) of $\mathbf{L_2^{Mes}}$. Hydrogen atoms have been omitted for clarity.

Single crystals of $\mathbf{L_2^{Mes}}$ suitable for X-ray diffraction were grown from a solution of the compound in a toluene/pentane mixture at ambient temperature, and the crystal structure was determined (Figure 3.1). The structure is unremarkable but serves to verify the successful installation of two phosphinimine groups on dibenzofuran. The structure also demonstrates a rather high degree of flexibility in the orientation of the phosphinimine arms, where free rotation about the C–P, P–N, and N–C bonds is evident, as the two phosphinimines in the structure

exist in significantly different orientations. The P–N bond lengths are in the expected range for a P–N double bond [P(1)–N(1) = 1.549(1) Å; P(2)–N(2) = 1.565(2) Å].[106–110]

3.3. Ligand Protonation

The route to complexation that was developed in Chapter 2 has also been exploited for the synthesis of cationic complexes in this chapter, whereby the ligand is first protonated with a suitable activator, and then the isolated aminophosphonium salt is reacted with an appropriate alkylzinc reagent. Starting from the neutral bis(phosphinimine) ligand 4,6-(MesN=PPh_2)$_2$dibenzofuran (**L_2^{Mes}**), protonation of the ligand was carried out using one equivalent of the reagent [$HNMe_2Ph^+$][$B(C_6F_5)_4^-$] to give a protonated salt of the formula [**$L_2^{Mes}H^+$**][$B(C_6F_5)_4^-$] (**8a**) in 80% yield. The analogous BPh_4^- salt has also been prepared, despite the fact that this anion is more prone to aryl abstraction.[92] The use of this anion was expected to promote superior crystallization properties, thereby expediting the solid-state characterization of the organozinc cations. [**$L_2^{Mes}H^+$**][BPh_4^-] (**8b**) was prepared by reacting the ligand with one equivalent of HCl and $NaBPh_4$, giving the desired compound in 80% yield. The cations of **8a** and **8b** display similar NMR spectroscopic properties, the most informative being the $^{31}P\{^1H\}$ NMR spectra, which for each derivative shows only a single broad resonance at δ 10.1 ($CDCl_3$ solvent). This indicates that the symmetry of the neutral ligand is retained despite the fact that only one of the phosphinimine groups should be protonated, suggesting rapid exchange of the proton on the NMR timescale. It is also interesting to note that

the chemical shift of this ^{31}P NMR resonance lies between those of the neutral ligand and the complex (*vide infra*).

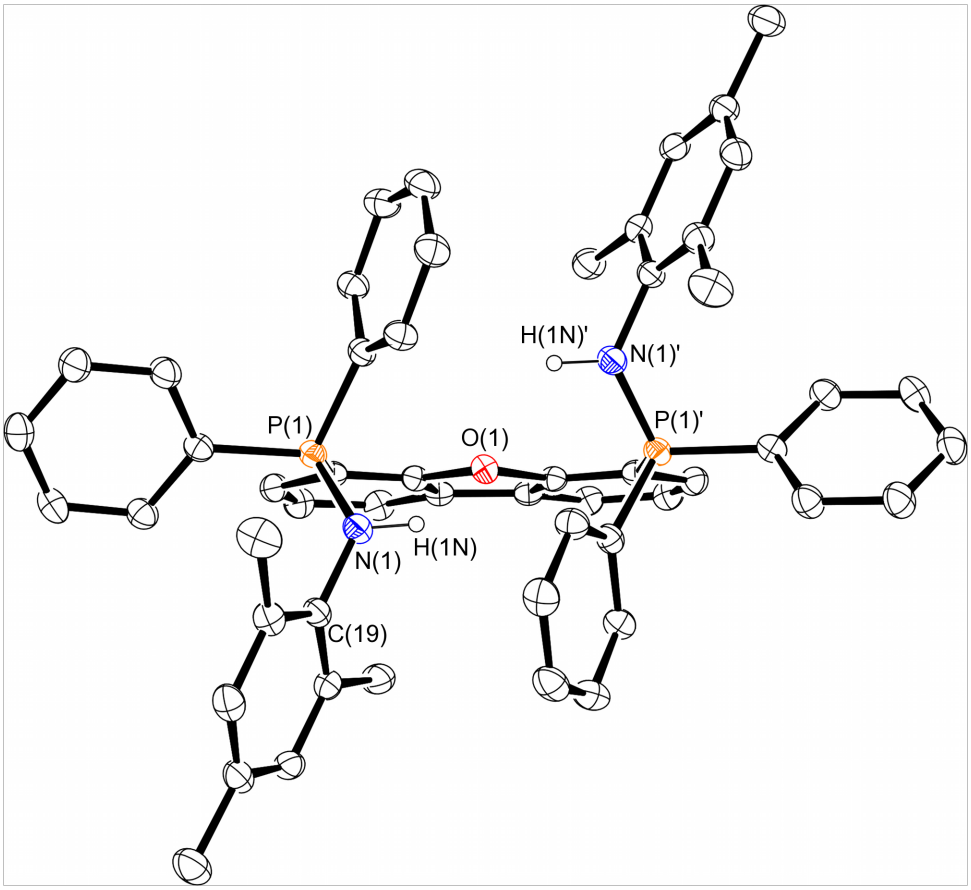


Figure 3.2. Displacement ellipsoid plot (30% probability) of the dication of **9**. Hydrogen atoms except H(1N) and solvent molecules have been omitted for clarity. The molecule rests on a two-fold axis of rotation.

Attempts to grow single crystals of **8a** using the typical array of solvents proved unsuccessful. Crystals were eventually obtained from an acetone solution of **8b**, but determination of the structure revealed the identity of the crystals to be the doubly protonated species [$\mathbf{L_2^{Mes}}$·$2H^{2+}$][BPh_4^-]$_2$·$CO(CH_3)_2$, (**9**·$CO(CH_3)_2$). Compound **9** is a probable component of a complex solution equilibrium involving **8b**, which, under the conditions employed, selectively crystallized from solution. It was also

found that this compound could be independently prepared by reacting $\mathbf{L_2^{Mes}}$ with 2 equivalents of HCl and $NaBPh_4$, which gave **9** as an analytically pure white powder in 91% yield. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum displays one sharp signal at δ 28.1, which is 18 ppm downfield of the singly protonated derivatives. Furthermore, the acidic protons resonate sharply in the ^1H NMR spectrum as a doublet at δ 8.14 with $^2J_{HP}$ = 9.7 Hz. The magnitude of the coupling is comparable to the protonated monophosphinimines studied in Chapter 2.

In the solid state, the cation of **9** lies on a site of 2-fold rotational symmetry, thereby rendering it C_2 symmetric (Figure 3.2). The acidic proton H(1N) was located on the electron density map and freely refined. Furthermore, there was no notable metal–anion interaction, as the ligand offers a substantial degree of steric protection. The P–N bond shows a small, but significant, degree of elongation as a result of protonation [P(1)–N(1) = 1.639(2) Å].

3.4. Synthesis and Characterization of Zinc Complexes

3.4.1. Methylzinc and Phenylzinc Complexes

Due to the disorder caused by the ethyl group in compound **6a** (Chapter 2), the analogous methylzinc complexes were targeted in the hope of minimizing disorder and simplifying crystallographic studies. Reaction of **8a** with a single equivalent of $ZnMe_2$ was facile, giving immediate effervescence of methane and complete conversion to a single product in under 5 minutes. This is a dramatic increase in reaction rate compared with the analogous reaction between protonated $\mathbf{L_1^{Dipp}}$ and $ZnEt_2$, which could be due to the higher denticity of the ligand. From the

reaction, the expected cationic zinc product [$\mathbf{L_2^{Mes}}$ZnMe$^+$][B(C_6F_5)$_4^-$], **10a**, was isolated. This complex has a single unique phosphorus environment which resonates in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.4 (C_6D_5Br solvent), approximately 41 ppm downfield of the free ligand. This downfield shift clearly indicates a coordinated phosphinimine, while the presence of only a single phosphorus environment implies that the cation of **10a** is at least C_2 or C_s symmetric on the NMR timescale and that both phosphinimine donors are bound to the zinc centre. The mesityl groups are also equivalent, with *ortho* and *para* methyls resonating at δ 1.34 and 2.05 in the ^1H NMR spectrum, respectively. The ^{11}B and ^{19}F NMR spectra show typical resonances associated with the B(C_6F_5)$_4^-$ anion and do not suggest significant interaction between anion and cation components in solution. In the ^1H NMR spectrum of this compound, a signal at δ –0.48, which integrates as 3H, is attributed to a single $ZnCH_3$ moiety. All other NMR spectroscopic signatures and elemental analyses are consistent with the proposed compound. Repeated crystallization attempts failed for **10a**, and thus, the solid-state structure was not ascertained.

In an attempt to garner detailed structural information about the complex, the tetraphenylborate anion was employed as a potentially more crystalline alternative. Reaction of **8b** with dimethylzinc proceeded rapidly, giving complete consumption of **8b** in less than 5 minutes at ambient temperature. Interestingly, the reaction generated a mixture of two products, with the major complex, identified as [$\mathbf{L_2^{Mes}}$ZnMe$^+$][BPh$_4^-$] (**10b**), resonating in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.7 (C_6D_5Br solvent). A single by-product resonates slightly downfield at δ 24.3. This

was revealed to be the phenylzinc compound [$\mathbf{L_2^{Mes}}$ZnPh$^+$][BPh_4^-] (**11**), by isolation of single crystals and determination of the solid-state structure (*vide infra*). Under the conditions employed, the reaction gave the two species in approximately a 7 to 1 ratio, as determined by integration of the $^{31}P\{^1H\}$ NMR resonances. The $ZnCH_3$ moiety of **10b** appears at δ –0.49 in the ^1H NMR spectrum, while the mesityl *ortho* and *para* methyls resonate at δ 1.33 and δ 2.04, respectively. All resonances closely match those for the cation of **10a**, suggesting that the nature of the cation is unaffected by the choice of tetraarylborate anion.

In the isolated mixture of **10b** and **11**, only the mesityl component of the ligand gives rise to clearly resolved and distinguishable resonances for these two compounds in the ^1H NMR spectrum. All remaining protons result in overlapping signals (C_6D_5Br). The *ortho* and *para* methyl groups of **11** appear at δ 1.03 and 2.09, respectively. Due to the similar properties of these two species, separation and purification could not be achieved. While the mechanism for the formation of **11** is currently not understood in great detail, the origin of the phenyl group is certainly the tetraphenylborate anion, which, as mentioned above, is known to be more prone to aryl abstraction than the $B(C_6F_5)_4^-$ anion. *In situ* observation of the $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture shows, in addition to a peak at δ –5.6 attributed to the tetraphenylborate anion, a signal at δ –10.4 corresponding to a methyltriphenylborate anion. This is expected to arise from Ph/Me exchange between zinc and the anion, and thus its observation, as well as the absence of a by-product in the synthesis of **10a**, lends further support to the conclusion that BPh_4^- is the source of the phenyl group.

Single crystals suitable for X-ray structural analysis were obtained at ambient temperature from a solution containing a mixture of **10b** and **11** in a mixture of benzene and bromobenzene. Determination of the structure revealed the identity of the crystals to be **10b**·0.5C_6H_6; the solid-state structure is depicted in Figure 3.3. Compound **10b** was found to contain no substantial cation–anion bonding interaction, which suggests that compounds **10a** and **10b** are solvent-separated ion pairs in solution. The zinc atom exhibits trigonal planar coordination geometry, is bound to the two nitrogen atoms in a *pseudo*-symmetric way, and does not interact notably with the dibenzofuran oxygen atom [Zn(1)–O(1) = 3.239(2) Å]. Zinc–nitrogen bond lengths of 2.033(4) and 2.044(4) Å, and a Zn(1)–C(79) distance of 2.034(9) Å, are similar in magnitude to those observed in the monophosphinimine complex **6b** (Chapter 2).

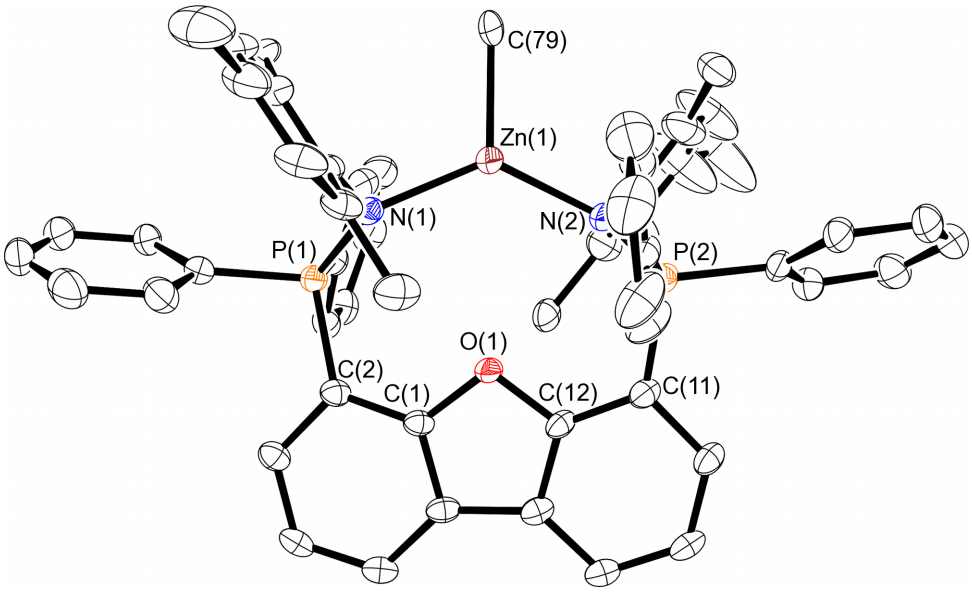


Figure 3.3. Displacement ellipsoid plot (30% probability) of the cation of **10b**. Hydrogen atoms have been omitted for clarity.

For zinc to be bound in this bidentate manner, the σ-symmetric orbitals of the phosphinimine nitrogen atoms must be orientated toward one another, but away from the dibenzofuran backbone (Figure 3.3). This requirement is achieved through orientation of each mesityl group such that one *ortho*-methyl closely approaches the oxygen of the dbf moiety, while the other remains in close proximity to the zinc centre, thereby maintaining a high level of steric protection. Rotational freedom about the C_{dbf}–P and P–N bonds are the major factors which allow this geometry to occur. Rotation about the former situates the nitrogen atoms at an ideal relative separation [C(1)–C(2)–P(1)–N(1) = –37.4(4)°; C(12)–C(11)–P(2)–N(2) = –41.0(4)°], while the latter influences the location and direction of the σ-donating lone pairs [C(2)–P(1)–N(1)–C(37) = –102.6(3)°; C(11)–P(2)–N(2)–C(46) = –89.2(4)°]. These rotations occur in both phosphinimines almost equally but in opposite directions, yielding a complex that is pseudo-C_2-symmetric, thereby placing the zinc centre within an axially chiral binding pocket. The other enantiomer is generated by a centre of inversion within the unit cell, and thus the compound exists as a racemic mixture in the solid state. The notable distortion from trigonal planarity at zinc is a result of the obtuse bite angle of the ligand [N(1)–Zn(1)–N(2) = 131.8(1)°]. Achieving a sharper bite angle would require further rotation about the P–N bond, which cannot be achieved due to the steric repulsion between the mesityl *ortho*-methyl groups and the dbf backbone.

The nearest contact between the tetraphenylborate anion and zinc exists at the *para* position of a closely approaching phenyl ring at a distance of 5.461(6) Å. The methyl group bound to zinc is disordered over two sites, with a concomitant

two-site disorder in the position of the approaching phenyl group of the anion. These disordered structures exist in a 7:3 ratio with the major one depicted in Figure 3.3. The secondary position of the disordered phenyl ring is slightly closer to the zinc centre [C_{anion}–Zn(1) = 5.20(1) Å], suggesting that this disorder may be caused by an interplay between electrostatic cation–anion attraction and steric repulsion between the ions.

To investigate the possibility of generating a dicationic zinc species through double protonolysis, the doubly protonated ligand derivative **9** was reacted with one equivalent of dimethylzinc. The material isolated from this reaction was again found to be a mixture of **10b** and **11**, but with a significant enhancement in the proportion of the phenyl-substituted species **11**, which accounted for 45% of the total material. From this mixture, single crystals of **11**·1.5C_6H_5Br were isolated, and the solid-state structure was obtained, confirming its identity. The solid-state molecular structure of **11** is shown in Figure 3.4. The zinc atom exists as a distorted trigonal planar, three-coordinate cation. The ligand coordinates in an orientation analogous to that observed in the structure of **10b**, with pseudo-C_2-symmetry and no binding to the dbf oxygen atom [Zn(1)–O(1) = 3.207(2) Å]. Zinc–nitrogen bond distances are shortened slightly, by an average of 0.024(8) Å [Zn(1)–N(1) = 2.016(2), Zn(1)–N(2) = 2.012(2) Å], an observation which is consistent with its position downfield of **10b** in the $^{31}P\{^1H\}$ NMR spectrum. These observations suggest that less donation to zinc from the phenyl substituent is compensated for by tighter binding of the ligand. The nitrogen atoms are positioned in similar locations to those of **10b**, [C(1)–C(2)–P(1)–N(1) = 42.5(3)°, C(12)–C(11)–P(2)–N(2) = 46.0(3)°], and

likewise the lone pairs on the nitrogen atoms are oriented in approximately the same direction, [C(2)–P(1)–N(1)–C(25) = 99.2(2)°, C(11)–P(2)–N(2)–C(46) = 94.7(2)°]. The bite angle in this complex thus remains very wide, and is, in fact, slightly greater than that observed for **10b** [N(1)–Zn(1)–N(2) = 133.1(1)°]. The closest Zn–C_{anion} contact is 6.384(3) Å, and as such, this compound can also be considered a solvent-separated ion pair in solution.

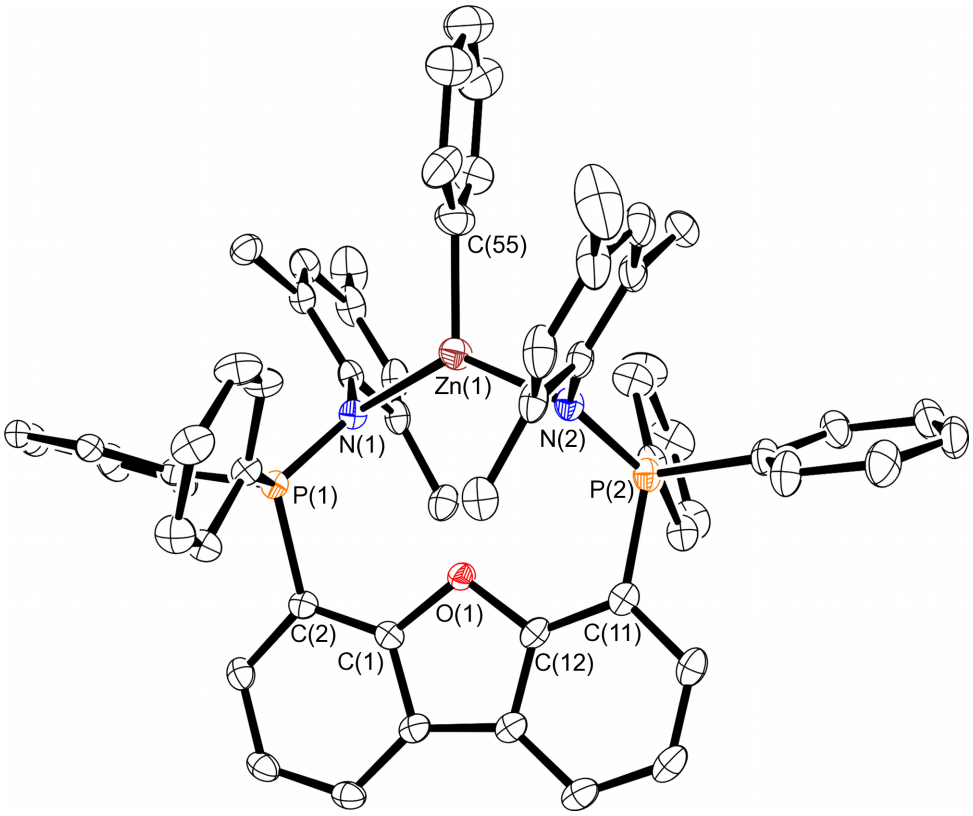


Figure 3.4. Displacement ellipsoid plot (30% probability) of the cation of **11**. Hydrogen atoms and a molecule of bromobenzene have been omitted for clarity.

3.4.2. A Zinc-Acetate Complex

The ability to utilize the above synthetic methodology for the preparation of zinc complexes bearing non-hydrocarbon functionalities would be advantageous. This would give these cationic zinc compounds a wider range of potential

applications, and in particular would likely promote improved performance for lactide polymerization. Attempts to generate alkoxides by reaction of **10a** or **10b** with an appropriate alcohol, such as *iso*propanol, or by reaction of **8a** or **8b** with zinc alkoxide precursors of the form $[RZnOR']_4$ have thus far met with little success. The latter route presumably failed due to the inherent stability of these tetrameric precursors. However, the desired reaction occurred in an attempt to install the acetate moiety by reaction of MeZnOAc with **8b**. When these reagents were combined the reaction proceeded rapidly, and in less than 5 minutes complete conversion to complex $[\mathbf{L_2^{Mes}}ZnOAc^+][BPh_4^-]$, **12**, was achieved. Contrary to what occurred in the preparation of **10b**, only a single product was generated. Compound **12** displays a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 28.3 (C_6D_5Br), which is significantly downfield relative to the methylzinc and phenylzinc cations (**10a**, **10b**, **11**) previously discussed. All other NMR signatures are similar, clearly indicating either C_2 or C_s symmetry, and suggesting no notable cation–anion interactions on the NMR timescale. The acetate methyl group resonates at δ 1.80 in the ^1H NMR spectrum and cleanly integrates as 3H confirming the anticipated ratio of one acetate group per ligand.

Single crystals of **12**·$2C_6H_6$ suitable for X-ray diffraction were obtained by slow cooling of a solution of the compound in a mixture of benzene and bromobenzene (1:1) from 100 °C to ambient temperature. The nearest $Zn–C_{anion}$ contact distance in the structure is 6.229(3) Å. Contrary to the solid-state structures of **10b** and **11**, the zinc centre in this compound is four-coordinate, with highly distorted tetrahedral geometry on account of the wide bite angle of $\mathbf{L_2^{Mes}}$ [N(1)–

Zn(1)–N(2) = 141.7(1)°] and the acute bite angle of the chelating acetate moiety [O(2)–Zn(1)–O(3) = 63.8(2)°] (Figure 3.5). The acetate oxygen atoms bind to zinc at nearly equal distances, with an average bond length of 2.086(4) Å. At 1.972(3) and 1.971(3) Å, the zinc–nitrogen bond distances are noticeably shorter in this complex.

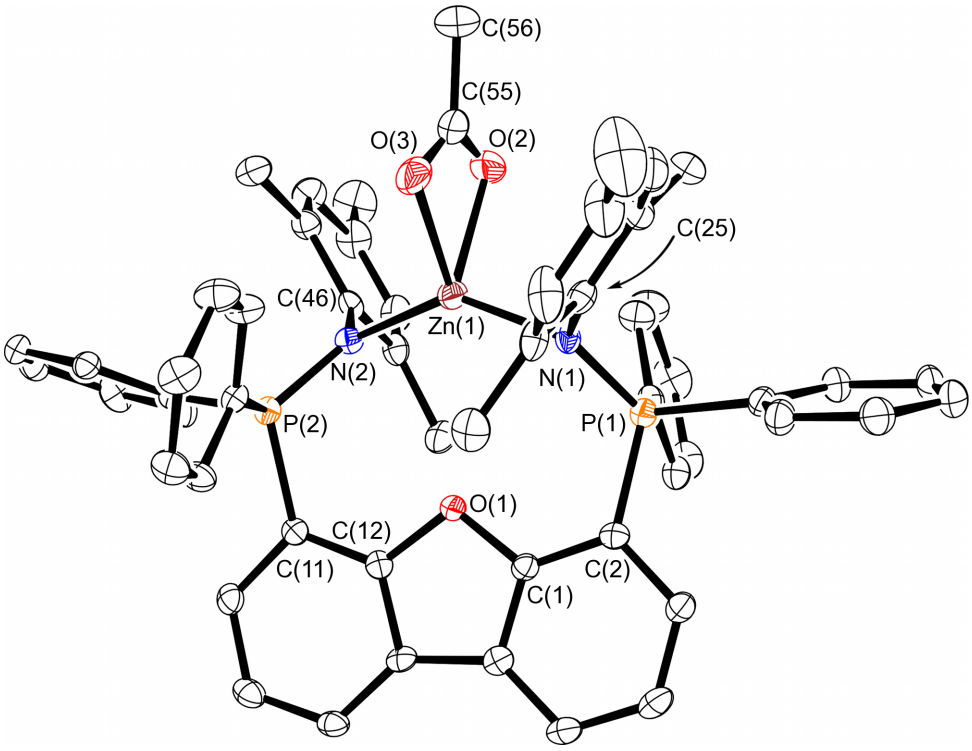


Figure 3.5. Displacement ellipsoid plot (30% probability) of the cation of **12**. Hydrogen atoms have been omitted for clarity.

As for **11**, the shortened P–N bond distances are likely a result of reduced electron donation from the acetate to zinc, which is compensated for by tighter binding of the ligand. The ligand adopts a similar orientation as that elucidated for the structures of **10a** and **11**, but with a substantially different bite angle, which is widened by approximately 10°. This increase in ligand bite angle stems from very subtle changes in the geometry of the ligand and is primarily due to a shift in the position of the zinc atom slightly further into the binding pocket. As a consequence,

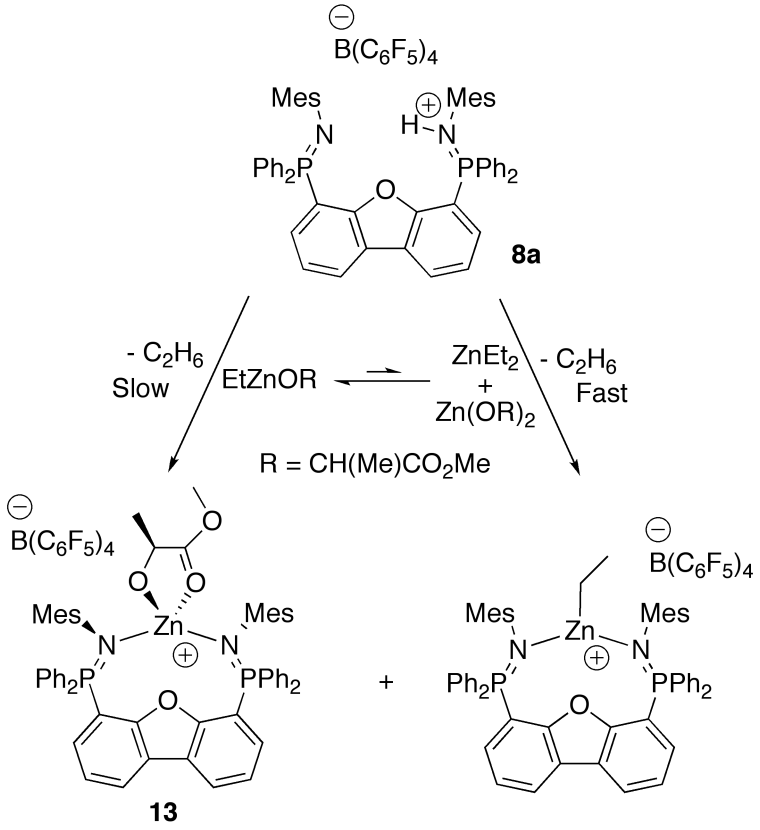
the zinc centre sits marginally closer to the dbf oxygen atom [Zn(1)–O(1) = 3.059(2) Å], but remains at a distance outside the range of a meaningful bonding interaction. The shortened zinc–nitrogen bond distances are consistent with the noted downfield shift in the $^{31}P\{^{1}H\}$ NMR spectrum, all of which suggest a greater partial positive charge on the zinc atom and increased donation of electron density from the phosphinimine functionalities.

3.4.3. A Zinc Lactate Complex

Preliminary studies of **10a** and **12** as catalysts for ROP of lactide have revealed these compounds to be inactive under moderate conditions (60 °C). Exposure to more harsh reaction conditions (100 °C) in the presence of lactide monomer resulted in complex decomposition. Because the methyl and acetate groups of **10a** and **12**, respectively, are known to be poor initiating groups for this transformation, the result is not particularly surprising. As mentioned above, simple alkoxide analogues could not be prepared, and thus, it was difficult to determine whether the lack of activity was due to the nature of the initiating group, or rather, an inherent property of the cationic catalyst design. To further probe this question, attempts to prepare a complex bearing a methyl-L-lactate initiating group were undertaken. This initiating group serves as an excellent structural and electronic mimic of the growing polymer chain, as it is a close representation of the product that would result from a single insertion of lactide into the Zn–C bond of complex **10a**.

By reaction of **8a** with 1.1 equivalents of EtZn(methyl-L-lactate), 85% of **8a** was converted to **13**, with the remainder being transformed into a by-product

which was established to be [$\mathbf{L_2^{Mes}}$ZnEt][$B(C_6F_5)_4$] (Scheme 3.1). Heteroleptic zinc species of the form RZnOR′ are known to exist in a complex equilibrium, with comproportionation giving rise to small concentrations of homoleptic ZnR_2 in solution. Because **8a** reacts significantly faster with $ZnEt_2$ than with EtZn(methyl-L-lactate), some formation of the [$\mathbf{L_2^{Mes}}$ZnEt$^+$][$B(C_6F_5)_4^-$] is not unexpected. Separation of the two complexes could not be achieved, thus studies assessing the utility of **13** as a lactide polymerization catalyst were undertaken using an 85:15 mixture of these two species. These studies are described in detail in Section 3.5.



Scheme 3.1. Synthesis of complex **13** with concomitant formation of [$\mathbf{L_2^{Mes}}$ZnEt$^+$][$B(C_6F_5)_4^-$].

At ambient temperature in bromobenzene-d_5, complex **13** exhibits two broad, but distinct, resonances at δ 24.5 and 25.1 in the $^{31}P\{^1H\}$ NMR spectrum

(Figure 3.6). Upon warming to 50 °C, these peaks coalesce into one signal at δ 25.0, which sharpens further at 70 °C. This dynamic behaviour could arise from two possible mechanisms. Firstly, the presence of two signals could be due to the asymmetric lactate moiety, which breaks the C_2 symmetry and renders the phosphinimines chemically inequivalent. Rapid rotation of the lactate group on the NMR timescale at elevated temperatures could account for averaging of these signals. Alternatively, these observations could be due to the fact that both the C_2 symmetric ligand and the lactate moiety are chiral, which results in two possible diastereomers (Scheme 3.2), each of which may give rise to one average signal in the ^{31}P NMR spectrum. Rapid interconversion between the two diastereomers at elevated temperatures would cause coalescence of the two peaks, thereby accounting for the spectral observations.

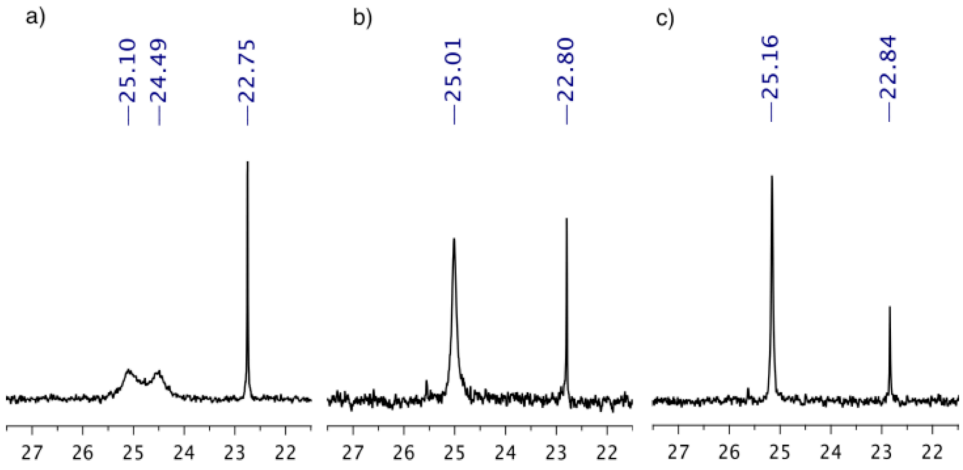
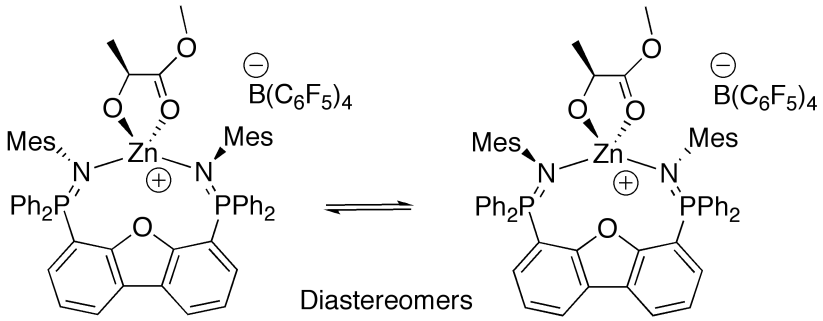


Figure 3.6. $^{31}P\{^{1}H\}$ NMR spectra of the methyl-(S)-lactate complex **13** and the LZnEt by-product in C_6D_5Br solution at ambient temperature (a), at 50 °C (b), and at 70 °C (c).



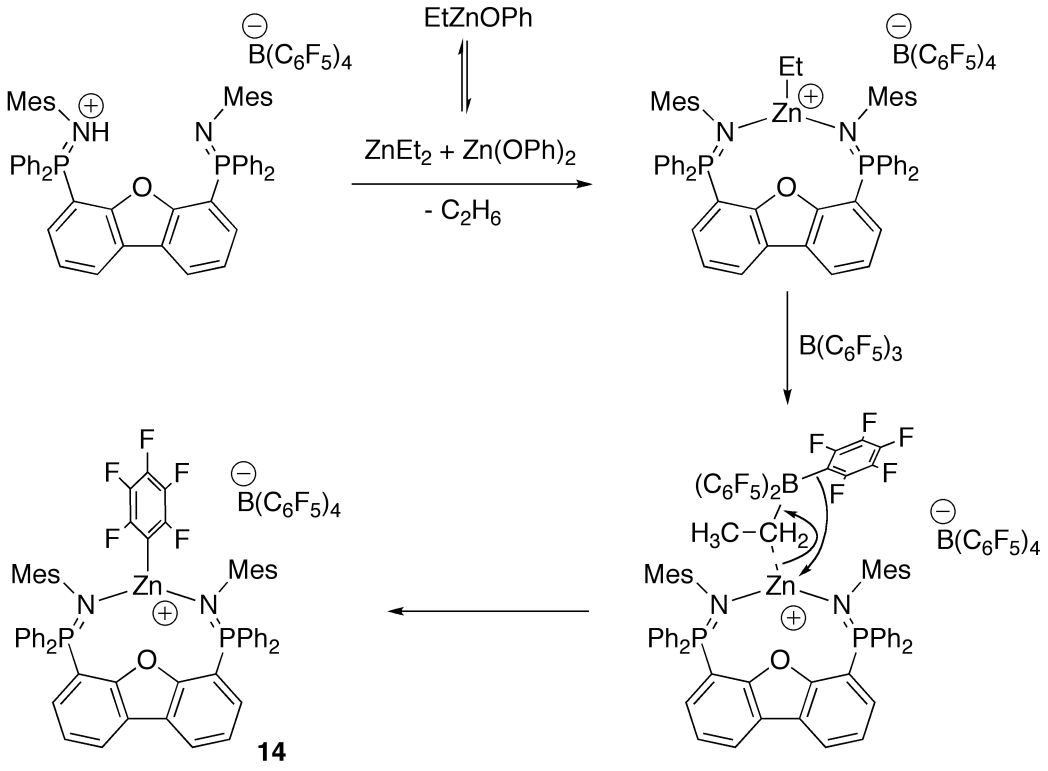
Scheme 3.2. Possible diastereomers of complex **13**.

It has not been possible to unambiguously establish which of these two competing theories is better. At 50 °C, a quartet at δ 4.28, a doublet at δ 1.29, and a singlet at δ 2.78 attributed to the methine, methyl and CO_2CH_3 of the methyl-L-lactate group, respectively, are observed in the ^{1}H NMR spectrum. Interestingly, the mesityl *ortho*-methyls are split into two separate resonances at δ 1.74 and 1.70, suggesting restricted rotation about the N–C bonds.

3.4.4. Unexpected Preparation of a ZnC_6F_5 Complex

Reaction of the **8a** with EtZnOPh was also performed, with the aim of cleanly producing a zinc-phenoxide complex. However, this gave a result similar to the synthesis of complex **13**, with only partial conversion to the targeted zinc-phenoxide complex and concomitant formation of the alkylzinc by-product. With the desire to promote more complete and rapid conversion, the reaction was performed with one equivalent of added $B(C_6F_5)_3$, in hopes that this strong Lewis acid might assist in the protonolysis by transferring the ethide group to the acidic proton. While this reaction did give clean conversion to a new species, analysis of the NMR spectra revealed the product to be the arylzinc species [$\mathbf{L_2^{Mes}}ZnC_6F_5^+$][$B(C_6F_5)_4^-$], **14**, arising from transfer of a C_6F_5 group from the borane. The identity of this compound

was corroborated by elemental analysis. A single sharp $^{31}P\{^{1}H\}$ NMR resonance appears at δ 26.6 ($CDCl_3$ solvent), while other NMR features are similar to the cationic zinc complexes of this ligand discussed above. In addition to the expected set of peaks arising from the anion in the ^{19}F NMR spectrum, resonances at –114.5, –160.8, and –155.4 are attributed to the *ortho*, *meta*, and *para* fluorines of the ZnC_6F_5 moiety, respectively.



Scheme 3.3. Proposed mechanism of formation of the cationic complex **14**.

A proposed mechanism for the formation of complex **14** is depicted in Scheme 3.3. The first step involves generation of an alkylzinc species, which is known to be a product of the reaction. This is followed by formation of an adduct with the borane, whereby partial abstraction of the ethyl group may occur. Then transfer of a C_6F_5 group to the highly electropositive zinc centre is a plausible final

step, giving rise to compound **14**. One could also envision the similar mechanism going through the zinc-phenoxide cation rather than the alkylzinc cation, and it is possible that both routes are operative. This manner of transfer of a C_6F_5 group from $B(C_6F_5)_3$ to zinc is not unprecedented, and has been described for a zinc calixarene system.[128] Additionally, the reaction between simple dialkylzinc species and $B(C_6F_5)_3$ in the absence of a chelating ligand or coordinating solvent has been shown by Bochmann et al. to result in double aryl transfer, giving rise to $Zn(C_6F_5)_2$.[129] Although **14** is not a step toward the goal of producing an active lactide polymerization catalyst, it does represent an interesting route to this novel cationic arylzinc compound.

3.4.5. A Zinc Aryloxide Complex

The problems encountered in the attempted synthesis of cationic zinc alkoxide and aryloxide species are proposed to be primarily due to the resistance of the heteroleptic zinc precursors toward protonolysis reactions. To test this hypothesis, the protonated ligand **8a** was reacted with the zinc aryloxide precursor $EtZnOC_6F_5$. Due to the electron withdrawing nature of the C_6F_5 group, this precursor exists as a dimer in solution rather than a tetramer, thereby rendering the zinc atoms trigonal planar and coordinatively unsaturated.[61] For these reasons, protonolysis of this reagent was expected to be much more facile. This was indeed found to be the case, and it was possible to drive the reaction to completion under relatively mild conditions (50 °C, 1 hour), giving the salt $[\mathbf{L_2^{Mes}}ZnOC_6F_5^+][B(C_6F_5)_4^-]$ (**15a**) as an analytically pure powder in 87% yield. The $^{31}P\{^1H\}$ NMR resonance at δ 28.3 is downfield of **14** and the ^{19}F NMR spectrum clearly indicates the presence of

the C_6F_5 group in the Zn complex, with peaks at δ –167.5, –168.5, and –180.5 for the *ortho*, *meta*, and *para* fluorine atoms, respectively.

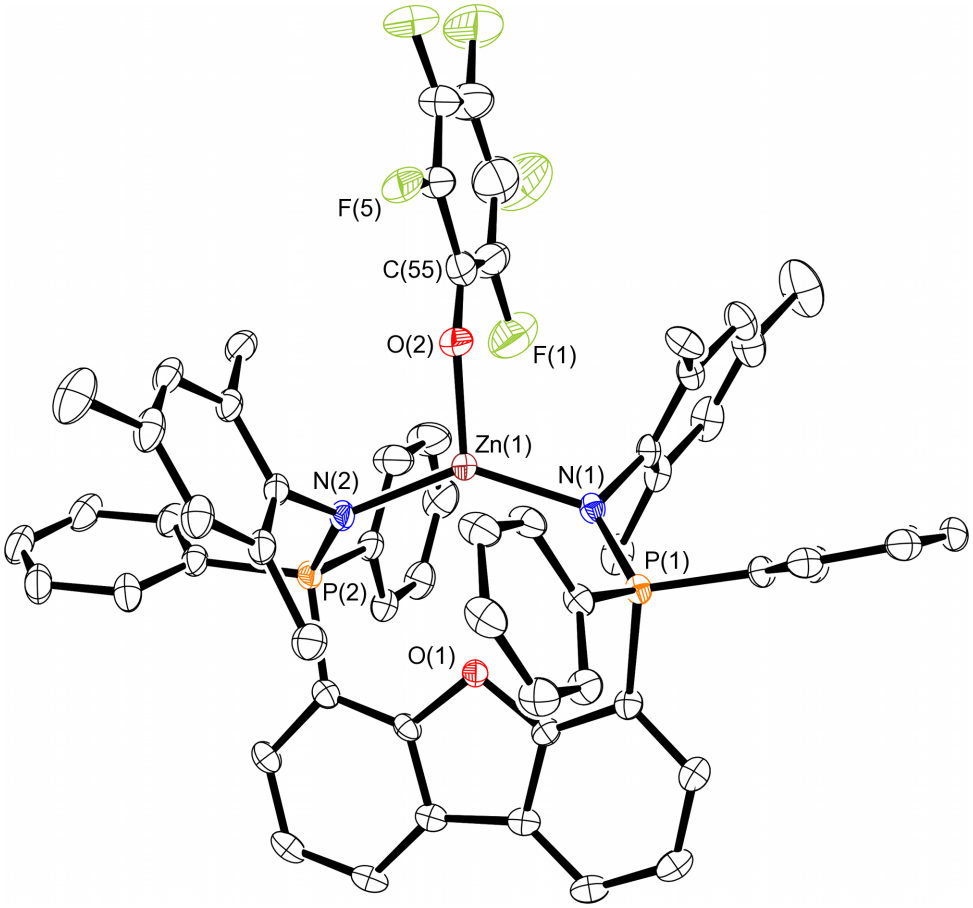


Figure 3.7. Displacement ellipsoid plot (30% probability) of the cation of **15b**. Hydrogen atoms, disordered atomic positions, and a molecule of chloroform have been omitted for clarity.

Crystals of this compound proved exceedingly difficult to obtain, and thus a small amount of **8b** was reacted with $EtZnOC_6F_5$ and crystals of $[\mathbf{L_2^{Mes}}ZnOC_6F_5^+][BPh_4^-]\cdot CHCl_3$ (**15b**·$CHCl_3$) were obtained from the reaction mixture, allowing for determination of the solid-state structure (Figure 3.7). The structure is similar in many ways to the preceding molecular structures discussed in this chapter. In particular, the ligand adopts a C_2 orientation and the zinc centre is three-coordinate trigonal planar. There exists no notable interaction between zinc

and the dbf oxygen [Zn(1)–O(1) = 3.096(2) Å], nor is there any significant cation–anion contact. The Zn–N bond distances are rather short, averaging 1.970(2) Å, which suggests tight binding of the ligand to compensate for the withdrawal of electron density by the C_6F_5 group. The bite angle of the ligand is 139.98(8)°, which is most similar to the zinc-acetate complex **11**. Complex **15** was unfortunately found to be inactive toward polymerization of lactide. However, this represents the first example of a stable cationic heteroleptic zinc aryloxide to arise from this thesis, and is an important step toward targeted zinc-alkoxide species.

3.5. Polymerization Studies

While complex **13** was found to catalyse the ROP of *rac*-lactide extremely slowly at ambient temperature, significantly enhanced activity was noted at warmer but still relatively mild temperatures. A coordination-insertion mechanism is evident upon *in situ* observation of polymerization of 10 equivalents of *rac*-lactide at 50 °C in $CDCl_3$ solution. After 30 minutes at 50 °C, complex **13** was almost entirely converted to a new species, presumably the product of one or more insertions of lactide monomer, which resonates slightly downfield (δ 25.5) in the $^{31}P\{^1H\}$ NMR spectrum (Figure 3.8). A concomitant change of the methyl-L-lactate end group was observed in the ^1H NMR spectrum, with replacement of the OCH_3 resonance at δ 2.80 by a new peak at δ 3.42. After nearly complete loss of the signals associated with **13**, observation of the methine resonances in the ^1H NMR spectrum indicates only 36% consumption of monomer (approximately 4 equiv), suggesting comparable rates of initiation versus propagation for this catalyst system. It is

important to note that the [$\mathbf{L_2^{Mes}}$ZnEt$^+$][B(C_6F_5)$_4^-$] impurity shows no reactivity toward the lactide monomer under these conditions.

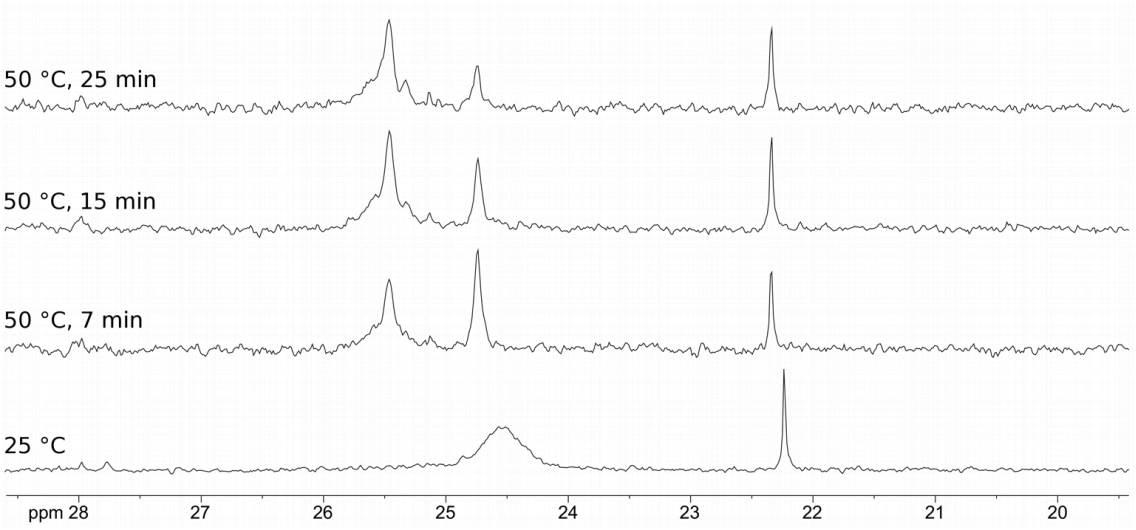


Figure 3.8. $^{31}P\{^1H\}$ NMR spectra of **13** and the impurity [$\mathbf{L_2^{Mes}}$ZnEt][B(C_6F_5)$_4$] after addition of 50 equivalents of *rac*-lactide, showing gradual conversion to a new species at 50 °C.

In situ observation of polymerization of 50 equivalents of *rac*-lactide was carried out in C_6D_5Br solvent at 60 °C. Under these conditions and with $[LA]_0$ = 0.25 M, 90% conversion to atactic polylactide was achieved in 3.5 hours. Isolated polymer samples were obtained from larger scale polymerizations carried out under identical reaction conditions. The methyl-L-lactate end group is clearly observed in the ^1H NMR spectrum of the isolated polymer (Figure 3.9), providing further evidence for a coordination-insertion mechanism. Specifically, the OCH_3 moiety appears at δ 3.74 ($CDCl_3$) as two distinct but very closely spaced peaks of approximately equal intensity. These peaks likely correspond to opposite enantiomers of the first inserted monomer. Additionally, MALDI-ToF analysis detected only oligomer fragments consistent with the presence of a methyl-L-lactate

end group (Figure 3.10). Peaks are separated by m/z = 72, suggesting significant rates of intrachain transesterification.

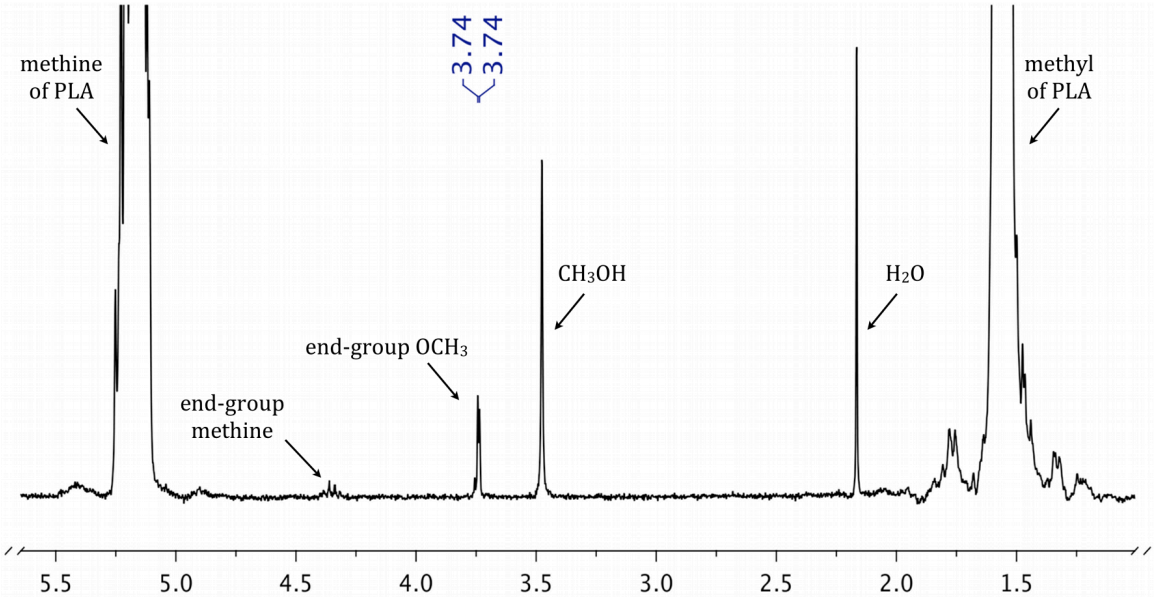


Figure 3.9. ^{1}H NMR spectrum of isolated PLA sample prepared with [*rac*-LA]$_0$/[**13**] = 200.

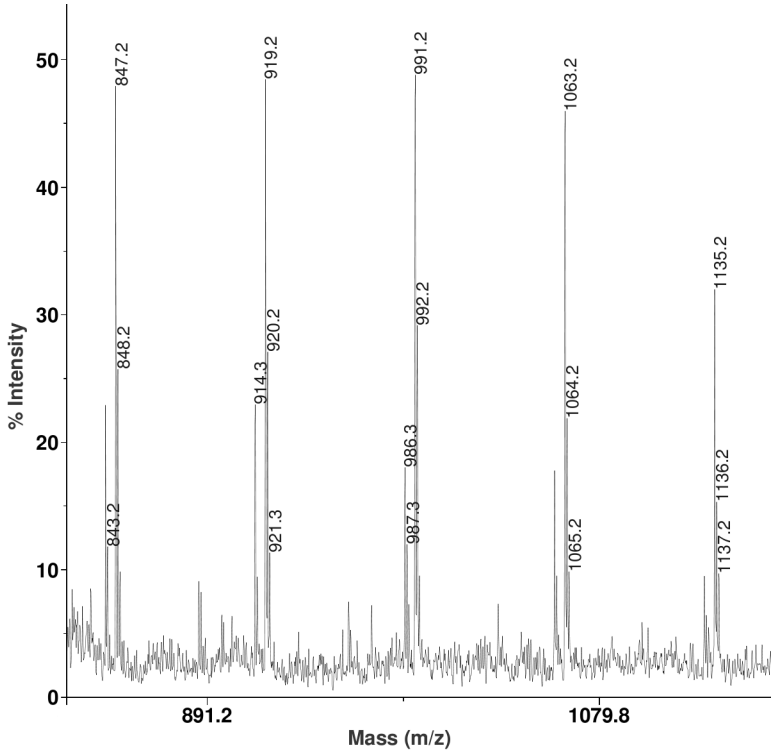


Figure 3.10. Section of MALDI-ToF mass spectrum of PLA sample ([*rac*-LA]$_0$/[**13**] = 200).

Despite the likely transesterification side-reactions, analysis of the polymer samples revealed reasonable molecular weight control. Specifically, samples produced using a monomer to initiator ratio of 50:1, as described above, had PDI values ranging from 1.2–1.3, with molecular weights of approximately 18 kg mol^{-1}, approximately triple the expected value.

Table 3.1. GPC data for PLA samples prepared with [*rac*-LA]$_0$/[**13**] = 50.

$M_{n,\,calc}$ (kg mol^{-1})	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
7.3	18.5	22.6	1.22
7.3	17.7	22.5	1.27
7.3	12.2	15.3	1.25

3.6. Conclusions

The cationic/activated ethylzinc complexes of $\mathbf{L_1^{Dipp}}$ discussed in Chapter 2 required harsh conditions to prepare. In contrast, the synthesis of alkylzinc complexes of $\mathbf{L_2^{Mes}}$ was facile. Attempts to install functionalities with less electron rich oxygen donors were successful (OAc, OC_6F_5), but these compounds were not active in polymerization studies. However, such coordinatively unsaturated cationic zinc complexes have rarely been structurally characterized, and these compounds are thus interesting from a fundamental perspective.

The preparation of simple zinc-alkoxide complexes of the bis(phosphinimine) architecture remains fraught with difficulty. However, the zinc-lactate complex **13** was synthesized more successfully, and it has been shown to indeed exhibit substantially improved lactide polymerization properties. While the

activity of this compound is modest compared with many of the known classes of neutral zinc catalysts discussed in Chapter 1, it represents a new family of lactide polymerization catalyst with significant potential for further development.[130]

Chapter 4. Varying the Steric Bulk of the Bis(Phosphinimine) Framework: Cationic Organozinc Complexes

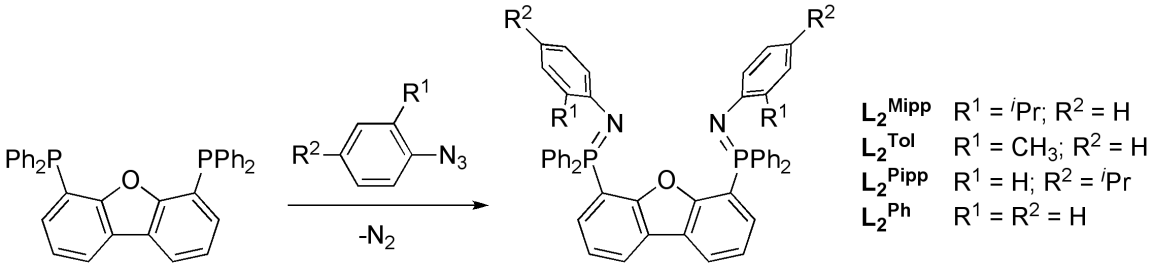
4.1. Introduction

The structurally characterized complexes of $\mathbf{L_2^{Mes}}$ discussed in Chapter 3 were all highly sterically hindered. Furthermore, in order for the ligand to bind in a bidentate manner, the mesityl groups were required to occupy a position in which one *ortho*-methyl of each mesityl group sterically crowded the dbf backbone. The studies discussed in Chapters 4 and 5 all stem from the idea that reduction of the steric bulk at this *ortho* position could substantially alleviate strain and allow the ligand to adopt a more energetically favourable orientation. It was hoped that such an achievement would allow a more facile synthesis of zinc-lactate complexes while also improving the catalytic activity of the resultant complexes.

In particular, this chapter focuses on varying the steric bulk of the N-aryl groups, whereby one *ortho* site is left unoccupied while the other *ortho* substituent is either H ($\mathbf{L_2^{Ph}}$), Me ($\mathbf{L_2^{Tol;}}$ Tol = *o*-tolyl), or ^{i}Pr ($\mathbf{L_2^{Mipp}}$; Mipp = 2-*iso*propylphenyl). In addition to these three derivatives, a ligand ($\mathbf{L_2^{Pipp}}$) incorporating *para*-*iso*propylphenyl (Pipp) groups has been investigated. The corresponding methylzinc complexes were prepared and structurally characterized, and these studies have provided a great deal of insight into the properties of the bis(phosphinimine) framework. All of the ligand variations employed were found capable of stabilizing

trigonal planar zinc cations, although significant variations in solid-state geometry and solution dynamics were observed.

4.2. Ligand Synthesis and Characterization



Scheme 4.1. Synthesis of bis(phosphinimine) ligands of varying steric bulk.

The ligands $\mathbf{L_2^{Mipp}}$, $\mathbf{L_2^{Tol}}$, $\mathbf{L_2^{Pipp}}$, and $\mathbf{L_2^{Ph}}$ were easily prepared from the bis(phosphine) precursor and the appropriate aryl azide (Scheme 4.1) in isolated yields between 72 and 85%, giving analytically pure, thermally stable solids. All show similar NMR spectroscopic features in the $^{31}P\{^1H\}$ NMR spectrum (C_6D_6 solvent), with each displaying one sharp singlet in the region between δ –6 and –4, suggesting C_{2v} symmetry in solution. The *iso*propyl groups of $\mathbf{L_2^{Mipp}}$ appear in the expected regions in the ^1H NMR spectrum at δ 4.28 and 1.52, for the methine and methyl protons, respectively. The NMR spectroscopic signatures of $\mathbf{L_2^{Pipp}}$ are very similar, with *iso*propyl ^1H resonances appearing at δ 2.73 and 1.16. The characteristic *ortho*-methyl groups of $\mathbf{L_2^{Tol}}$ resonate at δ 2.74 in the ^1H NMR spectrum.

All derivatives of the ligand have been studied crystallographically. Single crystals of $\mathbf{L_2^{Mipp}}\cdot CH_2Cl_2$ and $\mathbf{L_2^{Pipp}}\cdot C_5H_{12}$ suitable for X-ray diffraction studies were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the compound at –35

°C, while single crystals of $\mathbf{L_2^{Tol}}$ and $\mathbf{L_2^{Ph}}\cdot C_6H_6$ were obtained by slow diffusion of pentane into a benzene solution of the compound at ambient temperature. The solid-state molecular structures of $\mathbf{L_2^{Mipp}}$, $\mathbf{L_2^{Tol}}$, $\mathbf{L_2^{Pipp}}$, and $\mathbf{L_2^{Ph}}$ are depicted in Figure 4.1–Figure 4.4, respectively, and selected metrical parameters for each can be found in Table 4.1. All of the structures are unremarkable, but serve to verify the successful preparation of the desired compounds. Each structure exists in a somewhat different orientation as compared to the others, which is most likely governed by crystal packing effects. This again demonstrates the rather high degree of flexibility associated with the phosphinimine arms of the ligand, which corresponds primarily to rotation about the C–P, P–N, and N–C bonds.

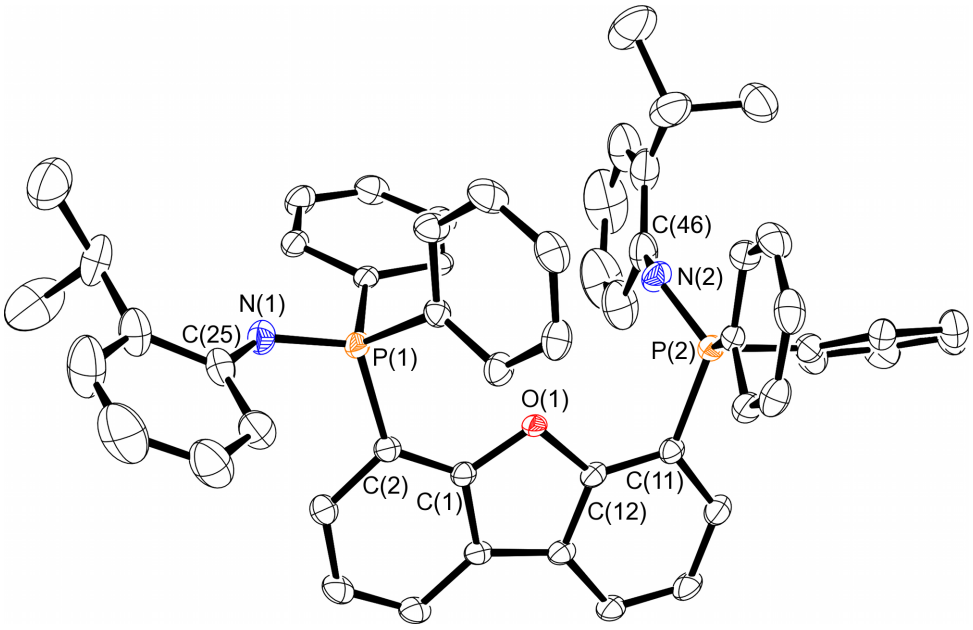


Figure 4.1. Displacement ellipsoid plot (30% probability) of $\mathbf{L_2^{Mipp}}$. Hydrogen atoms and a molecule of dichloromethane have been omitted for clarity.

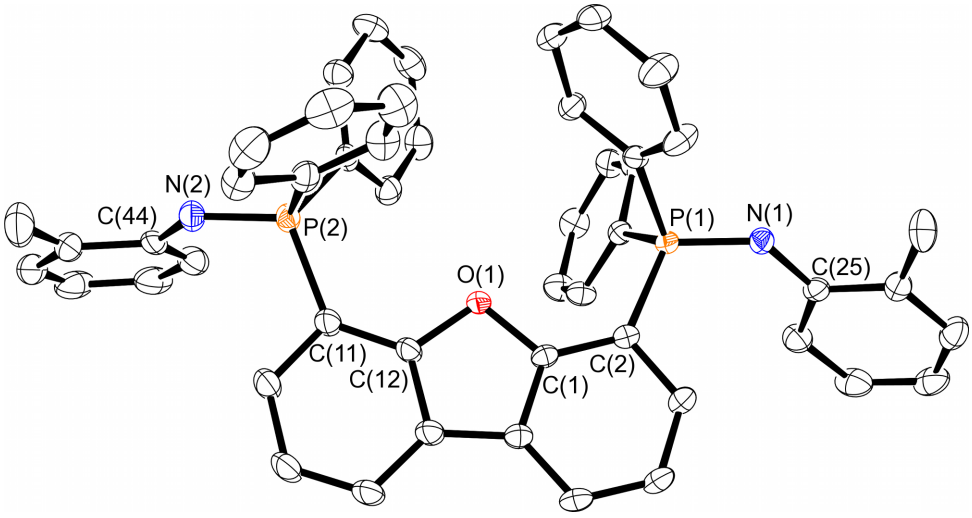


Figure 4.2. Displacement ellipsoid plot (30% probability) of $\mathbf{L_2^{Tol}}$. Hydrogen atoms have been omitted for clarity.

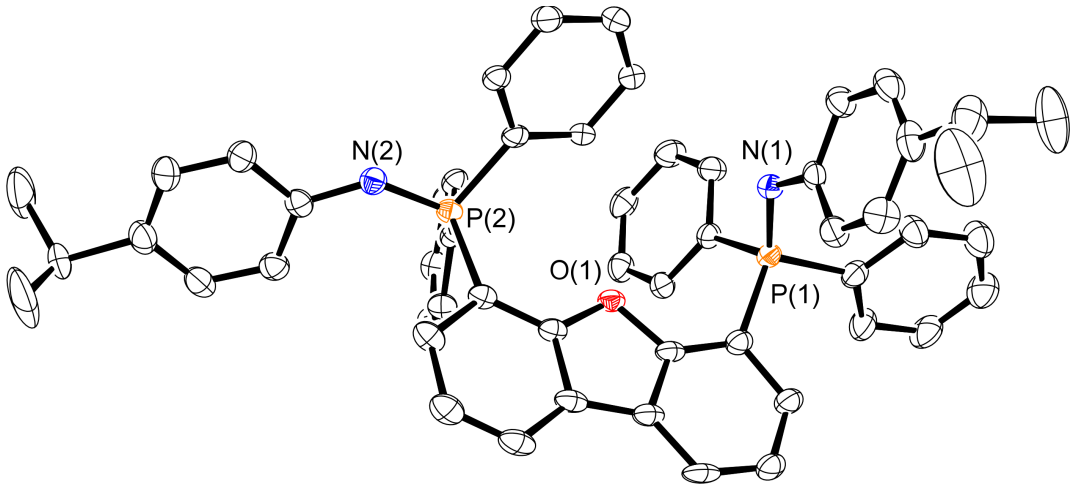


Figure 4.3. Displacement ellipsoid plot (30% probability) of $\mathbf{L_2^{Pipp}}$. Hydrogen atom, a molecule of pentane, and disordered atomic positions have been omitted for clarity.

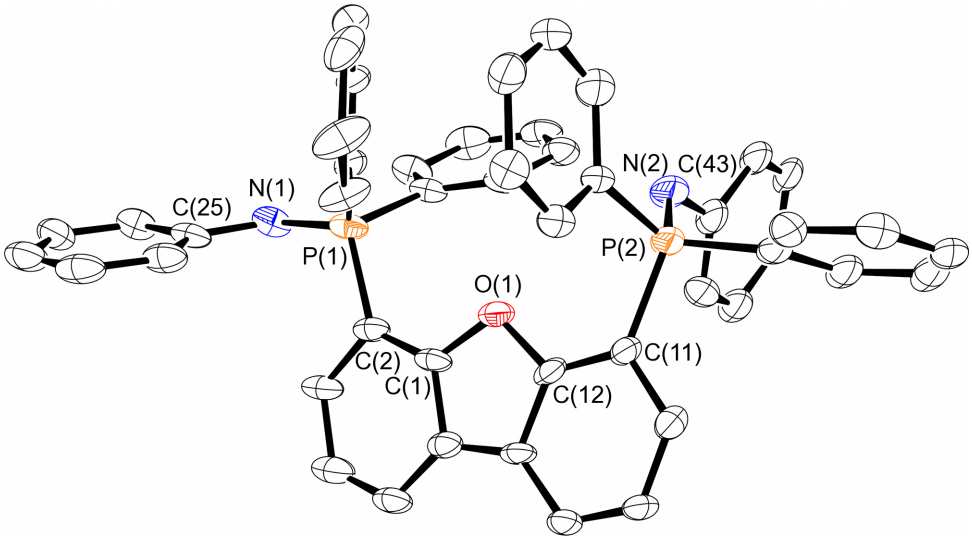


Figure 4.4. Displacement ellipsoid plot (30% probability) of $\mathbf{L_2^{Ph}}$. Hydrogen atoms and a molecule of benzene have been omitted for clarity.

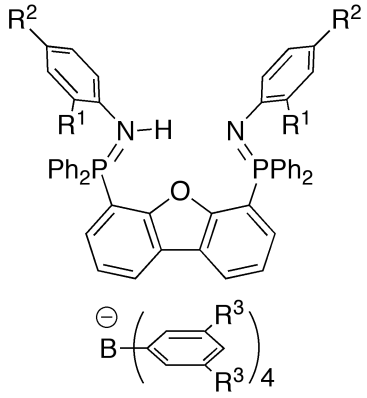
Table 4.1. Selected bond lengths (Å) and angles (°) for the four derivatives of $\mathbf{L_2}$.

Bond/Angle	$\mathbf{L_2^{Mipp}}$	$\mathbf{L_2^{Tol}}$	$\mathbf{L_2^{Pipp}}$	$\mathbf{L_2^{Ph}}$
C(2)–P(1)	1.821(4)	1.822(1)	1.818(3)	1.821(5)
C(11)–P(2)	1.812(6)	1.817(2)	1.831(3)	1.821(5)
P(1)–N(1)	1.560(4)	1.564(2)	1.559(3)	1.581(4)
P(2)–N(2)	1.542(4)	1.576(2)	1.558(3)	1.568(5)
N(1)–C(25)	1.380(5)	1.390(2)	1.392(4)	1.426(5)
N(2)–C(x)[a]	1.381(7)	1.411(3)	1.383(4)	1.408(7)
C(2)–P(1)–N(1)	114.4(2)	112.14(8)	116.2(1)	112.2(2)
C(11)–P(2)–N(2)	117.8(2)	111.94(9)	113.3(1)	118.5(3)
P(1)–N(1)–C(25)	129.1(4)	131.3(1)	127.3(2)	127.1(3)
P(2)–N(2)–C(x)[a]	127.5(4)	125.8(1)	134.5(2)	126.3(4)

[a] $\mathbf{L_2^{Mipp}}$: x = 46; $\mathbf{L_2^{Tol}}$: x = 44; $\mathbf{L_2^{Pipp}}$: x = 46; $\mathbf{L_2^{Ph}}$: x = 43.

4.3. Synthesis and Characterization of Methylzinc Complexes

4.3.1. Ligand Protonation



16a: R^1 = ^{i}Pr R^2 = H R^3 = CF_3
16b: R^1 = ^{i}Pr R^2 = H R^3 = H
17a: R^1 = CH_3 R^2 = H R^3 = CF_3
17b: R^1 = CH_3 R^2 = H R^3 = H
18a: R^1 = H R^2 = ^{i}Pr R^3 = CF_3
18b: R^1 = H R^2 = ^{i}Pr R^3 = H
19a: R^1 = H R^2 = H R^3 = CF_3
19b: R^1 = H R^2 = H R^3 = H

Figure 4.5. Protonated ligand salts of each ligand derivative.

In the present chapter, the same synthetic methodology has been used for the preparation of cationic organozinc complexes that was developed in Chapter 2 and further exploited in Chapter 3. Thus, each of these ligands was first protonated using a suitable Brønsted acid, and the resulting salts were isolated and fully characterized. Brookhart's acid, $[H(OEt_2)_2^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$, was used to protonate each ligand, giving salts of the formula $[LH^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$, **16a**–**19a** (Figure 4.5). Also, due to the success in crystallographically characterizing the BPh_4^- salts studied in Chapter 3, this strategy was further pursued for these sterically modified ligands. Thus each ligand was protonated using HCl, followed by reaction with sodium tetraphenylborate, affording the salts of the formula $[LH^+][BPh_4^-]$, **16b**–**19b**. All protonated ligand species were isolated in high yield (*ca.* 90% for **16a**–**19a**) as analytical pure powders and are indefinitely stable at ambient temperature when stored under an inert atmosphere. Compounds **16b**–**19b** were

stable enough for their syntheses to be performed without exclusion of atmospheric air and moisture, but were subsequently stored under argon. Each protonated ligand displays only a single peak in the $^{31}P\{^{1}H\}$ NMR spectrum, suggesting rapid proton exchange on the NMR timescale, and apparent average C_{2v} symmetry in solution. As is usual for phosphinimine systems of this type, protonation causes the ^{31}P NMR resonance to shift downfield of the neutral ligand by approximately 20 ppm. Peaks appear in the $^{31}P\{^{1}H\}$ NMR spectra between δ 14.3 and 19.2 for **16a**–**19a** in CD_2Cl_2 solvent, and between δ 12.6 and 14.5 for **16b**–**19b** in acetone-d_6 solvent. The acidic proton is difficult to observe in CD_2Cl_2, but is observed as a broad singlet in the ^{1}H NMR spectra of **16b**–**19b** (acetone-d_6) in the range δ 4–5.

Table 4.2. $^{31}P\{^{1}H\}$ NMR chemical shifts of **16a**–**19a** (CD_2Cl_2) and **16b**–**19b** (acetone-d_6).

	16	**17**	**18**	**19**
a	15.8	14.3	16.2	19.2
b	13.7	12.6	14.2	14.5

4.3.2. Complex of L_2^{Mipp}

Generation of the cationic methylzinc complexes [$\mathbf{L_2^{Mipp}}$ZnMe$^+$][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **20a**, and [$\mathbf{L_2^{Mipp}}$ZnMe$^+$][BPh_4^-], **20b**, was easily achieved by reaction of $ZnMe_2$ with **16a** and **16b**. Surprisingly, there was no evidence for abstraction of a phenyl group from the BPh_4^- anion in **20b**, which is contrary to what was observed in the synthesis of the analogous $\mathbf{L_2^{Mes}}$ complex **10b**, and thus the synthesis provided compound **20b** cleanly. This observation is attributed to greater steric protection of the metal centre by the bulky *iso*propyl groups. The NMR

spectroscopic signatures of **20a** and **20b** are similar, with the organometallic methyl group resonating at δ –0.88 in the ^{1}H NMR spectra. A single sharp peak is observed in the $^{31}P\{^{1}H\}$ NMR spectrum at δ 22.7 (CD_2Cl_2) for each, which is shifted downfield by 6.9 ppm relative to the protonated ligand. This trend is consistent with that observed in previously studied systems and suggests a tightly bound zinc cation in a complex with symmetrically bound phosphinimines. The *iso*propyl CH_3 groups split into two resonances at δ 0.84 and 0.36 in the ^{1}H NMR spectrum, with the corresponding methine appearing as a septet at δ 3.23. Coalescence of these diastereotopic methyl groups can be explained by a *syn*–*syn* interconversion process as depicted in Scheme 4.2, which is consistent with the solid-state molecular structure (*vide supra*).

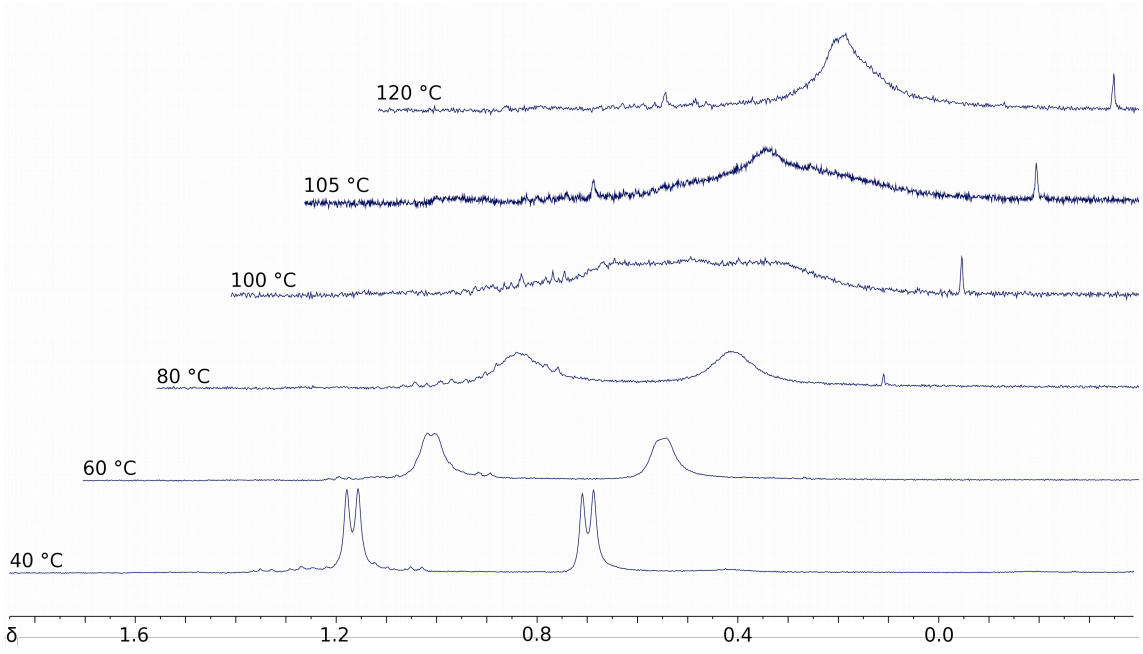
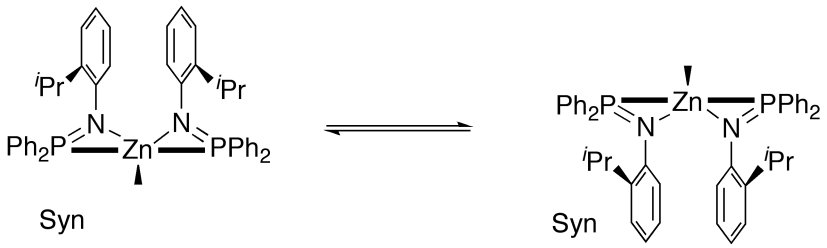


Figure 4.6. Variable-temperature ^{1}H NMR spectra of the *iso*propyl methyl groups of **20a** in C_6D_5Br solvent.



Scheme 4.2. Proposed fluxional process of compound **20a**. The dbf group is represented by a solid black line.

$$k_r = \kappa \frac{k_b T_{coal}}{h} e^{-\frac{\Delta G^{\ddagger}}{RT_{coal}}} \quad (\mathbf{4.1})$$

$$\Delta G^{\ddagger}_{coal} = 1.914 \times 10^{-2} (T_{coal})[9.972 + \log \frac{T_{coal}}{\Delta v}] \quad (\mathbf{4.2})$$

To determine the energy barrier associated with the *syn–syn* interconversion, a variable-temperature ^{1}H NMR study was performed (Figure 4.6). The energy barrier for such a process can be determined using the Eyring rate equation (Equation 4.1). A simplified and commonly used form of this equation for NMR exchange systems has been derived by Sandstrøm, which uses base-10 logarithms and assumes a transmission coefficient (κ) of 1 (Equation 4.2).[131] From the simplified equation, the required experimental parameters for energy barrier determination are the temperature of coalescence [T_{coal} (K)] and the maximum peak separation [$\Delta\nu$ (Hz)]. The two unique *iso*propyl doublets take on the appearance of broad singlets at 60 °C and above, and coalesce to a single broad peak at 105 °C (C_6D_5Br). The ambient temperature peak separation of 144.8 Hz is taken to be the maximum for this system, as there is no substantial reduction in the peak separation until the temperature reaches 80 °C. From this experimental data, an energy barrier of $\Delta G^{\ddagger}_{coal}$ = 75.3(8) kJ mol^{-1} was calculated using Equation 4.2. The coalesced peak

remains very broad at temperatures up to 120 °C, at which point decomposition of the compound begins to occur at a significant rate.

A solid-state molecular structure of **20b** has been determined crystallographically and is depicted in Figure 4.7, with selected bond lengths and angles provided in Table 4.3. The zinc centre is bound in a bidentate manner by the phosphinimines, with no interaction occurring between zinc and the dbf oxygen. The orientation and binding mode of the ligand within **20b** is unique compared with the previously studied compounds of the bis(phosphinimine) architecture, wherein the N-aryl groups bend away from the binding pocket in the same direction, resulting in a *syn* orientation and a C_s-symmetric complex. Conversely, all complexes of the ligand $\mathbf{L_2^{Mes}}$, discussed in Chapter 3, exhibited the *anti* configuration of the ligand, resulting in C_2-symmetric complexes. Apart from this unexpected relative orientation, the N-aryl groups behave in the expected manner, whereby the unsubstituted *ortho* site of each group is positioned near the dbf backbone. This places the *iso*propyl groups around the binding pocket, thereby resulting in a substantial degree of steric protection. There is evidence for a weak interaction between a methine hydrogen and zinc in the solid state, with an approximate Zn–H distance of 2.4 Å. The *syn* orientation of the ligand results in a rather sharp bite angle [N(1)–Zn(1)–N(2) = 113.30(5)°], although the coordination geometry at zinc is best described as three-coordinate trigonal planar. The Zn–N distances average 2.053(1) Å, which are noticeably longer than in the analogous complexes of the other $\mathbf{L_2}$ ligand variants (*vide infra*). This apparent weaker binding could be a result

of excessive steric repulsion from the *iso*propyl groups preventing the ligand from adopting an optimal orientation.

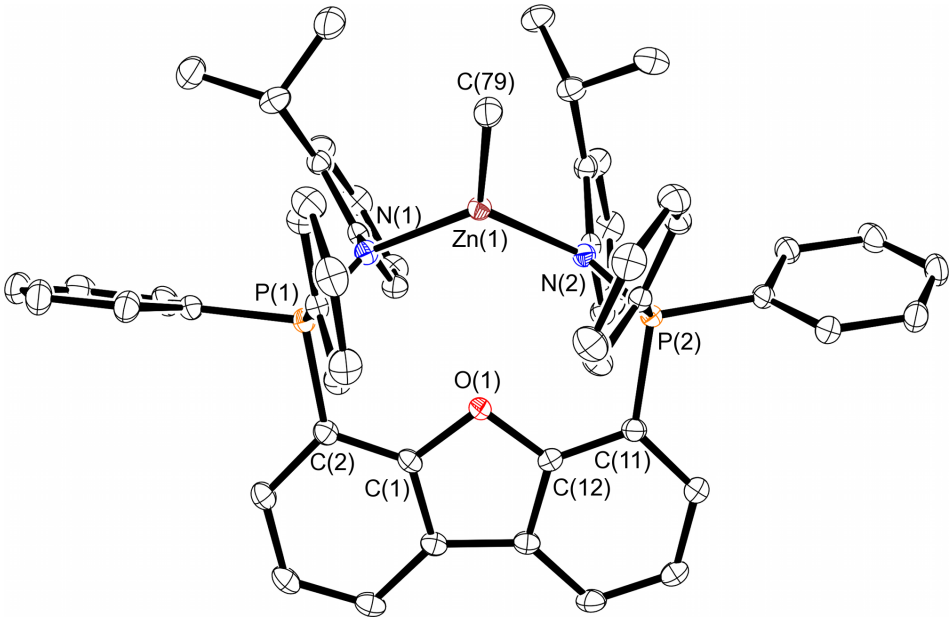


Figure 4.7. Displacement ellipsoid plot (30% probability) of the cation of **20b**. Hydrogen atoms and a molecule of benzene have been omitted for clarity.

Table 4.3. Selected bond lengths (Å) and angles (°) for compounds **20b**, **21b**, **22b**, and **23c**.

	20b	**21b**	**22b**	**23c**
Zn(1)–N(1)	2.050(1)	2.013(2)	2.044(2)	2.004(2)
Zn(1)–N(2)	2.056(1)	2.020(2)	2.051(3)	2.002(2)
Zn(1)–O(1)	3.125(1)	3.326(2)	2.284(2)	3.276(2)
Zn(1)–C(*x*)[a]	1.961(2)	1.967(4)	2.002(5)	1.977(2)
P(1)–N(1)	1.601(1)	1.599(2)	1.599(2)	1.601(2)
P(2)–N(2)	1.607(1)	1.602(2)	1.608(3)	1.600(2)
N(1)–Zn(1)–N(2)	113.30(5)	124.20(9)	112.5(1)	125.52(8)
N(1)–Zn(1)–C(*x*)[a]	123.67(7)	117.6(2)	122.4(2)	116.12(8)
N(2)–Zn(1)–C(*x*)[a]	122.37(7)	118.2(2)	124.6(2)	118.36(8)

[a]**20b**: *x* = 79; **21b**: *x* = 75; **22b**: *x* = 55; **23c**: *x* = 49

4.3.3. Complex of L_2^{Tol}

Reaction of dimethylzinc with the protonated ligands **17a** and **17b** rapidly generated the methylzinc complexes [$\mathbf{L_2^{Tol}}$ZnMe$^+$][B(*m*-(CF_3)$_2$-C_6H_3)$_4^-$], **21a**, and [$\mathbf{L_2^{Tol}}$ZnMe$^+$][BPh_4^-], **21b**, respectively. The synthesis afforded **21a** as an analytically pure powder in 97% yield. Unlike the corresponding methylzinc complexes of the other ligand variants discussed in this chapter, this compound shows two relatively broad resonances in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature which appear at δ 24.0 and 22.0 (C_6D_5Br) in a 1:1 ratio. This is not due to a lack of symmetry in the complex, but rather arises from the presence of two distinct $ZnCH_3$ peaks at δ –0.39 and –0.84 in the ^1H NMR spectrum. This conclusion has been further validated by variable temperature NMR studies (Figure 4.8), wherein it is observed that the two peaks in the $^{31}P\{^1H\}$ NMR spectrum ($\Delta\nu_{max}$ = 327.6 Hz) coalesce to a single broad resonance at 56 °C, which sharpens significantly at higher temperatures. Using Equation 4.1, the energy barrier for this process was calculated to be $\Delta G^{\ddagger}$ = 62.8(4) kJ mol^{-1}. A concomitant coalescence and sharpening of the unique ^1H NMR resonances are also noted, with the $ZnCH_3$ appearing at δ –0.40 (100 °C). Below ambient temperature, the NMR signatures of both isomers sharpen substantially while maintaining a 1:1 ratio. It is proposed that these peaks correspond to *anti* (C_2) and *syn* (C_s) orientations of the ligand (Scheme 4.3). While the bulkier cation in **20a/20b** appeared locked in a *syn* geometry, this observation shows that by

reducing the steric constraints on the system, the flexibility significantly increases while the energy difference between the *anti* and *syn* geometries is reduced.

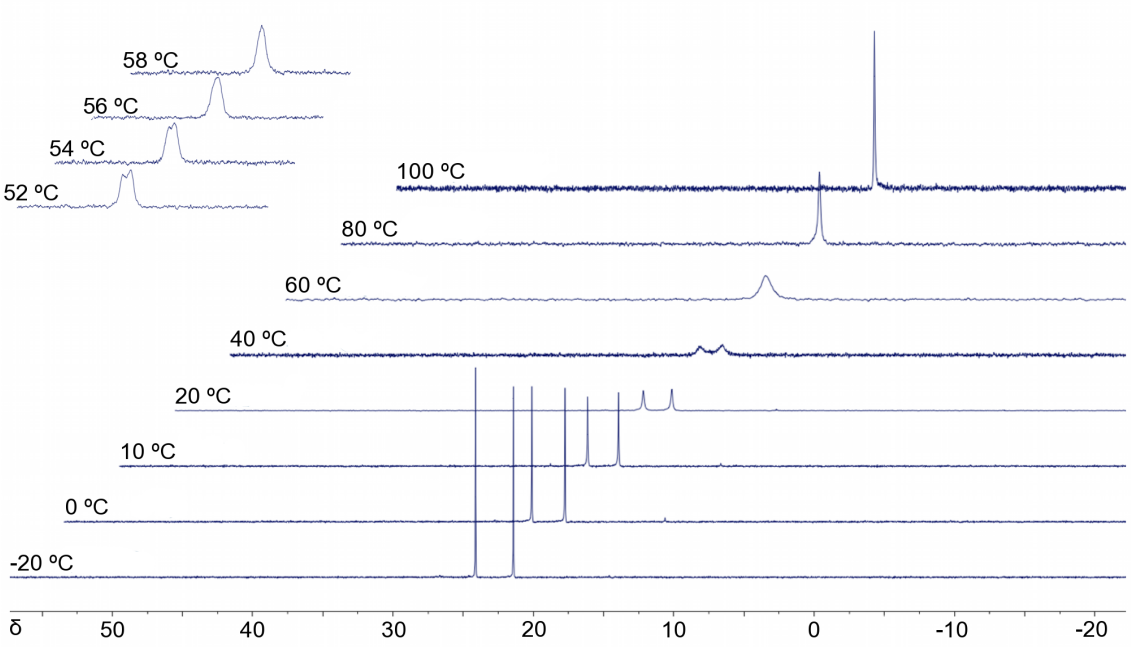
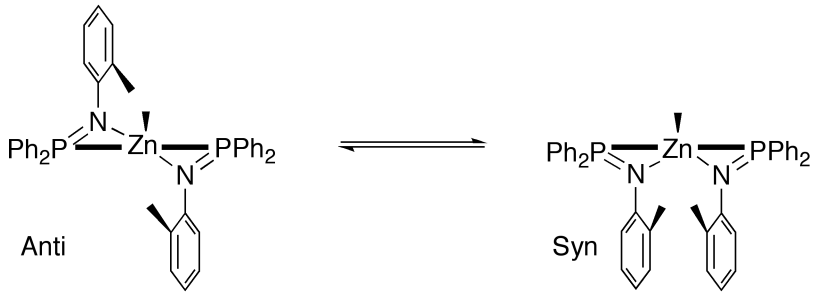


Figure 4.8. VT $^{31}P\{^{1}H\}$ NMR spectra of complex **21a**.



Scheme 4.3. Distinguishable structural isomers of complex **21a**. The dbf group is represented by a solid black line.

The synthesis of **21b** from **17a** and $ZnMe_2$ does not proceed cleanly, but also gives rise to the cationic zinc compound of the formula [$\mathbf{L_2^{Tol}}$ZnPh$^+$][$MeBPh_3^-$] (**21c**) as a by-product, in an approximate 60:40 ratio of **21b** to **21c**. Single crystals were

obtained from the mixture of **21b** and **21c**, and X-ray diffraction studies revealed the crystal to contain the cations of both compounds in a ratio of approximately 3:1. Only a single independent unit of the ligand and the zinc centre exist, and the presence of both components was modelled as a substitutional disorder of the methyl and phenyl groups.

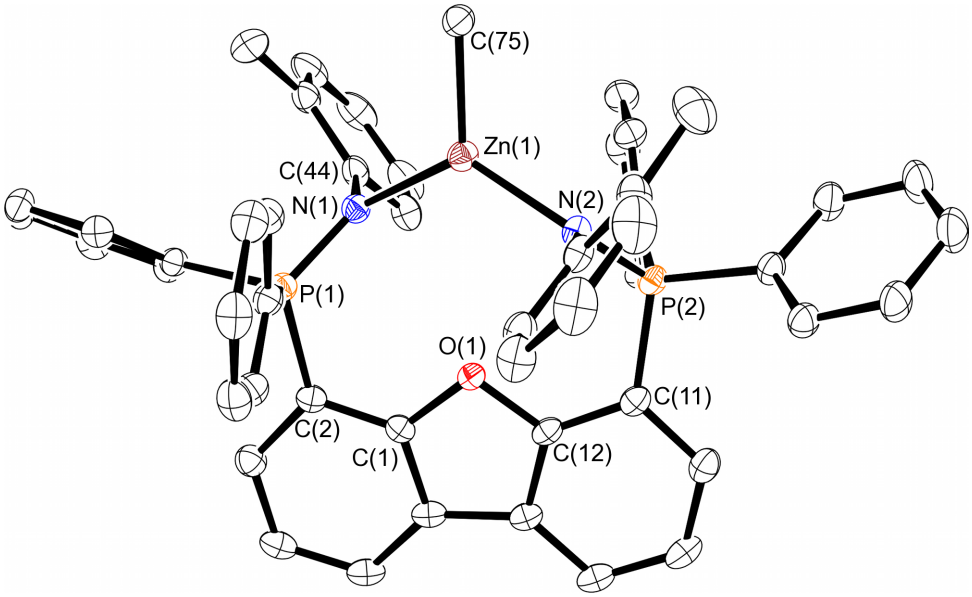


Figure 4.9. Displacement ellipsoid plot (30% probability) of the cation of **21b**. Hydrogen atoms and disordered atomic positions have been omitted for clarity.

The solid-state structure of **21b** is depicted in Figure 4.9 with the disorder omitted for clarity, and selected bond lengths and angles are presented in Table 4.3. The ligand is found to bind the zinc centre in a bidentate fashion, with no interaction between zinc and the dbf oxygen. The coordination geometry of zinc is thus best described as trigonal planar, and the sum of the bond angles about the zinc centre is 360.0(3)°. The ligand adopts an *anti* orientation rather the *syn* orientation noted in the structure of **20b**, and the complex is thereby *pseudo*-C_2-symmetric. The unsubstituted *ortho* sites of the *o*-tolyl groups are oriented toward the dibenzofuran

backbone, while the methyl groups occupy positions around the coordination sphere of the zinc atom, providing a modest degree of steric protection. Compared with the previously studied $\mathbf{L_2^{Mes}}$ analogue (**10b**), which was also C_2-symmetric in the solid state, the absence of a methyl group at one of the *ortho* sites allows the ligand to adopt a sharper bite angle much closer to the ideal 120° [N(1)–Zn(1)–N(2) = 124.29(9)°], resulting in a much less distorted trigonal planar geometry.

4.3.4. Complex of $\mathbf{L_2^{Pipp}}$

Reaction of **18a** with dimethylzinc in toluene afforded the cationic alkylzinc complex [$\mathbf{L_2^{Pipp}}$ZnMe$^+$][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **22a**. This reaction proved facile, proceeding to completion within several minutes at ambient temperature. The phosphinimine groups of complex **22a** are symmetry related in solution, whereby a single sharp resonance appears at δ 25.4 in the $^{31}P\{^1H\}$ NMR spectrum (C_6D_5Br solvent). There is no direct evidence for the existence of distinct *anti* and *syn* isomers for this complex, but it is reasonable to suggest that such isomers do occur, with interconversion between them very rapid on the NMR timescale due to the reduced steric demands of the system. In the ^1H NMR spectrum, the $ZnCH_3$ moiety appears at δ –0.79, while the diagnostic *iso*propyl methine and methyl groups shift upfield to δ 2.53 and δ 1.00, respectively. Despite repeated attempts, single crystals of **22a** suitable for X-ray diffraction studies remained elusive. However, upon utilization of the more crystalline tetraphenylborate counterion, single crystals of **22b**·$2.5C_6H_6$ were readily obtained. The synthesis of **22b** occurred similarly to **21b**, with formation of **22b** and the by-product [$\mathbf{L_2^{Pipp}}$ZnPh$^+$][$MeBPh_3^-$], **22c**, in a ratio of

3:1. The crystals contained both cationic species in a 72:28 ratio, and these were modelled as a substitutional disorder of the Me and Ph components.

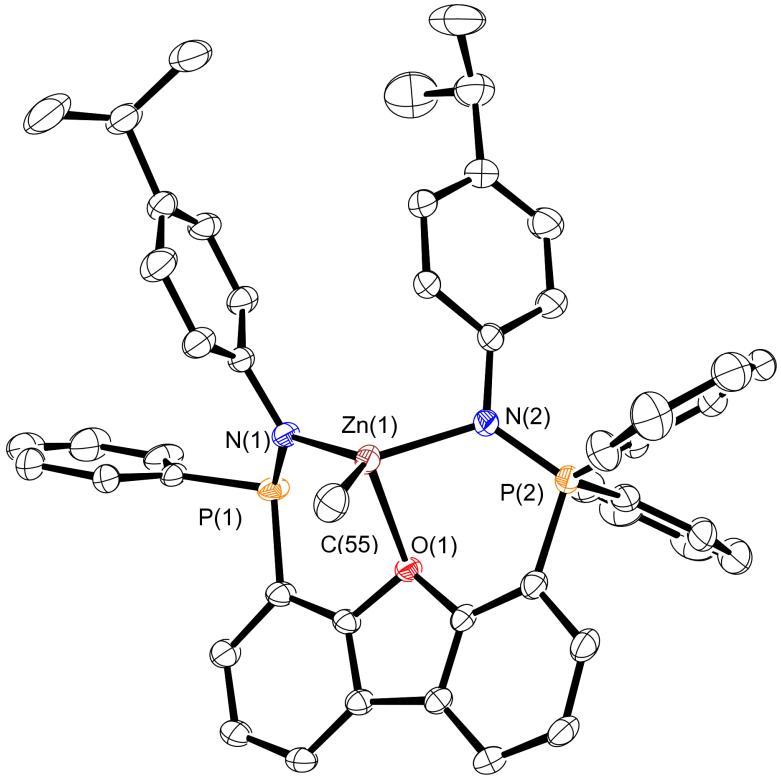


Figure 4.10. Displacement ellipsoid plot (30% probability) of the cation of **22b**. Hydrogen atoms, a phenyl ring of P(1), and disordered atomic positions have been omitted for clarity.

No significant interaction exists between the cation and the anion in the solid state, and thus the structure of the cation of **22b** can be considered an excellent representation of the cation of **22a**. Interestingly, this structure represents the first example of coordination of the dbf oxygen to zinc in the bis(phosphinimine) ligand framework. Due to this additional interaction, the geometry at zinc is 4-coordinate and best described as trigonal pyramidal, with the phosphinimines [Zn(1)–N(1) = 2.044(2) Å, Zn(1)–N(2) = 2.051(3) Å] and the methyl group [Zn(1)–C(55) = 2.002(5) Å] occupying the equatorial positions and the more weakly coordinated dbf oxygen

in the apical site [Zn(1)–O(1) = 2.284(2) Å]. The phosphinimine bite angle is slightly reduced from ideal [N(1)–Zn–N(2) = 112.5(1)°], although the sum of angles about the equatorial sites is 359.5(5)°. The coordination of the dbf oxygen is of significant interest given that such an interaction was not observed in analogous complexes of the bulkier ligands $\mathbf{L_2^{Mes}}$, $\mathbf{L_2^{Mipp}}$, and $\mathbf{L_2^{Tol}}$. Presumably, the reduced steric bulk of the Pipp groups renders this bonding mode possible.

4.3.5. Complex of $\mathbf{L_2^{Ph}}$

The cationic methylzinc complexes [$\mathbf{L_2^{Ph}}$ZnMe$^+$][*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **23a**, and [$\mathbf{L_2^{Ph}}$ZnMe$^+$][BPh_4^-], **23b**, were prepared similarly to the previously discussed complexes. The NMR spectra of **23a** are rather unremarkable, with the ZnMe moiety resonating in the ^{1}H NMR spectrum at δ –1.02, while a single peak is displayed the ^{31}P{^{1}H} NMR spectrum at δ 25.3. It is again probable that interconversion between *anti* and *syn* isomers can occur very rapidly on the NMR timescale, resulting in an average C_{2v} symmetry of the complex in solution.

Similarly to **21b** and **22b**, the synthesis of compound **23b** does not proceed cleanly, and a significant amount of a by-product with the formula [$\mathbf{L_2^{Ph}}$ZnPh$^+$][$MeBPh_3^-$] (**23c**) was formed with a ratio of 4:1 in favour of **23b**. Under the crystallization conditions employed, single crystals obtained from this mixture were enriched in the cation of **23c** (93%). Determination of the solid-state structure revealed a single molecule in the asymmetric unit, with the two compounds again modelled as a substitutional disorder of the phenyl and methyl groups. The solid-state structure of the cation of **23c** is depicted in Figure 4.11, while selected bond lengths and angles can be found in Table 4.3.

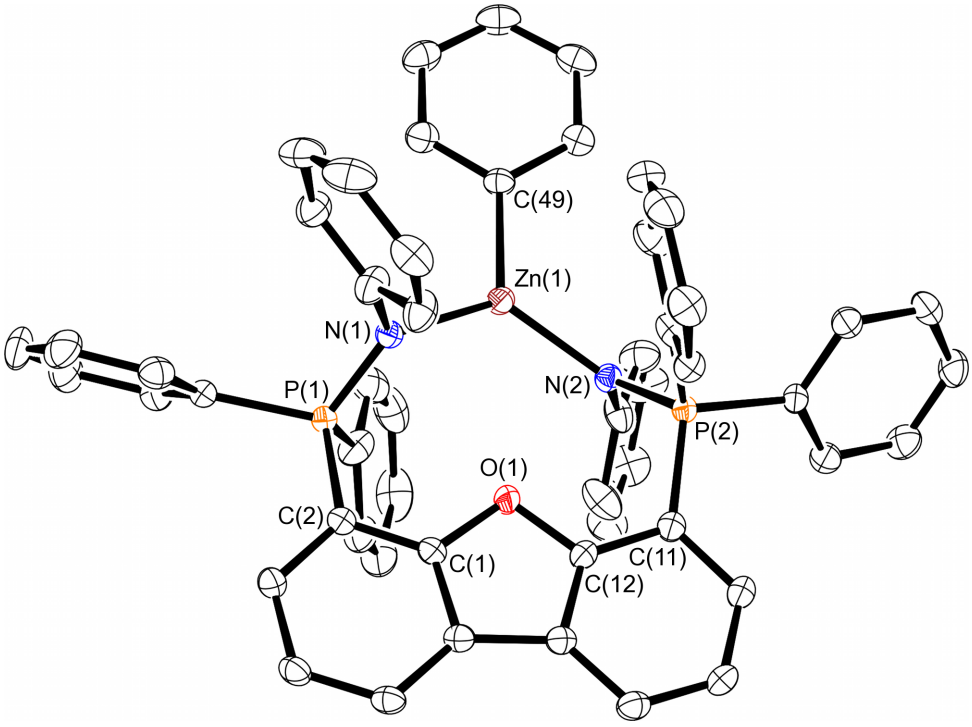


Figure 4.11. Displacement ellipsoid plot (30% probability) of the cation of **23c**. Hydrogen atoms and disordered P and N positions have been omitted for clarity.

The ligand binds to the zinc centre in a bidentate manner, with no significant interaction of the dbf oxygen, and the coordination geometry is again best described as trigonal planar. The lack of Zn–O bonding in this sterically unhindered complex is in surprising contrast to the structure of the $\mathbf{L_2^{Pipp}}$ analogue **22b**, and is probably best attributed to crystal packing effects. This suggests that the Zn–O bond observed in the sterically similar **22b** must be relatively weak. The ligand geometry exists primarily in a *pseudo*-C_2-symmetric *anti* configuration. However, both phosphinimine groups are significantly disordered, with the minor component of each occupying a *syn* configuration with respect to the major component of the other, lending support to the hypothesis that the complex undergoes rapid interconversion between *anti* and *syn* isomers in solution. This disorder was

modelled only as a positional disorder of the P and N atoms, in a ratio of 80:20 and 85:15 for P(1)–N(1) and P(2)–N(2), respectively (Figure 4.12). The bite angle of the ligand in its major *anti* orientation is very similar to that observed in complex **21b** (Table 4.3), though the bite angle of the *syn* orientation is notably sharper, and is comparable to that of complex **20b** [N(1)–Zn(1)–N(2b) = 114.6(3)°, N(1b)–Zn(1)–N(2) = 109.7(2)°].

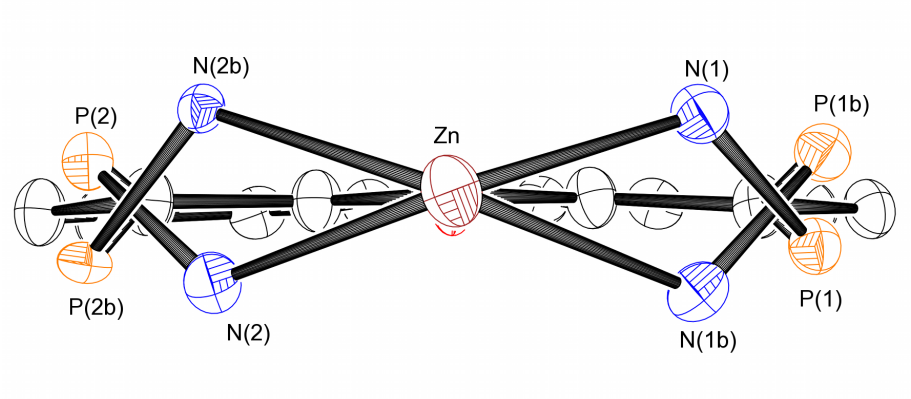


Figure 4.12. Displacement ellipsoid plot (30% probability) of the cation of **23c**, viewed down the dbf plane, showing only the dbf moiety, the Zn atom, and the disordered P and N atoms.

4.4. Conclusions

In summary, a series of closely related bis(phosphinimine) ligands (**L**$_2$), built using the dibenzofuran backbone, have been prepared. These ligands differ only in the steric bulk of the N-aryl substituents, where at least one *ortho* position of the N-aryl groups is left unsubstituted. Cationic methylzinc complexes of each ligand were prepared and characterized by multinuclear NMR spectroscopy and X-ray crystallography. The structural investigations revealed that the steric bulk of the N-aryl groups has a substantial impact on the orientation of the ligand in the complexes. In particular, a bulky *ortho* substituent

($\mathbf{L_2^{Mipp}}$) resulted in a C_s symmetric *syn* orientation, while a less sterically demanding *ortho* substituent ($\mathbf{L_2^{Tol}}$) brought about a system that slowly interconverts between *anti* and *syn* orientations. Most interesting is the observation that further reduction of the steric bulk allows the ligand $\mathbf{L_2^{Pipp}}$ to bind in a tridentate manner through an additional Zn–O interaction, giving a complex with trigonal pyramidal coordination geometry. The implications of these effects in regard to lactide polymerization have been explored, and these studies are the topic of Chapter 5.

Chapter 5: Synthesis, Structures, and Polymerization Properties of Cationic Zinc-Lactate Complexes

5.1. Introduction

A more complete understanding of the effects of ligand steric bulk on the structure of zinc complexes has now been gained through the studies described in Chapter 4. However, it is also desirable to understand what effect these modifications have on catalytic activity toward ring-opening polymerization of lactide. Unfortunately, the methylzinc complexes are inactive for this transformation. For that reason, the analogous zinc-lactate complexes have been prepared *via* the same synthetic route used for the synthesis of the zinc-lactate compound **13** discussed in Chapter 3. The present chapter details the synthesis and characterization of a series of zinc lactate complexes as well as a study of their efficacy as catalysts for the ring-opening polymerization of *rac*-lactide.

5.2. Synthesis and Characterization of Zn-Lactate Complexes

As mentioned above, it was necessary to install a suitable initiating group in order that lactide polymerization might be effectively performed. The findings of Chapter 3 suggest that a lactate initiating group will be most suitable due to the relative ease of synthesis compared with alkoxides and a relatively high rate of initiation compared with zinc alkyl complexes. The synthesis was performed by reaction of the protonated ligand salts of the formula $[LH^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$

with the reagent EtZn(methyl-L-lactate), which installs a lactate initiating group through a single protonolysis step. This is not only an excellent initiating group, but provides the added advantage of being a very close structural mimic of the growing polymer chain, and thus, characterization of such complexes provides a great deal of insight into the nature of the active catalyst species. The synthesis of these complexes requires rather harsh conditions relative to preparation of the related methylzinc compounds, and therefore the tetraphenylborate anion could not be employed. Additionally, the synthetic methodology proved ineffective for the most sterically hindered ligand $\mathbf{L_2^{Mipp}}$. For this reason, only zinc-lactate complexes of $\mathbf{L_2^{Tol}}$, $\mathbf{L_2^{Pipp}}$, and $\mathbf{L_2^{Ph}}$ have been prepared and studied.

5.2.1. Complex of $\mathbf{L_2^{Tol}}$

Reaction of **17a** with EtZn(methyl-L-lactate) for a period of 1 hour at 100 °C cleanly afforded [$\mathbf{L_2^{Tol}}$ZnOCH(Me)CO_2Me$^+$][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **24**, as a thermally stable white crystalline solid in 76% yield. Compound **24** displays dynamic solution behaviour similar to the methylzinc complex of the same ligand (**21**), with broad resonances appearing in the ^{1}H NMR spectrum. However, instead of two distinct isomers, the ^{31}P{^{1}H} NMR spectrum revealed three major isomers, which give rise to three broad resonances at ambient temperature (δ 27.0, 26.6, and 26.0 in C_6D_5Br solvent) with approximately equal intensity (Figure 5.1). These coalesce to a single broad resonance at 60 °C, corresponding to a slightly higher activation barrier of approximately $\Delta G^{\ddagger}$ = 67 kJ mol^{-1}, calculated using Equation 4.1 ($\Delta\nu_{max}$ = 120 Hz). This is taken as an approximate energy barrier due to the inability to achieve full peak separation at –20 °C, which approaches the lower temperature limit for C_6D_5Br

solvent. The peak sharpens considerably at elevated temperatures, giving a singlet at δ 27.2 in the $^{31}P\{^{1}H\}$ NMR spectrum at 80 °C. The ^{1}H NMR spectrum also exhibits sharp signals at this temperature, and the characteristic peaks of the methyl-lactate group are observed at δ 4.39 ($CHCH_3$), 2.89 (OCH_3), and 1.35 (CCH_3).[132] At temperatures below 20 °C, the $^{31}P\{^{1}H\}$ NMR spectrum becomes more complicated, with some regions displaying significant broadening, but at –20 °C the spectrum is dominated by two relatively sharp peaks at δ 26.7 and 25.7.

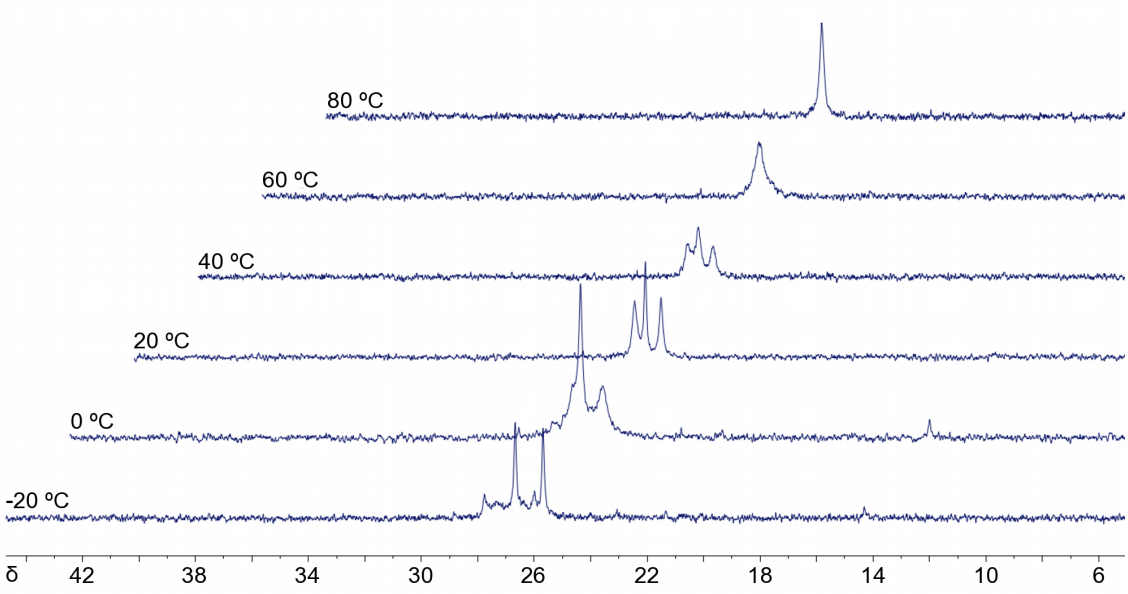
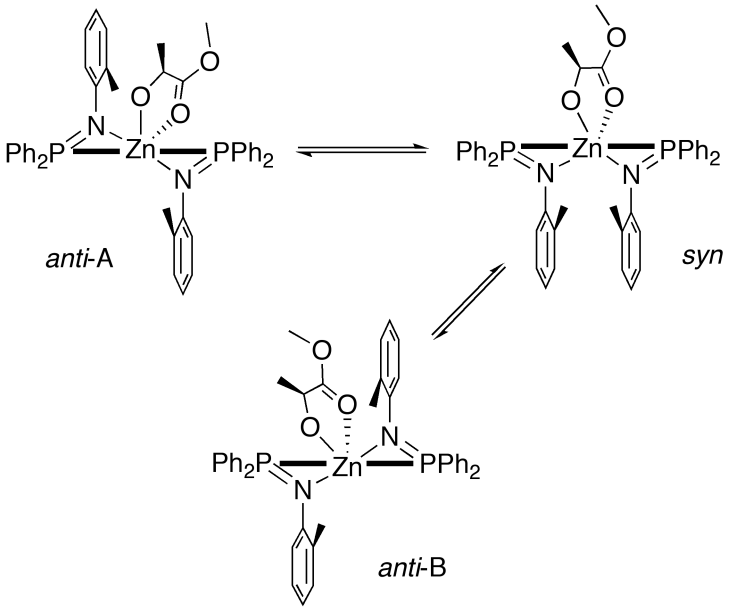


Figure 5.1. VT $^{31}P\{^{1}H\}$ NMR spectra of complex **24**.

The presence of three isomers is readily explained by considering the symmetry of the ligand in the *anti* and *syn* orientations and how these interact with the asymmetric methyl-lactate moiety. When the ligand exists in the C_2-symmetric orientation, two unique diastereomers can be distinguished for a given methyl-lactate enantiomer (*anti*-A and *anti*-B, Scheme 5.1), while for the C_2-symmetric orientation only a single diastereomer is possible (*syn*). For the opposite enantiomer

of the methyl-lactate moiety (if epimerization occurred during complex synthesis), the resulting isomers are enantiomers of the former, and would thus contribute to the same three peaks in the spectrum.



Scheme 5.1. Possible isomers of complex **24** for a methyl-L-lactate moiety, with a view down the plane of the dbf backbone. The dbf moiety is represented by a solid black line.

Single crystals of **24**·CH_2Cl_2 were grown by slow diffusion of pentane into a methylene chloride solution of the compound, and the solid-state structure was determined (Figure 5.2, Table 5.1). The molecular structure of **24** provides further insight into the dynamic solution properties of complexes of $\mathbf{L_2^{Tol}}$ discussed above and in the preceding chapter because it provides an example of the ligand in the *syn* configuration, rather than the *anti* configuration observed in the structure of the methylzinc complex **21b**. The ligand binds to the zinc centre in a bidentate manner, with no evidence for a significant interaction between zinc and the dbf oxygen atom. As expected, the methyl-lactate moiety also binds the zinc centre in a bidentate

mode, resulting in a 4-coordinate geometry that is best described as distorted trigonal pyramidal. The equatorial sites are occupied by the phosphinimine donors of the ligand and the formally anionic O(3) of the lactate group, with bond lengths in the expected ranges, and a sum of angles about the equatorial positions of the zinc centre of 358.7(3)°.

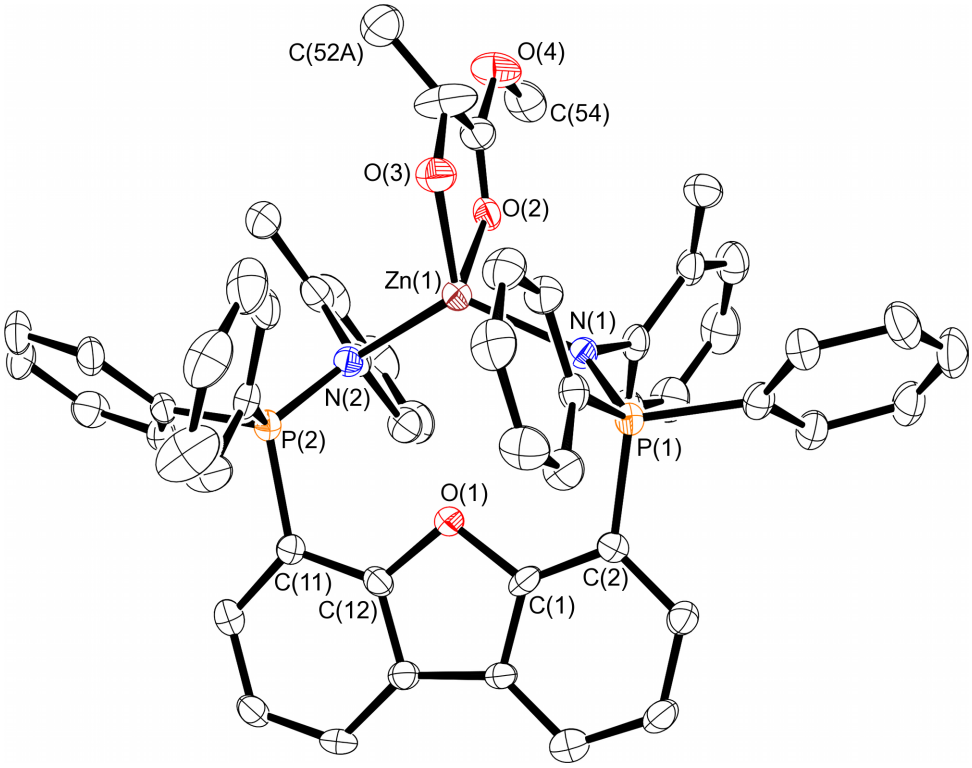


Figure 5.2. Displacement ellipsoid plot (30% probability) of the cation of **24**. Hydrogen atoms, disordered atomic positions, and a molecule of methylene chloride have been omitted for clarity.

The bite angle of the ligand in this *pseudo*-C_s-symmetric complex is 124.8(2)°, which is very similar to that of the C_2-symmetric ligand in the analogous methylzinc complex **21b** (124.21(9)°). This shows that the ligand is capable of adopting an ideal bite angle not just in the *anti* orientation, but also in the *syn* orientation. Although there is only one independent molecule in the asymmetric unit, the complex exists

as a racemic mixture, with the two enantiomers being modelled as a positional disorder of the methyl group C(52). This observation suggests racemization was caused by the harsh reaction conditions employed for the synthesis of **24**.

Table 5.1. Selected bond lengths (Å) and angles (°) for compounds **24**–**26**.

	24	**25**	**26**
Zn(1)–N(1)	2.014(5)	2.014(6)	2.016(3)
Zn(1)–N(2)	1.996(4)	2.000(5)	1.988(3)
Zn(1)–O(1)	3.247(4)	2.336(5)	2.367(2)
Zn(1)–O(2)	2.105(4)	2.120(6)	2.131(3)
Zn(1)–O(3)	1.921(4)	1.909(6)	1.904(3)
P(1)–N(1)	1.599(4)	1.591(5)	1.600(2)
P(2)–N(2)	1.593(5)	1.598(7)	1.597(4)
N(1)–Zn(1)–N(2)	124.8(2)	118.4(2)	116.2(1)
N(1)–Zn(1)–O(3)	115.3(2)	119.8(2)	122.3(1)
N(2)–Zn(1)–O(3)	118.6(2)	119.1(2)	117.6(1)
O(3)–Zn(1)–O(2)	83.2(2)	83.6(2)	83.3(1)
N(1)–Zn(1)–O(2)	99.6(2)	101.7(2)	103.2(1)
N(2)–Zn(1)–O(1)	N.A.	80.4(2)	83.7(1)
O(1)–Zn(1)–O(2)	N.A.	169.8(2)	168.3(1)

5.2.2. Complex of L_2^{Pipp}

[$\mathbf{L_2^{Pipp}}$ZnOCH(Me)CO_2Me^+][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **25**, was prepared by reaction of **18b** with EtZn(methyl-L-lactate) in bromobenzene at 100 °C for 2 hours. Characteristic signals for the lactate group of complex **25** were observed in the ^{1}H NMR spectrum at δ 3.19 (OCH_3), 3.76 (CHCH_3), and 0.94 (CHCH_3). Despite the

presence of the asymmetric lactate group, **25** exhibits apparent symmetry related phosphinimine groups in solution, with a single peak appearing in the $^{31}P\{^{1}H\}$ NMR spectrum at δ 28.9. The appearance of a single sharp peak contrasts observations made for complex **24**, and suggests rapid fluxional behaviour occurs in solution on the NMR timescale.

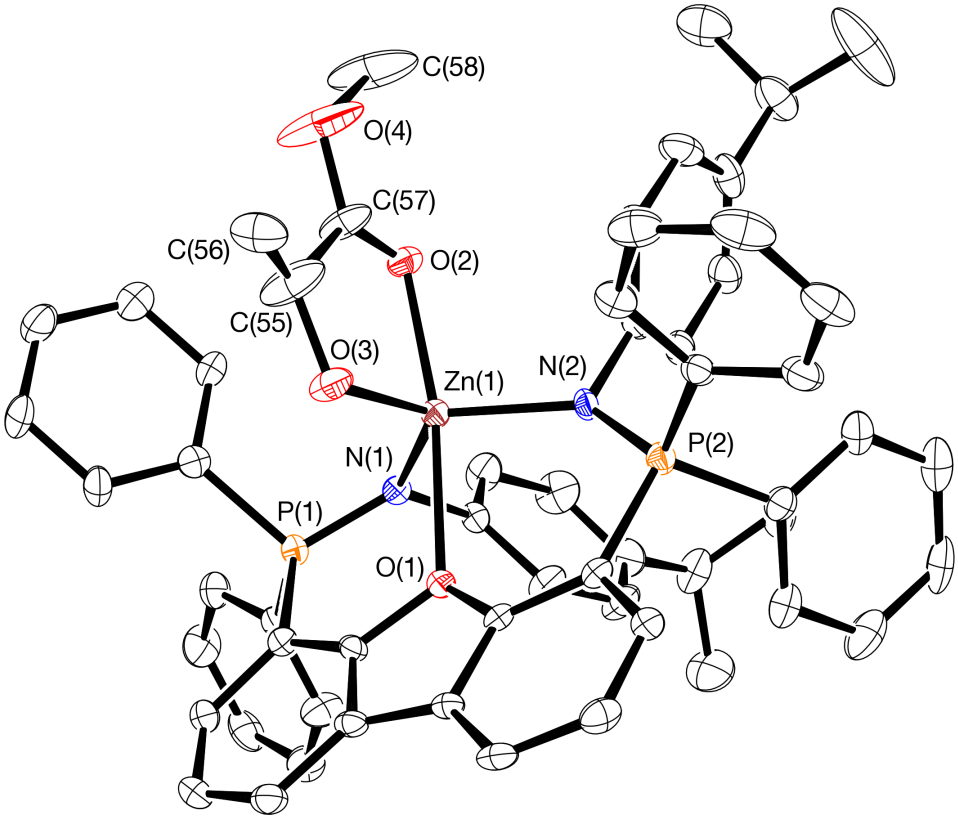


Figure 5.3. Displacement ellipsoid plot (30% probability) of the cation of **25**. Hydrogen atoms and disordered atomic positions have been omitted for clarity.

Single crystals of **25**·C_6H_6 were obtained by slowly cooling a benzene solution of the compound from 100 °C to ambient temperature. The solid-state structure of **25** is depicted in Figure 5.3 and selected metrical parameters are found in Table 5.1. The structure reveals a similar ligand binding mode as compared to the methylzinc complex of $\mathbf{L_2^{Pipp}}$ (**22b**), with strong coordination of both phosphinimine

donors [Zn(1)–N(1) = 2.014(6) Å; Zn(1)–N(2) = 2.000(5) Å] and weaker but significant coordination of the dbf oxygen [Zn(1)–O(1) = 2.336(5) Å]. The geometry at zinc is thus trigonal bipyramidal, with the phosphinimine nitrogen atoms and the formally anionic lactate oxygen, O(3), occupying the equatorial positions [Zn(1)–O(3) = 1.909(6) Å]. The sum of angles about the equatorial sites of the zinc atom is 357.3(6)°, with all angles slightly less than 120°. The lactate carbonyl oxygen occupies the apical site [Zn(1)–O(2) = 2.120(6) Å] opposite the dbf oxygen, which was vacant in complex **25**. The angle between these apical sites is 169.8(2)°. The lactate moiety exists as a 50:50 mixture of L and D isomers, which was modelled as a two-site positional disorder of the C(56) atom.

5.2.3. Complex of L_2^{Ph}

Reaction of **19a** with EtZn(methyl-L-lactate) for a period of 1 hour at 100 °C cleanly afforded [$\mathbf{L_2^{Ph}}$ZnOCH(Me)CO_2Me$^+$][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **26**, as a thermally stable powder in 72% yield. The NMR spectra of **26** are relatively simple, with sharp peaks arising at ambient temperature, including only a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 29.3. This indicates an average C_{2v} symmetry in solution, with fluxional behaviour between possible orientations that is rapid on the NMR timescale. However, examination of the ^1H NMR spectrum reveals the presence of two unique isomers, as evidenced by two distinct sets of signals for each proton of the cationic species. Specifically, peaks appear in the ^1H NMR spectrum from the lactate group at δ 3.42, 3.44, and 0.87, which correspond to the methine, methoxy, and methyl groups, respectively, while a second set appears at δ 4.07, 3.93, and 1.36

(CD_2Cl_2), with approximately equal intensity. The identity of these isomers is presently unknown, but may be related to the relative positions of the two coordinating methyl-lactate oxygen atoms with respect to axial and equatorial positions in the trigonal bipyramidal complex (*vide infra*). Single crystals of **26**·C_6H_5Br were obtained from a bromobenzene solution layered with pentane at –35 °C, and the solid-state molecular structure is depicted in Figure 5.4.

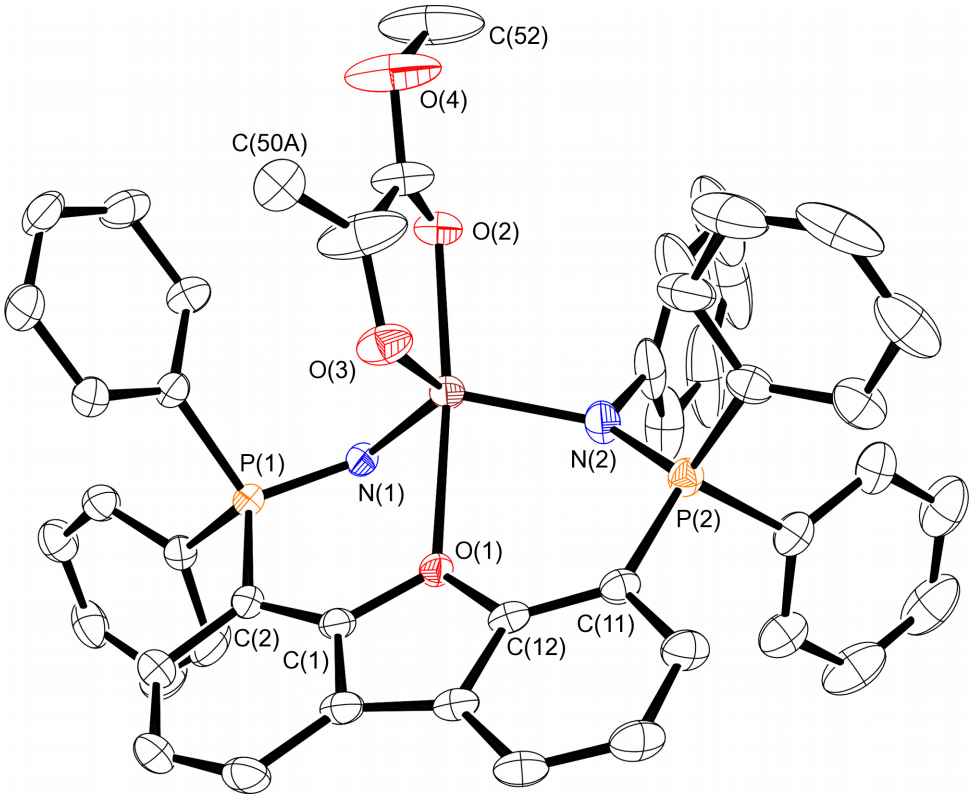


Figure 5.4. Displacement ellipsoid plot (30% probability) of the cation of **26**. Hydrogen atoms, an N–Ph group, disordered atomic positions, and a disordered molecule of bromobenzene have been omitted for clarity.

The molecular structure of **26** shows some significant differences compared with that of **24**, despite the seemingly small change in the ligand. Specifically, the zinc centre is bound by the ligand in a tridentate manner, with significant bonding of

the dbf oxygen [Zn(1)–O(1) = 2.367(2) Å]. The geometry is best described as 5-coordinate trigonal bipyramidal and is essentially isostructural with that of the $\mathbf{L_2^{Pipp}}$ analogue **25**. The equatorial sites are occupied by the phosphinimine N-donors and the formally anionic O(3) atom, and the sum of angles about these equatorial sites of the zinc centre is 356.1(2)°. The weaker, formally neutral oxygen donors occupy the axial sites, and the corresponding O–Zn–O angle is 168.3(1)°. As in the structures of **24** and **25**, the lactate moiety exists as a 50:50 mixture of L and D isomers, which is modelled as a positional disorder of C(50).

5.3. Polymerization Studies

5.3.1. General Trends in Polymerization Rate

Compound **24** shows little activity for polymerization of *rac*-LA at ambient temperature and must be heated to 60 °C to achieve polymerization at a reasonable rate. In $CDCl_3$ solvent at 60 °C, with an initial monomer concentration of 1 M and a catalyst loading of 0.5 mol% ($[LA]_0/[\mathbf{24}] = 200$), polymerization occurs under first-order kinetics with an observed rate constant of $3.65(2)\times10^{-4}$ s^{-1}. This rate is only slightly greater than that observed for the bulkier $\mathbf{L_2^{Mes}}$ analogue discussed in Chapter 3 (**13**), despite the significant reduction in steric bulk.

Complex **25** is a highly active catalyst for the polymerization of lactide at ambient temperature, giving 90% conversion of 200 equivalents of *rac*-lactide in 50 minutes (25 °C, CD_2Cl_2 solvent). Remarkably, such activity is comparable to some of the most highly active zinc-based catalyst systems known.[133] Measurement of the

rate under these conditions confirmed the reaction was first order in [LA], with an observed rate constant of $8.65(4)\times10^{-4}$ s^{-1}.

Compound **26** also displays high activity at ambient temperature, and in CH_2Cl_2 solvent the observed first-order rate constant at 25 °C was established to be $5.11(3)\times10^{-4}$ s^{-1}. Interestingly, this rate is somewhat lower than that determined for **25** ($8.65(4)\times10^{-4}$ s^{-1}) under identical conditions, despite their similar steric bulk. The modest reduction in activity cannot be attributed to steric crowding, and therefore the difference must arise predominantly from electronic effects. It is proposed that the lack of a *para-iso*propyl group on the N-aryl ring reduces the electron donating capacity of the ligand, thereby rendering the zinc centre modestly more electropositive in **26** compared with **25**. This demonstrates a high dependence of activity on the electrophilicity of the metal centre in these systems and suggests that better moderation of the electrophilicity leads to improved activity. This observation also leads to the conclusion that the reason for the large reduction in activity of **24** versus **25** and **26**, which is not commensurate with the difference in steric bulk, is due largely to the difference in the coordination geometry of the ligand. Specifically, the interaction between the cationic zinc centre and the dbf oxygen, which is only present in sterically unhindered complexes (**25** and **26**), appears to have a substantial impact on the moderation of the electrophilicity of the metal. It can thus be concluded that reduced steric bulk with concomitant reduction in metal electrophilicity act synergistically to promote enhanced LA polymerization activity in cationic zinc complexes stabilized by dbf-based bis(phosphinimine) pincer ligands.

All of these systems display living characteristics, whereby complete consumption of monomer does not result in catalyst death, and addition of more monomer results in continued consumption by the active catalyst and continued growth of the polymer chain. This living character has been quantified using complex **25** as catalyst. Five hours after initiating the polymerization of 200 equivalents of *rac*-LA, a second portion of monomer of equal amount was added, which was consumed under well-behaved first order kinetics with an observed rate constant of $8.1(1)\times10^{-4}$ s^{-1}, representing only a very slight reduction in rate (Figure 5.5).

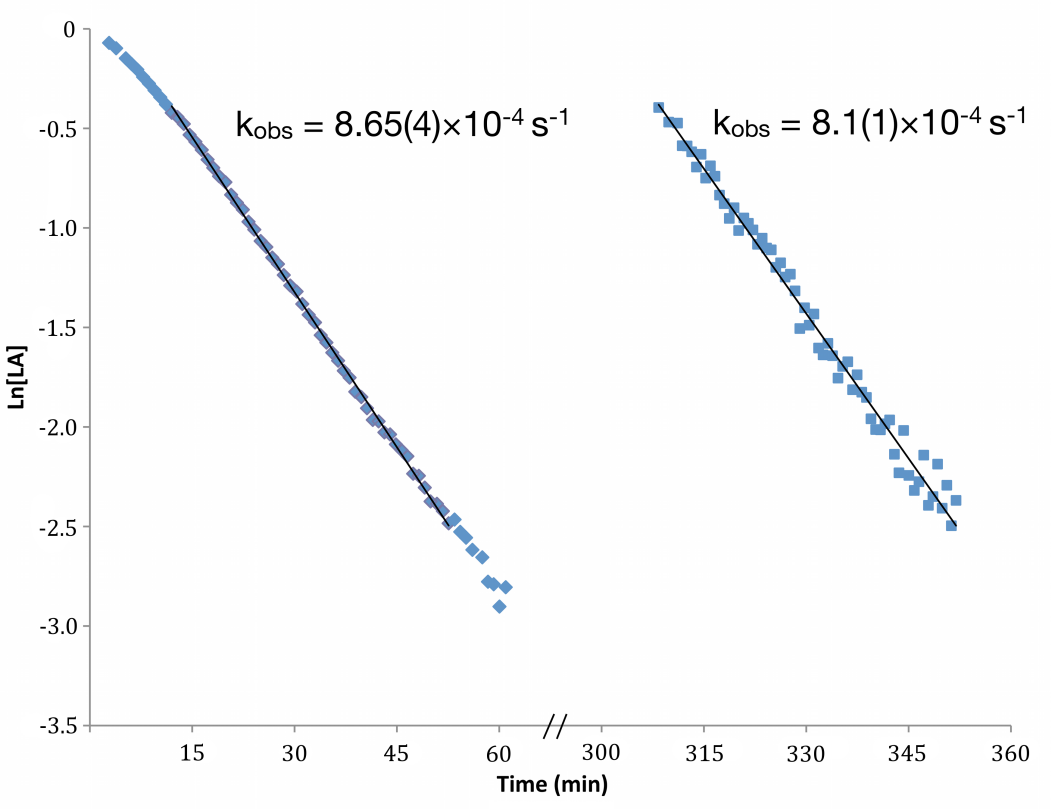


Figure 5.5. Determination of k_{obs} for complete polymerization of 200 equivalents of *rac*-LA by **25**, followed by polymerization of a second batch of *rac*-LA, demonstrating living behaviour.

5.3.2. Microstructure Analysis

Stereosequences of PLA can be resolved in the methine region of ^{1}H NMR spectra using simple homonuclear decoupling experiments, which give tetrad resolution at the field strength of most modern NMR instruments.[134] For poly(*rac*-lactide), four possible tetrad stereosequences can be observed. The chemical shifts in $CDCl_3$ solvent and their corresponding stereosequence assignments can be found in Table 5.2, where "i" represents an isotactic linkage and "s" represents a syndiotactic linkage (e.g., sis = -RSSR- and -SRRS- sequences). Based on Bernoullian statistics, completely atactic poly(*rac*-lactide), assuming no epimerization, should show peaks with relative intensities of 1:1:1:3:2. Deviations from these relative intensities represent either a heterotactic bias (increase in "isi" and "sis" sequences) or an isotactic bias (increase in the "iii" sequence). For heterotactic enriched PLA, the tacticity can be quantified using the formula $P_r^2/2$ = [sis], where P_r is the probability of heterotactic enchainment that equals 0.5 for atactic PLA and 1 for completely heterotactic PLA. The probability of isotactic enchainment (P_m) is then given by the simple relation $P_r + P_m = 1$.

Table 5.2. Assignment of stereosequences of atactic poly(*rac*-lactide).

Chemical Shift (ppm)	Stereosequence	Relative Intensity
5.24	sis	0.125
5.22 / 5.19	sii/iis	0.125/0.125
5.18	iii	0.375
5.17	isi	0.25

Stereosequence analysis of polymer samples prepared using catalysts **24**–**26** was performed using the method described above, and the resulting spectra are shown in Figure 5.6. It was found that catalysts **24** and **25** generate polymer with a similar modest heterotactic enrichment, with P_r values of 0.62 and 0.61, respectively. This enrichment is most likely due to a chain-end control process.[12f] However, it has been found that catalyst **26** promotes enhanced stereocontrol, with isolated polymer samples showing significant heterotactic enrichment (P_r = 0.70). This level of stereoregularity is uncommon for room-temperature active zinc systems and represents the best stereocontrol yet to be reported for polymerization of *rac*-lactide by a cationic metal complex. The result is surprising given that this catalyst is less bulky than **24** or **25**, where chain-end control is generally enhanced for bulkier catalysts. However, the improved control relative to **25** could be a consequence of the modestly reduced activity of this system.

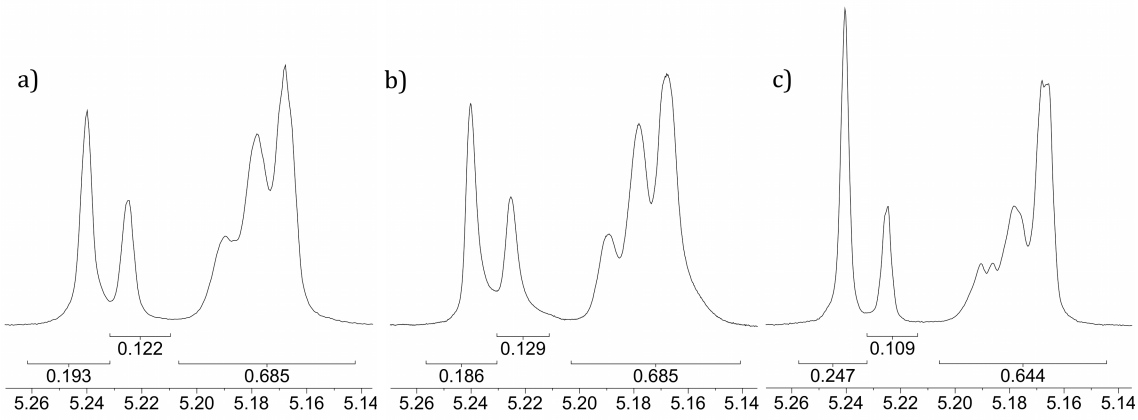


Figure 5.6. The methine region of the homonuclear decoupled ^{1}H NMR spectrum of PLA prepared using **24** (a), **25** (b) and **26** (c).

5.3.3. Mechanistic Studies

Complex **25** displayed the best activity of the series, and thus this system was chosen for more detailed mechanistic and kinetic studies. Upon exposure of **25** to excess *rac*-LA, immediate conversion to a new species with a $^{31}P\{^{1}H\}$ NMR chemical shift (at δ 29.4) slightly downfield of the initial catalyst (δ 28.9) was observed. More notably, the lactate end group gives rise to a singlet at δ 3.64 in the ^{1}H NMR spectrum, corresponding to the OCH_3 group, which is 0.45 ppm downfield of complex **25**. The methine signal, however, was not observed and is likely obscured beneath the LA/PLA signals. The very slight change in ligand resonances coupled with the very large change in the methyl-lactate OCH_3 resonance suggest that this new species is the product of insertion of one or more monomer units, thereby providing strong evidence for a coordination-insertion mechanism.

In addition, a low molecular weight polymer sample ($[LA]_0/[\mathbf{25}]$ = 50) was analysed by MALDI-ToF mass spectrometry, and the observed masses of all oligomer fragments were consistent with the presence of a methyl-lactate end-group (Figure 5.7). The mass peaks are separated by m/z 72, which suggests that intermolecular transesterification occurs to a significant degree during polymerization. Mass spectra of polymer samples prepared using **24** and **26** gave similar results.

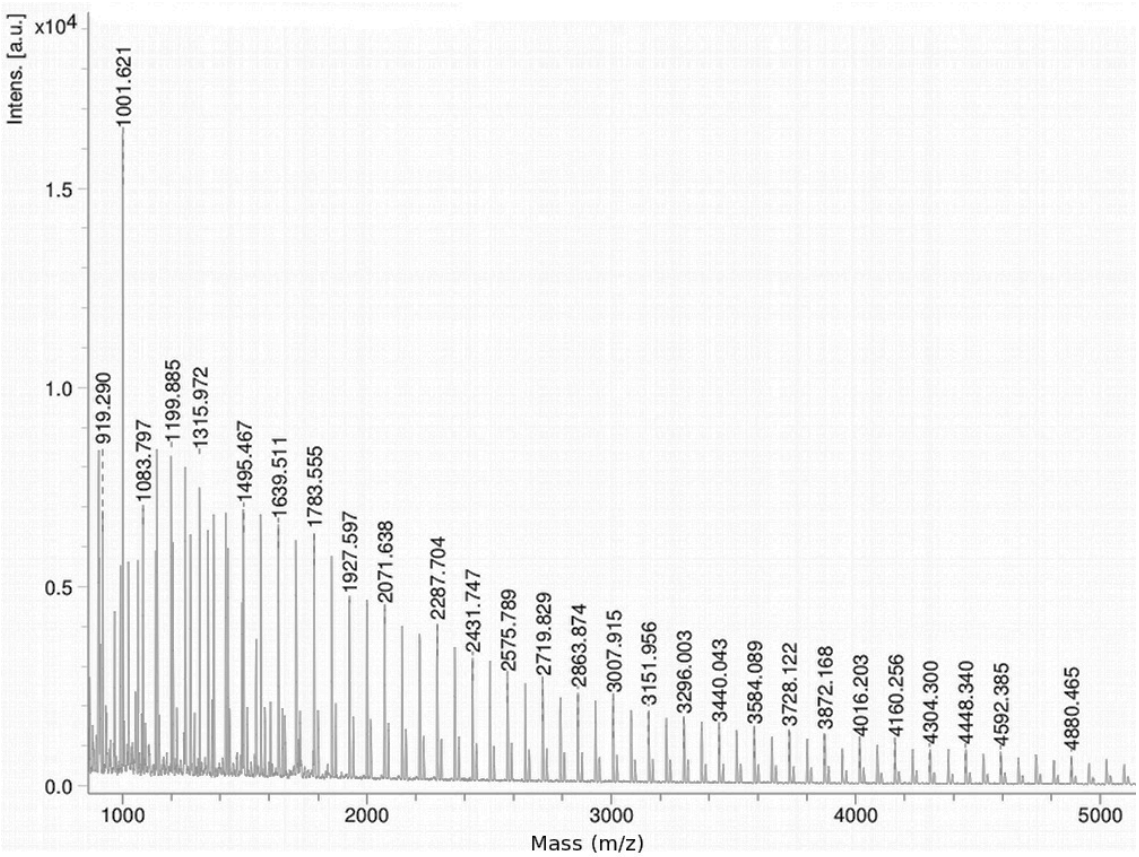


Figure 5.7. MALDI-ToF mass spectrum of a polymer sample prepared using complex **25** as the catalyst, with a catalyst loading of 2%.

5.3.4. Kinetic and Thermodynamic Studies

While it has already been established that the polymerization proceeds with first order kinetics in [LA], the reaction order with respect to catalyst has not been established. Therefore, the observed rate constant was measured at various concentrations of **25** (Table 5.3). A plot of k_{obs} versus [**25**] is linear (Figure 5.8), establishing the polymerization to be first order in catalyst concentration, giving an overall second order rate law (rate = k[**25**][LA]). Moreover, the second-order rate constant was taken from the slope of this graph, which gave k = 0.17(1) s^{-1} M^{-1}.

Table 5.3. Measured values of k_{obs} for polymerization of *rac*-LA at various concentrations of **25** as catalyst.

[**25**] (mol L^{-1})	k_{obs} (s^{-1})
0.01	$1.65(1) \times 10^{-3}$
0.008	$1.317(7) \times 10^{-3}$
0.006	$1.081(4) \times 10^{-3}$
0.005	$8.65(4) \times 10^{-4}$
0.004	$8.43(4) \times 10^{-4}$
0.002	$1.921(5) \times 10^{-4}$
0	0

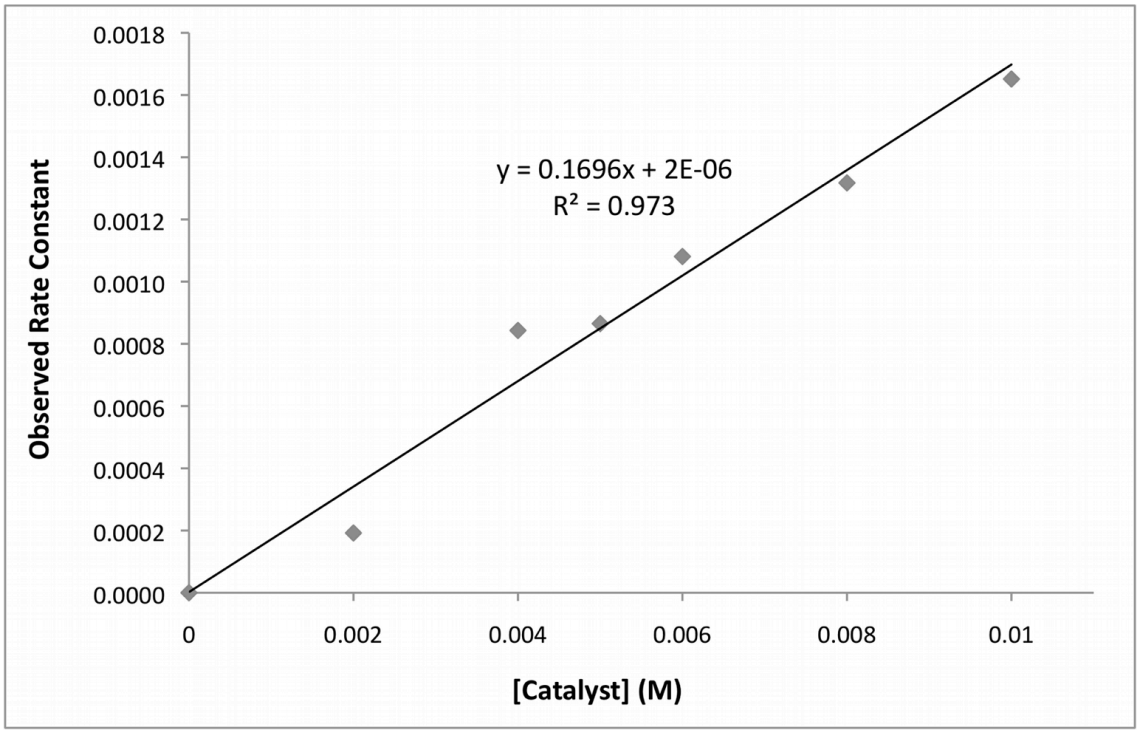


Figure 5.8. Plot of k_{obs} versus [**25**] used to determine the second order rate constant.

Determination of the activation parameters for the polymerization of *rac*-LA by **25** was accomplished by measuring the rate of reaction at temperatures ranging from 37 °C to –7 °C (Table 5.4). An Eyring plot of the data is an excellent linear fit (R^2 = 0.998) and provides the activation parameters $\Delta H^{\ddagger}$ = 47(1) kJ mol^{-1} and $\Delta S^{\ddagger}$ = –147(4) J K^{-1} mol^{-1} (Figure 5.9). These values closely match activation parameters for other known coordination-insertion lactide polymerization catalysts and are indicative of a well-controlled polymerization process.[135] The result also serves to fully establish an operative coordination-insertion mechanism.

Table 5.4. Data obtained for the measurement of activation parameters of the ring-opening polymerization of *rac*-LA by **25**.

Temperature (°C)	k_{obs} (s^{-1})	Ln(k_{obs}/T) (mol s^{-1} K^{-1})
37.03	1.94(1) × 10^{-3}	–11.98
31.48	1.265(5) × 10^{-3}	–12.39
25.92	8.65(4) × 10^{-4}	–12.75
14.80	3.90(2) × 10^{-4}	–13.51
3.70	1.90(1) × 10^{-4}	–14.19
–7.41	7.58(6) × 10^{-5}	–15.07

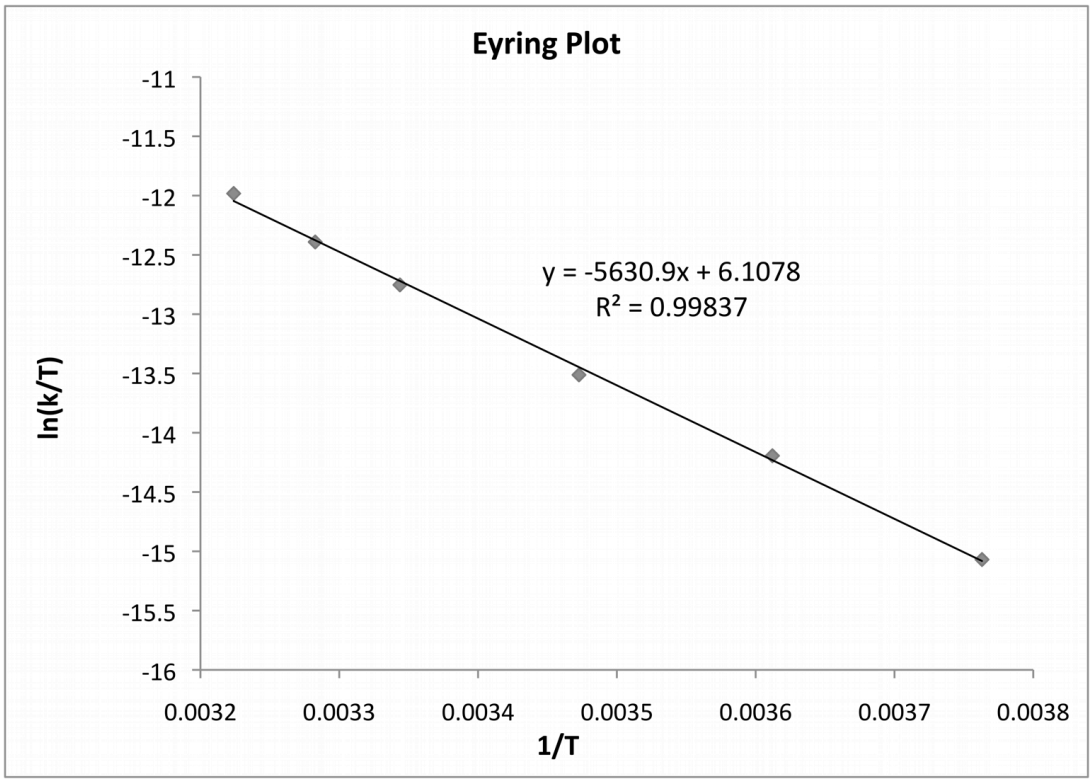


Figure 5.9. Plot of Ln(k_{obs}/T) versus 1/T for the determination of the activation parameters in the polymerization of *rac*-LA using **25**.

5.3.5. Polymer Characterization by GPC

Table 5.5. GPC data for PLA prepared using catalysts **24**–**26**, at M:I = 200.

	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
24	18.0	24.7	1.37
25	28.7	33.0	1.15
26	18.9	25.8	1.36

Molecular weight determination was performed by GPC for PLA samples prepared using each catalyst. The polymer samples were prepared with a catalyst loading of 0.5 mol%, with $[LA]_0$ = 1 M, in CH_2Cl_2 solvent at ambient temperature (**25**

and **26**) or at 40 °C (**24**). The M_n, M_w, and PDI data are presented in Table 5.5. In general, the molecular weights are in close agreement with the calculated value ($M_{n,calc}$ = 28.8 kg mol^{-1}), and the polydispersities are low, which is indicative of good molecular weight control. Catalyst **25** exhibits control that is superior to the other two systems, giving molecular weights very closely matching the expected values (28.7 kg mol^{-1}), and a very low PDI (1.15). On the other hand, polymer samples prepared using **24** and **26** had substantially greater PDIs and lower molecular weights.

Table 5.6. Molecular weight data determined by GPC for PLA samples prepared using various loadings of **25** as catalyst.

Entry	M:I	Isolated Yield (%)	Time (h)	Calc. M_n (kg mol^{-1})	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	100	99	1	14.3	12.9	17.3	1.34
2	200	98	1	28.3	28.7	33.0	1.15
3	300	92	1.5	39.8	35.0	37.8	1.08
4	400	90	2.5	51.9	33.4	36.5	1.09
5	500	98	2.5	70.6	41.9	50.7	1.21
6	1000	99	5	142.7	49.9	63.4	1.30
7	400[a]	98	3[a]	56.5	31.5	38.2	1.21

[a] Sample prepared by sequentially polymerizing two batches of 200 equiv of *rac*-Lactide for 90 minutes at each stage.

Due to the superior molecular weight control of **25**, this system was chosen for more detailed GPC studies. In particular, polymer samples were prepared using various catalyst loadings to determine the relationship between the M:I ratio and

the properties of the resulting polymers. The initial monomer concentration was left constant while the M:I ratio was varied from 100 to 1000. The molecular weight analyses of these polymers were then performed by GPC, and the results can be found in Table 5.6.

At high concentrations of catalyst **25** ($[LA]_0/[\mathbf{25}]$ = 100 and 200), the molecular weights of the resulting polymer samples closely approximate the calculated values (Figure 5.10). However, at lower concentrations of **25**, the molecular weights drop off significantly. For example, a number-average molecular weight (M_n) slightly less than 50 kg mol^{-1}, which is only ~35% of the calculated value, was achieved when $[LA]_0/[\mathbf{25}]$ = 1000. This observation is consistent with the presence of monomer impurities acting as chain-transfer agents. The molecular weight distribution is narrow for all samples (PDI = 1.08–1.34), with the most narrow distributions occurring at intermediate catalyst loadings ($[LA]_0/[\mathbf{25}]$ = 300 and 400). A plausible reason for higher PDI's at high catalyst loading is slow initiation relative to propagation, which becomes statistically less relevant at lower catalyst concentrations. Higher PDI values at lower catalyst loading are most likely a result of transesterification, which was observed to be occurring by MALDI-ToF mass spectrometry (*vide supra*). The broadening effect of transesterification on molecular weight distribution should necessarily depend on reaction times for the polymerization experiment, which are longer at lower catalyst loading.

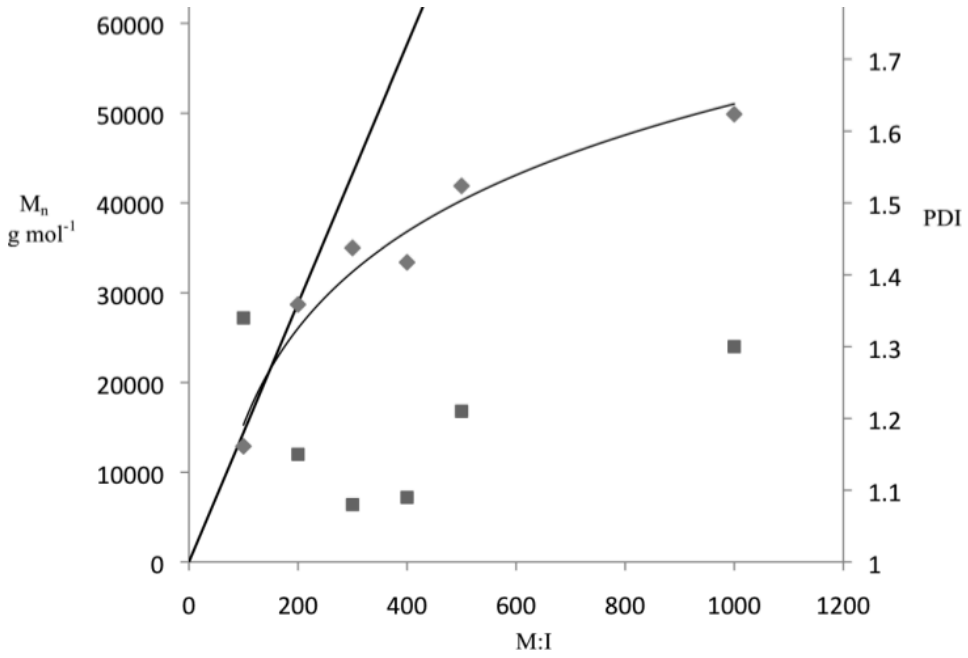


Figure 5.10. Plot of observed M_n (◆) and PDI (■) as a function of the monomer to catalyst ratio. The straight line represents calculated M_n values (M_n = $[LA]_0/[\mathbf{25}]\times144.13$), while the curved line shows the general trend for experimental M_n values.

As a further test of the livingness of **25** for LA polymerization, a polymer sample was prepared by sequentially polymerizing two batches of 200 equivalents of *rac*-LA. Analysis of the resulting polymer by GPC showed molecular weights similar to those determined for the single-step polymerization of 400 equivalents of *rac*-LA (M_n = 31.5 kg mol^{-1} vs. 33.4 kg mol^{-1}). The molecular weight distribution broadened slightly (PDI = 1.21), likely as a result of the longer duration of the polymerization experiment.

5.4. Conclusions

In summary, the first cationic zinc systems capable of catalysing the ring-opening polymerization of lactide at ambient temperature have been prepared (**25** and **26**). In fact, at the time of publication, complex **25** represented the first cationic

metal complex with ambient temperature activity for ROP of lactide ever to be reported.[136] The mechanism of polymerization has been unambiguously established not to occur *via* a cationic process, but rather, by a well-controlled coordination-insertion mechanism.

Comparison of ligands differing in steric bulk has shown these variations to have a significant impact on the polymerization activity of the resultant complexes. For instance, removal of only a single methyl substituent from the N-aryl group resulted in remarkable improvement in activity. This increased activity is attributed not only to the reduced steric constraints, but also to the additional stabilizing interaction between zinc and the dbf oxygen, which occurs only within the less sterically encumbered complexes. Furthermore, complex **26** displays notable stereoselectivity, giving modestly heteroenriched PLA (P_r = 0.70), which is the best stereocontrol yet observed for a well-defined cationic metal complex.

Chapter 6: Activity Enhancement from an Alkyl-Substituted Ligand

6.1. Introduction

In this chapter, a substantial modification of the bis(phosphinimine) architecture is reported, wherein the ligand bears alkyl substituents on the phosphinimine groups. Given the observation in Chapter 5 that polymerization activity is highly dependent on the electrophilicity of the metal centre, whereby a small reduction in electrophilicity resulted in marked improvement in performance, a more strongly electron donating ligand was expected to further enhance activity. The incorporation of alkyl groups at the P and N sites of the phosphinimine was thus expected to give this desired electronic effect, while also further reducing the steric hindrance of the system. A preliminary study of such modifications has been performed and is the subject of the present chapter.

6.2. Ligand Synthesis and Characterization

6.2.1. Synthesis of a P-Alkyl Bis(phosphine)

Preparation of the alkylated bis(phosphine) precursor 4,6-bis(diethylphosphino)dibenzofuran was targeted due to its reduced steric bulk relative to the known di*iso*propylphosphino analogue, and its improved electron donation relative to the diphenylphosphino compound. A similar, but modified, synthetic route was used, whereby efficient dilithiation of dibenzofuran was

accomplished using only 2.0 equivalents of ^{t}BuLi, rather than a significant excess of ^{sec}BuLi or ^{n}BuLi employed in previous reports.[137] Reaction of the resulting dilithio species with $ClPEt_2$ then afforded 4,6-bis(diethylphosphino)dibenzofuran, **27**, in 88% yield as a red oil, which was estimated to be 84% pure by integration of $^{31}P\{^{1}H\}$ NMR resonances. This novel bis(phosphine) has one sharp peak in the $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) at δ –19.01, with multiplets arising in the ^{1}H NMR spectrum from the diastereotopic CH_2 groups at δ 2.10 and 1.89 (Figure 6.1).

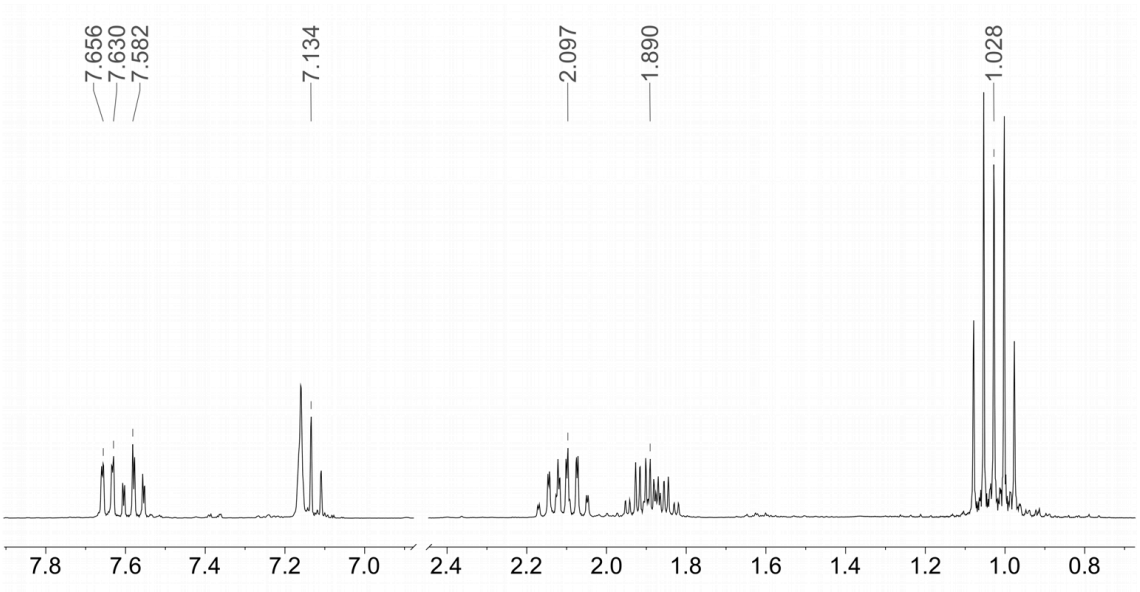


Figure 6.1. ^{1}H NMR spectrum of compound **27**.

6.2.2. An Alkyl-Substituted Bis(phosphinimine) Ligand

Synthesis of $\mathbf{L_3}$ from 4,6-bis(diethylphosphino)dibenzofuran and benzyl-azide under standard Staudinger conditions[112] is highly exothermic and proceeded to completion within minutes at ambient temperature. Work-up was simple and efficient, with high yield of analytically pure crystalline material being produced simply by addition of excess pentane to the reaction mixture. A single peak appears

in the $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) at δ 14.4. In the ^{1}H NMR spectrum, the diastereotopic PCH_2 resonances overlap, giving a complicated multiplet, while the benzylic CH_2 resonates as a doublet at δ 4.73 ($^{3}J_{PH}$ = 18.4 Hz). Single crystals of **L$_3$** were grown from a toluene solution of the compound at –35 °C, and the molecular structure was determined crystallographically (Figure 6.2). The P–N bond lengths are similar to those of the related bis(phosphinimine) ligands discussed in the preceding chapters [P(1)–N(1) = 1.568(1) Å; P(2)–N(2) = 1.550(2) Å].

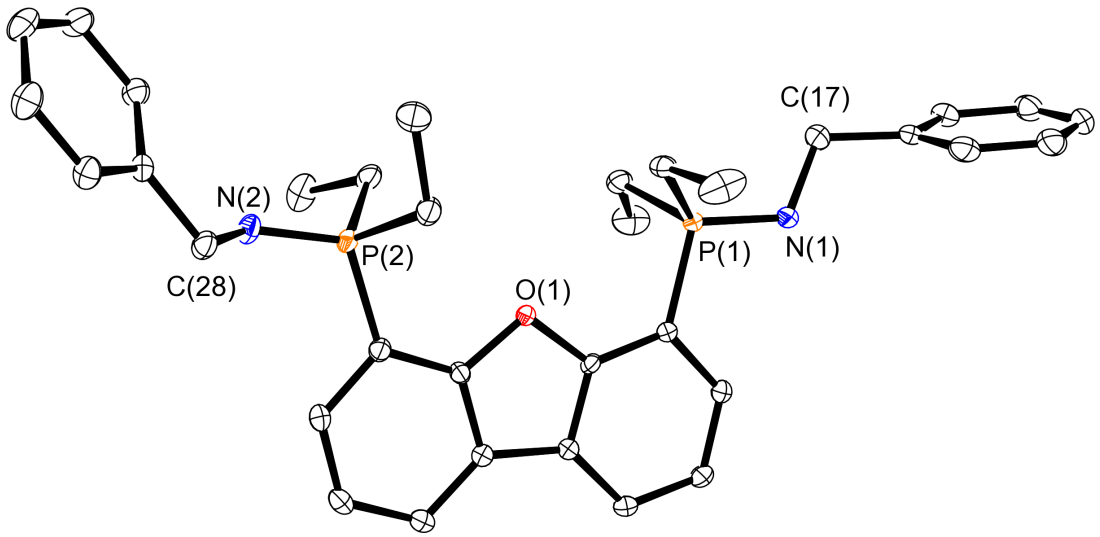


Figure 6.2. Displacement ellipsoid plot (30% probability) of **L$_3$**. Hydrogen atoms have been omitted for clarity.

6.3. Complex Synthesis and Characterization

6.3.1. Ligand Protonation

As with previous generations of the ligand discussed in the preceding chapters, the synthesis of cationic zinc complexes is most efficiently performed by first protonating the ligand with an appropriate Brønsted acid, thereby providing

access to an irreversible alkane elimination pathway upon reaction with alkylzinc precursors. Reaction of **L$_3$** with [H(OEt$_2$)$_2^+$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] rapidly generated [**L$_3$**H$^+$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$], **28**, which was isolated in high yield as an analytically pure light yellow powder. Unlike the protonated species of the general formula [**L$_2$**H$^+$][BAr$_4^-$] described in Chapters 3 and 4, compound **28** maintains relatively sharp NMR signals, with a single peak appearing in the ^{31}P{^{1}H} NMR spectrum at δ 39.5. This suggests more rapid exchange of the proton between the phosphinimine groups, possibly on account of the reduced steric bulk of the system compared with the analogous **L$_2$** ligands. The hydrogen atoms of the ethyl groups resonate similarly in the ^{1}H NMR spectrum compared with the neutral ligand, though the diastereotopic methylene groups are not as clearly resolved, resulting in one large overlapping multiplet at δ 2.31 (CD_2Cl_2). The acidic proton appears as a broad singlet at δ 5.45, which integrates as 1H, while the diagnostic benzylic methylene doublet is shifted slightly upfield to δ 4.03 ($^3J_{PH}$ = 16.5 Hz).

6.3.2. A Methylzinc Complex of L$_3$

The methylzinc complex [**L$_3$**ZnMe$^+$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$], **29**, was prepared by reaction of the protonated ligand **28** with dimethylzinc at ambient temperature for 1 hour, giving an analytically pure white powder in 90% yield. A single peak in the ^{31}P{^{1}H} NMR spectrum (δ 46.6, CD_2Cl_2) is indicative of symmetry related phosphinimines. Characteristic resonances in the corresponding ^{1}H NMR spectrum include a doublet at δ 4.00 from the benzylic CH_2 ($^3J_{PH}$ = 19.2 Hz), and a doublet of quartets from PCH_2. The $ZnCH_3$ moiety appears upfield in the spectrum at δ –0.95, which is similar to the cationic methylzinc complexes that were studied in the

preceding chapters. Unsurprisingly, this compound is inactive toward lactide polymerization, and thus, the zinc-lactate complex was targeted.

6.3.3. A Zinc-lactate Complex of L_3

Synthesis of the zinc-lactate complex [$\mathbf{L_3}$ZnOCH(Me)CO_2Me$^+$][B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$], **30**, was performed by reacting **28** with EtZn(methyl-L-lactate). This route proved much more efficient than for the previously prepared zinc-lactate complexes, with 95% yield of crystalline material being achieved, providing an excellent overall yield of 64% in four synthetic steps from dibenzofuran. Despite the presence of the asymmetric lactate moiety, only a single sharp peak is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 46.8. Characteristic methyl-lactate signals appear in the ^1H NMR spectrum at δ 4.66 (C*H*CH_3), 3.69 (OC*H*$_3$), and 1.41 (CHC*H*$_3$). The NMR signals of the ligand do not deviate significantly from those of **29**, with the exception of a more complex overlapping multiplet attributed to the PCH_2 groups. Additionally, examination of the $^{13}C\{^1H\}$ NMR spectrum reveals the existence of two inequivalent ethyl groups and two inequivalent phenyl groups in the compound, a phenomenon not observed in **29**. This suggests a loss of symmetry on the NMR timescale, likely corresponding to a reduction from average C_{2v} to either C_2 or C_s symmetry.

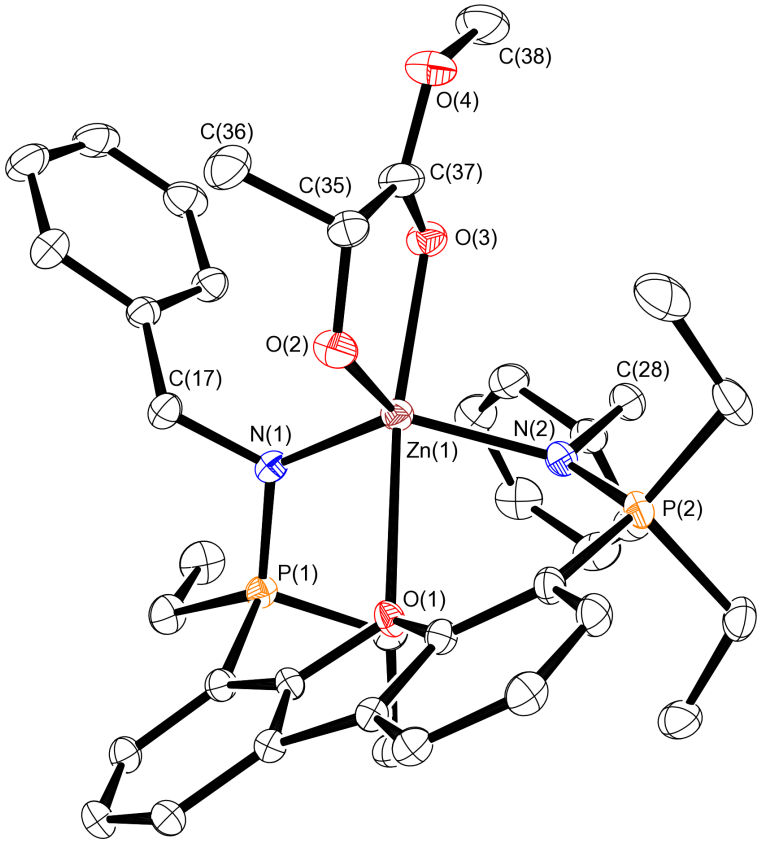


Figure 6.3. Displacement ellipsoid plot (30% probability) of the cation of **30**. Hydrogen atoms and disordered atomic positions have been omitted for clarity.

Large single crystals of **30** suitable for X-ray diffraction were grown from CH_2Cl_2 solvent, and the solid-state molecular structure was determined crystallographically (Figure 6.3, Table 6.1). As expected, the ligand coordinates to the metal centre in a tridentate mode, while the methyl-lactate moiety binds in a bidentate fashion, resulting in approximate five-cooordinate, trigonal bipyramidal geometry. The strongest donors bind at the equatorial sites, including the phosphinimines [Zn(1)–N(1) = 2.013(1) Å, Zn(1)–N(2) = 2.009(2) Å] and the anionic oxygen atom [Zn(1)–O(2) = 1.923(2) Å]. The sum of angles about these equatorial positions of the zinc centre is 356.5(1)°. The neutral oxygen-donors bind in the axial

positions, wherein the interaction with the lactate carbonyl is in the expected range [Zn(1)–O(3) = 2.173(1) Å], while that of the dbf oxygen is relatively long [Zn(1)–O(1) = 2.525(1) Å]. The angle between these is distorted somewhat from 180° [O(1)–Zn(1)–O(3) = 168.57(5)°], presumably due to steric repulsion of a nearby benzyl group. Interestingly, the interaction with the dbf oxygen is longer than that observed in the analogous complexes of $\mathbf{L_2^{Pipp}}$ (**25**) and $\mathbf{L_2^{Ph}}$ (**26**) by 0.189(5) and 0.158(2) Å, respectively. This lengthened Zn–O_{dbf} bond distance can be attributed to decreased Lewis acidity of the metal centre.

Table 6.1. Selected bond lengths (Å) and angles (°) for compound **30**.

	Length		Angle
Zn(1)–N(1)	2.013(1)	N(1)–Zn(1)–N(2)	131.35(6)
Zn(1)–N(2)	2.009(2)	N(1)–Zn(1)–O(2)	109.06(6)
Zn(1)–O(1)	2.525(1)	N(2)–Zn(1)–O(2)	116.10(6)
Zn(1)–O(2)	1.923(2)	O(2)–Zn(1)–O(3)	82.02(6)
Zn(1)–O(3)	2.173(1)	N(1)–Zn(1)–O(1)	83.26(5)
P(1)–N(1)	1.608(2)	N(1)–Zn(1)–O(3)	108.05(6)
P(2)–N(2)	1.605(1)	O(1)–Zn(1)–O(3)	168.57(5)

6.4. Polymerization Studies

Compound **30** is an extremely active catalyst for the polymerization of *rac*-lactide, giving 90% conversion of 200 equivalents of monomer to atactic (P_r = 0.50) PLA in under 20 minutes at 25 °C. Examination of the reaction kinetics by *in situ* NMR studies revealed well-behaved first-order kinetics with an observed rate

constant of 1.88(1) × 10^{-3} s^{-1} and no notable induction period. This measured rate is greater than that of the previous most active catalyst to arise from this work (compound **25**) by a factor of 2.2.

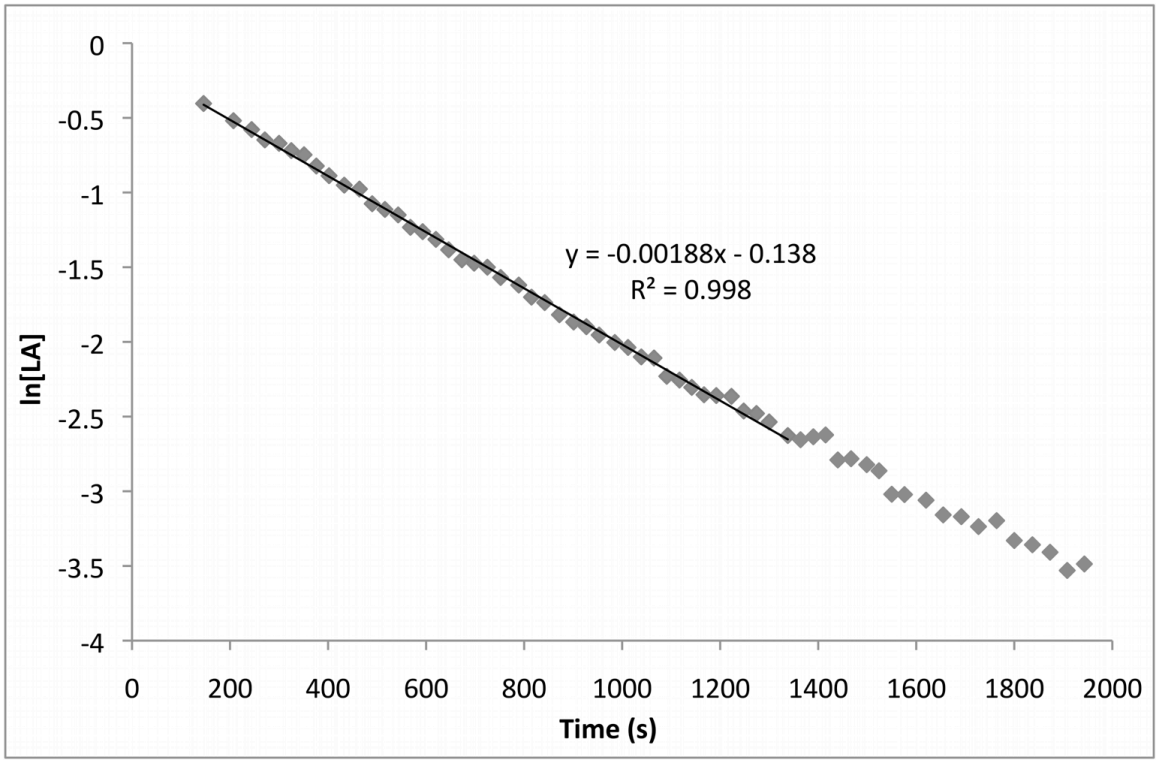


Figure 6.4. Linear plot of ln[LA] versus time (s) for polymerization of *rac*-LA with **30**, demonstrating well-behaved *pseudo*–first-order behaviour.

A MALDI-ToF mass-spectrum was obtained for a polymer sample prepared with a catalyst loading of 2% (Figure 6.5). Mass peaks are consistent with sodium adducts of polymer chains of the form H-[OCH(Me)CO]$_n$-OCH(Me)CO_2Me, bearing a methyl-lactate end-group, suggesting a controlled coordination-insertion process. However, peaks are separated by 72 u, suggesting appreciable rates of transesterification for this catalyst system, similar to the results discussed in Chapter 5. However, visual inspection of the spectrum reveals that peaks with even

integer values of n are appreciably more intense than peaks with odd integers values, which suggests a relatively slow rate of transesterification versus the rate of propagation.

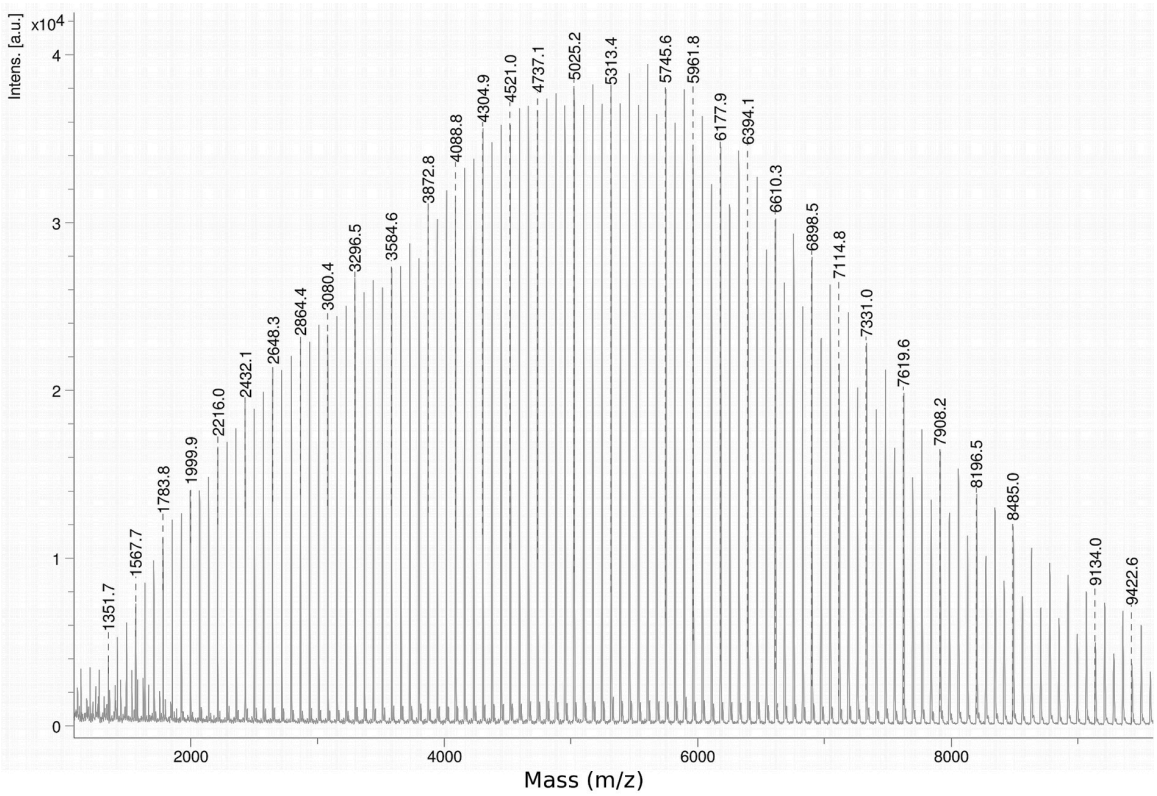


Figure 6.5. MALDI-ToF mass spectrum of PLA prepared using **30** as catalyst, with a catalyst loading of 2 mol% ($[LA]_0/[\mathbf{30}] = 50$).

GPC analyses of polymer samples prepared at various catalyst loadings of **30** have been undertaken (Table 6.2, Figure 6.6). At higher catalyst loadings ($[LA]_0/[\mathbf{30}]$ = 100 and 200), very good molecular weight control was achieved, yielding polymer samples with relatively low polydispersity (1.24–1.25) and molecular weights reasonably similar to theoretical values. Further reduction of catalyst loading ($[LA]_0/[\mathbf{30}]$ = 300, 400, and 500) resulted in reduced molecular weight control, giving larger molecular weight distributions (PDI = 1.39–1.43) and

molecular weights significantly lower than expected. We attribute these observations to appreciable rates of transesterification and chain-transfer side reactions, respectively. Catalyst decomposition is an unlikely cause as it has been found that the catalyst remains active upon completion of the polymerization experiment. Specifically, after complete consumption of 200 equivalents of *rac*-lactide, addition of further monomer resulted in continued polymerization. Consecutive polymerization of two portions of 200 equivalents of *rac*-lactide gave polymer with molecular weights similar to those measured for single step polymerization of 400 equivalents of *rac*-lactide.

Table 6.2. Molecular weight data for PLA samples prepared using different concentrations of **30**.

$[LA]_0/[\mathbf{30}]$	Isolated Yield (%)	Calc. M_n ($\times 10^3$)[a]	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI
100	90	13.0	10.2	12.6	1.25
200	96	27.7	18.9	23.5	1.24
300	96	41.5	17.3	24.2	1.39
400	92	53.0	19.7	28.3	1.43
500	71	51.2	23.4	31.0	1.32
400[b]	99	57.1	20.0	31.5	1.57

[a] Calculated using the formula $M_n = ([LA]_0/[\mathbf{30}]) \times 144.13 \times \text{conversion}$.

[b] Sequential polymerization of two portions of 200 equivalents of *rac*-LA.

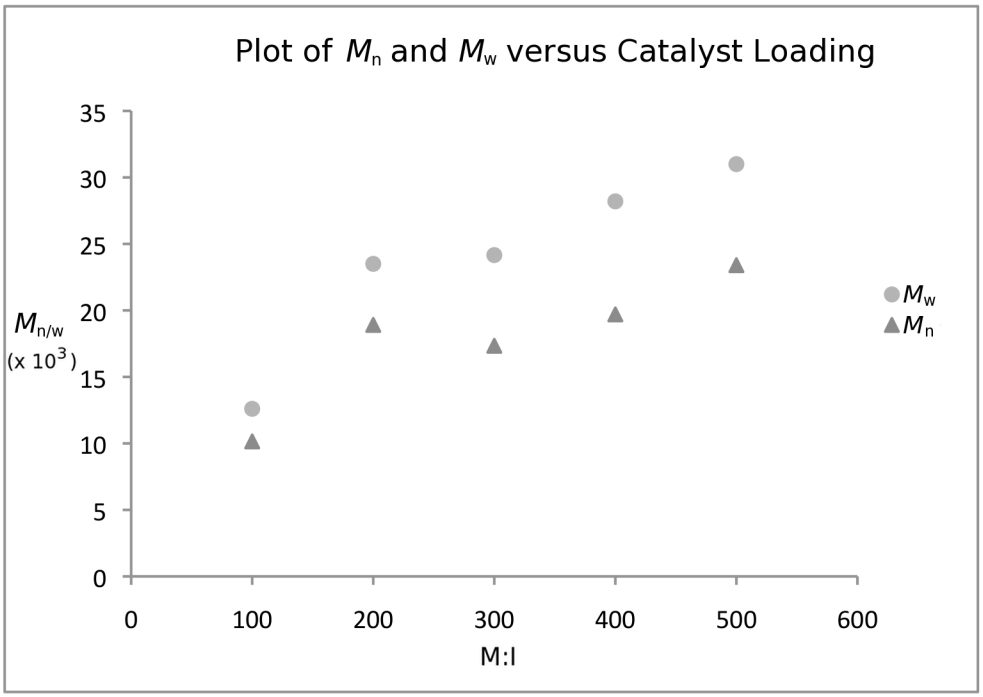


Figure 6.6. Plot of M_w (●) and M_n (▲) versus catalyst loading for polymerization of *rac*-LA with **30**.

In an attempt to gain an improved understanding of the polymerization process, a variety of samples were prepared under identical conditions and quenched at different stages of completion. A plot of M_n versus conversion gave a curve rather than the expected straight line (Figure 6.7). During the early stages (40–60% conversion) the polymerization is well controlled (PDI = 1.11–1.13), while in the later stages, the M_n values begin to drop off relative to the calculated molecular weight, with a concomitant increase in M_w and PDI (Table 6.3). This demonstrates that the rates of transesterification, chain-transfer, and other possible competing reactions become increasingly significant relative to propagation as monomer concentration decreases in the later stages of the polymerization.

Table 6.3. GPC data for PLA samples quenched after varying degrees of conversion.

t (min)	Isolated Yield (%)	Calculated Conversion (%)[a]	Calc. M_n ($\times 10^3$)[a]	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI
4.5	39	40	11.2	11.3	12.6	1.11
8	53	60	15.3	12.4	13.9	1.13
11	74	70	21.3	12.8	16.1	1.26
14	78	80	22.5	13.1	16.5	1.27
20	84	90	24.2	12.6	17.0	1.35
42	89	99	26.6	10.7	14.4	1.35

[a] Calculated based on the observed rate constant (k_{obs} = 0.00188 s^{-1}) measured under identical conditions, using the equation $\ln[LA] = -k_{obs} \times t$. This is expected to give a more accurate depiction of conversion than the isolated yield.

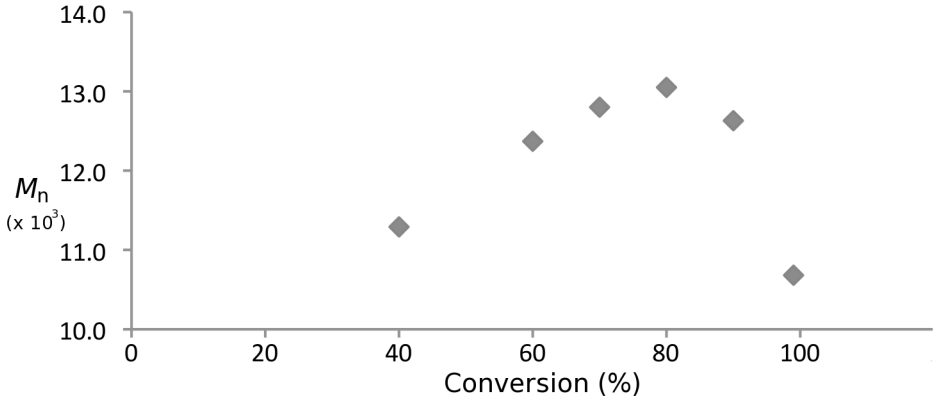


Figure 6.7. Plot of M_n versus calculated conversion for polymerization of *rac*-LA with **30**.

6.5. Conclusions

In summary, a new alkyl-substituted bis(phosphinimine) pincer ligand has been prepared and has been used as an ancillary ligand for the preparation of the cationic zinc-lactate complex **30**. This complex is a much more active lactide

polymerization catalyst than the analogous complexes of the phenyl-substituted bis(phosphinimine) ligands discussed in Chapter 5, but also displays a modest reduction in molecular weight and stereochemical control. This improved activity is attributed to better moderation of the Lewis acidity of the metal centre and reduced steric constraints, while the diminished molecular weight and stereochemical control is likely due to reduced steric protection.

Chapter 7: Conclusions and Future Directions

7.1. Future Work

7.1.1. Rational Ligand Modifications

It is apparent from the thesis work described in Chapters 3–5 that *ortho*-substituents on the N-aryl groups of the **L$_2$** ligand framework significantly inhibit the polymerization activity of the zinc-lactate complexes. On the other hand, reduced steric bulk was also shown in some instances to have a negative impact on molecular weight control. For these reasons it has been difficult to strike the desired balance between high activity and good control. Complex **25** exhibits possibly the best overall balance between activity and control among all of the catalyst systems examined in this thesis. These superior properties are attributed to the lack of bulky *ortho* substituents on the N-aryl groups, with steric protection instead being achieved by placement of *iso*propyl groups at the *para* positions. It is thus evident that steric bulk is beneficial if not placed too near the metal centre. Furthermore, the *iso*propyl groups were also demonstrated to enhance activity due to their subtle effect on the Lewis acidity of the metal centre. Armed with this knowledge, the future of the project can be directed with some degree of rational design.

In particular, it would be of interest to consider a series of bulkier N-aryl groups with unsubstituted *ortho* sites so as to potentially maintain high activity while inhibiting transesterification and other possible competing reactions. Examples of some azides that would be relatively simple to prepare are listed in

Figure 7.1, which, when reacted with the requisite bis(phosphine), would produce the desired sterically bulky bis(phosphinimine) ligands. The increased bulk of such ligands could have the additional desirable effect of enhancing the chain-end control of the resultant catalyst systems, thereby promoting improved polymer tacticity. Initially, one could prepare bulkier analogues of $\mathbf{L_2^{Pipp}}$ by replacing the *iso*propyl with larger groups such as ^{t}Bu or CPh_3. This would be relatively straightforward given that the requisite anilines 4-*tert*-butylaniline and 4-tritylaniline are commercially available compounds. Alternatively, substitution of the *meta* sites should also be feasible, and some proposed initial targets would incorporate methyl, *iso*propyl, and ^{t}butyl at these positions. The requisite 3,5-disubstituted anilines are either commercially available (3,5-dimethylaniline and 3,5-di^{t}butylaniline) or have well-established synthetic protocols for their preparation from other commercially available compounds, as is the case for 3,5-di*iso*propylphenylazide.[138] Such aryl groups would offer a great deal more steric protection while possibly not preventing the important $Zn–O_{dbf}$ bonding interaction from occurring.

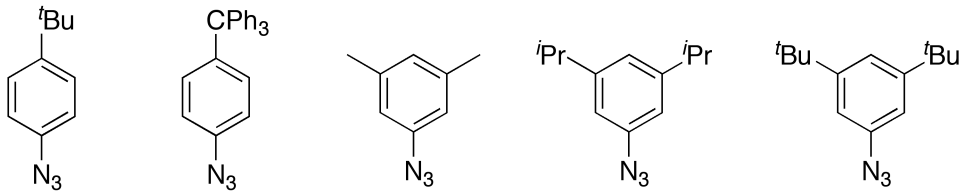
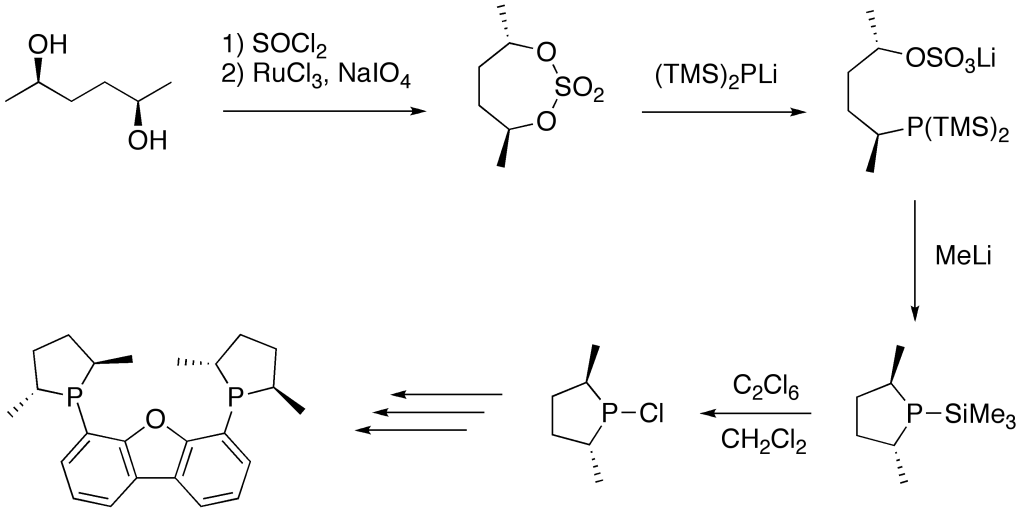


Figure 7.1. List of suggested azides that could be used to prepare bulkier derivatives of the ligand

7.1.2. Chiral Ligands

It would be of great interest to prepare chiral analogues of the bis(phosphinimine) framework employed in this thesis, as such ligands may promote stereoselective lactide polymerization *via* an enantiomorphic site-control

mechanism. This has the potential to generate isotactic stereocomplexed PLA from *rac*-lactide, which is a form of PLA that is highly sought after industrially due to its unique physical properties compared with isotactic L-PLA.[139] The most obvious site at which to install chirality is at the phosphorus centre of the phosphinimines. While on-going work in the Hayes group is pursuing a number of possible routes to such ligands, the author suggests that one of the most effective methods would be the installation of a chiral phospholane functionality. One well-established and effective chiral ligand is DuPhos,[140] a bis(phospholane) with a benzene backbone, which has been employed with much success in asymmetric hydrogenation reactions.[140]

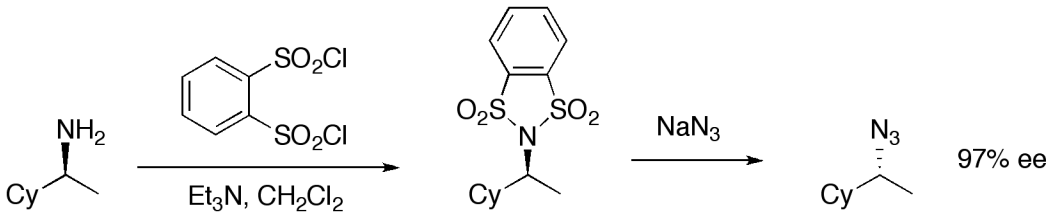


Scheme 7.1. Synthesis of a chiral bis(phospholane) compound.

Preparation of the dibenzofuran analogue of DuPhos should be relatively straightforward using the route shown in Scheme 7.1. Starting from commercially available, enantiopure 1,4-diols, Burk et al. have established the synthesis of the corresponding 1,4-diol cyclic sulphates.[141] From there, the TMS-phospholane can be prepared using the synthetic methodology developed by Holtz et al.,[142] which in turn can be used to prepare the corresponding chlorophospholane.[143] This

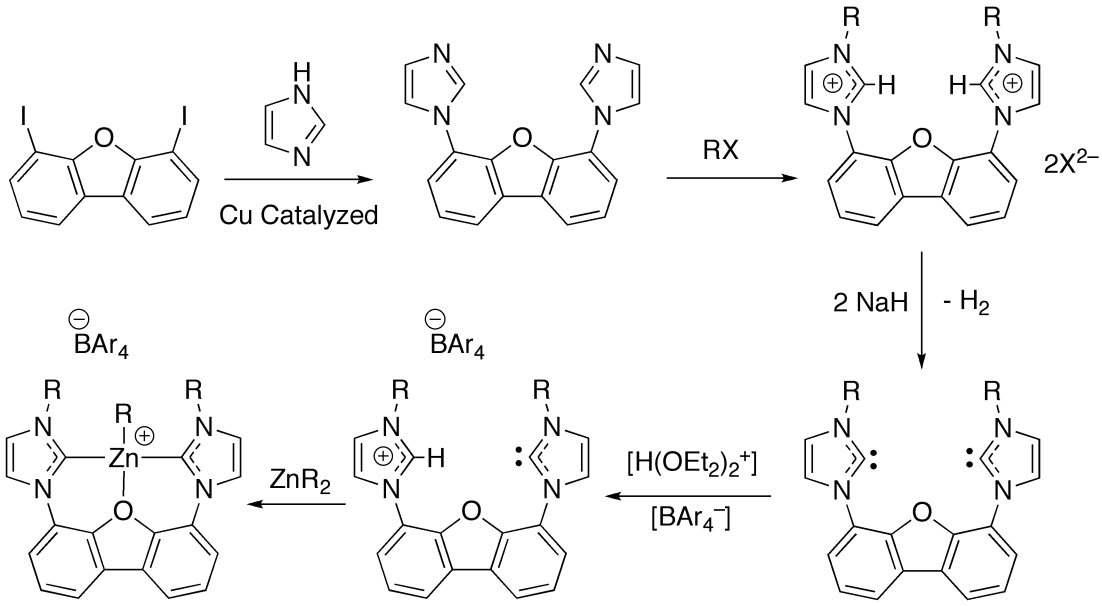
chlorophospholane can then be readily installed onto dibenzofuran using the same synthetic methodology employed in this thesis work to generate the diethylphosphino and diphenylphosphino analogues. The resultant chiral bis(phospholane) would then be easily converted to the bis(phosphinimine) *via* a Staudinger reaction.

An alternative strategy to the synthesis of a chiral ligand is the installation of chirality at the N site of the phosphinimines. This may actually be a more effective approach to achieving enantiomorphic site-control as it would potentially result in placement of the chiral moieties closer to the zinc centre. In order to synthesize such a ligand, one must first obtain the requisite chiral azide. The author proposes starting from the relatively inexpensive, commercially available chiral amine (R)-1-cyclohexylethylamine, which can be converted to the corresponding chiral azide according to a procedure by Fiksdahl et al. in a 1998 report (Scheme 7.2).[144] This process is relatively simple, giving 97% enantiomeric excess with inversion of configuration in just two synthetic steps from the amine.



Scheme 7.2. Preparation of a chiral azide which could be used to prepare chiral derivatives of the bis(phosphinimine) ligand.

7.1.3. Beyond Phosphinimines



Scheme 7.3. Synthesis of a dbf-based rigid bis(NHC) ligand.

It is evident from the results discussed in Chapter 2 that the phosphinimine functionality is not as strong a σ-donor as was initially desired at the outset of the project. Furthermore, the remainder of the thesis has continually demonstrated the importance of maximizing the electron-donating capacity of the ancillary ligand within these cationic complexes. For these reasons, it may ultimately be most productive to move away from phosphinimines to another choice of formally neutral functional group. The author suggests the N-heterocyclic carbene (NHC) functionality would be a particularly suitable replacement for this task. It should be possible to make a directly analogous bis(NHC) ligand using the route outlined in Scheme 7.3. Starting from 4,6-diiodo-dibenzofuran,[145] the imidazoles can be installed using a suitable copper(I) catalyst via an Ullman condensation.[146] The bis(NHC) compound can then be generated by reaction of the bis(imidazole)

compound with an appropriate alkyl halide, giving the imidazolium salt, which can be readily converted to the bis(NHC) by deprotonation using sodium hydride. The end result is a neutral pincer ligand with a geometry very similar to the bis(phosphinimine) framework employed in this thesis. For this reason, cationic zinc complexes should be relatively simple to prepare using a methodology similar to what has been used in this thesis.

7.2. Summary and Conclusions

The work presented in this thesis has described the synthesis, characterization, and lactide polymerization reactivity of a series of cationic zinc complexes stabilized by neutral phosphinimine ligands. Through the studies presented in Chapter 2, it was demonstrated that the most effective synthetic route to cationic zinc complexes was *via* protonation of the ligand, followed by protonolysis of an alkylzinc precursor. In this way, both a cationic and an "activated" alkylzinc complex of the monophosphinimine ligand $\mathbf{L_1^{Dipp}}$ were prepared, but these were unfortunately found to be poor catalysts for polymerization of lactide.

In Chapter 3 it was shown that the bis(phosphinimine) scaffold $\mathbf{L_2^{Mes}}$ was a more suitable ancillary ligand for stabilization of cationic zinc species. A series of coordinatively unsaturated, cationic zinc complexes were prepared and structurally characterized, which is significant given the rarity of such compounds. Of all the complexes of $\mathbf{L_2^{Mes}}$ studied, only the complex bearing a methyl-lactate initiating group was found to effectively promote the coordination-insertion polymerization of lactide, albeit only slowly at 60 °C.

In Chapter 4, a systematic study of the steric bulk of the $\mathbf{L_2}$ framework was performed, whereby the N-aryl groups were modified. A series of cationic methylzinc complexes were prepared and fully characterized by X-ray crystallography and NMR solution studies. The ligand was found to prefer certain very specific orientations upon complexation to zinc, depending on the steric bulk of the N-aryl group. Most interesting was the observation that only in the case of $\mathbf{L_2^{Pipp}}$ was the zinc centre bound to the dbf oxygen, while in all other examples the ligand adopted a bidentate mode, with only the phosphinimines coordinated.

In Chapter 5, a series of zinc-lactate complexes of the ligands studied in Chapter 4 were prepared. Structural investigations revealed that coordination of the dbf oxygen only occurs in the less bulky ligands $\mathbf{L_2^{Pipp}}$ and $\mathbf{L_2^{Ph}}$. Interestingly, only complexes of these less bulky ligands display ambient temperature activity for polymerization of lactide, demonstrating an apparent dependence of activity on the presence of this interaction. These complexes represented the first examples of cationic metal complexes capable of promoting the coordination-insertion polymerization of lactide at ambient temperature. Complex **25** was most active, and the polymerization properties of this system were studied in detail. The catalyst gives good molecular weight control at commonly employed catalyst loadings (0.5–0.25%), but with slow rates of transesterification resulting in a loss of control at further reduced catalyst concentrations. Complex **25** also displays living characteristics, suggesting a very stable active species.

In Chapter 6, a significant modification was made to the ligand system so as to examine the effects of replacing the phosphinimine N-aryl and P-phenyl groups

with more electron donating alkyl groups. The result was $\mathbf{L_3}$, which was efficiently synthesized in excellent yield. The zinc-lactate complex of this ligand (**30**) was prepared and fully characterized, and was found to be a tridentate complex with a significant interaction between the zinc centre and the dbf oxygen. This compound is remarkably active for the polymerization of *rac*-lactide, giving 90% monomer consumption in 20 minutes at ambient temperature, which is increased by a factor of 2.2 compared with complex **25**.

Chapter 8: Experimental Details

8.1. General Methods

Except where otherwise noted, all experimental work was performed under an inert argon atmosphere using a double-manifold high vacuum line[147] or an MBraun Labmaster glove box. All glassware (reaction vessels, swivel frits, vials, pipettes, NMR tubes, etc.) was thoroughly dried in an oven at 110 °C and either assembled and evacuated on the vacuum line while hot, or placed in the glove box antechamber and evacuated while hot.

8.1.1. Solvents

Except where otherwise noted, all solvents were rigorously dried prior to use. Benzene, toluene, pentane, heptane, tetrahydrofuran (THF), diethylether, and dichloromethane (DCM) were dried and purified using an MBraun solvent purification system. Aromatic and alkane solvents were then stored over "titanocene" to ensure dryness, while sodium/benzophenone ketal (THF, diethylether) or CaH_2 (DCM, methanol) were used to further purify the other solvents. Bromobenzene and methanol were obtained from commercial sources and dried over CaH_2. Solvents were introduced to reaction vessels *via* vacuum transfer, with cooling of the receiving flask to –78 °C using a dry ice/acetone bath. Deuterated solvents (benzene-d_6, bromobenzene-d_5, $CDCl_3$, CD_2Cl_2, acetone-d_6, toluene-d_8) were dried using appropriate drying agents, distilled, and stored over 4 Å molecular sieves.

8.1.2. Materials

The compounds dibenzofuran, ^{t}BuLi, ^{n}BuLi, $ClPPh_2$, $ClPEt_2$, N,N,N′,N′-tetramethylethylenediamine (TMEDA), methyl-L-lactate, Pipp-NH_2, Dipp-NH_2, Mes-NH_2, *o*-Tol-NH_2, Ph-NH_2, Mipp-NH_2, triflic acid, $ZnCl_2$, $Zn(C_6F_5)_2$, $ZnEt_2$, $ZnMe_2$, $[HNMe_2Ph^+][B(C_6F_5)_4^-]$, $NaBPh_4$, $B(C_6F_5)_3$, C_6F_5OH, Phenol, $NaBF_4$, $NaNO_2$, and NaN_3 were obtained from commercial sources (Sigma-Aldrich, Strem, VWR, Acros Organics, Fisher Scientific) and used without further purification. *Rac*-Lactide and L-lactide were obtained from VWR and were routinely purified by recrystallization from toluene followed by 2 or 3 sublimations under rigorously air and moisture free conditions prior to use. The compounds EtZnOAc,[148] EtZnLactate,[149] $EtZnOC_6F_5$,[61] EtZnOPh,[61,65] Dipp–N_3,[150] Mes–N_3,[151] Mipp–N_3,[152] Pipp–N_3,[108c] Ph-N_3,[153] Benzyl–N_3,[154] and $[H(OEt_2)_2^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$[95] were prepared according to literature methods.

8.1.3. Instrumentation and Analysis

NMR spectra (^{1}H (300.1 MHz), $^{13}C\{^1H\}$ (75.5 MHz), ^{19}F (282.4 MHz), $^{31}P\{^1H\}$ (121.5 MHz)) were collected at ambient temperature using a Bruker 300 MHz Advance II UltraShield NMR spectrometer. Spectra were referenced to residual proteo signals of the solvent for ^{1}H and ^{13}C and an external standard for all other nuclei (^{31}P: triphenylphosphine in benzene-d_6; δ –5.1; ^{19}F: trifluorotoluene in dichloroethane-d_4; δ –65.8; ^{11}B: boron trifluoride diethyletherate in benzene-d_6; δ 0). ^{1}H and ^{13}C peak assignments were facilitated by COSY, HSQC, and DEPT experiments.

For PLA samples prepared using **6a**, **6b**, and **13** as catalyst, GPC data were collected on a Viscotek Triple Detector GPC System outfitted with a model 270 Dual Detector Platform (Four Capillary Viscometer and Light Scattering Detector) and a Refractive Index Detector. Samples were run in THF at a concentration of 1 mg/mL. For PLA samples prepared using **25** or **30** as catalyst, GPC analyses were performed on a Waters 2695 equipped with a Waters 410 refractive index detector and a Wyatt light scattering detector. Solutions of the polymer samples were prepared in THF to a concentration of approximately 5 mg/mL, except for the samples with M:I = 100, which were prepared at higher concentration to improve signal strength. All samples were filtered (0.2 μm) prior to performing the analysis, and were run at a temperature of 40 °C. Light scattering data were processed using dn/dc = 0.049. For PLA samples prepared using compounds **24** and **26** as catalyst, GPC data were obtained on a Varian PL-GPC 50 Plus instrument and measured against polystyrene standards. The molecular weight values were scaled by the accepted Mark-Houwink parameter of 0.58.[155]

MALDI-ToF mass spectra were obtained using an ultraflexXtreme™ MALDI-ToF/ToF (Bruker Daltonics, Billerica, MA, USA) mass spectrometer in positive MS mode courtesy of the University of Alberta. MALDI-ToF mass spectra were obtained using 2-[(2E)-3-(4-tert-butylphenyl)-2-methylpro*p*-2-enylidene]malononitrile (DCTB) as the matrix compound, with primarily Na(+) added as the cationizing agent, with a smaller proportion of NH_4(+) also added in some cases as a secondary cationizing agent. The solution of the matrix compound was prepared in CH_2Cl_2 with a final concentration of 15 mg/mL. The sample was dissolved in CH_2Cl_2 with a

concentration of approximately 0.1–1 mg/mL and mixed with an equal volume of the matrix solution. A MALDI plate was then loaded with 0.5–1 μL of the sample/matrix solution and allowed to dry.

Elemental analyses were performed using an Elementar Vario Microcube instrument running in CHNS mode. The instrument was calibrated using sulfanilamide standards, and measurements were made using 2 mg samples sizes. Air sensitive samples were sealed in tin capsules inside a glovebox.

8.2. Polymerization Studies

8.2.1. Chapter 2

***In situ* observation: 6a** (5.3 mg, 0.0069 mmol) or **6b** (9.0 mg, 0.0069 mmol) were combined with 690 μL of a solution of L-lactide in 1:1 C_6D_6/C_6D_5Br (1.0 M, 0.69 mmol) in a J-Young NMR tube. The tube was then sealed and polymerizations were carried out at 100 °C by heating in an oil bath. The tubes were periodically removed from heat and conversions determined by integration of the methine region of the ^1H NMR spectra.

Large scale polymerization with 6a: 6a (21.4 mg, 0.028 mmol), L-lactide (400 mg, 2.8 mmol), and solvent (2.8 mL of 1:1 C_6D_6/C_6D_5Br) were combined in a 4 mL Teflon sealed vial equipped with a stir bar. The resulting solution was heated to 100 °C in an oil bath for 9 hours. The solution was then exposed to the atmosphere, and the complete contents of the vial were added to cold wet methanol (10 mL, 0 °C), resulting in precipitation of the polymer. This material was then isolated by

centrifugation and decantation of the supernatant, washed with methanol, and dried under high vacuum for 18 hours.

Large scale polymerization with 6b: 6b (30.0 mg, 0.023 mmol), L-lactide (332 mg, 2.3 mmol), and solvent (2.3 mL of 1:1 C_6D_6/C_6D_5Br) were combined in a 4 mL Teflon sealed vial equipped with a stir bar. The resulting solution was heated to 100 °C with stirring for 6 hours. Isolation of the polymer was performed as described above.

8.2.2. Chapter 4

***In Situ* Observation:** 4.1 mg (0.0025 mmol) of **13** and 18.0 mg (0.125 mmol) of *rac*-lactide were combined, and dissolved in 0.50 mL of C_6D_5Br in a J-Young NMR tube. The tube was sealed and heated to 60 °C using an oil bath, and periodically removed to obtain NMR spectra. Observations were continued until conversion reached 90% (3.5 hours total heating time), as determined by integration of the methine region of the ^1H NMR spectrum. *In situ* observation of polymerization of 10 equivalents of *rac*-lactide at 50 °C followed the same methodology.

Large Scale Preparation: 28.9 mg (0.0175 mmol) of **13** and 126 mg (0.874 mmol) of *rac*-lactide were combined with 3.50 mL of bromobenzene in a Teflon sealed vial. After 3.5 hours the reaction was quenched by addition of excess methanol (5 mL). All solvents were then removed *in vacuo*, and the crude material was reconstituted in methylene chloride. The polymer was then precipitated by addition of cold methanol (5 mL) and isolated by centrifugation and decanting the solvent, followed by drying *in vacuo* for 2 hours.

8.2.3. Chapters 5 and 6

***In Situ* Observation:** An NMR tube was loaded with an appropriate amount of catalyst (e.g. 4.0 mg for $[LA]_0/[\mathbf{25}] = 200$) and 72.1 mg of *rac*-LA), to which 0.50 mL of cold (–35 °C) $CDCl_3$ (**24**) or CD_2Cl_2 (**25** and **26**) was then added. The tube was immediately sealed with a rubber septum, removed from the glove box, cooled to –78 °C with dry ice, and transported to a temperature stabilized (60 °C for **24** and 25 °C for **25** and **26**) and pre-shimmed NMR instrument. The tube was then allowed to warm and was inserted into the probe after complete dissolution of the *rac*-LA was observed, and measurements were begun immediately. For rate measurements used in the determination of activation parameters, temperatures were calibrated using calibration data, which gave the relation $T_{actual} = 1.111T_0 - 1.8505$.

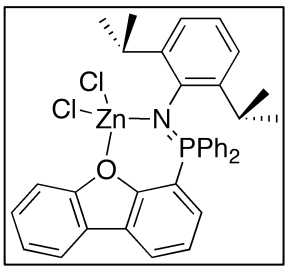
Large Scale Preparation using 25, 26, and 30: In a glove box with an ambient temperature of approximately 26 °C, a 20 mL scintillation vial was loaded with 144.1 mg of *rac*-lactide and an appropriate amount of catalyst (e.g. 9.2 mg of **25** for $[LA]_0/[\mathbf{25}] = 200$). To the vial 1.0 mL of CH_2Cl_2 was added using a syringe and the resulting solution was stirred for an appropriate period of time. Following this, the vial was removed from the glove box and exposed to the atmosphere. To the solution 10 mL of cold (–35 °C) wet methanol was added, causing the polymer to precipitate. The vial was centrifuged and the solvent decanted. The isolated polymer was redissolved in 1 mL of CH_2Cl_2 and reprecipitated and isolated by the same procedure. The polymer sample was then dried *in vacuo* for 24 hours.

Large Scale Preparation using 24: This was done similarly except at a temperature of 40 °C. Under these conditions, the polymerization required 8 hours to achieve high conversion.

8.3. Experimental Details of Chapter 2

For complete details of the synthesis of $\mathbf{L_1^{Mes}}$ and $\mathbf{L_1^{Dipp}}$, see the M.Sc. thesis of Mr. Benjamin J. Ireland.[156]

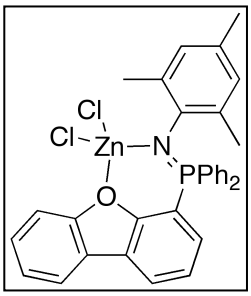
Synthesis of $\boldsymbol{L_1^{Dipp}ZnCl_2}$ *(**1**):*



$\mathbf{L_1^{Dipp}}$ (100 mg, 0.190 mmol) and $ZnCl_2$ (25.8 mg, 0.190 mmol) were combined in a glass bomb[147] with 5 mL of toluene, resulting in dissolution of the ligand and a suspension of the zinc dichloride. This mixture was heated to 120 °C for 24 hours, resulting in a clear yellow solution with all material dissolved. Allowing this to cool caused the solution to become cloudy. This solution was transferred to a vial and left at ambient temperature to crystallize for 48 hours, resulting in the formation of white crystals of the compound. The supernatant was decanted and the crystals were washed with pentane (3 x 1 mL) and dried *in vacuo*, giving **2** in 64.8% yield (81.5 mg, 0.123 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.36 (d, 1H, $^3J_{HH}$ = 7.7 Hz, 1-dbf), 8.10 (d, 1H, $^3J_{HH}$ = 7.7 Hz, 9-dbf), 7.91 (br s, 1H, 6-dbf), 7.67–7.58 (ov m, 3H, *p*-Ph + 7-dbf), 7.58–7.37 (ov m, 10H, *o*-Ph + *m*-Ph + 2-dbf + 8-dbf), 7.18–6.94 (ov m, 4H, *m*-Dipp + *p*-Dipp + 3-dbf), 3.35 (sp, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH_3)$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.23 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR

(CD_2Cl_2): δ 30.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 158.55 (s, Aromatic C), 156.36 (s, Aromatic C), 147.16 (d, J_{CP} = 5.4 Hz, Aromatic C), 138.51 (d, J_{CP} =7.9 Hz, Aromatic C), 134.72 (d, $^2J_{CP}$ = 10.0 Hz, *o*-Ph), 134.18 (d, $^2J_{CP}$ = 11.1 Hz, 3-dbf), 133.90 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 129.68 (s, 8-dbf), 129.48 (d, $^3J_{CP}$ = 12.5 Hz, *m*-Ph), 127.43 (s, 1-dbf), 127.08 (d, $^1J_{CP}$ = 97.1 Hz, *ipso*-Ph), 126.30 (d, $^5J_{CP}$ = 3.5 Hz, *p*-Dipp), 125.23 (s, 7-dbf), 124.71 (d, $^3J_{CP}$ = 2-dbf), 124.62 (d, $^4J_{CP}$ = 5.0 Hz, *m*-Dipp), 123.00 (s, Aromatic C), 121.63 (s, 9-dbf), 113.53 (s, 6-dbf), 109.74 (d, $^1J_{CP}$ = 112.8 Hz, 4-dbf), 29.39 (s, *C*H(CH_3)$_2$), 25.72 (s, CH(*C*H_3)$_2$), 22.62 (CH(*C*H_3)$_2$). One quaternary ^{13}C signal was unobserved. Anal. Calcd. (%) for $C_{36}H_{34}Cl_2NOPZn$: C: 65.12; H: 5.16; N: 2.11; found: C: 64.82; H: 4.94; N: 2.44.

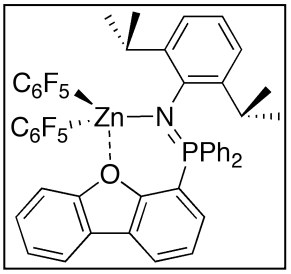
Synthesis of ***$L_1^{Mes}ZnCl_2$ (2)****:*



L_1^{Mes} (200 mg, 0.412 mmol) and $ZnCl_2$ (56.1 mg, 0.412 mmol) were combined in a bomb with 20 mL of toluene. The resulting suspension was heated to 120 °C with stirring for a period of 48 hours. During this time, $ZnCl_2$ was observed to eventually dissolve, followed by gradual formation of a white precipitate. The volume of toluene was reduced to 10 mL *in vacuo*, and an equivalent amount of pentane was added to encourage complete precipitation of product. The solvent was decanted and the resulting white solid was dried under vacuum, giving **1** in 88.6% yield (227 mg, 0.365 mmol). Solubility of the compound is too low in normal organic solvents to obtain ^{13}C NMR spectra. ^1H NMR (CD_2Cl_2): δ 8.19 (d, 1H, $^3J_{HH}$ = 7.7 Hz, 1-dbf), 7.93 (d, 1H, $^3J_{HH}$ = 7.7 Hz, 9-dbf), 7.75 (dd, 4H, $^3J_{PH}$ = 12.7 Hz, $^3J_{HH}$ = 7.7 Hz, *o*-

Ph), 7.67 (tq, 2H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.8 Hz, $^{5}J_{PH}$ = 1.8 Hz, *p*-Ph), 7.51 (td, 4H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 3.5 Hz, *m*-Ph), 7.45–7.23 (ov m, 5H, 2-dbf + 3-dbf + 6-dbf + 7-dbf + 8-dbf), 6.45 (s, 2H, *m*-Mes), 2.01 (s, 6H, *o*-C*H*$_3$ Mes), 1.87 (s, 3H, *p*-C*H*$_3$ Mes). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 28.0 (s). Anal. Calcd. (%) for $C_{33}H_{28}Cl_2NOPZn$: C: 63.74; H: 4.54; N: 2.25; found: C: 64.16; H: 4.75; N: 2.18.

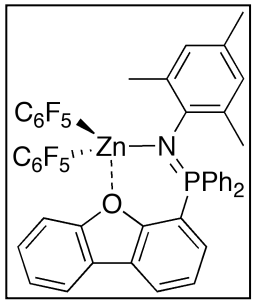
Synthesis of ***L*$_1^{Dipp}$*Zn(C$_6$F$_5$)$_2$ (3):***



L$_1^{Dipp}$ (100 mg, 0.190 mmol) and $Zn(C_6F_5)_2$ (76.0 mg, 0.190) were combined in a scintillation vial and dissolved in 1 mL of toluene, giving a clear yellow solution. This solution was layered with 3 mL of pentane and placed in a –35 °C freezer. White crystals of the compound formed after 4 days. The supernatant was decanted, the crystals were washed with pentane (3 x 1 mL) and dried *in vacuo*, giving **3** in 81.1% yield (143 mg, 0.154 mmol). ^{1}H NMR (C_6D_6): δ 7.59 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 9-dbf), 7.56–7.48 (ov m, 2H, 6-dbf + 1-dbf), 7.32 (br m, 4H, *o*-Ph), 7.22–7.12 (m, 1H, obscured by solvent, 8-dbf), 7.12–6.87 (ov m, 6H, 7-dbf + *p*-Dipp + *m*-Dipp + *p*-Ph), 6.80 (td, 4H, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{PH}$ = 3.0 Hz, *m*-Ph), 6.76–6.68 (ov m, 2H, 2-dbf + 3-dbf), 3.84 (sp, 2H, $^{3}J_{HH}$ = 6.7 Hz, *C*H(CH$_3$)$_2$), 1.11 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, CH(*C*H$_3$)$_2$), 0.38 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, CH(*C*H$_3$)$_2$). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 28.5 (s). $^{19}F\{^{1}H\}$ NMR (C_6D_6): δ –114.5 (m, 4F, *o*-C_6F_5), –156.8 (t, 2F, *p*-C_6F_5), –160.8 (m, 4F, *m*-C_6F_5). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 158.23 (s, Aromatic C), 156.88 (s, Aromatic C), 148.58 (br dd, $^{1}J_{CF}$ = 226 Hz, $^{2}J_{CF}$ = 28 Hz, *o*-C_6F_5), 147.41 (d, J_{CP} = 5.8 Hz, Aromatic C), 140.34 (br d, $^{1}J_{CF}$ = 238 Hz, *p*-C_6F_5), 139.74 (d, J_{CP} = 8.2 Hz, Aromatic C), 137.04 (br d, $^{1}J_{CF}$ = 248 Hz, *m*-C_6F_5),

134.32 (d, $^{2}J_{CP}$ = 9.7 Hz, *o*-Ph), 133.88 (d, $^{4}J_{CP}$ = 2.4 Hz, *p*-Ph), 133.76 (s, 3-dbf), 129.39 (s, 7-dbf), 129.33 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-Ph), 126.89 (d, $^{4}J_{CP}$ = 2.7 Hz, 1-dbf), 126.66 (d, $^{5}J_{CP}$ = 3.6 Hz, *p*-Dipp), 126.64 (br d, $^{1}J_{CP}$ = 101.5 Hz, *ipso*-Ph), 126.30 (d, J_{CP} = 6.8 Hz, Aromatic C), 125.18 (d, $^{4}J_{CP}$ = 3.4 Hz, *m*-Dipp), 124.61 (s, 8-dbf), 123.68 (d, $^{3}J_{CP}$ = 11.3 Hz, 2-dbf), 123.31 (br t, $^{2}J_{CF}$ = 70 Hz, *ipso*-C_6F_5), 122.69 (d, J_{CP} = 0.9 Hz, Aromatic C), 121.04 (s, 9-dbf), 113.31 (s, 6-dbf), 111.10 (d, $^{1}J_{CP}$ = 100.6 Hz, 4-dbf), 29.04 (s, *C*H(CH_3)$_2$), 25.28 (s, CH(*C*H_3)$_2$), 23.96 (s, CH(*C*H_3)$_2$). Anal. Calcd. (%) for $C_{48}H_{34}F_{10}NOPZn$: C: 62.18; H: 3.70; N: 1.51; found: C: 62.27; H: 3.92; N: 1.95.

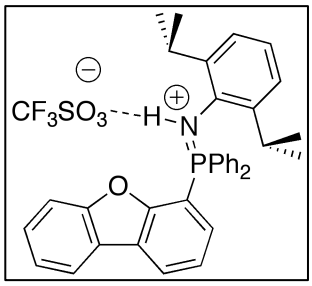
Synthesis of ***L*$_1^{Mes}$*Zn(C_6F_5)$_2$ (4):***



This was prepared similarly to **3** using $\mathbf{L_1^{Mes}}$ (100 mg, 0.206 mmol) and $Zn(C_6F_5)_2$ (82.3 mg, 0.206 mmol), affording pale yellow crystals of **4** in 87.8% yield (160 mg, 0.181 mmol). ^{1}H NMR (C_6D_6): δ 7.60–7.45 (ov m, 3H, 1-dbf + 6-dbf + 9-dbf), 7.38 (dd, 4H, $^{3}J_{PH}$ = 12.5 Hz, $^{3}J_{HH}$ = 7.9 Hz, *o*-Ph), 7.20–7.10 (ov m, 1H, 7-dbf, obscured by solvent signal), 7.06 (td, 1H, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.1 Hz, 8-dbf), 6.94 (tq, 2H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, $^{5}J_{PH}$ = 1.5 Hz, *p*-Ph), 6.86–6.72 (ov m, 6H, *m*-Ph + 2-dbf + 3-dbf), 6.39 (s, 2H, *m*-Mes), 2.12 (s, 6H, *o*-CH_3 Mes), 1.84 (s, 3H, *p*-CH_3 Mes). ^{31}P{^{1}H} NMR (C_6D_6): δ 25.7 (s). ^{19}F{^{1}H} NMR (C_6D_6): δ –114.5 (m, 4F, *o*-C_6F_5), –157.1 (t, 2F, *p*-C_6F_5), –161.3 (m, 4F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (C_6D_6): δ 157.67 (s, Aromatic C), 156.29 (s, Aromatic C), 148.03 (br dd, $^{1}J_{CF}$ = 222 Hz, $^{2}J_{CF}$ = 28 Hz, *o*-C_6F_5), 140.03 (d, J_{CP} = 7.6 Hz, Aromatic C), 139.60 (br d, $^{1}J_{CF}$ = 240 Hz, *p*-C_6F_5), 136.27 (br d, $^{1}J_{CF}$ = 250 Hz, *m*-C_6F_5), 136.10 (d, J_{CP} = 5.7 Hz, Aromatic C), 133.80 (d, J_{CP} = 3.9

Hz, Aromatic C), 133.49 (d, $^{2}J_{CP}$ = 9.9 Hz, *o*-Ph), 133.20 (d, $^{4}J_{CP}$ = 2.9 Hz, *p*-Ph), 131.95 (d, $^{3}J_{CP}$ = 8.4 Hz, 3-dbf), 129.40 (d, $^{4}J_{CP}$ = 3.3 Hz, *m*-Mes), 128.66 (s, 7-dbf), 128.52 (d, $^{3}J_{CP}$ = 12.5 Hz, *m*-Ph), 126.13 (d, $^{4}J_{CP}$ = 2.7 Hz, 1-dbf), 126.03 (d, $^{1}J_{CP}$ = 103.0 Hz, *ipso*-Ph), 125.79 (d, J_{CP} = 6.6 Hz, Aromatic C), 123.86 (s, 8-dbf), 122.89 (d, $^{3}J_{CP}$ = 11.3 Hz, 2-dbf), 122.11 (t, $^{2}J_{CF}$ = 67 Hz, *ipso*-C_6F_5), 122.08 (s, Aromatic C), 120.48 (s, 9-dbf), 112.95 (s, 6-dbf), 111.17 (d, $^{1}J_{CP}$ = 99.0 Hz, 4-dbf), 20.70 (br s, *o*-*C*H_3 Mes), 20.10 (d, $^{6}J_{CP}$ = 1.4 Hz, *p*-*C*H_3 Mes). Anal. Calcd. (%) for $C_{45}H_{28}F_{10}NOPZn{\cdot}C_5H_{12}$: C: 62.74; H: 4.21; N: 1.46; found: C: 62.67; H: 3.96; N: 1.43.

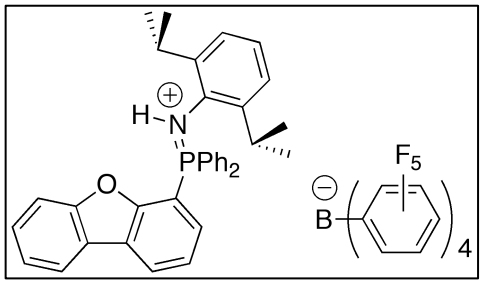
*Synthesis of [**L**$_1^{Dipp}$**H**$^+$][$SO_3CF_3^-$] (**5a**):*



A slight excess of triflic acid (0.170 mL, 1.92 mmol) was added to a solution of **L**$_1^{Dipp}$ (1.00 g, 1.90 mmol) in 30 mL of benzene. Upon addition of triflic acid, a color change of the solution from yellow to pale yellow was observed. The solution was allowed to stir for 30 minutes at ambient temperature, at which time the benzene was removed under vacuum. The crude product was then stirred in 30 mL of pentane for 30 minutes and filtered. The crude residue was washed with pentane (3 x 10 mL) and dried under vacuum to yield **5a** as an analytically pure white powder in 85% yield (1.10 g, 1.62 mmol). ^{1}H NMR (1:1 C_6D_6/C_6D_5Br): δ 9.31 (d, 1H, $^{2}J_{PH}$ = 11.7 Hz, N*H*), 7.73 (ov m, 5H, *o*-Ph + Aromatic H), 7.61 (dd, 1H, *J* = 14 Hz, 8.1 Hz, Aromatic H), 7.53 (d, 1H, *J* = 6.6 Hz, Aromatic H), 7.20–7.00 (ov m, 9H, Aromatic H), 6.92–6.80 (ov m, 2H, Aromatic H), 6.73 (d, 2H, $^{2}J_{HP}$ = 7.5 Hz, *m*-Dipp), 3.23 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$(CH_3)_2$), 0.85 (br s, 12H, CH(C*H*$_3)_2$). ^{31}P{^{1}H} NMR (1:1

C_6D_6/C_6D_5Br): δ 33.5 (s). $^{19}F\{^1H\}$ NMR (1:1 C_6D_6/C_6D_5Br): δ –77.5 (s). $^{13}C\{^1H\}$ NMR (1:1 C_6D_6/C_6D_5Br): δ 157.45 (d, J_{CP} = 2.5 Hz), 156.97 (s), 149.25 (d, J_{CP} = 3.8 Hz), 135.37 (d, J_{CP} = 3.0 Hz), 134.64 (d, J_{CP} = 11.3 Hz), 133.15 (d, J_{CP} = 7.6 Hz), 130.95 (d, J_{CP} = 5.0 Hz), 130.13 (s), 129.48 (s), 129.41 (d, J_{CP} = 2.3 Hz), 126.59 (d, J_{CP} = 7.4 Hz), 124.72 (d, J_{CP} = 11.6 Hz), 124.66 (d, J_{CP} = 11.0 Hz), 124.57 (s), 122.99 (s), 122.64 (d, J_{CP} = 1.2 Hz), 121.75 (s), 121.60 (s), 112.94 (s), 105.20 (d, J_{CP} = 105.5 Hz), 30.06 ($CH(CH_3)_2$), 24.20 ($CH(CH_3)_2$). One quaternary aromatic C not observed. Anal. Calcd. (%) for $C_{37}H_{35}F_3NO_4PS$: C: 65.57; H: 5.21; N: 2.07; S: 4.73; found: C: 66.09; H: 5.33; N: 2.14; S: 4.93.

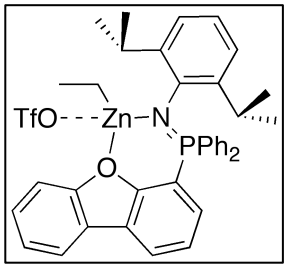
*Synthesis of [**L₁^Dipp**H⁺][B(C₆F₅)₄⁻] (**5b**):*



L_1^{Dipp} (0.098 g, 0.186 mmol) was combined with one equivalent of the anilinium activator $[HNMe_2Ph^+][B(C_6F_5)_4^-]$ (0.150 g, 0.187 mmol) in 2 mL of benzene. Immediately upon combining the reagents, the formation of a pale yellow oil was observed. The reaction mixture was stirred for 5 minutes at ambient temperature, and then the benzene was decanted. The remaining oil was washed twice with pentane and dried under vacuum to generate **5b** as a white powder in 97% yield (0.217 g, 0.180 mmol). ^1H NMR (3:1 C_6D_6/C_6D_5Br): δ 7.84 (d, 1H, 7.8 Hz, Aromatic H), 7.61 (m, 1H, Aromatic H), 7.14–7.05 (ov m, 8H, Aromatic H) 6.96 (ov m, 5H, *m*-Ph + Aromatic H), 6.90 (d, 1H, *J* = 6.9 Hz, Aromatic H), 6.86–6.72 (ov m, 2H, Aromatic H), 6.68 (d, 2H, *J* = 7.8 Hz, *m*-Dipp), 4.96 (d, 1H, $^2J_{HP}$ = 9.3 Hz, N*H*), 2.66 (sp, 2H, *J* = 6.9 Hz, C*H*$(CH_3)_2$),

0.56 (d, 12H, J = 6.9 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ 36.1 (s). ^{19}F{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ –131.7 (d, 8F, *o*-C$_6F_5$), –162.4 (t, 4F, *p*-C$_6F_5$), –166.3 (t, 8F, *m*-C$_6F_5$). ^{13}C{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ 156.80 (d, J_{CP} = 1.4 Hz), 156.09(s), 150.37 (br, C_6F_5), 147.56 (d, J_{CP} = 3.0 Hz), 147.22 (br, C_6F_5), 138.33 (br, C_6F_5), 136.00 (d, J_{CP} = 2.3 Hz), 135.10 (br, C_6F_5), 133.40 (d, J_{CP} = 11.3 Hz), 131.66 (d, J_{CP} = 9.0 Hz), 130.02 (d, J_{CP} = 14 Hz), 128.77 (d, J_{CP} = 3.0 Hz), 127.98 (d, JCP = 5.6 Hz), 126.45 (d, J_{CP} = 6.9 Hz), 124.86 (s), 124.54 (d, J_{CP} = 2.0 Hz), 124.10 (d, J_{CP} = 12.0 Hz), 121.59 (d, J_{CP} = 1.2 Hz), 121.57 (s), 118.45 (s), 117.01 (s), 111.45 (s), 105.65 (d, J_{CP} = 99.2 Hz), 28.97 (*C*H(CH$_3$)$_2$), 22.83 (CH(*C*H$_3$)$_2$). One quaternary aromatic C was not observed. Anal. Calcd. (%) for $C_{60}H_{35}BF_{20}NOP$: C: 59.67; H: 2.92; N: 1.16; found: C: 59.97; H: 3.37; N: 1.37.

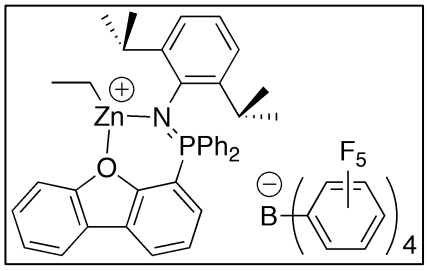
Synthesis of ***L$_1^{Dipp}$ZnEt(SO$_3$CF$_3$) (6a)****:*



A slight excess of diethylzinc (80 µL, 0.486 mmol) was added to a solution of **5a** (303 mg, 0.447 mmol) in benzene (50 mL). The reaction mixture was then allowed to stir at 100 °C for 24 hours. The benzene solvent was removed under vacuum, yielding the crude product as an off-white solid. The residue was dissolved in a minimum amount of bromobenzene and precipitated as a white powder by addition of pentane. The solvent was decanted, and the product was washed again with a small portion of pentane. Drying under vacuum gave **6a** as a white powder in 83% yield (288 mg, 373 mmol). ^{1}H NMR (1:1 C_6D_6/C_6D_5Br): δ 7.70 (ov m, 2H, Aromatic H), 7.58 (d, 1H, J = 6.6 Hz, Aromatic H), 7.44 (br m, 4H, *o*-Ph),

7.15–6.70 (ov m, 13H, Aromatic H), 3.51 (sp, 2H, J = 6.9 Hz, CH(CH$_3$)$_2$), 1.36 (t, 3H, J = 8.1 Hz, CH$_2$CH_3), 1.32 (d, 6H, J = 6.9 Hz, CH(CH_3)$_2$), 0.80 (q, 2H, J = 8.1 Hz, CH_2CH$_3$), 0.32 (d, 6H, J = 6.9 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ 26.9 (s). ^{19}F{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ –77.8 (s). ^{13}C{^{1}H} NMR (1:1 C_6D_6/C_6D_5Br): δ 158.78 (s), 156.97 (s), 147.14 (d, J_{CP} = 5.3 Hz), 139.07 (d, J_{CP} = 8.3 Hz), 134.60 (d, J_{CP} = 9.8 Hz), 133.88 (d, J_{CP} = 10.7 Hz), 133.85 (d, J_{CP} = 3.0 Hz), 129.83 (s), 129.61 (d, J_{CP} = 12.1 Hz), 127.73 (d, J_{CP} = 6.8 Hz), 126.86 (d, J_{CP} = 3.8 Hz), 125.27 (s), 125.15 (d, J_{CP} = 3.0 Hz), 124.53 (d, J_{CP} = 12.8 Hz), 123.38 (d, J_{CP} = 0.8 Hz), 121.94 (s), 119.07 (s), 112.98 (s), 110.02 (d, J_{CP} = 113.7 Hz), 29.73 (CH(CH$_3$)$_2$), 25.86 (CH(CH_3)$_2$), 23.05 (CH(CH_3)$_2$), 12.61 (CH$_2$CH_3), 2.34 (d, $^3J_{CP}$ = 2.7 Hz, CH_2CH$_3$). 2 quaternary aromatic C atoms were not observed. Anal. Calcd. (%) for $C_{39}H_{39}F_3NO_4PSZn$: C: 60.74; H: 5.10; N: 1.82; S: 4.16; found: C: 60.45; H: 5.05; N: 1.94; S: 4.49.

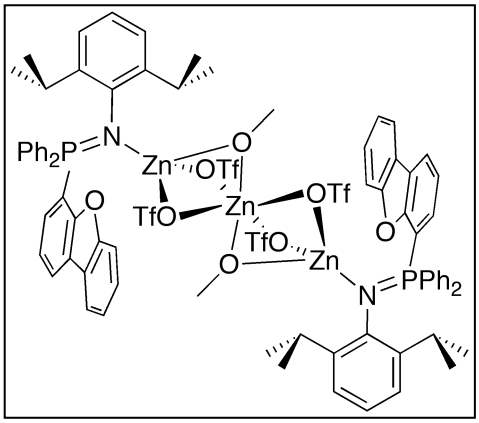
*Synthesis of [**L$_1^{Dipp}$**ZnEt$^+$][B(C$_6$F$_5$)$_4^-$] (**6b**):*



A slight excess of diethylzinc (21 µL, 0.127 mmol) was added to a solution of **5b** (150 mg, 0.124 mmol) in 5 mL of toluene. The reaction mixture was heated to 100 °C for 16 hours, and the solvent was then removed under vacuum. The crude product was dissolved in a minimum amount of bromobenzene and precipitated as a pale yellow oil by addition of pentane. The solvent was decanted, the oil was washed twice with pentane, and dried under vacuum to yield **6b** as a white powder in 87% yield (141 mg, 0.108 mmol). ^{1}H NMR (1:1 C_6D_6/C_6D_5Br): δ 7.85 (d, J = 7.5 Hz, 1H, Aromatic H), 7.66 (dd,

1H, *J* = 4.8 Hz, 3.0 Hz, Aromatic H), 7.25–6.96 (ov m, 15H, Aromatic H), 6.83–6.73 (ov m, 3H, *m*-Dipp + Aromatic H), 2.72 (sp, 2H, *J* = 6.9 Hz, C*H*(CH_3)$_2$), 1.00 (t, 3H, *J* = 7.8 Hz, CH_2CH_3), 0.81 (d, 6H, *J* = 6.9 Hz, CH(CH_3)$_2$), 0.73 (q, 2H, *J* = 7.8 Hz, CH_2CH_3), 0.31 (d, 6H, *J* = 6.9 Hz, CH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (1:1 C_6D_6/C_6D_5Br): δ 30.1 (s). $^{19}F\{^1H\}$ NMR (1:1 C_6D_6/C_6D_5Br): δ –131.6 (d, 8F, *o*-C_6F_5), –162.4 (t, 4F, *p*-C_6F_5), –166.2 (t, 8F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (1:1 C_6D_6/C_6D_5Br): δ 157.11 (d, J_{CP} = 0.9 Hz), 156.38 (s), 150.96 (br, C_6F_5), 147.76 (br, C_6F_5), 146.88 (d, J_{CP} = 4.5 Hz), 138.88 (br, C_6F_5), 136.36 (d, J_{CP} = 3.0 Hz), 135.61 (br, C_6F_5), 134.07 (d, J_{CP} = 8.4 Hz), 133.40 (d, J_{CP} = 9.8 Hz), 132.68 (d, J_{CP} = 8.3 Hz), 131.03 (d, J_{CP} = 13 Hz), 130.37 (s), 126.90 (d, J_{CP} = 6.8 Hz), 126.28 (s), 125.58 (d, J_{CP} = 3.2 Hz), 125.47 (s), 122.62 (s), 122.50 (d, J_{CP} = 0.8 Hz), 121.62 (d, J_{CP} = 105.7 Hz), 111.68 (s), 111.68 (d, J_{CP} = 97.6), 29.68 (*C*H(CH_3)$_2$), 25.82 (CH(*C*H_3)$_2$), 21.68 (CH(*C*H_3)$_2$), 11.03 (CH_2*C*H_3), 4.65 (*C*H_2CH_3). 2 quaternary aromatic C atoms were not observed. Anal. Calcd. (%) for $C_{62}H_{39}BF_{20}NOPZn$: C: 57.23; H: 3.02; N: 1.08; found: C: 57.08; H: 3.10; N: 1.21.

Synthesis of ***L*$_1^{Dipp}$**$_2Zn_3(\mu_2\text{-}SO_3CF_3)_4(\mu_2\text{-}OCH_3)_2$ (**7**):



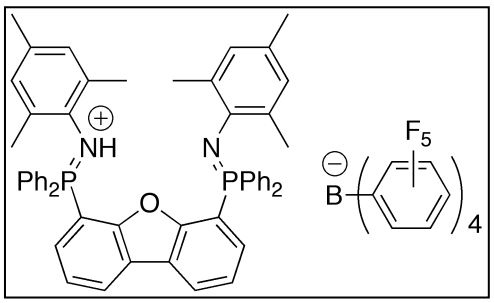
In a 20 mL Teflon-sealed vial, a stoichiometric amount of dry methanol (5.2 µL, 0.13 mmol) was added to a suspension of **6a** (100 mg, 0.130 mmol) in benzene (3 mL). The vial was sealed, heated to 100 °C for 1 hour, and then cooled to ambient temperature and left to stand for a period of 48 hours. A significant amount of material crystallized

during that time. The mother liquor was decanted, and the colourless crystals were washed with benzene (2 × 1 mL) and pentane (2 × 1 mL) and dried *in vacuo*, affording 7 as a white crystalline material in 92.4% yield (57.2 mg, 0.0300 mmol). The compound is too insoluble in non-coordinating solvents to allow characterization by NMR spectroscopy. Anal. Calcd. (%) for $C_{78}H_{74}F_{12}N_2O_{16}P_2S_4Zn_3$: C: 49.05; H: 3.91; N: 1.47; S: 6.72; found: C: 49.25; H: 4.07; N: 1.52; S: 6.68.

8.4. Experimental Details of Chapter 3

For complete details of the synthesis and characterization of $\mathbf{L_2^{Mes}}$, see the M.Sc. thesis of Mr. Benjamin J. Ireland.[156]

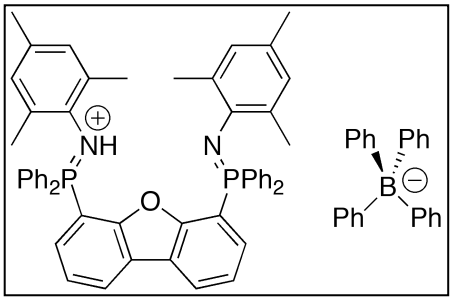
Synthesis of $[\boldsymbol{L_2^{Mes}H^+}][B(C_6F_5)_4^-]$ (***8a***)*:*



A 50 mL round bottom flask was charged with 0.271 g (0.338 mmol) of $\mathbf{L_2^{Mes}}$ and 0.266 mg (0.332 mmol) of $[HNMe_2Ph][B(C_6F_5)_4]$ to which 10 mL of benzene was added. The solution was allowed to stir for 10 minutes and the benzene was removed *in vacuo* affording an oily, light yellow solid containing the desired product and Me_2NPh. The flask was attached to a swivel frit apparatus and the solid was washed three times with 10 mL portions of pentane. During each washing procedure, the mixture was sonicated and allowed to stir for several minutes before filtration. The light yellow solid was dried *in vacuo* for 20 hours, affording the desired product. A total of 0.394 g (0.266 mmol)

of **8a** was recovered as a light yellow solid (80% yield). ^{1}H NMR ($CDCl_3$): δ 8.30 (d, $^{3}J_{HH}$ = 6.0 Hz, 2H, 1,9-dbf), 7.57–7.21 (br ov m, 24H, 2,8-dbf + 3,7-dbf + *o*-Ph + *m*-Ph + *p*-Ph), 6.58 (s, 4H, *m*-Mes), 5.72 (br s, 1H, N*H*), 2.17 (s, 6H, *p*-C*H*$_3$ Mes), 1.55 (s, 12H, *o*-C*H*$_3$ Mes). ^{31}P{^{1}H} NMR (C_6D_6): δ 10.1 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.4 (s). ^{19}F{^{1}H} NMR (C_6D_6): δ –130.8 (br d, $^{3}J_{FF}$ = 11 Hz, 8F, *o*-C_6F_5), –161.7 (t, $^{3}J_{FF}$ = 22 Hz, 4F, *p*-C_6F_5), –165.5 (m, 8F, *m*-C_6F_5). ^{11}B{^{1}H} NMR ($CDCl_3$): δ –16.7 (br s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.2 (s, Aromatic C), 134.6 (d, $^{3}J_{CP}$ = 5.3 Hz, 2,8-dbf), 134.0 (s, Aromatic C), 133.4 (s, Aromatic C), 132.6 (d, $^{2}J_{CP}$ = 10.6 Hz, *o*-Ph), 131.2 (s, Aromatic C), 130.0 (s, *p*-Ph), 129.8 (s, *m*-Ph), 129.5 (s, *m*-Mes), 127.1 (s, 1,9-dbf), 125.4 (s, Aromatic C), 124.0 (s, Aromatic C), 123.3 (s, Aromatic C), 20.8 (s, *p*-*C*H$_3$ Mes), 20.1 (s, *o*-*C*H$_3$ Mes); B(C_6F_5)$_4^-$ resonances are very broad and weak and are thus not reported and the *ipso*-Ph signal was not observed. Anal. Calcd. (%) for $C_{78}H_{49}BF_{20}N_2OP_2$: C: 63.17; H: 3.34; N: 1.89. Found: C: 63.34; H: 3.37; N: 1.95.

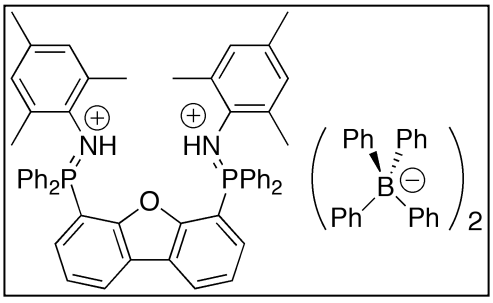
*Synthesis of [**L**$_2^{Mes}$H$^+$][BPh$_4^-$] (**8b**):*



Under aerobic conditions, 400 mg (0.498 mmol) of **L**$_2^{Mes}$ was dissolved in 1 mL of methanol, to which was added 0.50 mL of a 1M aqueous solution of HCl (0.50 mmol). A separate solution of $NaBPh_4$ (188 mg, 0.549 mmol) in 1 mL of methanol was added to this with stirring, which resulted in the immediate formation of a flocculent white precipitate. The precipitate was obtained by filtration, thoroughly washed with methanol, and dried *in vacuo*, giving **8b** in 80.5%

yield (450 mg, 0.401 mmol). ^{1}H NMR ($CDCl_3$): δ 8.14 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, 1,9-dbf), 7.46–7.31 (ov m, 24H, 1,9-dbf + 3,7-dbf + *o*-Ph + *p*-Ph + *o*-BPh_4), 7.30–7.19 (m, 8H, *m*-Ph), 6.95 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 6.1 Hz, 8H, *m*-BPh_4), 6.82 (t, $^{3}J_{HH}$ = 7.4 Hz, 4H, *p*-BPh_4), 6.58 (s, 4H, *m*-Mes), 5.69 (br s, 1H, N*H*), 2.18 (s, 6H, *p*-C*H*$_3$ Mes), 1.56 (s, 12H, *o*-C*H*$_3$ Mes). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.5 (s). ^{11}B{^{1}H} NMR ($CDCl_3$): δ –6.5 (br s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.4 (q, $^{1}J_{CB}$ = 49.1 Hz, *ipso*-BPh_4), 157.0 (s, Aromatic C), 136.5 (s, *m*-BPh_4), 134.5 (s), 133.9 (s, 2,6-dbf), 133.6 (s, Aromatic C), 132.5 (d, $^{2}J_{CP}$ = 9.8 Hz, *o*-Ph), 131.2 (s, Aromatic C), 129.6 (s, *p*-Ph), 129.3 (s, *m*-Ph), 128.5 (s, *m*-Mes), 127.4 (s, 1,9-dbf), 125.5 (s, *o*-BPh_4), 125.1 (s, Aromatic C) 124.2 (d, $^{2}J_{CP}$ = 6.0 Hz, 3,7-dbf), 123.4 (s, Aromatic C), 121.6 (s, *p*-BPh_4), 20.8 (s, *o*-*C*H$_3$ Mes)), 20.2 (s, *p*-*C*H$_3$ Mes). *ipso*-Ph not observed. Anal. Calcd. (%) for $C_{78}H_{69}BN_2OP_2$: C: 83.39; H: 6.20; N: 2.49. Found: C: 83.24; H: 6.11; N: 2.51.

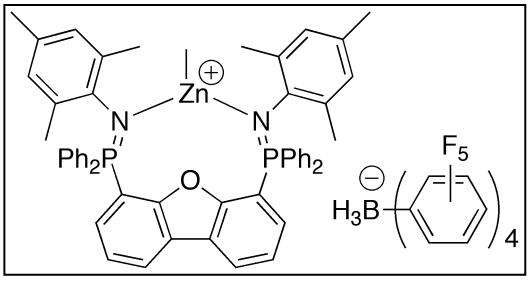
*Synthesis of [**L**$_2^{Mes}$2H^{2+}][BPh$_4^-$]$_2$ (**9**):*



An excess of 1M aqueous HCl (0.50 mL, 0.50 mmol) was added to a suspension of **L**$_2^{Mes}$ (0.110 g, 0.137 mmol) in methanol (5 mL). With stirring, a slight excess of $NaBPh_4$ (0.112 g, 0.327 mmol) in MeOH (5 mL) was added, immediately yielding a fluffy white precipitate. Stirring was continued for another 5 minutes. The precipitate was collected by filtration, washed three times with methanol, and dried *in vacuo* to give **9** in 91.2% yield (0.170 g, 0.125 mmol). ^{1}H NMR (acetone-d_6): δ 8.56 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 8.14 (d, 2H, $^{3}J_{HP}$ = 9.7 Hz,

N*H*), 8.08 (dd, 2H, $^{3}J_{HP}$ = 14.3 Hz, $^{3}J_{HH}$ = 7.8 Hz, 3,7-dbf), 7.61 (td, 2H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HP}$ = 1.4 Hz, 2,8-dbf), 7.06 (t, 4H, $^{3}J_{HH}$ = 7.4 Hz, *p*-PPh_2), 6.84 (td, 8H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 3.8 Hz, *m*-PPh_2), 6.78–6.65 (m, 24H, *o*-BPh_4^- + *o*-PPh_2), 6.47 (t, 16H, $^{3}J_{HH}$ = 7.2 Hz, *m*-BPh_4^-), 6.33 (t, 8H, $^{3}J_{HH}$ = 7.2 Hz, *p*-BPh_4^-), 6.22 (s, 4H, *m*-Mes), 1.63 (s, 6H, *p*-C*H*$_3$ Mes), 1.26 (s, 12H, *o*-C*H*$_3$ Mes). $^{31}P\{^{1}H\}$ NMR (acetone-d_6): δ 28.1 (s). $^{11}B\{^{1}H\}$ NMR (acetone-d_6): δ –6.5 (br s). $^{13}C\{^{1}H\}$ NMR (acetone-d_6): δ 165.0 (q, $^{1}J_{CB}$ = 49.4 Hz, *ipso*-BPh_4^-), 157.6 (d, J_{CP} = 3.4 Hz), 138.2 (s), 137.1 (q, $^{3}J_{CB}$ = 1.4 Hz, *m*-BPh_4^-), 137.0 (br s), 135.0 (s), 134.3 (d, J_{CP} = 11.4 Hz), 132.6 (s), 131.1 (s), 130.9 (s), 130.7 (d, J_{CP} = 1.9 Hz), 130.3 (s), 129.8 (s), 127.8 (s), 127.0 (d, J_{CP} = 11.7 Hz), 126.1 (q, $^{2}J_{CB}$ = 2.8 Hz, *o*-BPh_4^-), 122.3 (q, $^{4}J_{CB}$ = 0.5 Hz, *p*-BPh_4^-), 116.1 (s), 20.8 (s, *p*-*C*H$_3$ Mes), 19.8 (s, *o*-*C*H$_3$ Mes). Anal. Calcd. (%) for $C_{102}H_{90}B_2N_2OP_2 \cdot C_3H_6O$: C: 83.99; H: 6.44; N: 1.87. Found: C: 83.89; H: 6.19; N: 1.94.

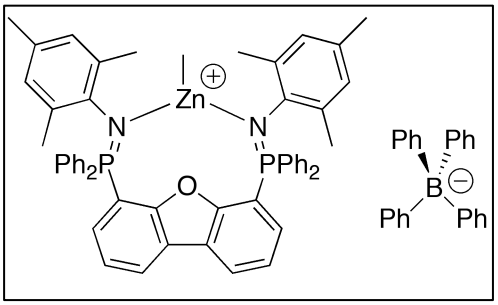
*Synthesis of [**L**$_2^{Mes}$ZnCH$_3^+$][B(C$_6$F$_5$)$_4^-$] (**10a**):*



An excess of 1.2 M dimethylzinc in toluene (65 µL, 0.0780 mmol) was added to a solution of **8a** (100 mg, 0.0674 mmol) in bromobenzene (2 mL). Effervescence of methane was immediately observed. After allowing the mixture to stand for 30 minutes at ambient temperature, the product was precipitated as a red/orange oil by addition of pentane (5 mL). The supernatant was decanted, the resulting oil was washed twice with 1 mL of pentane, then once with 2 mL of a 1:2 benzene/pentane mixture and dried *in vacuo*, giving **10a** as a pale yellow powder in 92.0% yield (96.6

mg, 0.0618 mmol). ^{1}H NMR (C_6D_5Br): δ 7.87 (d, 2H, $^{3}J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.32–7.19 (ov m, 4H, *p*-Ph; partially obscured by solvent), 7.19–7.06 (ov m, 10H, *o*-Ph + 2,8-dbf), 6.99 (td, 8H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 3.2 Hz, *m*-Ph), 6.77 (dd, 2H, $^{3}J_{PH}$ = 11.8 Hz, $^{3}J_{HH}$ = 7.6 Hz, 3,7-dbf), 6.41 (s, 4H, *m*-Mes), 2.05 (s, 6H, *p*-CH_3 Mes), 1.34 (s, 12H, *o*-CH_3 Mes), –0.48 (s, 3H, CH_3Zn). ^{31}P{^{1}H} NMR (C_6D_5Br): δ 23.4 (s). ^{19}F{^{1}H} NMR (C_6D_5Br): δ –133.2 (d, 8F, *o*-C_6F_5), –163.7 (t, 4F, *p*-C_6F_5), –167.5 (t, 8F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_5Br): δ –17.7 (br s). ^{13}C{^{1}H} NMR (C_6D_5Br): δ 157.60 (s, Aromatic C), 150.23 (br s, C_6F_5), 147.06 (br s, C_6F_5), 139.99 (br s, C_6F_5), 138.29 (d, J_{CP} = 7.9 Hz, Aromatic C), 136.55 (d, J_{CP} = 6.0 Hz, Aromatic C), 135.00 (br s, C_6F_5), 134.39 (d, J_{CP} = 4.1 Hz, Aromatic C), 134.12 (d, $^{4}J_{CP}$ = 2.6 Hz, *p*-Ph), 132.84 (d, $^{2}J_{CP}$ = 10.0 Hz, *o*-Ph), 132.36 (d, $^{2}J_{CP}$ = 6.8 Hz, 3,7-dbf), 129.81 (s, *m*-Mes), 129.49 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-Ph), 127.13 (d, $^{4}J_{CP}$ = 2.3 Hz, 1,9-dbf), 124.09 (d, $^{3}J_{CP}$ = 10.5 Hz, 2,8-dbf), 123.96 (d, J_{CP} = 8.9 Hz, Aromatic C), 114.75 (d, $^{1}J_{CP}$ = 92.0 Hz, 4,6-dbf), 20.75 (s, *p*-*C*H_3 Mes), 19.04 (s, *o*-*C*H_3 Mes). *ipso*-Ph not observed. Anal. Calcd. (%) for $C_{79}H_{51}BF_{20}N_2OP_2Zn{\cdot}C_6H_5Br$: C: 59.38; H: 3.28; N: 1.63; found: C: 59.44; H: 3.29; N: 1.71.

*Synthesis of [**L**$_2^{Mes}$ZnCH$_3^+$][BPh$_4^-$]/[L$_2^{Mes}$ZnPh$^+$][BPh$_4^-$] (**10b/11**):*



Method A: A small excess of dimethylzinc (0.160 mL of a 1.2 M solution in toluene, 0.192 mmol) was added to a solution of **8b** (200 mg, 0.178 mmol) in bromobenzene (1 mL). Immediate evolution of methane gas was observed, with a concomitant colour change of the solution

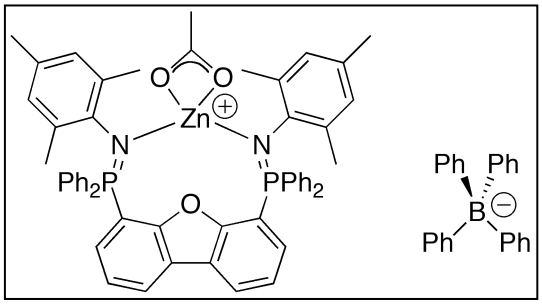
from pale yellow to pale orange. Within 15 minutes at ambient temperature, the reaction products crystallized from solution. The mother liquor was decanted from the white crystalline material, which was washed with benzene (3 x 1 mL) and pentane (2 x 1 mL), and dried *in vacuo*, giving an overall yield of 89.3% (191 mg, 0.159 mmol). The material was found to contain 87% **10b** and 13% **11**, by integration of the *ortho* methyl groups in the ^{1}H NMR spectrum.

Method B: A slight excess of dimethylzinc (0.050 mL of a 1.2 M solution in toluene, 0.060 mmol) was added to a suspension of **9** (80.7 mg, 0.0559 mmol) in bromobenzene (1 mL). All material dissolved within 1 min, and the resulting yellow solution was left to stand for 30 minutes. Within this time, the reaction products crystallized from solution. The mother liquor was decanted from the resulting white crystalline material, which was then washed with benzene (3 x 1 mL) and pentane (2 x 1 mL), and dried *in vacuo*, affording an overall 63.5% yield (42.7 mg, 0.0355 mmol). The material was found to contain 55% **10b** and 45% **11**, by integration of the *ortho* methyl groups in the ^{1}H NMR spectrum.

NMR data are reported for material isolated from Method B (55% **10b**, 45% **11**). ^{1}H NMR (C_6D_5Br): δ 7.83 (br m, 8H, *o*-BPh_4), 7.70 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.25–7.00 (ov m, 20H, *o*-Ph + *p*-Ph + *m*-BPh_4, partially obscured by solvent resonance), 7.00–6.83 (ov m, 14H, *p*-BPh_4 + *m*-Ph + 2,8-dbf, partially obscured by solvent resonances), 6.70 (dd, 2H, $^{3}J_{PH}$ = 12.0 Hz, $^{3}J_{HH}$ = 7.5 Hz, 3,7-dbf), 6.40 (s, 2.2H, *m*-Mes of **10b**), 6.37 (s, 1.8H, *m*-Mes of **11**), 2.08 (s, 2.7H, *p*-CH_3 Mes of **11**), 2.04 (s, 3.3H, *p*-CH_3 Mes of **10b**), 1.33 (s, 6.6H, *o*-CH_3 Mes of **10b**), 1.03 (s, 5.4H, *o*-CH_3 Mes of **11**), –0.49 (s, 1.65H, ZnCH_3). ^{31}P{^{1}H} NMR (C_6D_5Br): δ

23.6 (s, **10b**), 24.2 (s, **11**). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): δ –5.6 (s). Compound solubility and purity did not permit the collection and assignment of $^{13}C\{^{1}H\}$ NMR data.

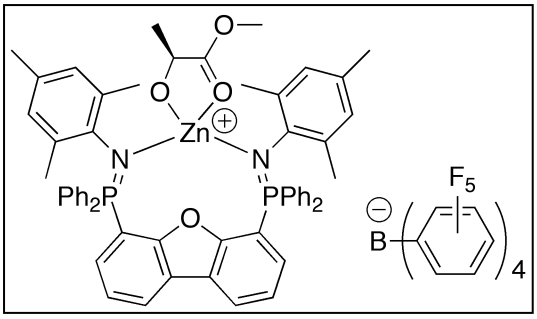
*Synthesis of [**L**$_2^{Mes}$ZnCO$_2$CH$_3^+$][BPh$_4^-$] (**12**):*



Complex **12** was prepared similarly to **10a**, by reaction of **8b** (200 mg, 0.178 mmol) and MeZnOAc (25 mg, 0.179 mmol). After combining the reagents in bromobenzene (1 mL), the resulting cloudy solution promptly clarified to give a yellow solution. After standing for 15 minutes at ambient temperature the product crystallized. The mother liquor was decanted, the white crystalline material was washed with benzene and pentane, and after drying under vacuum for 24 hours, **12** was isolated in 99% yield (220 mg, 0.176 mmol). ^{1}H NMR (C_6D_5Br): δ 7.83 (br s, 8H, *o*-BPh$_4$), 7.68 (d, 2H, $^{3}J_{HH}$ = 7.9 Hz, 1,9-dbf), 7.27–7.09 (m, 12H, *o*-Ph + *p*-Ph, partially obscured by solvent signal), 7.05 (t, 8H, $^{3}J_{HH}$ = 7.3 Hz, *m*-BPh$_4$), 7.01–6.93 (m, 10H, *m*-Ph + 2,8-dbf, partially obscured by solvent signal), 6.93–6.84 (m, 4H, *p*-BPh$_4$, partially obscured by solvent), 6.71 (dd, 2H, $^{3}J_{PH}$ = 12.2 Hz, $^{3}J_{HH}$ = 7.9 Hz, 3,7-dbf), 6.41 (s, 4H, *m*-Mes), 1.97 (d, 6H, $^{4}J_{HH}$ = 2.0 Hz, *p*-C*H*$_3$ Mes), 1.80 (s, 3H, CO$_2$C*H*$_3$), 1.40 (s, 12H, *o*-C*H*$_3$ Mes). $^{31}P\{^{1}H\}$ NMR (C_6D_5Br): δ 28.3 (s). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): δ –5.6 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br): δ 185.02 (s, *C*O$_2$CH$_3$), 164.80 (q, $^{1}J_{CB}$ = 49.2 Hz, *ipso*-BPh$_4$), 138.46 (d, J_{CP} = 8.0 Hz, Aromatic C), 136.89 (q, $^{2}J_{CB}$ = 1.3 Hz, *o*-BPh$_4$), 136.42 (d, J_{CP} = 5.7 Hz, Aromatic C),

134.66 (d, J_{CP} = 3.8 Hz, Aromatic C), 134.26 (s, *p*-Ph), 133.41 (d, $^{3}J_{CP}$ = 10.3 Hz, *m*-Ph), 132.38 (d, $^{2}J_{CP}$ = 10.4 Hz, 3,7-dbf), 131.45 (d, obscured by solvent, *o*-Ph), 130.04 (s, *m*-Mes), 129.44 (d, $^{3}J_{CP}$ = 12.9 Hz, *m*-Ph), 128.27 (s, 1,9-dbf), 125.86 (q, $^{3}J_{CB}$ = 2.7 Hz, *m*-BPh_4), 121.93 (s, *p*-BPh_4), 113.76 (d, $^{1}J_{CP}$ = 92.6 Hz, 4,6-dbf), 21.20 (s, CO_2CH_3), 20.80 (s, *p*-CH_3 Mes), 18.59 (s, *o*-CH_3 Mes). Signals for three quaternary carbons were not observed. Anal. Calcd. (%) for $C_{80}H_{71}BN_2O_3P_2Zn{\cdot}2C_6H_6$: C: 78.77; H: 5.96; N: 2.00; found: C: 78.58; H: 5.94; N: 2.11.

*Synthesis of [**L**$_2^{Mes}$ZnOCHMeCO$_2$Me$^+$][B(C$_6$F$_5$)$_4^-$] (**13**):*

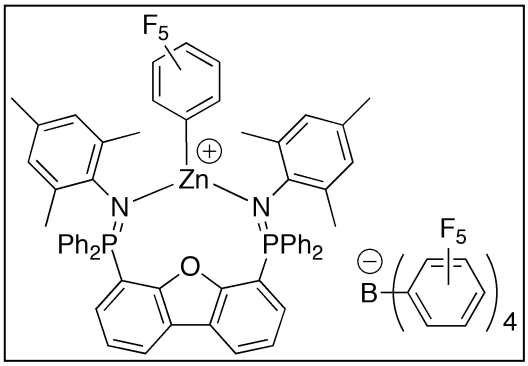


Complex **13** was prepared by reaction of **8a** (200 mg, 0.135 mmol) with a slight excess of EtZnOCHMeCO$_2$Me (29.3 mg, 0.148 mmol). The reagents were combined with bromobenzene (2 mL) in a Teflon sealed vial and heated to 80 °C for 2 hours with stirring. After cooling to ambient temperature, the product was precipitated as a red/orange oil by addition of pentane (5 mL). The supernatant was decanted, the material washed with a 1:1 mixture of benzene and pentane (3 x 2 mL) and then dried *in vacuo*, giving a pale red/orange powder in 62% yield (139 mg, 0.0842 mmol). The material was found to be contaminated with approximately 15% [**L**$_2^{Mes}$ZnEt][B(C$_6$F$_5$)$_4$] by integration of $^{31}P\{^{1}H\}$ NMR resonances. Due to the mixture of compounds, ^{13}C spectra were very complicated and are not reported. ^{1}H NMR (C_6D_5Br, 50 °C): δ 7.94 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.40–7.10 (ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.10–6.95 (ov m, 8H, *m*-

Ph obscured by solvent), 6.85 (dd, $^{3}J_{PH}$ = 11.7 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3,7-dbf), 6.39 (s, 4H, *o*-C*H*$_3$ Mes), 4.28 (q, 1H, $^{3}J_{HH}$ = 6.7 Hz, OC*H*MeCO$_2$Me), 2.78 (s, 3H, OCHMeCO$_2$*Me*), 1.97 (d, 6H, $^{4}J_{HH}$ = 2.0 Hz, *p*-C*H*$_3$ Mes), 1.74 (s, 6H, *o*-C*H*$_3$ Mes), 1.70 (s, 6H, *o*-C*H*$_3$ Mes), 1.29 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, OCH*Me*CO$_2$Me). ^{31}P{^{1}H} NMR (C_6D_5Br, 50 °C): δ 25.0 (s), 22.8 (s, LZnEt by-product). ^{19}F{^{1}H} NMR ($CDCl_3$, 50 °C): δ –132.4 (br s, 8F, *o*-C_6F_5), –163.7 (br t, 4F, *p*-C_6F_5), –167.2 (t, 8F, *m*-C_6F_5). ^{11}B{^{1}H} NMR ($CDCl_3$, 50 °C): δ –16.5 (br s).

*Synthesis of [**L**$_2^{Mes}$ZnC$_6$F$_5^+$][B(C$_6$F$_5$)$_4^-$] (**14**):*

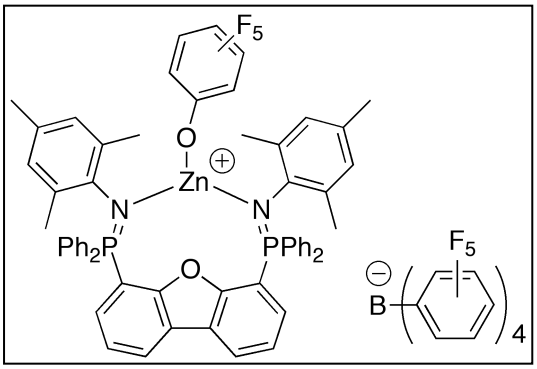
In a glass vial, **8a** (100 mg, 0.0674 mmol), EtZnOPh (12.4 mg, 0.0672 mmol), and $B(C_6F_5)_3$ (34.5 mg, 0.0674 mmol) were combined. These were dissolved in 1 mL of bromobenzene, and the resulting solution was heated to 100 °C for 90 minutes. After cooling to ambient temperature, a red/orange oil was precipitated from solution by addition of 4 mL of pentane. The supernatant was decanted, and the oil was washed with a 1:1 mixture of benzene and pentane (3 x 1 mL) and dried *in vacuo*, affording **14** as a light yellow powder in 89.6% yield (103.2 mg, 0.0602 mmol). ^{1}H NMR ($CDCl_3$): δ 8.26 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.55 (t, 4H, $^{3}J_{HH}$ = 7.6 Hz, *p*-Ph), 7.42 (td, 2H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 2.6 Hz, 2,8-dbf), 7.26 (td, 8H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 3.5 Hz, *m*-Ph), 7.08 (dd, 8H, $^{3}J_{PH}$ = 12.5 Hz, $^{3}J_{HH}$ = 7.6 Hz, *o*-Ph), 6.90 (dd, 2H, $^{3}J_{PH}$ = 12.1 Hz, $^{3}J_{HH}$ = 7.7 Hz, 3,7-dbf), 6.32 (s, 4H, *m*-Mes), 2.04 (d, 6H, $^{4}J_{HH}$ = 2.3 Hz, *o*-C*H*$_3$ Mes), 1.05 (s, 12H, *p*-C*H*$_3$ Mes). ^{31}P{^{1}H} NMR



($CDCl_3$): δ 26.6 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ –114.5 (m, 2F, *o*-ZnC_6F_5), –132.6 (br d, 8F, *o*-$B(C_6F_5)_4$), –155.4 (t, 1F, *p*-ZnC_6F_5), –160.75 (m, 2F, *m*-ZnC_6F_5), –163.2 (t, 4F, $^3J_{FF}$ = 20.6 Hz, *p*-$B(C_6F_5)_4$), –166.8 (br t, 8F, *m*-$B(C_6F_5)_4$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ –16.6 (br s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.83 (s, Aromatic C), 149.99 (br s, BC_6F_5), 146.70 (br s, BC_6F_5), 139.91 (br s, BC_6F_5), 138.10 (br s, BC_6F_5), 136.62 (d, J_{CP} = 8.1 Hz, Aromatic C), 136.52 (d, J_{CP} = 5.7 Hz, Aromatic C), 135.82 (d, J_{CP} = 4.0 Hz, Aromatic C), 134.82 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph), 133.02 (d, $^2J_{CP}$ = 9.7 Hz, *o*-Ph), 132.79 (d, $^2J_{CP}$ = 6.9 Hz, 3,7-dbf), 130.04 (d, $^3J_{CP}$ = 13.0 Hz, *m*-Ph), 129.85 (d, $^4J_{CP}$ = 3.1 Hz, *m*-Mes), 128.02 (d, $^4J_{CP}$ = 2.5 Hz, 1,9-dbf), 124.78 (d, $^3J_{CP}$ = 10.7 Hz, 2,8-dbf), 124.37 (dd, J_{CP} = 6.2 Hz, J_{CP} = 0.7 Hz, Aromatic C), 124.30 (d, $^1J_{CP}$ = 106.1 Hz, *ipso*-Ph), 114.26 (d, $^1J_{CP}$ = 92.9 Hz, 4,6-dbf), 20.82 (d, $^6J_{CP}$ = 1.4 Hz, *p*-CH_3 Mes), 18.81 (d, $^4J_{CP}$ = 1.4 Hz, *o*-CH_3 Mes). Resonances from ZnC_6F_5 are not observed. Anal. Calcd. (%) for $C_{84}H_{48}BF_{25}N_2OP_2Zn$: C: 58.85; H: 2.82; N: 1.63; found: C: 59.00; H: 2.77; N: 1.64.

*Synthesis of [**L**$_2^{Mes}$ZnOC$_6$F$_5^+$][B(C$_6$F$_5$)$_4^-$] (**15**):*

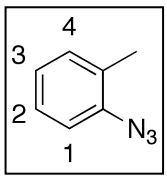
In a glass vial **8a** (100 mg, 0.0674 mmol) and $EtZnOC_6F_5$ (18.7 mg, 0.0674 mmol) were combined. These were dissolved in 1 mL of bromobenzene, and the resulting solution was heated to 50 °C for 1 hour. After cooling to ambient temperature, the product was precipitated as a red/orange oil by addition of pentane (3 mL). The supernatant was decanted and the oil was washed with a 1:1 benzene/pentane mixture (3 x 1 mL) and pentane (3 x



1 mL). The oil was then dried *in vacuo*, giving **15** as a white powder in 87.4% yield (102 mg, 0.0589 mmol). ^{1}H NMR ($CDCl_3$): δ 8.38 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.65 (t, 4H, $^{3}J_{HH}$ = 7.7 Hz, *p*-Ph), 7.54 (td, 2H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{PH}$ = 2.6 Hz, 2,8-dbf), 7.36 (td, 8H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 3.9 Hz, *m*-Ph), 7.27 (dd, 8H, $^{3}J_{PH}$ = 12.1 Hz, $^{3}J_{HH}$ = 7.7 Hz, *o*-Ph), 7.05 (dd, 2H, $^{3}J_{PH}$ = 12.1 Hz, $^{3}J_{HH}$ = 7.8 Hz, 3,7-dbf), 6.41 (s, 4H, *m*-Mes), 2.11 (d, 6H, $^{4}J_{HH}$ = 2.2 Hz, *o*-C*H*$_3$ Mes), 1.39 (s, 12H, *p*-C*H*$_3$ Mes). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.3 (s). ^{19}F{^{1}H} NMR ($CDCl_3$): δ –132.5 (br d, 8F, *o*-B(C_6F_5)$_4$), –163.2 (t, 4F, $^{3}J_{FF}$ = 20.6 Hz, *p*-B(C_6F_5)$_4$), –166.8 (br t, 8F, *m*-B(C_6F_5)$_4$), –167.5 (dd, 2F, $^{3}J_{FF}$ = 20.3 Hz, $^{4}J_{FF}$ = 9.4 Hz, *o*-OC_6F_5), –168.5 (t, 2F, $^{3}J_{FF}$ = 22.3 Hz, *m*-OC_6F_5), –180.5 (tt, 1F, $^{3}J_{FF}$ = 22.6 Hz, $^{4}J_{FF}$ = 9.7 Hz, *p*-OC_6F_5). ^{11}B{^{1}H} NMR ($CDCl_3$): δ –16.6 (br s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.53 (s, Aromatic C), 149.93 (br s, BC_6F_5), 146.75 (br s, BC_6F_5), 139.89 (br s, BC_6F_5), 138.04 (br s, BC_6F_5), 136.92 (d, J_{CP} = 8.2 Hz, Aromatic C), 136.39 (d, J_{CP} = 5.5 Hz), 135.92 (d, J_{CP} = 3.8 Hz), 135.01 (d, $^{4}J_{CP}$ = 2.7 Hz, *p*-Ph), 133.36 (d, $^{2}J_{CP}$ = 10.1 Hz, *o*-Ph), 132.87 (d, $^{2}J_{CP}$ = 6.9 Hz, 3,7-dbf), 130.02 (d, $^{3}J_{CP}$ = 12.8 Hz, *m*-Ph), 129.81 (d, $^{4}J_{CP}$ = 3.3 Hz, *m*-Mes), 128.16 (d, $^{4}J_{CP}$ = 2.9 Hz, 1,9-dbf), 125.25 (d, $^{3}J_{CP}$ = 11.3 Hz, 2,8-dbf), 124.44 (d, J_{CP} = 6.5 Hz, Aromatic C), 123.15 (d, $^{1}J_{CP}$ = 105.9 Hz, *ipso*-Ph), 113.97 (d, $^{1}J_{CP}$ = 94.2 Hz, 4,6-dbf), 20.65 (d, $^{6}J_{CP}$ = 1.4 Hz, *p*-*C*H$_3$ Mes), 19.11 (d, $^{4}J_{CP}$ = 1.3 Hz, *o*-*C*H$_3$ Mes); resonances from OC_6F_5 not observed. Anal. Calcd. (%) for $C_{84}H_{48}BF_{25}N_2O_2P_2Zn$: C: 58.30; H: 2.80; N: 1.62; found: C: 57.65; H: 2.88; N: 1.53.

8.5. Experimental Details of Chapter 4

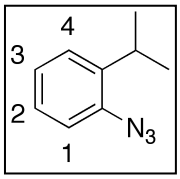
Synthesis of o-Tolyl-azide:



(Warning: Azides are thermally sensitive and a potential explosion hazard. Avoid heating these compounds and store them in a freezer.) In a 500 mL round bottom flask, 80 mL of water and 80 mL of concentrated HCl were stirred together. $NaBF_4$ (26.4 g, 0.240 mol) was dissolved in this mixture and the resulting solution was cooled to –20 °C. While maintaining this temperature, a solution of $NaNO_2$ (8.27 g, 0.120 mol) in 75 mL of water was added dropwise using a dropping funnel, followed by the dropwise addition of *o*-toluidine (12.0 mL, 0.113 mol), over a total period of 1 hour with vigorous stirring. This resulted in the formation of a red/brown mixture with a beige precipitate (the diazonium salt). The precipitate was collected by filtration and washed thoroughly with cold ether (cooled using dry ice), and then transferred to a separate 500 mL flask containing a solution of NaN_3 (23.4 g, 0.260 mol) in 200 mL of water cooled to 0 °C. The solution was stirred for 16 hours and allowed to gradually warm to ambient temperature. The product was then extracted with ether and the solvent was removed using a rotary evaporator, giving the product as a red liquid in 81% yield (12.2 g, 0.0916 mol). Dark impurities were removed by flash chromatography on a silica column using hexanes as the eluent, giving yellow liquid of high purity. ^{1}H NMR ($CDCl_3$): δ 7.22 (t, 1H, $^3J_{HH}$ = 7.5 Hz, 3-*o*-Tol), 7.15 (d, 1H, $^3J_{HH}$ = 7.5 Hz, 4-*o*-Tol), 7.10 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 1-*o*-Tol), 7.03 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 2-*o*-Tol), 2.21 (s, 3H,

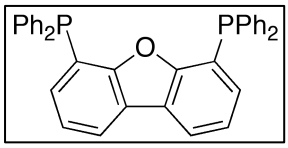
CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.53 (s, 6-*o*-Tol), 131.30 (s, 4-*o*-Tol), 129.74 (s, 5-*o*-Tol), 127.25 (s, 3-*o*-Tol), 124.74 (s, 2-*o*-Tol), 118.05 (s, 1-*o*-Tol), 17.40 (s, CH_3).

Synthesis of 2-^{i}PrPh-azide:



2-*i*PrPh-azide was prepared similarly to *o*-Tolyl-azide using 2-*iso*propylaniline (16.2 g, 0.120 mol) and all other reagents in the same quantities, giving the corresponding azide in 61% yield (11.8 g, 0.0732 mol). ^1H NMR ($CDCl_3$): δ 7.33–7.23 (ov m, 2H, 4-Mipp + 3-Mipp), 7.19–7.11 (ov m, 2H, 1-Mipp + 2-Mipp), 3.26 (sp, 1H, $^3J_{HH}$ = 7.0 Hz, C*H*(CH_3)$_2$), 1.25 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.18 (s, 6-Mipp), 137.33 (s, 5-Mipp), 127.11 (s, 3-Mipp), 126.77 (s, 4-Mipp), 125.12 (s, 2-Mipp), 118.22 (s, 1-Mipp), 28.08 (s, *C*H(CH$_3$)$_2$), 23.04 (s, CH(*C*H$_3$)$_2$).

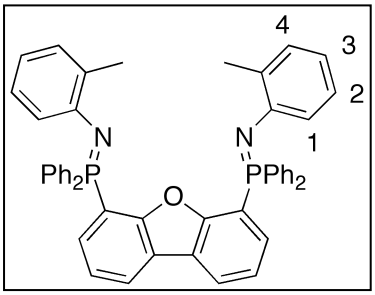
*Synthesis of 4,6-bis(diphenylphosphino)*dibenzofuran*:*



This compound was prepared by a modified literature procedure.[127] Dibenzofuran (3.00 g, 0.0178 mol) was placed in a 250 mL 2-neck round bottom flask attached to a reflux condenser and dissolved in 120 mL of heptane. To this solution TMEDA (5.7 mL, 0.038 mol) was added. The solution was cooled to 0 °C, and then a 1.7 M solution of tert-butyllithium in pentane (22.0 mL, 0.0374 mol) was added dropwise over a 30 minute period, resulting in the formation of a brown precipitate in a red solution. After addition was complete, the solution was allowed to warm to ambient temperature, and was then heated to reflux for one hour. The resulting solution was

then cooled to 0 °C, and 6.9 mL (0.038 mol) of $ClPPh_2$, diluted to a total volume of 20 mL in pentane, was added dropwise over 30 minutes with rapid stirring. The resulting reaction mixture was then allowed to warm to ambient temperature and was left stirring for 19 hours. The round bottom flask was then attached to a swivel-frit apparatus, wherein the pale brown precipitate was collected by filtration, washed with heptane (3 x 10 mL) and dried *in vacuo*, giving 8.60 g of a crude mixture containing the product and Li·TMEDA. Then, in the presence of air, the crude material was dissolved in dry toluene and filtered to remove the insoluble Li·TMEDA adduct. The solvent was then removed using a rotovap apparatus, washed with pentane (3 x 10 mL), and dried *in vacuo*, yielding the compound as a pale yellow powder in 57.3% yield (5.49 g, 0.0102 mol). The spectral data match the literature values.[127]

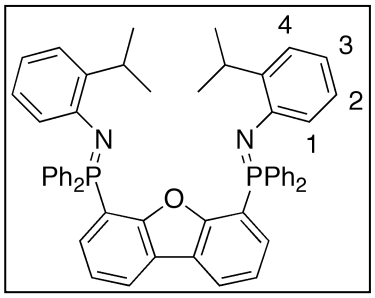
*Synthesis of 4,6-(o-Tol-N=PPh_2)$_2$-dbf (**L_2^{Tol}**):*



4,6-(PPh_2)$_2$-dbf (1.00 g, 1.86 mmol) was placed in a 100 mL 2-neck round bottom flask attached in a swivel-frit apparatus. 40 mL of toluene was added, giving a yellow solution. To this solution *o*-Tolyl-azide (0.52 g, 3.90 mmol) was added. The reaction mixture was heated to 70 °C and stirred for 18 hours. The solution was then filtered to remove trace solid impurities. The solution volume was reduced to 5 mL *in vacuo*, and 30 mL of pentane was added, causing precipitation of the product as a yellow oily material. Vigorously stirring for 1 hour produced a fine yellow precipitate. The

solid was collected by filtration, washed with pentane (3 x 10 mL), and dried *in vacuo*, affording $\mathbf{L_2^{Tol}}$ as a light yellow powder in 80.6% yield (1.12 g, 1.50 mmol). ^{1}H NMR (C_6D_6): δ 8.27 (dd, 2H, $^3J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 7.6 Hz, 3,7-H dbf), 7.64 (dd, 8H, $^3J_{PH}$ = 12.7 Hz, $^3J_{HH}$ = 7.4 Hz, *o*-Ph), 7.49(d, 2H, $^3J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.32(d, 2H, $^3J_{HH}$ = 7.0 Hz, 4-*o*-Tol), 6.95 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 2,8-dbf), 6.92–6.85 (ov m, 6H, *p*-Ph + 2-*o*-Tol), 6.81 (2H, $^3J_{HH}$ = 7.1 Hz, 3-*o*-Tol), 6.74 (td, 8H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.8 Hz, *m*-Ph), 6.58(d, 2H, $^3J_{HH}$ = 7.7 Hz, 1-*o*-Tol), 2.74 (s, 6H, CH_3 *o*-Tol). ^{31}P{^{1}H} NMR (C_6D_6): δ –5.9 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.80 (d, J_{CP} = 2.6 Hz), 150.30 (d, J_{CP} = 1.0 Hz), 135.02 (d, $^2J_{CP}$ = 6.5 Hz, 3,7-dbf), 133.47 (d, J_{CP} = 22.4 Hz), 132.67 (d, $^2J_{CP}$ = 10.2 Hz, *o*-Ph), 131.96 (d, $^1J_{CP}$ = 106.8 Hz, *ipso*-Ph), 131.85 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph), 131.03 (d, $^4J_{CP}$ = 2.0 Hz, 4-*o*-Tol), 129.02 (d, $^3J_{CP}$ = 12.5 Hz, *m*-Ph), 126.83 (s, 2-*o*-Tol), 125.10 (dd, J_{CP} = 6.5 Hz, J_{CP} = 0.9 Hz), 125.00 (d, $^4J_{CP}$ = 2.3 Hz, 1,9-dbf), 124.30 (d, $^3J_{CP}$ = 10.2 Hz, 2,8-dbf), 121.28 (d, $^3J_{CP}$ = 9.7 Hz, 1-*o*-Tol), 118.52 (s, 3-*o*-Tol), 117.52 (d, $^1J_{CP}$ = 87.4 Hz, 4,6-dbf), 20.62 (s). Anal. Calcd. (%) for $C_{50}H_{40}N_2OP_2$: C: 80.41; H: 5.40; N: 3.75; found: C: 80.34; H: 5.31; N: 3.78.

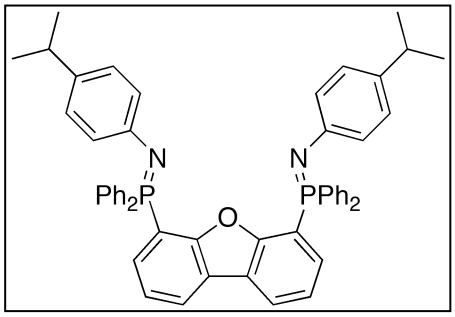
Synthesis of 4,6-(Mipp-N=PPh$_2$)$_2$-dbf ($\mathbf{L_2^{Mipp}}$):



$\mathbf{L_2^{Mipp}}$ was prepared similarly to $\mathbf{L_2^{Tol}}$ using 4,6-(PPh$_2$)$_2$-dbf (1.00, 1.86 mmol) and 2-*i*PrPh-azide (0.75 g, 4.65 mmol), yielding $\mathbf{L_2^{Mipp}}$ as a light yellow powder. Yield: 1.13 g (1.41 mmol), 75.8%. ^{1}H NMR (C_6D_6): δ 8.26 (dd, 2H, $^3J_{PH}$ = 13.6 Hz, $^3J_{HH}$ = 6.4 Hz, 3,7-H dbf), 7.64 (dd, 8H, $^3J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 7.0 Hz, *o*-Ph), 7.49 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-H dbf),

7.37(m, 2H, 4-Mipp), 7.00–6.80(ov m, 10H, *p*-Ph + 2,8-H dbf + 2-Mipp + 3-Mipp), 6.73 (td, 8H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 3.0 Hz, *m*-Ph), 6.63 (m, 2H, 1-Mipp), 4.28 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.52 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ –5.2 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 156.76 (d, *J* = 2.6 Hz), 149.07 (d, *J* = 1.1 Hz), 143.28 (d, $^{2}J_{CP}$ = 21.7 Hz), 135.06 (d, $^{2}J_{CP}$ = 6.6 Hz, 3,7-dbf), 132.66 (d, $^{3}J_{CP}$ = 10.2 Hz, *o*-Ph), 131.94 (d, $^{1}J_{CP}$ = 107.6 Hz, *ipso*-Ph), 131.83 (d, $^{4}J_{CP}$ = 2.9 Hz, *p*-Ph), 129.02 (d, $^{3}J_{CP}$ = 12.6 Hz, *m*-Ph), 126.44 (s, 3-Mipp), 126.18 (d, $^{4}J_{CP}$ = 2.2 Hz, 4-Mipp), 125.14 (dd, J_{CP} = 6.3 Hz, J_{CP} = 0.9 Hz), 125.00 (d, $^{4}J_{CP}$ = 2.5 Hz, 1,9-dbf), 124.35 (d, $^{3}J_{CP}$ = 9.9 Hz, 2,8-dbf), 121.78 (d, $^{3}J_{CP}$ = 10.1 Hz, 1-Mipp), 118.90 (d, $^{4}J_{CP}$ = 0.5 Hz, 2-Mipp), 117.60 (d, $^{1}J_{CP}$ = 85.6 Hz, 4,6-dbf), 29.20 (s, *C*H(CH_3)$_2$), 23.70 (s, CH(*C*H$_3$)$_2$). Anal. Calcd. (%) for $C_{54}H_{48}N_2OP_2$: C: 80.78; H: 6.03; N: 3.49; found: C: 80.48; H: 6.03; N: 3.29.

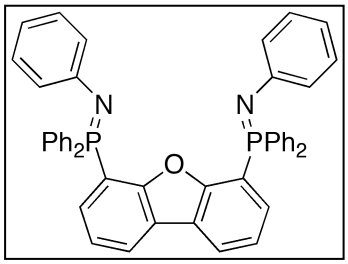
*Synthesis of 4,6-(Pipp-N=PPh$_2$)$_2$-dbf (**L$_2^{Pipp}$**):*



L$_2^{Pipp}$ was prepared similarly to **L$_2^{Tol}$** using 4,6-(PPh$_2$)$_2$-dbf (1.30 g, 2.42 mmol) and 4-*i*PrPh-azide (0.820 g, 5.09 mmol), yielding **L$_2^{Pipp}$** as a light yellow powder. Yield: 1.65 g, 84.6%. ^{1}H NMR (C_6D_6): δ 8.28 (dd, 2H, $^{3}J_{PH}$ = 13.7 Hz, $^{3}J_{HH}$ = 7.6 Hz, 3,7-dbf), 7.70 (dd, 8H, $^{3}J_{PH}$ = 12.7 Hz, $^{3}J_{HH}$ = 7.7 Hz, *o*-Ph), 7.49 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.02 (ov m, 8H, o,*m*-Pipp), 6.97–6.88 (ov m, 6H, 2,8-dbf + *p*-Ph), 6.86–6.77 (td, 8H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 3.0 Hz, *m*-Ph), 2.73 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.16 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ –5.1 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 156.86 (d, J_{CP} = 2.2 Hz), 149.77 (d, J_{CP} =

1.9 Hz), 138.20 (s), 135.02 (d, $^{2}J_{CP}$ = 7.1 Hz, 3,7-dbf), 132.92 (d, $^{2}J_{CP}$ = 10.2 Hz, *o*-Ph), 131.92 (d, $^{1}J_{CP}$ = 104.2 Hz, *ipso*-Ph), 131.79 (d, $^{4}J_{CP}$ = 2.8 Hz, *p*-Ph), 129.04 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-Ph), 127.43 (s, *m*-Pipp), 125.14 (dd, J_{CP} = 5.9 Hz, J_{CP} = 0.9 Hz), 124.90 (d, $^{4}J_{CP}$ = 2.4 Hz, 1,9-dbf), 124.14 (d, $^{3}J_{CP}$ = 10.5 Hz, 2,8-dbf), 124.12 (d, $^{3}J_{CP}$ = 17.7 Hz, *o*-Pipp), 117.20 (d, $^{1}J_{CP}$ = 91.1 Hz, 4,6-dbf), 34.13 (s, *C*H(CH$_3$)$_2$), 24.99 (s, CH(*C*H$_3$)$_2$). Anal. Calcd. (%) for $C_{54}H_{48}N_2OP_2$: C: 80.78; H: 6.03; N: 3.49; found: C: 80.52; H: 6.26; N: 3.29.

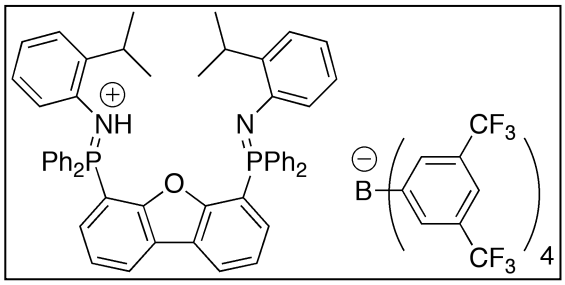
*Synthesis of 4,6-(Ph-N=PPh$_2$)$_2$-dbf (**L$_2^{Ph}$**):*



L$_2^{Ph}$ was prepared similarly to **L$_2^{Tol}$** using 4,6-(PPh$_2$)$_2$-dbf (1.00 g, 1.86 mmol) and phenyl-azide (0.47 g, 3.95 mmol). This reaction is much more facile, and reaction at ambient temperature for a 2 hour period proved sufficient to give complete conversion, affording **L$_2^{Ph}$** as a pale yellow powder in 82.3% yield (1.10 g, 1.53 mmol). ^{1}H NMR (C$_6$D$_6$): δ 8.24 (dd, 2H, $^{3}J_{PH}$ = 13.9 Hz, $^{3}J_{HH}$ = 7.6 Hz, 3,7-dbf), 7.68 (dd, 8H, $^{3}J_{PH}$ = 12.6 Hz, $^{3}J_{HH}$ = 7.6 Hz, *o*-Ph), 7.48 (d, 2H, $^{3}J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.18–7.04 (ov m, 8H, o+*m*-NPh), 6.98–6.88 (ov m, 6H, *p*-Ph + 2,8-dbf), 6.87–6.75 (ov m, 10H, *m*-Ph + *p*-NPh). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ –4.2 (s) ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 156.86 (d, J_{CP} = 2.2 Hz), 152.08 (d, J_{CP} = 1.9 Hz), 134.92 (d, $^{2}J_{CP}$ = 7.1 Hz, 3,7-dbf), 132.92 (d, $^{2}J_{CP}$ = 10.2 Hz, *o*-Ph), 131.87 (d, $^{4}J_{CP}$ = 3.0 Hz, *p*-Ph), 131.67 (d, $^{1}J_{CP}$ = 103.7 Hz, *ipso*-Ph), 129.54 (d, $^{4}J_{CP}$ = 1.2 Hz, *m*-NPh), 129.06 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-Ph), 125.14 (dd, J_{CP} = 6.4 Hz, J_{CP} = 0.9 Hz), 124.96 (d, $^{4}J_{CP}$ = 2.5 Hz, 1,9-dbf), 124.42 (d, $^{3}J_{CP}$ = 17.8 Hz, *o*-NPh), 124.14 (d, $^{3}J_{CP}$ = 10.4 Hz, 2,8-dbf), 118.42 (d,

$^5J_{CP}$ = 0.8 Hz, *p*-NPh), 116.96 (d, $^1J_{CP}$ = 93.0 Hz, 4,6-dbf). Anal. Calcd. (%) for $C_{48}H_{36}N_2OP_2$: C: 80.21; H: 5.05; N: 3.90; found: C: 80.23; H: 5.30; N: 3.48.

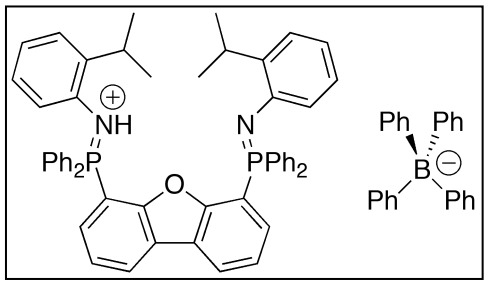
*Synthesis of [**L₂^Mipp**H⁺][B(m-(CF₃)₂-C₆H₃)₄⁻] (**16a**):*



The ligand **L₂^Mipp** (200 mg, 0.249 mmol) and the oxonium acid $[H(OEt_2)_2^+][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4^-]$ (252 mg, 0.249 mmol) were combined in a glass vial. To the vial 2 mL of benzene was added, and the mixture was triturated for several minutes until all material was dissolved, giving a clear red/orange solution. This mixture was allowed to stand for 5 minutes, and then 5 mL of pentane was added to precipitate the product as a red/orange oil. The supernatant was decanted, the oil was washed with pentane (3 x 1 mL) and dried *in vacuo* giving the product as a light yellow powder in 88.4% yield (367 mg, 0.220 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.46 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.74 (br s, 8H, *o*-BAr^F_4), 7.64 (td, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 2.4 Hz, 2,8-dbf), 7.56 (br s, 4H, *p*-BAr^F_4), 7.50 (tt, 4H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 3.1 Hz, *p*-Ph), 7.39 (dd, 2H, $^3J_{PH}$ = 11.6 Hz, $^3J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.36–7.21 (ov m, 16H, *o*-Ph + *m*-Ph), 7.08 (d, 2H, $^3J_{HH}$ = 7.6 Hz, 4-Mipp), 6.88 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 3-Mipp), 6.42 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 2-Mipp), 6.16 (d, 2H, $^3J_{HH}$ = 7.6 Hz, 1-Mipp), 3.19 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 0.94 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 15.8 (br s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –61.9 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.32 (q, $^1J_{CB}$ = 49.9 Hz, *ipso*-BAr^F_4), 158.15 (d, J_{CP} = 1.8 Hz, Aromatic C), 145.88 (d, J_{CP} = 10.6 Hz, Aromatic C), 135.36 (br s, *o*-BAr^F_4),

134.93 (br s, *p*-Ph), 133.83 (d, $^{2}J_{CP}$ = 6.6 Hz, 3,7-dbf), 133.10 (d, $^{2}J_{CP}$ = 10.4 Hz, *o*-Ph), 129.89 (d, $^{3}J_{CP}$ = 13.2 Hz, *m*-Ph), 129.43 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{3}J_{CB}$ = 2.9 Hz, *m*-BAr^{F}_{4}), 128.86 (s, Aromatic C), 128.37 (s, 1,9-dbf), 127.05 (d, $^{4}J_{CP}$ = 2.0 Hz, 2-Mipp), 126.80 (s, 4-Mipp), 125.62 (d, $^{3}J_{CP}$ = 5.8 Hz, 1-Mipp), 125.55 (d, $^{3}J_{CP}$ = 9.8 Hz, 2,8-dbf), 125.33 (br s, 3-Mipp), 125.14 (q, $^{1}J_{CF}$ = 272.4 Hz, *C*F_3), 125.01 (d, J_{CP} = 7.0 Hz, Aromatic C), 123.14 (br d, $^{1}J_{CP}$ = 110.5 Hz, *ipso*-Ph), 118.05 (sp, $^{3}J_{CF}$ = 3.9 Hz, *p*-BAr^{F}_{4}), 112.75 (br d, $^{1}J_{CP}$ = 74.1 Hz, 4,6-dbf), 28.41 (s, *C*H$(CH_3)_2$), 23.12 (s, CH(*C*$H_3)_2$). Anal. Calcd. (%) for $C_{78}H_{49}BF_{20}N_2OP_2$: C: 61.96; H: 3.69; N: 1.68; found: C: 62.00; H: 3.58; N: 1.83.

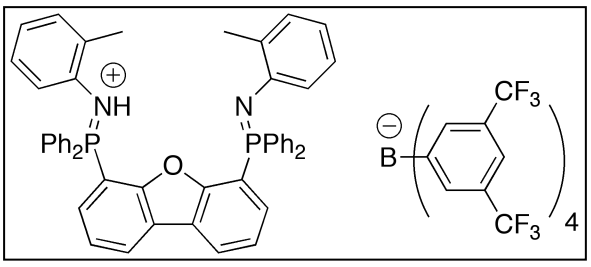
*Synthesis of [**$L_2^{Mipp}H^+$**][BPh_4^-] (**16b**):*



This was prepared similarly to **8b** from **L_2^{Mipp}** (0.50 g, 0.62 mmol), 1M HCl (0.62 mL, 0.62 mmol), and $NaBPh_4$ (234 mL, 0.68 mmol). A white powder was obtained in 63% yield (0.44 g, 0.39 mmol). ^{1}H NMR (acetone-d_6): δ 8.72 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 8.00 (dd, 2H, $^{3}J_{PH}$ = 13.6 Hz, $^{3}J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.78 (t, 2H, $^{3}J_{HH}$ = 7.7 Hz, 2,8-dbf), 7.60–7.46 (ov m, 14H, *o*-Ph + *p*-Ph), 7.40–7.25 (ov m, 16H, *o*-BPh_4 + *m*-Ph), 7.14 (d, 2H, $^{3}J_{HH}$ = 7.5 Hz, 4-Mipp), 6.91 (t, 8H, $^{3}J_{HH}$ = 7.4 Hz, *m*-BPh_4), 6.85 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, 3-Mipp), 6.76 (t, 4H, $^{3}J_{HH}$ = 7.2 Hz, *p*-BPh_4), 6.63 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, 2-Mipp), 6.48 (d, 2H, $^{3}J_{HH}$ = 7.9 Hz, 1-Mipp), 3.19 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$(CH_3)_2$), 0.94 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3)_2$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 13.7 (br s). ^{11}B{^{1}H} NMR (acetone-d_6): δ –6.5 (s). ^{13}C{^{1}H} NMR (acetone-d_6): δ 165.00

(q, $^{1}J_{CB}$ = 49.4 Hz, *ipso*-BPh_4), 157.70 (d, J_{CP} = 2.8 Hz), 145.24 (d, J_{CP} = 11.7 Hz), 137.10 (q, $^{2}J_{CB}$ = 1.4 Hz, *o*-BPh_4), 135.06 (d, $^{2}J_{CP}$ = 6.8 Hz, 3,7-dbf), 134.80 (br s, *p*-Ph), 133.65 (d, $^{2}J_{CP}$ = 10.8 Hz, *o*-Ph), 130.29 (d, $^{3}J_{CP}$ = 13.1 Hz, *m*-Ph), 128.88 (br s, 1,9-dbf), 126.94 (d, $^{4}J_{CP}$ = 1.3 Hz, 2-Mipp), 126.85 (br s, 4-Mipp), 126.20 (br s, 2,8-dbf), 126.07 (q, $^{3}J_{CB}$ = 2.8 Hz, *m*-BPh_4), 125.84 (dd, J_{CP} = 6.8 Hz, J_{CP} = 1.1 Hz), 125.25 (br s, 1-Mipp), 124.24 (br s, 3-Mipp), 122.30 (s, *p*-BPh_4), 28.61 (s, *C*H(CH_3)$_2$), 23.41 (s, CH(*C*H_3)$_2$); 3 quaternary carbons not observed. Anal. Calcd. (%) for $C_{78}H_{69}BN_2OP_2$: C: 83.41; H: 6.19; N: 2.49; found: C: 82.91; H: 6.07; N: 2.47.

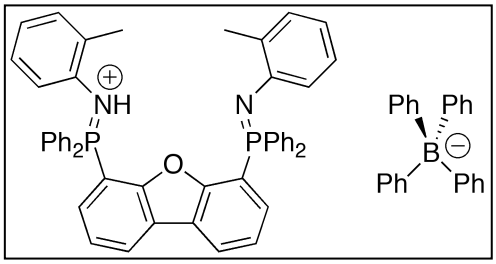
*Synthesis of [**L₂^Tol**H⁺][B(m-(CF₃)₂-C₆H₃)₄⁻] (**17a**):*



17a was prepared similarly to **16a** from $\mathbf{L_2^{Tol}}$ (200 mg, 0.268 mmol) and the oxonium acid [H(OEt_2)$_2^+$] [B(*m*-(CF_3)$_2$-C_6H_3)$_4^-$] (271 mg, 268 mmol), yielding **17a** as a light yellow powder in 90.7% yield (392 mg, 0.243 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.42 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.74 (s, 8H, *m*-BAr^F_4), 7.66–7.50 (ov m, 10H, 2,8-dbf + *p*-Ph + *p*-BAr^F_4), 7.48–7.28 (ov m, 18H, *o*-Ph + *m*-Ph + 3,7-dbf), 6.88 (d, 2H, $^{3}J_{HH}$ = 7.4 Hz, 4-*o*-Tol), 6.71 (t, 2H, $^{3}J_{HH}$ = 7.4 Hz, 3-*o*-Tol), 6.57 (t, 2H, $^{3}J_{HH}$ = 7.6 Hz, 2-*o*-Tol), 6.32 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1-*o*-Tol), 6.22 (s, 1H, N*H*), 1.84 (s, 6H, CH_3 *o*-Tol). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 14.3 (br s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –61.9 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.31 (q, $^{1}J_{CB}$ = 50.0 Hz, *ipso*-BAr^F_4), 158.10 (d, J_{CP} = 1.6 Hz, Aromatic C), 141.22 (d, J_{CP} = 3.5 Hz, Aromatic C), 135.61 (d, J_{CP} = 12.6 Hz, Aromatic C), 135.35 (br s, *o*-BAr^F_4), 134.53 (d, $^{4}J_{CP}$ = 3.0

Hz, *p*-Ph), 133.19 (d, $^{2}J_{CP}$ = 10.4 Hz, *o*-Ph), 133.17 (d, $^{3}J_{CP}$ = 7.0 Hz, 3,7-dbf), 131.22 (s, 4-*o*-Tol), 129.94 (d, $^{3}J_{CP}$ = 13.1 Hz, *m*-Ph), 129.42 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{3}J_{CB}$ = 2.9 Hz, *m*-$BAr^{F}{}_{4}$), 127.86 (d, $^{4}J_{CP}$ = 2.5 Hz, 1,9-dbf), 127.12 (d, $^{4}J_{CP}$ = 1.7 Hz, 2-*o*-Tol), 125.35 (d, $^{3}J_{CP}$ = 6.2 Hz, 2,8-dbf), 125.24 (d, $^{3}J_{CP}$ = 2.2 Hz, 1-*o*-Tol), 125.14 (q, $^{1}J_{CF}$ = 272.4 Hz, CF_3), 124.96 (dd, J_{CP} = 6.0 Hz, J_{CP} = 0.9 Hz, Aromatic C), 124.46 (d, $^{1}J_{CP}$ = 110.5 Hz, *ipso*-Ph), 124.10 (d, $^{5}J_{CP}$ = 1.9 Hz, 3-*o*-Tol), 118.04 (sp, $^{3}J_{CF}$ = 4.2 Hz, *p*-$BAr^{F}{}_{4}$), 112.94 (d, $^{1}J_{CP}$ = 86.7 Hz, 4,6-dbf), 18.87 (s, *o*-Tol CH_3). Anal. Calcd. (%) for $C_{82}H_{53}BF_{24}N_2OP_2$: C: 61.13; H: 3.32; N: 1.74; found: C: 61.03; H: 3.02; N: 1.85.

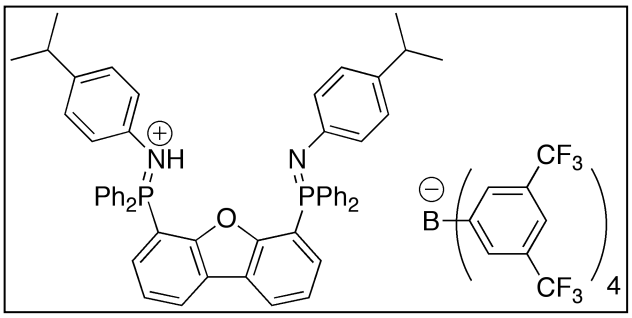
*Synthesis of [**L₂^Tol**H⁺][BPh₄⁻] (**17b**):*



17b was prepared similarly to **8b** from **L₂^Tol** (0.500 g, 0.670 mmol), 1M HCl (0.67 mL, 0.67 mmol), and $NaBPh_4$ (0.25 g, 0.73 mmol), yielding **L₂^Tol** as a white powder in 70.4% yield (0.504 g, 0.472 mmol). ^{1}H NMR (acetone-d_6): δ 8.70 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.90 (dd, 2H, $^{3}J_{PH}$ = 14.2 Hz, $^{3}J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.72 (td, 2H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 1.8 Hz, 2,8-dbf), 7.64–7.49 (ov m, 12H, *o*-Ph + *p*-Ph), 7.39–7.28 (ov m, 16H, *o*-BPh_4 + *m*-Ph), 7.02 (d, 2H, $^{3}J_{HH}$ = 7.3 Hz, 4-*o*-Tol), 6.91 (t, 8H, $^{3}J_{HH}$ = 7.3 Hz, *m*-BPh_4), 6.81–6.72 (ov m, 6H, *p*-BPh_4 + 3-*o*-Tol), 6.67 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, 2-*o*-Tol), 6.42 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1-*o*-Tol), 2.14 (s, 6H, CH_3 *o*-Tol). ^{31}P{^{1}H} NMR (acetone-d_6): δ 12.6 (br s). ^{11}B{^{1}H} NMR (acetone-d_6): δ –6.5 (s). ^{13}C{^{1}H} NMR (acetone-d_6): δ 165.00 (q, $^{1}J_{CB}$ = 49.4 Hz, *ipso*-BPh_4), 157.78 (d, J_{CP} = 2.2 Hz), 142.18 (br s, Aromatic C), 137.10 (q, $^{2}J_{CB}$ = 1.4 Hz, *o*-BPh_4), 135.21 (d, $^{2}J_{CP}$

= 7.6 Hz, 3,7-dbf), 134.60 (d, $^4J_{CP}$ = 2.1 Hz, *p*-Ph), 133.66 (d, $^2J_{CP}$ = 10.8 Hz, *o*-Ph), 131.39 (s, 4-*o*-Tol), 130.18 (d, $^3J_{CP}$ = 13.1 Hz, *m*-Ph), 128.61 (s, 1,9-dbf), 127.19 (d, $^4J_{CP}$ = 1.3 Hz, 2-*o*-Tol), 126.05 (q, $^3J_{CP}$ = 2.8 Hz, *m*-BPh_4), 125.88 (d, $^3J_{CP}$ = 10.6 Hz, 2,8-dbf), 125.80 (dd, J_{CP} = 6.6 Hz, J_{CP} = 1.1 Hz), 124.87 (br s, 1-*o*-Tol), 123.36 (br s, 3-*o*-Tol), 122.30 (s, *p*-BPh_4), 19.31 (s, CH_3 *o*-Tol), 3 quaternary carbons not observed. Anal. Calcd. (%) for $C_{74}H_{61}BN_2OP_2$: C: 83.29; H: 5.76; N: 2.63; found: C: 82.72; H: 6.30; N: 2.41.

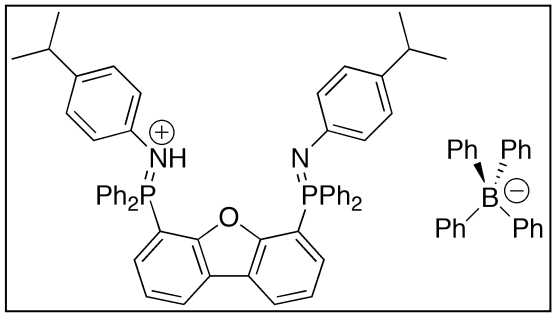
*Synthesis of [**L**$_2^{Pipp}$**H**$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**18a**):*



This was prepared similarly to **16a** from **L$_2^{Pipp}$** (0.500 g, 0.623 mmol) and the oxonium acid [H(OEt$_2$)$_2^+$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4^-$] (0.630 g, 0.622 mmol), affording **18a** as a pale yellow powder in 92% yield (0.955 g, 0.573 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.40 (d, 2H, $^3J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.75 (s, 8H, *o*-Ph Anion), 7.66–7.48 (ov m, 18H, *p*-Ph Anion + *o*-Ph + *p*-Ph + 2,8-dbf), 7.48–7.35 (ov m, 10H, *m*-Ph + 3,7-dbf), 6.82 (ov m, 5H, $^3J_{HH}$ = 8.2 Hz, *m*-Pipp + NH), 6.56 (d, 4H, $^3J_{HH}$ = 8.2 Hz, *o*-Pipp), 2.75 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.15 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 16.2 (br s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –62.8 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.33 (q, $^1J_{CB}$ = 49.7 Hz, *ipso*-BAr_4), 157.62 (s, Aromatic C), 143.74 (s, Aromatic C), 140.91 (s, Aromatic C), 135.37 (br s, *o*-BAr_4),

134.59 (d, $^4J_{CP}$ = 2.7 Hz, *p*-Ph), 133.47 (d, $^2J_{CP}$ = 10.6 Hz, *o*-Ph), 133.18 (d, $^2J_{CP}$ = 7.7 Hz, 3,7-dbf), 129.99 (d, $^3J_{CP}$ = 13.1 Hz, *m*-Ph), 129.44(qq, $^2J_{CF}$ = 31.5 Hz, $^3J_{CB}$ = 2.9 Hz, *m*-BAr_4), 127.78 (d, $^4J_{CP}$ = 1.9 Hz, 1,9-dbf), 127.60 (s, *m*-Pipp), 125.52 (q, $^1J_{CF}$ = 272.4 Hz, Anion CF_3), 125.49 (s, Aromatic C), 125.42 (d, $^3J_{CP}$ = 11.4 Hz, 2,8-dbf), 125.00 (d, $^3J_{CP}$ = 10.8 Hz, *o*-Pipp), 124.56 (d, $^1J_{CP}$ = 70.4 Hz, *ipso*-Ph), 118.05 (m, *p*-BAr_4), 111.98 (d, $^1J_{CP}$ = 95.3 Hz, 4,6-dbf), 33.83 (s, *C*H(CH_3)$_2$), 24.30 (s, CH(*C*H_3)$_2$). Anal. Calcd. (%) for $C_{86}H_{61}BF_{24}N_2OP_2$: C: 61.96; H: 3.69; N: 1.68; found: C: 61.96; H: 3.65; N: 1.69.

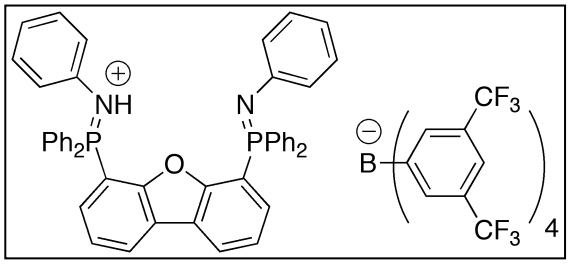
*Synthesis of [**L**$_2^{Pipp}$H$^+$][BPh$_4^-$] (**18b**):*



18b was prepared similarly to **8b** from **L**$_2^{Pipp}$ (0.50 g, 6.2 mmol), 1M HCl (0.62 mL, 6.2 mmol), and $NaBPh_4$ (0.23 g, 0.67 mmol). A white powder was obtained in 84% yield (0.58 g, 0.52 mmol). ^{1}H NMR (acetone-d_6): δ 8.66 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.86 (dd, 2H, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.78–7.64 (ov m, 10H, *o*-Ph + 2,8-dbf), 7.60 (t, 4H, J_{HH} = 7.6 Hz, *p*-Ph), 7.43 (td, 8H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 3.4 Hz, *m*-Ph), 7.34 (br s, 8H, *o*-BPh_4), 6.97–6.84 (ov m, 12H, *m*-BPh_4 + *m*-Pipp), 6.80–6.70 (ov m, 8H, *p*-BPh_4 + *o*-Pipp), 2.75 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.13 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 14.2 (br s). ^{11}B{^{1}H} NMR (acetone-d_6): δ –6.5 (s). ^{13}C{^{1}H} NMR (acetone-d_6): δ 165.00 (q, $^1J_{CB}$ = 49.4 Hz, *ipso*-BPh_4), 157.54 (d, *J* = 2.2 Hz), 142.34 (s), 142.27 (s), 137.11 (q, $^2J_{CB}$ = 1.4 Hz, *o*-BPh_4), 134.85 (d, $^4J_{CP}$ = 2.8 Hz,

p-Ph), 134.74 (d, $^{2}J_{CP}$ = 8.0 Hz, 3,7-dbf), 133.90 (d, $^{2}J_{CP}$ = 11.0 Hz, *o*-Ph), 130.48 (d, $^{3}J_{CP}$ = 13.2 Hz, *m*-Ph), 128.68 (d, $^{4}J_{CP}$ = 2.8 Hz, 1,9-dbf), 127.71 (s, *m*-Pipp), 126.06 (q, $^{3}J_{CB}$ = 2.8 Hz, *m*-BPh_4), 125.86 (d, $^{3}J_{CP}$ = 11.4 Hz, 2,8-dbf), 125.82 (dd, J_{PH} = 6.8 Hz, J_{CP} = 1.1 Hz), 124.54 (br s), 123.34 (d, $^{3}J_{CP}$ = 11.6 Hz, *o*-Pipp), 122.31 (s, *p*-BPh_4), 111.34 (d, J_{CP} = 4.2 Hz), 34.03 (s, *C*H(CH_3)$_2$), 24.47 (s, CH(*C*H_3)$_2$). Anal. Calcd. (%) for $C_{78}H_{69}BN_2OP_2$: C: 83.41; H: 6.19; N: 2.49; found: C: 82.84; H: 6.12; N: 2.38.

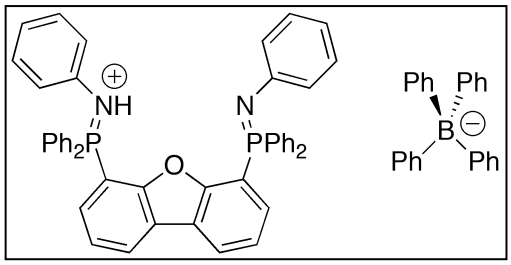
*Synthesis of [**L**$_2^{Ph}$H$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**19a**):*



19a was prepared similarly to **16a** from **L**$_2^{Ph}$ (0.200 g, 0.278 mmol) and the oxonium acid [H(OEt_2)$_2$][B(*m*-(CF$_3$)$_2$-C_6H_3)] (0.281 mg, 0.278 mmol), affording **19a** as a pale yellow powder in 89.2% yield (392 mg, 0.248 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.41 (dt, 2H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.4 Hz), 7.74 (br s, 8H, *o*-BAr^F_4), 7.69–7.58 (ov m, 6H, *p*-Ph + 2,8-dbf), 7.57–7.38 (ov m, 22H, *p*-BAr^F_4 + *o*-Ph + *m*-Ph + 3,7-dbf), 7.02–6.85 (ov m, 6H, *m*- + *p*-N-Ph), 6.65 (d, 4H, $^{3}J_{HH}$ = 8.2 Hz, *o*-N-Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.2 (br s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –62.8 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.34 (q, $^{1}J_{CB}$ = 50.0 Hz, *ipso*-BAr^F_4), 157.54 (d, J_{CP} = 1.4 Hz, Aromatic C), 142.26 (br s, Aromatic C), 135.38 (br s, *o*-BAr^F_4), 135.13 (d, $^{4}J_{CP}$ = 2.8 Hz, *p*-Ph), 133.53 (d, $^{2}J_{CP}$ = 10.9 Hz, *o*-Ph), 133.40 (d, $^{2}J_{CP}$ = 8.7 Hz, 3,7-dbf), 130.27 (d, $^{3}J_{CP}$ = 13.3 Hz, *m*-Ph), 129.89 (s, *m*-N-Ph), 129.46 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{3}J_{CB}$ = 2.9 Hz, *m*-BAr^F_4), 128.34 (d, $^{4}J_{CP}$ = 2.6 Hz, 1,9-dbf), 125.74 (d, $^{3}J_{CP}$ = 11.3 Hz, 2,8-dbf), 125.17 (q, $^{1}J_{CF}$ = 272.4 Hz, CF_3), 125.09 (dd, J_{CP} = 6.4 Hz, J_{CP} = 1.0

Hz, Aromatic C), 124.63 (d, $^3J_{CP}$ = 10.1 Hz, *o*-N-Ph), 123.71 (s, *p*-N-Ph), 123.56 (d, $^1J_{CP}$ = 106.9 Hz, *ipso*-Ph), 118.06 (br sp, $^3J_{CF}$ = 4.0 Hz, *p*-BAr^F_4), 110.87 (d, $^1J_{CP}$ = 96.2 Hz, 4,6-dbf). Anal. Calcd. (%) for $C_{80}H_{49}BF_{24}N_2OP_2$: C: 60.70; H: 3.12; N: 1.77; found: C: 60.54; H: 2.95; N: 1.76.

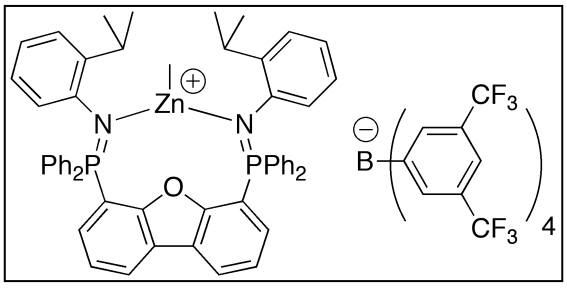
*Synthesis of [**L₂^Ph**H⁺][BPh₄⁻] (**19b**):*



19b was prepared similarly to **8b** from **L₂^Ph** (0.50 g, 0.70 mmol), 1M HCl (0.70 mL, 0.70 mmol), and $NaBPh_4$ (0.24 g, 0.70 mmol), giving **19b** as a white powder in 76% yield (0.55 g, 0.53 mmol). ^{1}H NMR (acetone-d_6): δ 8.67 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.90 (dd, 2H, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.7 Hz, 3,7-dbf), 7.78–7.64 (ov m, 10H, *o*-Ph + 2,8-dbf), 7.59 (t, 4H, $^3J_{HH}$ = 7.1 Hz, *p*-Ph), 7.44 (td, 8H, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 3.5 Hz, *m*-Ph), 7.35 (m, 8H, *o*-BPh_4), 7.02 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-NPh), 6.91 (t, 8H, $^3J_{HH}$ = 7.3 Hz, *m*-BPh_4), 6.82 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-NPh), 6.80–6.70 (ov m, 8H, *p*-BPh_4 + *o*-NPh). ^{31}P{^{1}H} NMR (acetone-d_6): δ 14.5 (br s). ^{11}B{^{1}H} NMR (acetone-d_6): δ –6.5 (s). ^{13}C{^{1}H} NMR (acetone-d_6): δ 165.00 (q, $^1J_{CB}$ = 49.4 Hz), 157.50 (d, J_{CP} = 2.4 Hz), 144.77 (s), 137.10 (q, J_{CB} = 1.4 Hz, *o*-BPh_4), 134.91 (d, J_{CP} = 3.0 Hz, *p*-Ph), 134.76(d, J_{CP} = 7.8 Hz, 3,7-dbf), 133.86 (d, $^2J_{CP}$ = 11.0 Hz, *o*-Ph), 130.50 (d, $^3J_{CP}$ = 13.2 Hz, *m*-Ph), 129.90 (d, $^4J_{CP}$ = 0.5 Hz, *m*-NPh), 128.76 (d, $^4J_{CP}$ = 2.6 Hz, 1,9-dbf), 126.06 (q, $^3J_{CB}$ = 2.8 Hz, *m*-BPh_4), 125.89 (s, 2,8-dbf), 125.79 (dd, J_{CP} = 6.8 Hz, J_{CP} = 1.1 Hz), 125.06 (d, $^1J_{CP}$ = 105.6 Hz, *ipso*-Ph), 123.39 (d, $^3J_{CP}$ = 11.7 Hz, *o*-NPh), 122.31 (s, *p*-BPh_4), 122.06

(s), 111.22 (d, $^{1}J_{CP}$ = 97.8 Hz, 4,6-dbf). Anal. Calcd. (%) for $C_{72}H_{57}BN_2OP_2$: C: 83.23; H: 5.53; N: 2.70; found: C: 82.69; H: 5.50; N: 2.54.

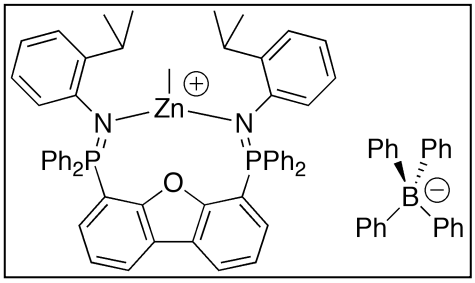
*Synthesis of [**L₂^Mipp**ZnCH₃⁺][B(m-(CF₃)₂-C₆H₃)₄⁻] (**20a**):*



In a 20 mL vial, 200 mg (0.120 mmol) of **16a** was dissolved in 1 mL of CH_2Cl_2. To this yellow solution an excess of $ZnMe_2$ was added as a 1.2 M solution in toluene (150 μL, 0.180 mmol). The resulting reaction mixture was allowed to stand at ambient temperature for 90 minutes. The solvent was then removed *in vacuo*, giving the crude product as a red/orange oil. The oil was washed with pentane (3 x 1 mL) and dried *in vacuo*, affording **20a** as a light yellow powder in 96.7% yield (202 mg, 0.116 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.51 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.74 (br s, 8H, *o*-BAr^{F}_4), 7.64 (t, 2H, $^{3}J_{HH}$ = 7.6 Hz, *p*-Ph), 7.60–7.43 (ov m, 12H, 2,8-dbf + *p*-BAr^{F}_4 + *p*-Ph + *o*-Ph), 7.38 (td, 4H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 3.5 Hz, *m*-Ph), 7.27 (td, 4H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 3.5 Hz, *m*-Ph), 6.99 (dd, 2H, $^{3}J_{PH}$ = 11.8 Hz, $^{3}J_{HH}$ = 7.5 Hz, 3,7-dbf), 6.92–6.75 (ov m, 8H, *o*-Ph + 3-Mipp + 4-Mipp), 6.43 (t, 2H, $^{3}J_{HH}$ = 7.9 Hz, 2-Mipp), 6.30 (d, 2H, $^{3}J_{HH}$ = 7.9 Hz, 1-Mipp), 3.23 (sp, 2H, $^{3}J_{HH}$ = 6.7 Hz, C*H*$(CH_3)_2$), 0.84 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, CH(C*H*$_3)_2$), 0.36 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, CH(C*H*$_3)_2$), –0.88 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.7 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –61.9 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.31 (q, $^{1}J_{CB}$ = 49.9 Hz, *ipso*-BAr^{F}_4), 158.43 (s, Aromatic C), 146.00 (d, J_{CP} = 9.2 Hz, Aromatic C), 140.99 (d, J_{CP} = 7.8 Hz, Aromatic C), 135.34 (br s, *o*-BAr^{F}_4), 135.03 (d, $^{4}J_{CP}$ = 2.8 Hz, *p*-Ph),

134.35 (d, $^{2}J_{CP}$ = 10.7 Hz, *o*-Ph), 134.19 (d, $^{2}J_{CP}$ = 4.8 Hz, 3,7-dbf), 134.13 (s, *p*-Ph), 133.65 (d, $^{2}J_{CP}$ = 9.1 Hz, *o*-Ph), 130.12 (d, $^{3}J_{CP}$ = 13.2 Hz, *m*-Ph), 129.42 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{3}J_{CB}$ = 2.9 Hz, *m*-BAr^{F}_{4}), 129.42 (d, $^{3}J_{CP}$ = 12.3 Hz, *m*-Ph), 128.06 (d, $^{4}J_{CP}$ = 2.4 Hz, 1,9-dbf), 127.57 (d, $^{3}J_{CP}$ = 6.0 Hz, 1-Mipp), 127.27 (d, $^{5}J_{CP}$ = 2.6 Hz, 3-Mipp), 126.79 (d, $^{4}J_{CP}$ = 3.2 Hz, 2-Mipp), 125.63 (d, $^{3}J_{CP}$ = 10.4 Hz, 2,8-dbf), 125.46 (d, $^{4}J_{CP}$ = 3.4 Hz, 4-Mipp), 125.13 (q, $^{1}J_{CF}$ = 272.5 Hz, CF_3), 124.64 (d, J_{CP} = 6.0 Hz, Aromatic C), 124.39 (d, $^{1}J_{CP}$ = 97.1 Hz, *ipso*-Ph), 123.74 (d, $^{1}J_{CP}$ = 117.6 Hz, *ipso*-Ph), 118.04 (br sp, $^{3}J_{CF}$ = 4.2 Hz, *p*-BAr^{F}_{4}), 114.15 (d, $^{1}J_{CP}$ = 90.3 Hz, 4,6-dbf), 27.90 (s, $CH(CH_3)_2$), 24.63 (s, $CH(CH_3)_2$), 23.19 (s, $CH(CH_3)_2$), –3.48 ($ZnCH_3$). Anal. Calcd. (%) for $C_{87}H_{63}BF_{24}N_2OP_2Zn{\cdot}0.5CH_2Cl_2$: C: 58.74; H: 3.61; N: 1.57; found: C: 58.73; H: 3.32; N: 1.63.

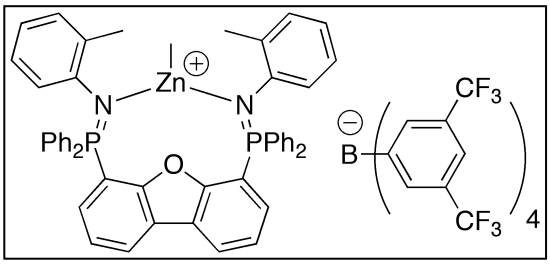
*Synthesis of [**L**$_2^{Mipp}$ZnCH$_3^+$][BPh$_4^-$] (**20b**):*



20b was prepared similarly to **10b** from **16b** (200 mg, 0.178 mmol) and dimethylzinc (1.2 M in toluene, 165 µL, 0.198 mmol), giving **20b** in quantitative yield (214 mg, 0.178 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.51 (d, 2H, $^{3}J_{HH}$ = 7.9 Hz, 1,9-dbf), 7.70–7.42 (ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.40–7.23 (ov m, 18H, *o*-BPh_4 + *m*-Ph + 3,7-dbf), 7.01 (t, 8H, $^{3}J_{HH}$ = 7.4 Hz, *m*-BPh_4), 6.91–6.75 (ov m, 8H, *p*-BPh_4 + 3-Mipp + 4-Mipp), 6.42 (t, 2H, $^{3}J_{HH}$ = 7.7 Hz, 2-Mipp), 6.29 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, 1-Mipp), 3.22 (sp, 2H, $^{3}J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.84 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.36 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), –0.90 (s, 3H, $ZnCH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.7 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6

(s). Material crystallized from CH_2Cl_2 was used for elemental analysis, and results were consistent with the presence of 0.5 equivalents of CH_2Cl_2. Anal. Calcd. (%) for $C_{79}H_{71}BN_2OP_2Zn{\cdot}0.5CH_2Cl_2$: C: 76.69; H: 5.83; N: 2.25; found: C: 76.54; H: 5.66; N: 2.36.

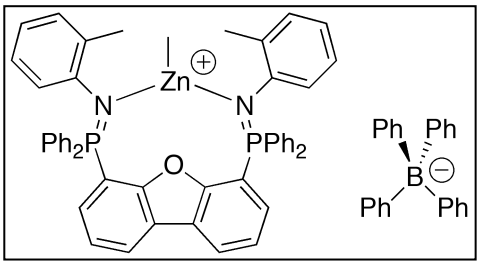
*Synthesis of [**L**$_2^{Tol}$ZnCH$_3^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**21a**):*



21a was prepared similarly to **20a** from **17a** (200 mg, 0.124 mmol) and dimethylzinc (150 µL of a 1.2 M solution in toluene, 180 mmol). After addition of $ZnMe_2$, the solution was triturated briefly and allowed to stand at ambient temperature for 2 hours. The majority of the solvent was removed *in vacuo* giving a red/orange oil. Addition of 1 mL of pentane to this resulted in crystallization of the product. The pale yellow crystals were washed with pentane (3 x 1 mL) and dried *in vacuo*, affording **21a** in 96.8% yield (203 mg, 0.120 mmol). ^{1}H NMR (C_6D_5Br, 0 °C): δ 8.27 (s, 8H, *o*-BAr$^F{}_4$), 7.88 (d, 1H, $^3J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.83 (d, 1H, $^3J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.52 (s, 4H, *p*-BAr$^F{}_4$), 7.42 (dd, 2H, $^3J_{PH}$ = 12.4 Hz, $^3J_{HH}$ = 7.8 Hz, *p*-Ph), 7.36–7.24 (ov m, 2H, obscured by solvent, *p*-Ph), 7.24–7.06 (ov m, 6H, *o*-Ph + 2,8-dbf), 7.06–6.65 (ov m, 16H, *m*-Ph + *o*-Ph + 3,7-dbf + 3-Mipp + 4-Mipp), 6.65–6.56 (ov m, 2H, 3-Mipp + 4-Mipp), 6.37 (br s, 1H, 2-Mipp), 6.25–6.11 (ov m, 2H, 2-Mipp + 1-Mipp), 5.86 (d, 1H, $^3J_{HH}$ = 7.8 Hz, 1-Mipp), 1.79 (s, 3H, *o*-Tol CH_3), 1.55 (s, 3H, *o*-Tol CH_3), –0.35 (s, 1.5H, ZnC*H*$_3$), –0.88 (s, 1.5H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Br, 0 °C): δ 24.1 (s), 21.7 (s). ^{19}F{^{1}H} NMR (C_6D_5Br, 25 °C): δ –61.5 (s). ^{11}B{^{1}H} NMR (C_6D_5Br, 25

°C): δ –5.8 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br, 0 °C): δ 162.37 (q, $^{1}J_{CB}$ = 49.8 Hz, *ipso*-BAr^{F}_4), 158.07 (s, Aromatic C), 157.62 (s), 142.82 (d, J_{CP} = 8.0 Hz), 140.86 (d, J_{CP} = 8.0 Hz), 136.39 (d, J_{CP} = 7.5 Hz), 135.26 (s), 135.07 (s, *o*-BAr^{F}_4), 134.36(s), 133.79 (d, J_{CP} = 6.5 Hz), 133.64 (s), 133.41 (d, J_{CP} = 10.3 Hz), 132.75 (d, J_{CP} = 9.6 Hz), 132.69 (d, J_{CP} = 10.1 Hz), 132.28 (d, J_{CP} = 9.6 Hz), 131.36 (s), 130.10 (s), 129.51 (d, J_{CP} = 13.3 Hz), 128.96 (d, J_{CP} = 8.9 Hz), 128.79 (d, J_{CP} = 8.7 Hz), 127.50 (d, J_{CP} = 10.9 Hz), 127.34 (br s), 126.83 (s), 126.32 (d, J_{CP} = 5.9 Hz), 125.80 (d, J_{CP} = 6.5 Hz), 124.96 (d, J_{CP} = 10.7 Hz), 124.76 (q, J_{CF} = 272.93 Hz, CF_3), 124.53 (d, J_{CP} = 10.4 Hz), 117.72 (br s, *p*-BAr^{F}_4), 112.94 (d, $^{1}J_{CP}$ = 79.4 Hz, 4,6-dbf), 111.74 (d, $^{1}J_{CP}$ = 79.4 Hz, 4,6-dbf), 19.31 (s, *o*-Tol *C*H_3), 18.08 (s, *o*-Tol *C*H_3), –3.42 (s, Zn*C*H_3), –6.77 (s, Zn*C*H_3). The resonances of several quaternary carbon atoms (6 total) are obscured by solvent or are too broad to be observed. Anal. Calcd. (%) for $C_{83}H_{55}BF_{24}N_2OP_2Zn$: C: 58.97; H: 3.28; N: 1.66; found: C: 58.93; H: 3.29; N: 1.66.

*Synthesis of [**L₂^Tol**ZnCH₃⁺][BPh₄⁻] (**21b**):*

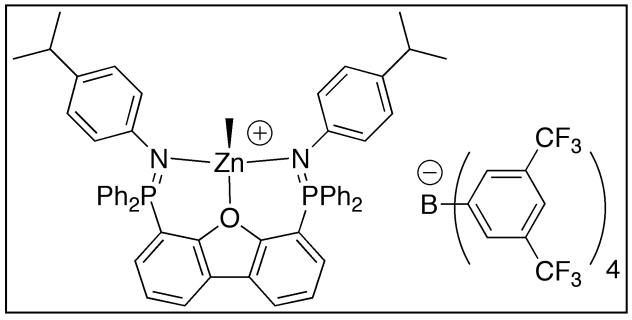


An excess of 1.2 M dimethylzinc in toluene (160 μL, 0.192 mmol) was added to a solution of **17b** (200 mg, 0.185 mmol) in toluene (4 mL). Effervescence of methane was immediately observed. After allowing the mixture to stand at ambient temperature for 60 minutes, the product was precipitated by addition of pentane, giving a yellow oil. The supernatant was decanted, and the product was washed with benzene and pentane and dried *in vacuo*, giving the material as predominantly **21b**, and

approximately 25% [$\mathbf{L_2^{Tol}}$ZnPh$^+$][BPh$_4^-$] (**21c**), with a combined quantitative yield (212 mg, 185 mmol). Single crystals grown from this mixture were found to also contain an approximate 3:1 ratio of these methylzinc and phenylzinc products, respectively. Only the resonances of the primary product (**21b**) are listed below. ^{1}H NMR (CD_2Cl_2): δ 8.49 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 1,9-dbf), 7.70–7.40 (br ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.38–7.22 (br ov m, 16H, *m*-Ph + *o*-BPh$_4$), 7.12 (br s, 2H, 3,7-dbf), 7.00 (t, 8H, $^3J_{HH}$ = 7.5 Hz, *m*-BPh$_4$), 6.85 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-BPh$_4$), 6.77 (br ov m, 4H, 3-*o*-Tol + 4-*o*-Tol), 6.39 (br s, 2H, 2-*o*-Tol), 6.14 (br s, 1H, 1-*o*-Tol), 5.95 (br s, 1H, 1-*o*-Tol), 1.78 (br s, 3H, *o*-Tol CH_3), 1.61 (br s, 3H, *o*-Tol CH_3), –0.60 (br s, 1.5H, ZnCH_3), –0.93 (br s, 1.5H, ZnCH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.2 (br s), 23.9 (br s). ^{11}B{^{1}H} (CD_2Cl_2): –6.6 (s).

*Synthesis of [**L$_2^{Pipp}$**ZnCH$_3^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**22a**):*

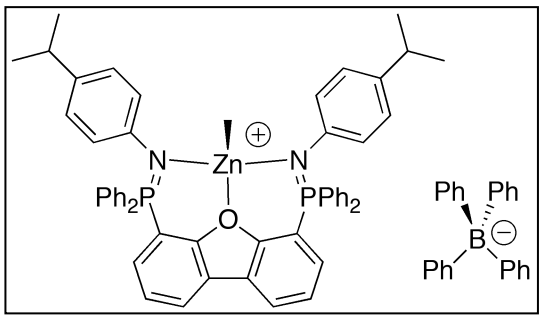
To a solution of **18a** (100 mg, 0.0600 mmol) in benzene (1 mL), dimethylzinc (1.2 M in toluene, 50 µL, 0.0600 mmol) was added. The resulting solution was triturated briefly and then left to stand for 30 minutes at ambient temperature. Pentane was added (~1 mL) to precipitate the product as a red/orange oil. The supernatant was decanted, and the oily product was thoroughly washed with pentane (3 x 1 mL). The resulting oil was dried *in vacuo*, yielding **22a** as an analytically pure white powder in 81.3% yield (85.2 mg, 0.0488 mmol). ^{1}H NMR



(C_6D_5Br): δ 8.21 (s, 8H, *o*-BAr^F_4), 7.78 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.54 (s, 4H, *p*-BAr^F_4), 7.40 (dd, 8H, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.25(t, 4H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph), 7.20–7.00 (ov m, 12H, *m*-Ph + 2,8-dbf + 3,7-dbf), 6.60 (d, 4H, *m*-Pipp, $^3J_{HH}$ = 8.4 Hz), 6.52 (dd, 4H, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 1.5 Hz, *o*-Pipp), 2.53 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*$(CH_3)_2$), 1.00 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3)_2$), –0.79 (s, 3H, ZnC*H*$_3$). $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 25.4 (s). $^{19}F\{^1H\}$ NMR (C_6D_5Br): δ –61.5 (s). $^{11}B\{^1H\}$ NMR (C_6D_5Br): δ –5.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_5Br): δ 162.3 (q, $^1J_{BH}$ = 49.9 Hz, *ipso*-BAr^F_4), 156.06 (s), 143.58 (d, J_{CP} = 2.8 Hz), 142.31 (d, J_{CP} = 5.4 Hz), 135.07 (s, *o*-BAr^F_4), 133.82 (d, $^4J_{CP}$ = 2.8 Hz, *p*-Ph), 133.18 (d, $^2J_{CP}$ = 10.3 Hz, *o*-Ph), 131.74 (d, $^3J_{CP}$ = 8.4 Hz, 2,8-dbf), 129.28 (d, $^3J_{CP}$ = 12.7 Hz, *m*-Ph), 127.16 (s, *m*-Pipp), 126.96 (s, 1,9-dbf), 125.62 (d, $^3J_{CP}$ = 9.6 Hz, *o*-Pipp), 125.36 (d, $^2J_{CP}$ = 11.7 Hz, 3,7-dbf), 125.20 (s), 124.74 (q, $^1J_{CF}$ = 272.9 Hz, *C*F_3), 124.03 (d, J_{CP} = 5.8 Hz), 123.96 (d, J_{CP} = 8.7 Hz), 117.68 (sp, $^3J_{CF}$ = 3.7 Hz, *p*-BAr^F_4), 112.62 (d, $^1J_{CP}$ = 107.5 Hz, 4,6-dbf), 33.23 (s, *C*H$(CH_3)_2$), 23.96 (s, CH(*C*$H_3)_2$), –11.30 (s, Zn*C*H_3). Anal. Calcd. (%) for $C_{87}H_{63}BF_{24}N_2OP_2Zn$: C: 59.83; H: 3.64; N: 1.60; found: C: 59.66; H: 3.71; N: 1.65.

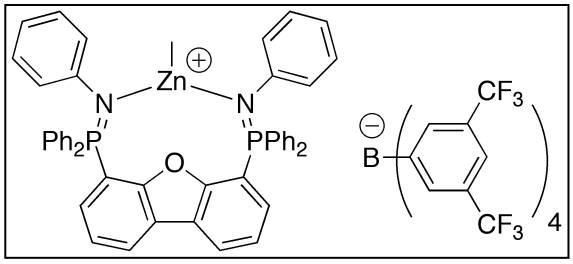
*Synthesis of [**L**$_2^{Pipp}$ZnCH$_3^+$][BPh$_4^-$] (**22b**):*

22b was prepared similarly to **10b** from **18b** (200 mg, 0.178 mmol) and dimethylzinc (1.2 M in toluene, 150 μL, 180 mmol), giving compound **22b** in approximately 75% purity, as determined by ^1H and ^{31}P NMR spectroscopy. The impurity was identified to be the aryl



analogue [$\mathbf{L_2^{Pipp}}$ZnPh$^+$][BPh$_4^-$], which was produced by transfer of a phenyl group from the BPh$_4$ anion. The material was isolated in a combined yield of 97.2% (208 mg, 0.173 mmol).^{1}H NMR (C_6D_5Br): δ 7.87 (br s, 8H, *o*-BPh$_4$), 7.68 (d, 2H, $^3J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.39 (dd, 8H, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.6 Hz), 7.23 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.15–6.88 (ov m, 24H, *m*-BPh$_4$ + *p*-BPh$_4$ + *m*-Ph + 2,8-dbf + 3,7-dbf), 6.60 (d, 4H, $^3J_{HH}$ = 8.6 Hz, *m*-Pipp), 6.54 (dd, 4H, $^3J_{HH}$ = 8.6 Hz, $^4J_{PH}$ = 1.3 Hz, *o*-Pipp), 2.52 (sp, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.00 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), –0.79 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Br): δ 25.7 (s, **22b**), 27.3 (s, [$\mathbf{L_2^{Pipp}}$ZnPh$^+$][BPh$_4^-$]). ^{11}B{^{1}H} NMR (C_6D_5Br): δ –5.6 (s, BPh$_4^-$), –10.3 (s, H$_3$CBPh$_3^-$).

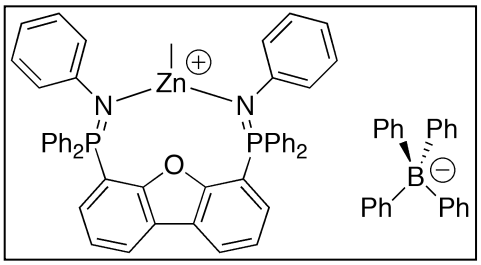
*Synthesis of [**L**$_2^{Ph}$ZnCH$_3^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**23a**):*



In a 20 mL glass vial, 200 mg (0.126 mmol) of **19b** was dissolved in 1 mL of CH_2Cl_2. To the resulting clear yellow solution an excess of dimethylzinc as a 1.2 M solution in toluene (150 µL, 180 mmol) was added. The solution was then left to stand at ambient temperature for 1 hour. The solvent was removed *in vacuo*, giving a red/orange oil. The oil was washed with pentane (3 x 1 mL) and dried *in vacuo*, giving the product as a light yellow powder in 93.3% yield (196 mg, 118 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.38 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 1,9-dbf), 7.75 (br s, 8H, *o*-BAr$^F_4$), 7.70–7.50 (ov m, 18H, 2,8-dbf + *p*-Ph + *o*-Ph + *p*-BAr$^F_4$), 7.45 (dd, 8H, $^3J_{PH}$ = 7.6 Hz, $^3J_{HH}$ = 3.3 Hz, *m*-Ph), 7.31 (dd, 2H, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.7 Hz, 3,7-dbf), 6.87–6.69 (ov m, 6H, *m*-NPh + *p*-NPh), 6.58 (m, 4H, *o*-NPh), –1.02 (s, 3H, ZnC*H*$_3$).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 25.3 (s). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2): δ –61.9 (s). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): δ –6.6 (s). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 162.31 (q, $^{1}J_{CB}$ = 49.8 Hz, *ipso*-BAr^{F}_4), 156.78 (s, Aromatic C), 145.57 (d, J_{CP} = 5.4 Hz, Aromatic C), 135.36 (br s, *o*-BAr^{F}_4), 134.53 (d, $^{3}J_{CP}$ = 3.0 Hz), 133.85 (d, $^{2}J_{CP}$ = 10.3 Hz, *o*-Ph), 132.61 (d, $^{4}J_{CP}$ = 8.2 Hz, 3,7-dbf), 129.95 (d, $^{3}J_{CP}$ = 12.7 Hz, *m*-Ph), 129.42 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{3}J_{CB}$ = 2.9 Hz, *m*-BAr^{F}_4), 129.71 (s, *m*-NPh), 127.89 (d, $^{4}J_{CP}$ = 2.6 Hz, 1,9-dbf), 126.20 (d, $^{4}J_{CP}$ = 11.6 Hz, *p*-Ph), 126.16 (d, $^{3}J_{CP}$ = 9.9 Hz, *o*-NPh), 125.13 (q, $^{1}J_{CF}$ = 272.4 Hz, *C*F_3), 124.96 (d, $^{1}J_{CP}$ = 99.1 Hz, *ipso*-Ph), 124.86 (d, J_{CP} = 6.3 Hz, Aromatic C), 123.54 (d, $^{5}J_{CP}$ = 2.6 Hz), 118.04 (sp, $^{3}J_{CF}$ = 4.0 Hz), 113.27 (d, $^{1}J_{CP}$ = 107.7 Hz, 4,6-dbf), –11.95 (s, Zn*C*H_3). Anal. Calcd. (%) for $C_{81}H_{51}BF_{24}N_2OP_2Zn{\cdot}CH_2Cl_2$: C: 57.42; H: 3.07; N: 1.64; found: C: 57.42; H: 2.77; N: 1.59.

*Synthesis of [**L₂^Ph**ZnCH₃⁺][BPh₄⁻] (**23b**):*

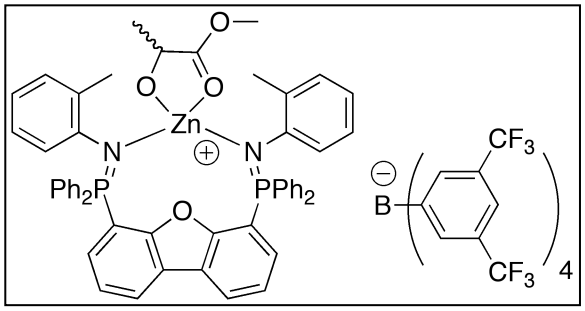


23b was prepared similarly to **10a** from **L_2^{Ph}** (200 mg, 192 mmol) and dimethylzinc (1.2 M in toluene, 165 µL, 198 mmol), giving the compound as a 4 to 1 mixture with [**L_2^{Ph}**$ZnPh^+$][BPh_4^-] (**23c**) in a combined yield of 96.1% (207 mg, 185 mmol). Only the resonances of **23b** are listed below. ^{1}H NMR (CD_2Cl_2): δ 8.36 (d, 2H, $^{3}J_{HH}$ = 7.9 Hz, 1,9-dbf), 7.73–7.48 (ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.44 (td, 8H, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 3.4 Hz, *m*-Ph), 7.35–7.20 (ov m, 10H, *o*-BPh_4 + 3,7-dbf), 7.00 (t, 8H, $^{3}J_{HH}$ = 7.5 Hz, *m*-BPh_4), 6.84 (t, 4H, $^{3}J_{HH}$ = 7.5, *p*-BPh_4), 6.80–6.69

(ov m, 6H, *m*-NPh + *p*-NPh), 6.57 (d, 4H, $^{3}J_{HH}$ = 7.2 Hz, *o*-NPh), –1.04 (s, 3H, ZnCH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 25.4 (s). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): δ –6.6 (s).

8.6. Experimental Details of Chapter 5

*Synthesis of [**L₂^Tol**ZnOCHMeCO₂Me⁺][B(m-(CF₃)₂-C₆H₃)₄⁻] (**24**):*

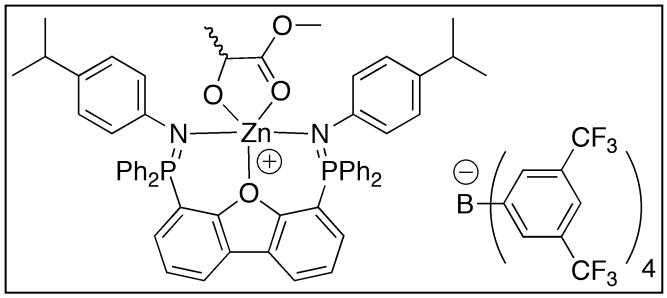


Stoichiometric amounts of **17a** (200 mg, 0.124 mmol) and ethylzinc lactate (24.5 mg, 0.124 mmol) were combined in a glass bomb with 3 mL of bromobenzene. The bomb was sealed and the yellow solution was heated, with stirring, to 100 °C for 2 hours. The solution was then allowed to cool to ambient temperature and was filtered through celite into a glass vial. To this light yellow solution 1 mL of benzene and 10 mL of pentane were added, resulting in a cloudy solution. After letting stand at ambient temperature for 18 hours, the compound crystallized as a white microcrystalline material. The supernatant was decanted, the crystals were washed with pentane (3 x 1 mL) and dried *in vacuo*, giving 118 mg of the product. The supernatant was placed in a freezer at –35 °C, and after 6 days an additional crop of 50 mg was obtained, giving an overall yield of 76.1% (168 mg, 0.0945 mmol). ^{1}H NMR (C_6D_5Br, 80 °C): δ 8.11 (s, 8H, *o*-BAr^{F}_4), 7.99 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, 1,9-dbf), 7.57 (s, 4H, *p*-BAr^{F}_4), 7.40–7.13 (br ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.12–6.88 (br ov m, 10H, *m*-Ph + 3,7-dbf), 6.73–6.63 (ov m, 4H, 3-*o*-Tol + 4-*o*-Tol), 6.57–6.38 (br ov m, 4H, 1-*o*-Tol + 2-*o*-Tol), 4.39 (q, 1H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*MeCO$_2$Me), 2.89 (s, 3H, OCHMeCO$_2$*Me*),

1.56 (s, 3H, *o*-Tol CH_3), 1.35 (d, 3H, $^3J_{HH}$ = 6.8 Hz, OCH*Me*CO_2Me). Additionally, a small amount of a second isomer of the compound is evident, only in unique resonances of methyl-lactate CH and OCH_3 groups. These appear at δ 4.07 and 3.64, respectively, and are too weak to be observed in the ^{13}C NMR spectrum. $^{31}P\{^1H\}$ NMR (C_6D_5Br, 80 °C): δ 27.2 (s). $^{19}F\{^1H\}$ NMR (C_6D_5Br): δ –61.5 (s). $^{11}B\{^1H\}$ NMR (C_6D_5Br): δ –5.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 80 °C): δ 190.56 (s, OCHMe*C*O_2Me), 162.24 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-BAr^F_4), 158.11 (s, Aromatic c), 142.93 (d, J_{CP} = 9.1 Hz, Aromatic C), 137.16 (d, J_{CP} = 7.1 Hz, Aromatic C), 135.10 (s, *o*-BAr^F_4), 133.79 (br s, *o*-Ph), 133.61 (d, $^2J_{CP}$ = 6.5 Hz, 3,7-dbf), 133.27 (br s, Aromatic C), 132.40 (d, $^4J_{CP}$ = 10.4 Hz, *p*-Ph), 130.54 (s, 3-*o*-Tol), 129.04 (br m, *m*-Ph), 128.50 (d, $^3J_{CP}$ = 5.7 Hz, 1-*o*-Tol), 127.02 (s, 1,9-dbf), 126.54 (s, 2-*o*-Tol), 125.00 (d, $^4J_{CP}$ = 3.5 Hz, 4-*o*-Tol), 124.80 (q, $^1J_{CF}$ = 273 Hz, CF_3), 124.32 (d, $^3J_{CP}$ = 10.7 Hz, 2,8-dbf), 117.62 (s, *p*-BAr^F_4), 113.08 (d, $^1J_{CP}$ = 92.7 Hz, 4,6-dbf), 70.92 (s, O*C*HMeCO_2Me), 53.25 (s, OCHMeCO_2*Me*), 23.35 (s, OCH*Me*CO_2Me), 17.91 (s, CH_3 *o*-Tol). Signals for *ipso*-Ph and *m*-BAr^F_4 were not observed. Anal. Calcd. (%) for $C_{86}H_{59}BF_{24}N_2O_4P_2Zn$: C: 58.08; H: 3.34; N: 1.58; found: C: 58.20; H: 3.00; N: 1.59.

*Synthesis of [**L**$_2^{Pipp}$ZnOCHMeCO$_2$Me$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**25**):*

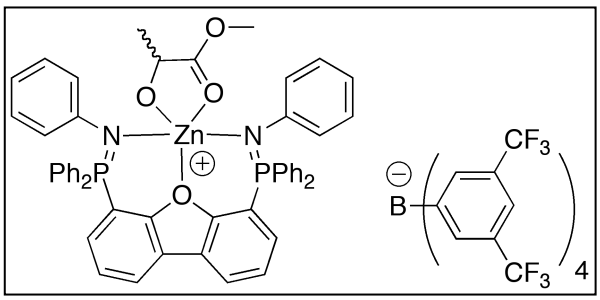
In a glass bomb equipped with a magnetic stir bar **18a** (200 mg, 0.120 mmol) was combined with a stoichiometric amount of EtZn(OCHMeCO$_2$Me) (23.7 mg, 0.120 mmol) and dissolved in 3 mL of



bromobenzene. The solution was then heated to 100 °C with stirring for 2 hours. After cooling to ambient temperature, the solution was transferred to a 20 mL scintillation vial. The product was precipitated from solution as a red oil by addition of 5 mL of pentane. The resulting oil was twice redissolved in bromobenzene (1 mL) and reprecipitated by addition of pentane (2 mL). The product was washed twice with pentane and dried *in vacuo*, giving **25** in 56.8% yield (125 mg, 0.0681 mmol). A single sharp resonance appears in the $^{31}P\{^{1}H\}$ NMR spectrum at δ 28.9 (C_6D_5Br), which at ambient temperature coexists with a very broad resonance between δ 33 and δ 30, with corresponding broad resonances occurring in the ^{1}H NMR spectrum. At elevated temperatures, these ^{31}P NMR signals coalesce to a single sharp peak. At all temperatures, two distinct structural isomers are apparent in the ^{1}H NMR spectrum, with a ratio of 3:1. ^{1}H NMR (C_6D_5Br, 80 °C): δ 8.10 (s, 8H, *o*-BAr^F_4), 7.86 (d, 2H, $^{3}J_{HH}$ = 6.9 Hz, 1,9-dbf), 7.57 (s, 4H, *p*-BAr^F_4), 7.54–7.36 (m, 8H, *o*-Ph), 7.30–6.96 (ov m, 16H, *p*-Ph + *m*-Ph + 2,8-dbf + 2,7-dbf), 6.78 (d, 1H, $^{3}J_{HH}$ = 8.6 Hz, *o*-Pipp), 6.65 (d, 3H, $^{3}J_{HH}$ = 8.3 Hz, *o*-Pipp), 6.60 (d, 1H, $^{3}J_{HH}$ = 8.6 Hz, *m*-Pipp), 6.50 (dd, 3H, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{PH}$ = 2.4 Hz, *m*-Pipp), 4.07 (q, 0.25H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*$MeCO_2Me$), 3.78 (q, 0.75H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*$MeCO_2Me$), 3.64 (s, 0.75H, OCH$MeCO_2$*Me*), 3.19 (s, 2.25H, OCH$MeCO_2$*Me*), 2.59 (sp, 2H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$(CH_3)_2$), 1.34 (d, 0.75H, $^{3}J_{HH}$ = 6.8 Hz, OCH*Me*CO_2Me), 1.06 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3)_2$), 1.02 (d, 9H, $^{3}J_{HH}$ = 6.9 Hz, CH(C*H*$_3)_2$), 0.94 (d, 2.25H, $^{3}J_{HH}$ = 6.8 Hz, OCH*Me*CO_2Me). $^{31}P\{^{1}H\}$ NMR (C_6D_5Br, 80 °C): δ 29.2 (s). $^{19}F\{^{1}H\}$ NMR (C_6D_5Br): δ –61.5 (s). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): δ –5.8 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br, 80 °C): (Note: Resonances are listed for both isomers where possible, with the exception of quaternary carbons, which are too weak to be

observed for the minor isomer. The *ipso*-Ph signal was not observed for either isomer due to obscuring solvent signals) δ 190.95 (s, OCHMe*C*O$_2$Me), 162.21 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-BAr$_4$), 157.49 (s, Aromatic C), 144.74 (d, J_{CP} = 3.8 Hz), 142.18 (d, J_{CP} = 6.8 Hz), 135.08 (br s, *o*-BAr$_4$), 133.84 (d, $^4J_{CP}$ = 2.9 Hz, *p*-Ph), 133.60 (d, $^2J_{CP}$ = 9.9 Hz, *o*-Ph), 133.38 (d, $^4J_{CP}$ = 3.1 Hz, *p*-Ph), 133.26 (d, $^2J_{CP}$ = 9.9 Hz, *o*-Ph), 132.79 (d, $^3J_{CP}$ = 10.5 Hz, 2,8-dbf), 132.42 (d, $^2J_{CP}$ = 8.3 Hz, 3,7-dbf), 131.86 (s, Aromatic C), 129.30 (d, $^3J_{CP}$ = 13.3 Hz, *m*-Ph), 128.92 (d, $^3J_{CP}$ = 12.5 Hz, *m*-Ph), 128.35 (d, $^3J_{CP}$ = 7.6 Hz, *o*-Pipp), 128.28 (s, Aromatic C), 127.16 (s, *m*-Pipp), 126.58 (s, *m*-Pipp), 126.55 (s, 1,9-dbf), 125.45 (d, J_{CP} = 3.3 Hz, Aromatic C), 125.03 (d, $^3J_{CP}$ = 10.0 Hz, *o*-Pipp), 124.74 (q, $^1J_{CF}$ = 272.9 Hz, *C*F$_3$), 124.54 (d, $^3J_{CP}$ = 11.8 Hz, 2,8-dbf), 117.60 (br s, *p*-BAr$^F_4$), 111.64 (d, $^1J_{CP}$ = 106.1 Hz, 4,6-dbf), 69.89 (s, O*C*HMeCO$_2$Me), 67.33 (s, O*C*HMeCO$_2$Me), 53.68 (s, CHMeCO$_2$*Me*), 53.16 (s, CHMeCO$_2$*Me*), 33.30 (s, *C*H(CH$_3$)$_2$), 23.88 (s, CH(*C*H$_3$)$_2$), 23.77 (s, CH(*C*H$_3$)$_2$), 23.46 (s, CH*Me*CO$_2$Me), 23.31 (s, CH*Me*CO$_2$Me). Anal. Calcd. (%) for $C_{90}H_{67}BF_{24}N_2O_4P_2 \cdot C_6H_5Br$: C: 57.89; H: 3.64; N: 1.41; found: C: 58.02; H: 3.80; N: 1.43.

*Synthesis of [**L**$_2^{Ph}$ZnOCHMeCO$_2$Me$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**26**):*



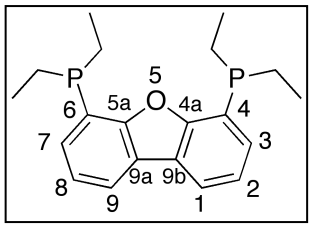
A stoichiometric amount of **19a** (100 mg, 0.063 mmol) and ethyl zinc lactate (12.5 mg, 0.063 mmol) were combined in a glass bomb with 5 mL of bromobenzene. The bomb was sealed and heated to 100 °C for two hours while stirring. The resulting red/orange solution was cooled to ambient

temperature, and then filtered through celite into a glass vial. The volume was reduced under vacuum to ~ 3 mL and 10 mL of pentane was added to precipitate the product. The resulting cloudy solution was placed in a freezer at –35 °C for 24 hours. During this time, the product precipitated as a red/orange oil. The supernatant was decanted and the oil was washed with pentane (3 x 1 mL) and dried *in vacuo*, giving 62 mg of the compound as a light red/orange powder. The supernatant was returned to –35 °C for three more days, and an additional 18 mg of product was obtained, for an overall yield of 72% (80 mg, 0.046 mmol). Two distinct structural isomers are apparent in the ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (CD_2Cl_2): δ 8.47 (dt, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1,9-dbf), 8.43 (dt, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1,9-dbf), 7.77 (br s, 8H, *m*-BAr^{F}_{4}), 7.72–7.40 (ov m, 28H, *o*-Ph + *m*-Ph + *p*-Ph + *p*-BAr^{F}_{4} + 2,8-dbf + 3,7-dbf), 7.00 (t, 2H, $^{3}J_{HH}$ = 7.8 Hz, *p*-NPh), 6.92–6.84 (ov m, 4H, *m*-NPh), 6.69 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, *o*-NPh), 6.57 (m, *o*-NPh), 4.06 (q, 0.5H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*MeCO$_2$Me), 3.93 (s, 1.5H, OCHMeCO$_2$*Me*), 3.44 (q, 0.5H, $^{3}J_{HH}$ = 6.8 Hz, OC*H*MeCO$_2$Me), 3.42 (s, 1.5H, OCHMeCO$_2$*Me*), 1.36 (d, 1.5H, $^{3}J_{HH}$ = 6.8 Hz, OCH*Me*CO$_2$Me), 0.87 (d, 1.5H, $^{3}J_{HH}$ = 6.8 Hz, OCH*Me*CO$_2$Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 29.3 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –61.9 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). Resonances of both isomers are listed in the ^{13}C NMR spectrum. The spectrum contains 3 unique resonances for both the *o*-Ph and *p*-Ph atoms, suggesting a splitting of these signals for one of the two isomers. The quaternary carbons, with the exception of the lactate moiety, do not display distinct signals for the two isomers. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 191.4 (s, OCHMe*C*O$_2$Me), 185.48 (s, OCHMe*C*O$_2$Me), 162.31 (q, $^{1}J_{CB}$ = 49.9 Hz, *ipso*-BAr^{F}_{4}), 157.97 (s, Aromatic C), 145.20

(d, J_{CP} = 6.6 Hz, Aromatic C), 135.36 (br s, *o*-BAr^F_4), 134.61 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph), 134.28 (d, $^2J_{CP}$ = 10.0 Hz, *o*-Ph), 134.27 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph), 134.09 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph), 133.82 (d, $^2J_{CP}$ = 10.1 Hz, *o*-Ph), 133.51 (d, $^2J_{CP}$ = 8.4 Hz, 3,7-dbf), 133.43 (d, $^2J_{CP}$ = 10.7 Hz, *o*-Ph), 133.16 (d, $^2J_{CP}$ = 8.0 Hz, 3,7-dbf), 131.36 (d, $^1J_{CP}$ = 101.4 Hz, *ipso*-Ph), 130.04 (d, $^3J_{CP}$ = 13.1 Hz, *m*-Ph), 129.70 (s, *p*-NPh), 129.60 (d, $^2J_{CP}$ = 12.7 Hz, *m*-Ph), 129.43 (qq, $^2J_{CF}$ = 31.3 Hz, $^3J_{CB}$ = 2.8 Hz, *m*-BAr^F_4), 129.23 (d, $^4J_{CP}$ = 2.8 Hz, *m*-NPh), 129.01 (d, $^3J_{CP}$ = 7.5 Hz, *o*-NPh), 127.80 (d, $^4J_{CP}$ = 2.3 Hz, 1,9-dbf), 127.55 (s, Aromatic C), 127.54 (d, $^4J_{CP}$ = 2.6 Hz, 1,9-dbf), 125.51 (d, $^3J_{CP}$ = 3.3 Hz, 2,8-dbf), 125.37 (d, $^3J_{CP}$ = 3.6 Hz, 2,8-dbf), 125.14 (q, $^1J_{CF}$ = 272.4 Hz, CF_3), 124.94 (d, $^3J_{CP}$ = 11.3 Hz, *o*-NPh), 124.45 (d, $^4J_{CP}$ = 3.6 Hz, *m*-NPh), 118.04 (sp, $^3J_{CF}$ = 4.1 Hz, *p*-BAr^F_4), 111.72 (d, $^1J_{CP}$ = 106.1 Hz, 4,6-dbf), 69.80 (s, O*C*HMeCO_2Me), 67.79 (s, O*C*HMeCO_2Me), 54.69 (s, OCHMeCO_2*Me*), 54.23 (s, OCHMeCO_2*Me*), 24.12 (s, OCH*Me*CO_2CH_3), 13.47 (s, OCH*Me*CO_2Me). Anal. Calcd. (%) for $C_{84}H_{55}BF_{24}N_2O_4P_2Zn$: C: 57.64; H: 3.17; N: 1.60; found: C: 57.77; H: 2.85; N: 2.03.

8.7. Experimental Details of Chapter 6

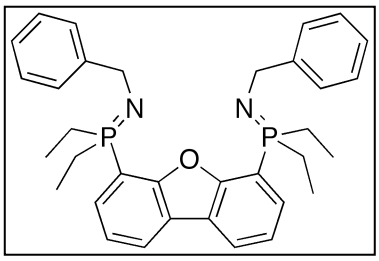
*Synthesis of 4,6-(PEt_2)$_2$-dbf (**27**):*



TMEDA (1.8 mL, 12.1 mmol) was added to a suspension of dibenzofuran (1.00 g, 5.95 mmol) in 50 mL of heptane. The resulting solution was cooled to 0 °C and 2 equivalents of 1.7 M ^{t}BuLi solution in pentane (7.0 mL, 11.9 mmol) were added over 30 minutes. The solution was allowed to warm to ambient

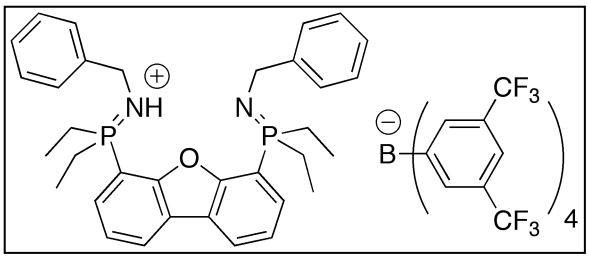
temperature, and was then heated to reflux for a period of 1 hour. The resulting suspension of doubly lithiated dibenzofuran was then cooled to 0 °C, and 1.48 g of Et_2PCl, diluted to 10 mL in pentane, was added dropwise over a period of 20 minutes. The solution was allowed to stir for 30 minutes at 0 °C, and then warmed to ambient temperature and continued stirring for another 60 minutes. The solution was filtered to remove LiCl·TMEDA, and the solvent was removed *in vacuo* to give the crude compound as a viscous red oil. The material was dissolved in 3 mL of pentane and cooled to –35 °C for 18 hours, resulting in precipitation of the product as a red oil. The supernatant was removed and the material was dried *in vacuo*, yielding 1.81 g (5.26 mmol, 88.3%) of **27** as a red oil in *ca.* 84% purity. ^{1}H NMR (C_6D_6): δ 7.64 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1,9-dbf), 7.58 (td, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 3,7-dbf), 7.13 (t, 2H, $^3J_{HH}$ = 7.5 Hz, 2,8-dbf), 2.11 (dqd, 4H, $^2J_{HaHb}$ = 13.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^2J_{PH}$ = 1.2 Hz, PCH_aH$_b$CH$_3$), 1.88 (dqd, 4H, $^2J_{HaHb}$ = 13.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^2J_{PH}$ = 3.3 Hz, PCH$_a$$H_bCH_3$), 1.03 (dt, 12H, $^3J_{PH}$ = 15.4 Hz, $^3J_{HH}$ = 7.7 Hz, PCH$_2$CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ –19.0 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 158.98 (d, $^2J_{CP}$ = 4.8 Hz, 4a,5a-dbf), 132.96 (d, $^2J_{CP}$ = 21.9 Hz, 3,7-dbf), 124.34 (dd, $^3J_{CP}$ = 1.3 Hz, $^4J_{CP}$ = 0.7 Hz, 9a,9b-dbf), 123.55 (d, $^3J_{CP}$ = 6.9 Hz, 2,8-dbf), 123.08 (d, $^1J_{CP}$ = 25.4 Hz, 4,6-dbf), 121.87 (s, 1,9-dbf), 19.15 (d, $^1J_{CP}$ = 11.2 Hz, PCH$_2$CH$_3$), 10.76 (d, $^2J_{CP}$ = 14.4 Hz, PCH$_2$$CH_3$).

*Synthesis of 4,6-(Bn-N=PEt$_2$)$_2$-dbf (**L$_3$**):*



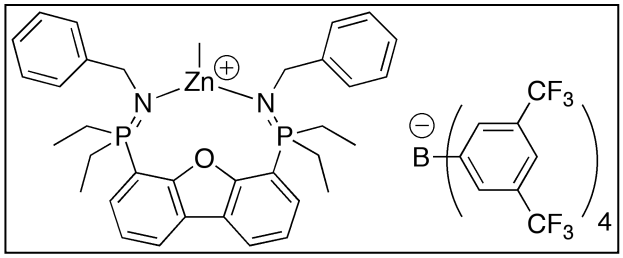
A solution of benzyl-azide (177 mg, 1.33 mmol) in benzene (2 mL) was added dropwise to a solution of the **27** (218 mg, 0.633 mmol) with stirring. The resulting yellow solution was left to stand at ambient temperature for 30 minutes. The solution was concentrated to a volume of 1 mL, and 10 mL of pentane was added, causing the solution to become cloudy. Cooling to –35 °C for 19 hours resulted in the formation of yellow crystals. The mother liquor was decanted and the crystals were washed with pentane (3 x 1 mL) and dried *in vacuo*, giving **L$_3$** in 80% yield (279 mg, 0.503 mmol). ^{1}H NMR (C_6D_6): δ 8.24 (dd, 2H, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 7.6 Hz, 3,7-dbf), 7.88 (d, 4H, $^3J_{HH}$ = 7.1 Hz, *o*-CH_2Ph), 7.56 (d, 2H, $^3J_{HH}$ = 7.6 Hz, 1,9-dbf), 7.40 (t, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-CH_2Ph), 7.22 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-CH_2Ph), 7.13 (td, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.1 Hz, 2,8-dbf), 4.73 (d, 4H, $^3J_{PH}$ = 18.4 Hz, C*H*$_2$Ph), 2.10–1.85 (ov m, 8H, PC*H*$_2$CH$_3$), 0.95 (dt, 12H, $^3J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 7.6 Hz, PCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 14.4 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.72 (d, J_{CP} = 2.9 Hz, Aromatic C), 147.70 (d, J_{CP} = 17.9 Hz, Aromatic C), 134.08 (d, J_{CP} = 4.7 Hz, 3,7-dbf), 128.65 (s, *m*-CH_2Ph), 127.84 (s, *o*-CH_2Ph), 126.39 (s, *p*-CH_2Ph), 124.36 (dd, J_{CP} = 5.7 Hz, J_{CP} = 0.7 Hz, Aromatic C), 124.18 (s, 1,9-dbf), 124.11 (d, J_{CP} = 5.8 Hz, 2,8-dbf), 117.90 (d, $^1J_{CP}$ = 75.8 Hz, 2,6-dbf), 49.68 (d, J_{CP} = 3.8 Hz, *C*H$_2$Ph), 21.78 (d, $^1J_{CP}$ = 67.5 Hz, P*C*H$_2$CH$_3$), 6.75 (d, $^2J_{CP}$ = 4.9 Hz, PCH$_2$*C*H$_3$). Anal. Calcd. (%) for $C_{34}H_{40}N_2OP_2$: C: 73.63; H: 7.27; N: 5.05; found: C: 73.47; H: 7.00; N: 5.12.

*Synthesis of [**L**$_3$H$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**28**):*



L$_3$ (320 mg, 0.577 mmol) and [H(OEt$_2$)$_2^+$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (584 mg, 0.577 mmol) were combined in a 20 mL glass vial with 2 mL of benzene. The resulting mixture was triturated briefly, giving a clear red solution, and left to stand for 5 minutes. Addition of 2 mL of pentane resulted in precipitation of a red oil. The supernatant was decanted, the oil was washed with pentane (3 x 2 mL) and dried *in vacuo*, affording **28** as a pale yellow powder in 95.7% yield (783 mg, 0.552 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.26 (d, 2H, $^3J_{HH}$ = 7.3 Hz, 1,9-dbf), 7.75 (br s, 8H, *o*-BAr$^F_4$), 7.65–7.50 (ov m, 8H, *p*-BAr$^F_4$ + 3,7-dbf + 2,8-dbf), 7.26–7.10 (ov m, 10H, *o*- + *m*- + *p*-CH$_2$Ph), 5.45 (br s, 1H, N*H*), 4.03 (d, 4H, $^3J_{PH}$ = 16.5 Hz, C*H*$_2$Ph), 2.50–2.15 (ov m, 8H, PC*H*$_a$*H*$_b$CH$_3$), 1.10 (dt, 12H, $^3J_{PH}$ = 18.9 Hz, $^3J_{HH}$ = 7.6 Hz, PCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 39.5 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –62.8 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.30 (q, $^1J_{CB}$ = 49.8 Hz, *ipso*-BAr$^F_4$), 157.38 (s, Aromatic C), 141.08 (d, J_{CP} = 11.4 Hz, Aromatic C), 135.35 (s, *o*-BAr$^F_4$), 130.72 (d, $^2J_{CP}$ = 6.0 Hz, 3,7-dbf), 129.41 (qq, $^2J_{CF}$ = 31.5 Hz, $^3J_{CB}$ = 2.8 Hz, *m*-BAr$^F_4$), 128.96 (s, CH$_2$Ph), 128.13 (s, CH$_2$Ph), 127.98 (s, CH$_2$Ph), 127.40 (s, 1,9-dbf), 125.26 (d, $^3J_{CP}$ = 9.8 Hz, 2,8-dbf), 125.14 (q, $^1J_{CF}$ = 272.4 Hz, CF$_3$), 124.64 (d, J_{CP} = 5.8 Hz, Aromatic C), 118.03 (sp, $^3J_{CF}$ = 3.8 Hz, *p*-BAr$^F_4$), 109.90 (d, $^1J_{CP}$ = 83.5 Hz, 4,6-dbf), 48.00 (d, $^2J_{CP}$ = 3.0 Hz, *C*H$_2$Ph), 17.57 (d, $^1J_{CP}$ = 34.8 Hz, P*C*H$_2$CH$_3$), 5.82 (d, $^2J_{CP}$ = 4.2 Hz, PCH$_2$*C*H$_3$). Anal. Calcd. (%) for $C_{66}H_{53}BF_{24}N_2OP_2$: C: 55.87; H: 3.77; N: 1.97; found: C: 55.74; H: 3.87; N: 2.26.

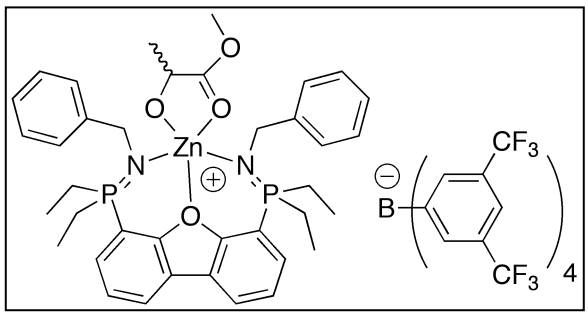
*Synthesis of [**L**$_3$ZnCH$_3^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**29**):*



A slight excess of a 1.2 M solution of dimethylzinc in toluene (120 µL, 144 mmol) was added to a solution of **28** (200 mg, 141 mmol) in bromobenzene (1 mL). The solution was left to stand for 1 hour, then 2 mL of pentane was added, precipitating the product as a red oil. The supernatant was decanted, the material was washed with pentane (3 x 1 mL) and then dried *in vacuo*, giving **29** as an off-white powder in 90.0% yield (190 mg, 127 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.34 (dt, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.1 Hz, 1,9-dbf), 7.73 (br s, 8H, *o*-BAr$^F_4$), 7.64 (td, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 2.4 Hz, 2,8-dbf), 7.56 (br s, 4H, *p*-BAr$^F_4$), 7.53 (ddd, 2H, $^3J_{PH}$ = 10.4 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.1 Hz), 7.19–7.13 (ov m, 6H, *m*- + *p*-CH_2Ph), 7.07–7.01 (m, *o*-CH_2Ph), 4.00 (d, 4H, $^3J_{PH}$ = 19.2 Hz, C*H*$_2$Ph), 2.30 (dq, 8H, $^2J_{PH}$ = 11.8 Hz, $^3J_{HH}$ = 7.7 Hz, PC*H*$_2$CH$_3$), 1.07 (dt, 12H, $^3J_{PH}$ = 18.7 Hz, $^3J_{HH}$ = 7.6 Hz, PCH$_2$C*H*$_3$), –0.95 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 46.6 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –62.8 (s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ –6.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.29 (q, $^1J_{CB}$ = 49.7 Hz, *ipso*-BArF$_4$), 157.13 (s, Aromatic C), 141.37 (d, J_{CP} = 9.7 Hz, Aromatic C), 135.34 (br s, *o*-BAr$^F_4$), 130.82 (d, $^2J_{CP}$ = 6.4 Hz, 3,7-dbf), 129.40 (qq, $^2J_{CF}$ = 31.4 Hz, $^3J_{CB}$ = 2.8 Hz, *m*-BAr$^F_4$), 129.31 (s, CH_2Ph), 128.06 (s, CH_2Ph), 127.36 (d, $^4J_{CP}$ = 2.1 Hz, 1,9-dbf), 127.29 (s, *o*-CH_2Ph), 125.79 (d, $^3J_{CP}$ = 9.9 Hz, 2,8-dbf), 125.14 (q, $^1J_{CF}$ = 272.4 Hz, CF_3), 124.68 (d, J_{CP} = 6.3 Hz, Aromatic C), 118.02 (sp, $^3J_{CF}$ = 3.9 Hz, *p*-BAr$^F_4$), 111.28 (d, $^1J_{CP}$ = 85.8 Hz, 4,6-dbf), 50.11 (d, $^2J_{CP}$ = 4.2 Hz, *C*H$_2$Ph), 17.84 (d, $^1J_{CP}$ = 65.2 Hz, P*C*H$_2$CH$_3$),

5.94 (d, $^2J_{CP}$ = 4.2 Hz, PCH_2CH_3), –8.81 (s, $ZnCH_3$). Anal. Calcd. (%) for $C_{67}H_{55}BF_{24}N_2OP_2Zn$: C: 53.71; H: 3.70; N: 1.87; found: C: 53.35; H: 3.54; N: 2.20.

*Synthesis of [**L**$_3$ZnOCHMeCO$_2$Me$^+$][B(m-(CF$_3$)$_2$-C$_6$H$_3$)$_4^-$] (**30**):*



The protonated ligand **28** (400 mg, 282 mmol) and ethylzinc-lactate (55.7 mg, 282 mmol) were dissolved in 5 mL of bromobenzene and sealed in a glass bomb. The solution was heated to 100 °C for 1 hour and cooled to ambient temperature. The solution was transferred to a glass vial and concentrated to 2 mL *in vacuo*. Addition of 4 mL of pentane caused the precipitation of the product as a pale yellow powder. The supernatant was decanted and the solid was washed with a 1:1 benzene/pentane mixture (2 mL) and pentane (2 x 2 mL) and dried *in vacuo*, giving 282 mg of compound **30**. The combined supernatant and washings were reduced to dryness and redissolved in 1 mL of bromobenzene. A further 141 mg of the compound was isolated from this solution in the same manner as described above, giving **30** in an overall yield of 94.6% (423 mg, 267 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.35 (dt, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1,9-dbf), 7.73 (s, 8H, *o*-BAr^F_4), 7.61 (td, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 2.4 Hz, 2,8-dbf), 7.55 (s, 4H, *p*-BAr^F_4), 7.48 (ddd, 2H, $^3J_{PH}$ = 9.5 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 3,7-dbf), 7.18–7.08 (ov m, 6H, *m*- + *p*-CH_2Ph), 7.05–6.98 (ov m, 4H, *o*-CH_2Ph), 4.66 (q, 1H, $^3J_{HH}$ = 6.8 Hz, OC*H*$MeCO_2Me$), 3.98 (d, 4H, $^3J_{PH}$ = 23.1 Hz, CH_2Ph), 3.69 (s, 3H, $OCHMeCO_2$*Me*), 2.45–2.24 (ov m, 8H, PCH_2CH_3), 1.41 (d, 3H, $^3J_{HH}$ = 6.8 Hz,

OCH*Me*CO_2Me), 1.04 (q, 6H, $^3J_{PH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, PCH_2CH_3), 0.98 (q, 6H, $^3J_{PH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.8 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ –62.8 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ –6.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 191.96 (s, OCHMe*C*O_2Me), 163.33 (q, $^1J_{BH}$ = 49.8 Hz, *ipso*-$BAr^F{}_4$), 157.15 (s, Aromatic C), 141.34 (d, J_{CP} = 5.6 Hz, Aromatic C), 135.39 (s, *o*-$BAr^F{}_4$), 130.90 (d, $^2J_{CP}$ = 4.8 Hz, 3,7-dbf), 129.45 (qq, $^2J_{CF}$ = 31.5 Hz, $^3J_{CB}$ = 2.9 Hz, *m*-$BAr^F{}_4$), 128.86 (s, *m*-CH_2Ph), 128.28 (s, *o*-CH_2Ph), 128.00 (s, *p*-CH_2Ph), 127.24 (d, $^4J_{CP}$ = 2.3 Hz, 1,9-dbf), 125.34 (d, $^3J_{CP}$ = 9.1 Hz, 2,8-dbf), 125.18 (q, $^1J_{CF}$ = 272.5 Hz, CF_3), 124.45 (d, J_{CP} = 6.2 Hz, Aromatic C), 118.06 (sp, $^3J_{CF}$ = 4.0 Hz, *p*-$BAr^F{}_4$), 112.49 (d, $^1J_{CP}$ = 77.8 Hz, 4,6-dbf), 71.49 (s, O*C*HMeCO_2Me), 54.73 (s, OCHMeCO_2*Me*), 51.26 (d, $^2J_{CP}$ = 5.6 Hz, *C*H_2Ph), 24.65 (s, OCH*Me*CO_2Me), 16.65 (d, $^1J_{CP}$ = 68.7 Hz, P*C*H_2CH_3), 16.30 (d, $^1J_{CP}$ = 68.3 Hz, P*C*H_2CH_3), 5.80 (d, $^2J_{CP}$ = 3.3 Hz, PCH_2CH_3), 5.74 (d, $^2J_{CP}$ = 3.3 Hz, PCH_2CH_3). Anal. Calcd. (%) for $C_{70}H_{59}BF_{24}N_2O_4P_2Zn$: C: 53.00; H: 3.75; N: 1.77; found: C: 53.13; H: 3.92; N: 2.09.

8.8. Details of Crystallographic Studies

X-ray diffraction data were collected on a Bruker AXS Smart Apex II X-ray diffractometer [Mo Kα (λ = 0.71073 Å)]. Suitable crystals of the compounds were coated in paratone oil, mounted on a glass fibre, and flash frozen to 173(2) K. Unit cell parameters were determined and refined on all reflections and data were integrated using APEX2 software.[157] Data reduction and correction for Lorentz polarization were performed using Saint-plus,[158] and scaling and absorption

corrections were performed using the SADABS software package.[159] Structure solution by direct methods and least-squares refinement on F^2 were performed using the SHELXTL software suite.[160] Non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in calculated positions and refined with a riding model. Structural figures were generated with ORTEP-3.[161]

In some cases, large solvent occupied voids existed and solvent molecules could not be modelled explicitly, and thus the SQUEEZE subroutine of the PLATON software package[162, 163] was used to account for the electron density of these solvent molecules, which were then included in the respective formulae. For **3**·1.5C_7H_8, 41 electrons were removed from a void volume of 232 Å^3 and assigned to 1 molecule of toluene (0.5 per asymmetric unit). For **7**·C_6H_6, 100 electrons were removed from a void volume of 612 Å^3 and assigned to 2 molecules of benzene (1 per asymmetric unit). For **10b**·0.5C_6H_6, 31 electrons were removed from a void volume of 137 Å^3 and were assigned to one molecule of benzene (0.5 per asymmetric unit). For $\mathbf{L_2^{Tol}}$, 13 electrons were removed from a void volume of 140 Å^3 and were left unassigned. For $\mathbf{L_2^{Pipp}}$·C_5H_{12}, 24 electrons were removed from a void volume of 396 Å^3 and were left unassigned. For **11**·1.5C_6H_5Br, 142 electrons were removed from a void volume of 646 Å^3 and were assigned to 2 molecules of bromobenzene (0.5 per asymmetric unit). For **12**·2C_6H_6, 160 electrons were removed from a void volume of 986 Å^3 and were assigned to 4 molecules of benzene (1 per asymmetric unit). For **22b**·2.5C_6H_6, 120 electrons were removed from a void volume of 433 Å^3 and assigned to 3 molecules of benzene (1.5 molecules per asymmetric unit). For **23c**·2C_6H_6, 70

electrons were removed from a void volume of 365 Å^3 and were assigned to 2 molecules of benzene (1 per asymmetric unit).

Many of the crystal structures also contained significant positional or substitutional disorder. While the most significant of these were described in the main body of the thesis, many other disorders should also be noted. These are only discussed briefly here, but for more details the reader is encouraged to refer to the crystal data in CIF format, which can be found on the attached compact disc. In **5b**, there is a positional disorder of the triflate SO_3 group, which was modelled as a 94:6 disorder of the oxygen atoms over two sites. The atoms of the less abundant component were modelled isotropically. In **15b**·$CHCl_3$, there exists a substitutional disorder whereby the coordination site of zinc is occupied by either the OC_6F_5 moiety or a phenyl group in a 62:38 ratio. When the smaller phenyl group is present, a molecule of chloroform is also present. In the structure of $\mathbf{L_2^{Pipp}}$·C_5H_{12}, an isopropyl group is modelled as a 63:37 positional disorder over two sites. In the structure of 22b, a phenyl group of the ligand is modelled as a 72:28 disorder over two sites, while a phenyl group of the anion is modelled as a 84:16 disorder over two sites. In the structure of **25**·C_6H_6, an isopropyl group of the ligand is modelled as 62:38 disorder over two sites. Additionally, the fluorine atoms of many CF_3 groups of the B(*m*-$(CF_3)_2$-$C_6H_3)_4^-$ anion in the structures of **24**·CH_2Cl_2, **25**·C_6H_6, **26**·C_6H_5Br, and **30** are similarly disordered over two sites, as is commonly observed for this anion.

Basic crystallographic data and refinement details are found in Tables 8.1–8.7. For more complete details, including full tables of atomic coordinates, bond

lengths, angles, torsion angles, and anisotropic displacement parameters see Appendix 2, which is included in digital format on the attached compact disc.

Table 8.1. Crystallographic data for $\mathbf{L_1^{Dipp}}$, **1**, **2**·C_7H_8, and **3**·1.5C_7H_8.

	$\mathbf{L_1^{Dipp}}$	**1**	**2 · C_7H_8**	**3 · 1.5 C_7H_8**
Empirical formula	$C_{36}H_{34}NOP$	$C_{36}H_{34}Cl_2NOPZn$	$C_{66}H_{56}Cl_4N_2O_2P_2Zn_2 \cdot C_7H_8$	$C_{48}H_{34}F_{10}NOPZn \cdot 1.5\ C_7H_8$
Formula weight	527.61	663.88	1335.7	1065.37
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	Pbca	*P*-1	*P*-1	*P*-1
a (Å)	a = 11.1269(7)	9.3247(4)	9.5777(5)	a = 12.3644(7)
b (Å)	b = 17.6285(11)	10.7683(4)	13.5073(7)	b = 13.2795(7)
c (Å)	c = 29.3704(18)	16.9837(7)	14.889(1)	c = 17.704(1)
α (°)	90	78.32	114.568(1)	α= 70.327(1)
β (°)	90	83.58	92.957(1)	β= 70.849(1)
γ (°)	90	75.89	108.823(1)	γ = 71.903(1)
Volume (Å^3)	5761.0(6)	1616.1(1)	1619.1(2)	2519.4(2)
Z	8	2	2	2
ρ_{calcd} (Mg m^{-3})	1.217	1.364	1.370	1.344
μ (mm^{-1})	0.125	1.004	1.003	0.595
F(000)	2240	688	690	1044
Crystal size (mm^3)	0.25x0.21x0.17	0.39x0.32x0.25	0.24x0.17x0.12	0.30x0.26x0.24
θ range (°)	2.57 to 25.03	2.64 to 26.37	2.60 to 26.37	2.56 to 25.03
Reflections collected	52904	17389	21637	24263
Independent reflections	5077 [*R*(int) = 0.0618]	6576 [*R*(int) = 0.0115]	6586 [*R*(int) = 0.0283]	8863 [*R*(int) = 0.0219]
Completeness to theta = 25.03°	100%	99.2%	99.5%	99.6%
Data / restraints / parameters	5077/ 0 / 356	6576 / 0 / 383	6586 / 99 / 407	8863 / 0 / 615
Goodness-of-fit (GOF)	1.101	1.068	1.034	1.045
R indices [I>2σ(I)]	R_1 = 0.0486, wR_2 = 0.1115	R_1 = 0.0223, wR_2 = 0.0612	R_1 = 0.0377, wR_2 = 0.0979	R_1 = 0.0366, wR_2 = 0.0998
R indices (all data)	R_1 = 0.0657, wR_2 = 0.1202	R_1 = 0.0238, wR_2 = 0.0620	R_1 = 0.0495, wR_2 = 0.1051	R_1 = 0.0433, wR_2 = 0.1033
Largest diff. peak/hole (e Å^{-3})	0.382 and -0.322	0.394 and -0.251	1.531 and -0.359	0.553 and -0.479

Table 8.2. Crystallographic data for **4**·C_5H_{12}, **5b**, **6b**, and **7**·C_6H_6.

	4 · C_5H_{12}	**5b**	**6b**	**7· C_6H_6**
Empirical formula	$C_{45}H_{28}F_{10}NOPZn \cdot C_5H_{12}$	$C_{40}H_{38}F_3NO_4PSZn$	$C_{39}H_{39}F_3NO_4PSZn$	$C_{78}H_{74}F_{12}N_2O_{16}P_2S_4Zn_3 \cdot C_6H_6$
Formula weight	957.17	716.74	771.11	1987.96
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P-1	P-1	P-1
a (Å)	15.274(1)	9.2135(5)	9.6030(9)	12.729(2)
b (Å)	14.196(1)	10.9472(6)	12.3790(12)	13.861(2)
c (Å)	21.311(2)	18.2092(10)	16.7009(16)	14.226(2)
α (°)	90	77.0560(10)	75.1590(10)	86.308(1)
β (°)	98.317(1)	88.6580(10)	83.3150(10)	89.135(1)
γ (°)	90	87.1610(10)	74.0350(10)	84.456(1)
Volume (Å^3)	4572.3(7)	1787.61(17)	1842.8(3)	2492.9(5)
Z	4	2	2	2
ρ_{calcd} (Mg m^{-3})	1.390	1.332	1.390	1.272
μ (mm^{-1})	0.651	0.194	0.823	0.908
F(000)	1960	750	800	976
Crystal size (mm^3)	0.30x0.26x0.18	0.50x0.39x0.29	0.32x0.16x0.11	0.28x0.26x0.13
θ range (°)	2.62 to 25.03	1.91 to 25.03	2.60 to 25.03	2.59 to 25.03
Reflections collected	43393	17259	17771	23701
Independent reflections	8076 [*R*(int) = 0.0310]	6284 [*R*(int) = 0.0146]	6479 [*R*(int) = 0.0313]	8770 [*R*(int) = 0.0381]
Completeness to theta = 25.03°	99.9%	99.7%	99.6%	99.6%
Data / restraints / parameters	8076 / 0 / 582	6284 / 6 / 472	6479 / 1200 / 591	8770 / 0 / 534
Goodness-of-fit (GOF)	1.025	1.023	1.015	1.023
R indices [I>2σ(I)]	R_1 = 0.0365, wR_2 = 0.0883	R_1 = 0.0422, wR_2 = 0.1128	R_1 = 0.0360, wR_2 = 0.0806	R_1 = 0.0408, wR_2 = 0.1026
R indices (all data)	R_1 = 0.0513, wR_2 = 0.0972	R_1 = 0.0463, wR_2 = 0.1166	R_1 = 0.0570, wR_2 = 0.0891	R_1 = 0.0664, wR_2 = 0.1102
Largest diff. peak/hole (e Å^{-3})	0.482 and -0.304	0.792 and -0.487	0.347 to 0.295	0.645 and -0.329

Table 8.3. Crystallographic data for $\mathbf{L_2^{Mes}}$, **9**·$CO(CH_3)_2$, **10b**·0.5C_6H_6, and **11**·1.5C_6H_5Br.

	$\mathbf{L_2^{Mes}}$	**9** · $\mathbf{CO(CH_3)_2}$	**10b** · 0.5 $\mathbf{C_6H_6}$	**11** · 1.5 $\mathbf{C_6H_5Br}$
Empirical formula	$C_{54}H_{48}N_2OP_2$	$C_{102}H_{90}B_2N_2OP_2$ · $CO(CH_3)_2$	$C_{81}H_{72}BN_2OP_2Zn$ · 0.5 C_6H_6	$C_{84}H_{73}BN_2OP_2Zn$ · 1.5 C_6H_5Br
Formula weight	802.88	1501.4	1241.55	1500.10
Temperature (K)	173(2)	173(2) K	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	P2(1)/n	Pbcn	P(-1)	P2(1)/c
a (Å)	9.0464(6)	17.2935(9)	11.435(1)	17.7836(9)
b (Å)	16.3859(11)	20.5469(11)	15.818(1)	21.818(1)
c (Å)	28.9463(19)	23.7107(13)	19.206(2)	19.887(1)
α (°)	90	90	86.685(1)	90
β (°)	95.4910(10)	90	75.823(1)	100.504(1)
γ (°)	90	90	82.763(1)	90
Volume (Å^3)	4271.1(5)	8425.1(8)	3340.0(5)	7587.0(7)
Z	4	4	2	4
ρ_{calcd} (Mg m^{-3})	1.249	1.184	1.235	1.245
μ (mm^{-1})	0.144	0.105	0.464	0.941
F(000)	1696	3184	1290	2960
Crystal size (mm^3)	0.44x0.40x0.36	0.42x0.20x0.20	0.26x0.15x0.13	0.56x0.52x0.39
θ range (°)	2.58 to 25.03	2.08 to 25.03	2.58 to 25.03	2.08 to 25.03
Reflections collected	40610	97914	40680	90928
Independent reflections	7537 [*R*(int) = 0.0256]	7433 [*R*(int) = 0.1083]	11774 [*R*(int) = 0.0712]	13399 [*R*(int) = 0.0398]
Completeness to theta = 25.03°	99.9%	99.9%	99.7%	100%
Data / restraints / parameters	7537 / 0 / 538	7433 / 0 / 516	11774 / 1475 / 822	13399 / 0 / 877
Goodness-of-fit (GOF)	1.036	1.028	1.032	1.051
R indices [I>2σ(I)]	R_1 = 0.0350, wR_2 = 0.0863	R_1 = 0.0466, wR_2 = 0.1008	R_1 = 0.0662 wR_2 = 0.1554	R_1 = 0.0492 wR_2 = 0.1337
R indices (all data)	R_1 = 0.0420, wR_2 = 0.0912	R_1 = 0.0838, wR_2 = 0.1183	R_1 = 0.1351 wR_2 = 0.1883	R_1 = 0.0634 wR_2 = 0.1410
Largest diff. peak/hole (e Å^{-3})	0.279 and -0.318	0.196 and -0.317	0.557 and -0.895	1.017 and -0.767

Table 8.4. Crystallographic data for **12**·2C_6H_6, **15b**·$CHCl_3$, $\mathbf{L_2^{Mipp}}$·0.2CH_2Cl_2, and $\mathbf{L_2^{Tol}}$.

	12 · 2 C_6H_6	**15b·1.38 $CHCl_3$**	**L_2^{Mipp}·0.2 CH_2Cl_2**	**L_2^{Tol}**
Empirical formula	$C_{86}H_{77}BN_2O_3P_2Zn$ · 2 C_6H_6	$C_{84}H_{70}BF_{3.10}N_2O_{1.62}P_2Zn$ · 1.38 $CHCl_3$	$C_{54}H_{48}N_2OP_2$ · 0.2 CH_2Cl_2	$C_{50}H_{40}N_2OP_2$
Formula weight	1480.94	1494.99	819.87	746.78
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P-1	P2(1)/c
a (Å)	17.7836(9)	17.4192(12)	11.5434(11)	18.0198(9)
b (Å)	21.818(1)	21.5109(15)	14.8956(15)	14.0045(7)
c (Å)	19.887(1)	20.0888(14)	15.1659(15)	16.7584(9)
α (°)	90	90	62.3130(10)	90
β (°)	100.504(1)	99.3290(10)	86.1340(10)	109.6460(10)
γ (°)	90	90	78.1150(10)	90
Volume (Å^3)	7587.0(7)	7427.8(9)	2258.4(4)	3982.9(4)
Z	4	4	2	4
ρ_{calcd} (Mg m^{-3})	1.245	1.337	1.206	1.245
μ (mm^{-1})	0.941	0.580	0.161	0.150
F(000)	2784	3095	865	1568
Crystal size (mm^3)	0.56x0.52x0.39	0.93x0.41x0.17	0.58x0.22x0.13	0.46x0.25x0.21
θ range (°)	2.08 to 25.03	1.72 to 26.37	2.60 to 25.03	2.58 to 25.02
Reflections collected	90928	98561	26448	37535
Independent reflections	13399 [*R*(int) = 0.1224]	15188 [*R*(int) = 0.0256]	7960 [*R*(int) = 0.0611]	7010 [*R*(int) = 0.0267]
Completeness to theta = 25.03°	99.8%	100%	99.6%	99.8%
Data / restraints / parameters	13330 / 48 / 755	15188 / 48 / 994	7960 / 1 / 563	7010 / 0 / 498
Goodness-of-fit (GOF)	1.051	1.076	1.11	1.081
R indices [I>2σ(I)]	R_1 = 0.0492 wR_2 = 0.1337	R_1 = 0.0476, wR_2 = 0.1294	R_1 = 0.0646, wR_2 = 0.1472	R_1 = 0.0394, wR_2 = 0.1041
R indices (all data)	R_1 = 0.0634 wR_2 = 0.1410	R_1 = 0.0578, wR_2 = 0.1371	R_1 = 0.1432, wR_2 = 0.1827	R_1 = 0.0465, wR_2 = 0.1079
Largest diff. peak/hole (e Å^{-3})	0.880 and -0.434	1.388 and -0.645	0.690 and -0.308	0.533 and -0.585

Table 8.5. Crystallographic data for $\mathbf{L_2^{Pipp}}\cdot C_5H_{12}$, $\mathbf{L_2^{Ph}}\cdot C_6H_6$, **20b**$\cdot C_6H_6$, and **21b**.

	$\mathbf{L_2^{Pipp}\cdot C_5H_{12}}$	$\mathbf{L_2^{Ph}\cdot C_6H_6}$	$\mathbf{20b\cdot C_6H_6}$	**21b**
Empirical formula	$C_{54}H_{48}N_2OP_2 \cdot C_5H_{12}$	$C_{51}H_{39}N_2OP_2$	$C_{85}H_{77}BN_2OP_2Zn \cdot C_6H_6$	$C_{76.18}H_{63.47}BN_2OP_2Zn$
Formula weight	875.03	757.78	1280.61	1160.98
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	Pca2(1)	P-1	P-1	P-1
a (Å)	26.938(3)	9.373(11)	14.3702(7)	9.9214(8)
b (Å)	18.8282(18)	13.769(17)	15.2542(7)	17.1175(13)
c (Å)	10.2745(10)	17.95(2)	17.2588(8)	18.4747(14)
α (°)	90	104.285(15)	81.4510(10)	86.7540(10)
β (°)	90	90.990(14)	66.4690(10)	78.7250(10)
γ (°)	90	92.535(15)	76.8670(10)	80.8590(10)
Volume (Å^3)	5211.1(9)	2242(5)	3370.8(3)	3036.9(4)
Z	4	2	2	2
ρ_{calcd} (Mg m^{-3})	1.115	1.123	1.262	1.270
μ (mm^{-1})	0.123	0.134	0.462	0.505
F(000)	1864	794	1348	1215
Crystal size (mm^3)	0.49x0.15x0.14	0.27x0.12x0.08	0.60x0.50x0.19	0.42x0.21x0.04
θ range (°)	2.16 to 25.03	2.14 to 25.03	2.27 to 25.03	2.58 to 25.03
Reflections collected	61302	26495	32672	36687
Independent reflections	9201 [*R*(int) = 0.0504]	7900 [*R*(int) = 0.1176]	11879 [*R*(int) = 0.0203]	10686 [*R*(int) = 0.0643]
Completeness to theta = 25.03°	99.9%	99.7%	99.7%	99.7%
Data / restraints / parameters	9201 / 77 / 613	7900 / 0 / 433	11879 / 0 / 834	10686 / 84 / 784
Goodness-of-fit (GOF)	1.106	0.915	1.016	1.012
R indices [I>2σ(I)]	R_1 = 0.0517, wR_2 = 0.1195	R_1 = 0.0794, wR_2 = 0.1825	R_1 = 0.0302, wR_2 = 0.0785	R_1 = 0.0445, wR_2 = 0.0849
R indices (all data)	R_1 = 0.0602, wR_2 = 0.1238	R_1 = 0.1780, wR_2 = 0.2141	R_1 = 0.0370, wR_2 = 0.0825	R_1 = 0.0878, wR_2 = 0.0987
Largest diff. peak/hole (e Å^{-3})	0.265 and -0.177	0.236 and -0.238	0.337 and -0.287	0.338 and -0.327
Absolute Structure Param.	-0.01(9)			

Table 8.6. Crystallographic data for **22b**·2.5C_6H_6, **23c**·2C_2H_6, **24**·0.83CH_2Cl_2, and **25**·C_6H_6.

	22b · 2.5 C_6H_6	**23c · 2 C_6H_6**	**24**·0.83 CH_2Cl_2	**25 · C_6H_6**
Empirical formula	$C_{73}H_{85}BN_2OP_2Zn$ · 2.5 C_6H_6	$C_{80.65}H_{63.86}BN_2O$ P_2Zn · 2 C_6H_6	$C_{86}H_{59}BF_{24}N_2O_4$ P_2Zn·0.83 CH_2Cl_2	$C_{90}H_{67}BF_{24}N_2O_4$ P_2Zn · C_6H_6
Formula weight	1339.92	1371.44	1848.96	1912.68
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P2(1)/c
a (Å)	9.878(7)	9.9023(5)	11.4655(17)	19.0867(15)
b (Å)	17.426(11)	16.8670(9)	19.564(3)	26.603(2)
c (Å)	21.932(14)	20.7112(11)	19.662(3)	19.5381(15)
α (°)	80.235(8)	101.9740(10)	99.640(2)	90
β (°)	82.751(8)	91.1140(10)	103.416(2)	116.1330(10)
γ (°)	80.160(8)	95.2960(10)	92.916(2)	90
Volume (Å^3)	3647(4)	3366.9(3)	4210.9(11)	8906.6(12)
Z	2	2	2	4
ρ_{calcd} (Mg m^{-3})	1.095	1.199	1.458	1.426
μ (mm^{-1})	0.423	0.459	0.487	0.415
F(000)	1264	1270	1874	3904
Crystal size (mm^3)	0.58x0.40x0.14	0.45x0.38x0.21	0.35x0.07x0.05	0.27x0.15x0.09
θ range (°)	2.58 to 25.03	2.58 to 25.03	1.65 to 25.12	1.92 to 20.81
Reflections collected	44021	40833	41317	72717
Independent reflections	12848 [*R*(int) = 0.0270]	11870 [*R*(int) = 0.0212]	14955 [*R*(int) = 0.1034]	9322 [*R*(int) = 0.0803]
Completeness to theta = 25.03°	99.7%	99.7%	99.3%	99.9%
Data / restraints / parameters	12848 / 252 / 927	11870 / 0 / 829	14955 / 225 / 1170	9322 / 699 / 1298
Goodness-of-fit (GOF)	1.035	1.069	1.02	1.275
R indices [I>2σ(I)]	R_1 = 0.0507, wR_2 = 0.1231	R_1 = 0.0387, wR_2 = 0.1026	R_1 = 0.0785, wR_2 = 0.1742	R_1 = 0.0761, wR_2 = 0.1605
R indices (all data)	R_1 = 0.0621, wR_2 = 0.1284	R_1 = 0.0465, wR_2 = 0.1073	R_1 = 0.1704, wR_2 = 0.2148	R_1 = 0.0932, wR_2 = 0.1665
Largest diff. peak/hole (e Å^{-3})	0.536 and -0.525	0.684 and -0.421	0.724 and -0.665	0.486 and -0.424

Table 8.7. Crystallographic data for **26**·C_6H_5Br, $\mathbf{L_3}$ and **30**.

	26 · $C_6H_5Br_{0.38}$	$\mathbf{L_3}$	**30**
Empirical formula	$C_{84}H_{55}BF_{24}N_2O_4P_2Zn \cdot C_6H_5Br_{0.38}$	$C_{34}H_{40}N_2OP_2$	$C_{70}H_{59}BF_{24}N_2O_4P_2Zn$
Formula weight	1857.89	554.62	1586.31
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	P-1	P-1
a (Å)	18.7810(11)	10.8628(14)	15.0190(19)
b (Å)	27.1179(16)	11.1264(15)	15.4530(19)
c (Å)	18.6506(11)	13.9234(18)	16.072(2)
α (°)	90	72.3880(10)	104.9790(10)
β (°)	116.7850(10)	88.627(2)	101.2910(10)
γ (°)	90	69.7920(10)	95.3630(10)
Volume (Å^3)	8479.6(9) Å^3	1499.1(3)	3492.5(8)
Z	4	2	2
ρ_{calcd} (Mg m^{-3})	1.455 Mg/m^3	1.229	1.508
μ (mm^{-1})	0.612 mm^{-1}	0.174	0.512
F(000)	3761	592	1612
Crystal size (mm^3)	0.47x0.35x0.28	0.32x0.32x0.12	0.52x0.33x0.27
θ range (°)	2.56 to 25.03	2.05 to 26.37	2.66 to 26.37
Reflections collected	101702	20286	47147
Independent reflections	14960 [*R*(int) = 0.0443]	6118 [*R*(int) = 0.0225]	14217 [*R*(int) = 0.0184]
Completeness to theta = 25.03°	99.9%	99.6%	99.5%
Data / restraints / parameters	14960 / 815 / 1339	6118 / 0 / 356	14217 / 231 / 1056
Goodness-of-fit (GOF)	1.117	1.025	1.024
R indices [I>2σ(I)]	R_1 = 0.0613, wR_2 = 0.1516	R_1 = 0.0357, wR_2 = 0.0885	R_1 = 0.0340, wR_2 = 0.0868
R indices (all data)	R_1 = 0.0797, wR_2 = 0.1617	R_1 = 0.0445, wR_2 = 0.0940	R_1 = 0.0398, wR_2 = 0.0904
Largest diff. peak/hole (e Å^{-3})	0.852 and -0.636	0.393 and -0.296	0.660 and -0.427

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Appendix 1: Publications Arising from the Thesis

Portions of this thesis have been included in the publications listed below. The author's contributions make up the majority of publication 1, while the second author (Mr. Benjamin J. Ireland) played a supporting role with the preparation and characterization of the ligand. Publication 2 is a literature review that was primarily written by the author, for which Mr. Ireland is also credited with a supporting role. The contents of publication 3 are primarily the work of Mr. Ireland, but the author played a significant role, including the synthesis and characterization of $\mathbf{L_2^{Mes}}$ and all crystallographic studies ($\mathbf{L_2^{Mes}}$, **9**, and the magnesium complex [$\mathbf{L_2^{Mes}}$·Mg^{n}Bu$^+$] [BPh_4^-]), and also a supporting role in manuscript preparation. The author was responsible for all material presented in publications 4 and 5. Additionally, the work presented in this thesis has led directly to the pursuit of American and Canadian patents, for which provisional status has been granted.

Publications

1) Wheaton, C. A.; Ireland, B. J.; Hayes, P. G., Activated Zinc Complexes Supported by a Neutral, Phosphinimine-Containing Ligand: Synthesis and Efficacy for the Polymerization of Lactide. *Organometallics* **2009**, *28*, 1282-1285.

2) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J., Complexes of Mg, Ca and Zn as homogeneous catalysts for lactide polymerization. *Dalton Trans.* **2009**, 4832-4846.

3) Ireland, B. J.; Wheaton, C. A.; Hayes, P. G., Cationic Organomagnesium Complexes as Highly Active Initiators for the Ring-Opening Polymerization of epsilon-Caprolactone. *Organometallics* **2010**, *29*, 1079-1084.

4) Wheaton, C. A.; Hayes, P. G., Cationic organozinc complexes of a bis(phosphinimine) pincer ligand: synthesis, structural and polymerization studies. *Dalton Trans.* **2010**, *39*, 3861-3869.

5) Wheaton, C. A.; Hayes, P. G., Cationic zinc complexes: a new class of catalyst for living lactide polymerization at ambient temperature. *Chem. Commun.* **2010**, *46*, 8404-8406.

Published Patent Applications

1) P. G. Hayes and C. A. Wheaton, "Catalysts for the polymerization of cyclic esters", US Patent No. 20100130753, filed Nov. 24, 2009.

2) P. G. Hayes and C. A. Wheaton, "Catalysts for the polymerization of cyclic esters", Canadian Patent No. CA 2686355, filed Nov. 24, 2009.

Appendix 2: Crystallographic Data Tables, Atomic Coordinates, Anisotropic Displacement Parameters and Metrical Data

Table A.1: Crystal data and structure refinement for $\mathbf{L_1^{Dipp}}$.

Empirical formula	$C_{36}H_{34}NOP$	
Formula weight	527.61	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.1269(7) Å	α= 90°.
	b = 17.6285(11) Å	β= 90°.
	c = 29.3704(18) Å	γ = 90°.
Volume	5761.0(6) $Å^3$	
Z	8	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	2240	
Crystal size	0.25 x 0.21 x 0.17 mm^3	
Theta range for data collection	2.57 to 25.03°.	
Index ranges	-13<=h<=13, -20<=k<=20, -34<=l<=34	
Reflections collected	52904	
Independent reflections	5077 [R(int) = 0.0618]	
Completeness to theta = 25.03°	1.00	
Max. and min. transmission	0.9792 and 0.9693	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5077 / 0 / 356	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1115	
R indices (all data)	R1 = 0.0657, wR2 = 0.1202	
Largest diff. peak and hole	0.382 and -0.322 $e.Å^{-3}$	

Table A.2: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_1^{Dipp}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	168(1)	698(1)	3745(1)	25(1)	C(18)	1964(2)	65(1)	3172(1)	37(1)
O(1)	203(1)	-1102(1)	3681(1)	33(1)	C(19)	1328(2)	541(1)	4167(1)	27(1)
N(1)	-424(2)	1500(1)	3748(1)	29(1)	C(20)	2348(2)	997(1)	4147(1)	35(1)
C(1)	-879(2)	-756(1)	3765(1)	27(1)	C(21)	3245(2)	929(2)	4469(1)	45(1)
C(2)	-1022(2)	20(1)	3829(1)	27(1)	C(22)	3112(3)	418(2)	4823(1)	46(1)
C(3)	-2186(2)	259(1)	3924(1)	31(1)	C(23)	2093(3)	-23(2)	4852(1)	43(1)
C(4)	-3145(2)	-248(1)	3945(1)	34(1)	C(24)	1203(2)	34(1)	4525(1)	34(1)

C(5)	-2976(2)	-1013(1)	3866(1)	33(1)	C(25)	131(2)	2196(1)	3855(1)	26(1)
C(6)	-1829(2)	-1272(1)	3773(1)	28(1)	C(26)	534(2)	2683(1)	3505(1)	28(1)
C(7)	-1298(2)	-1997(1)	3667(1)	30(1)	C(27)	1062(2)	3370(1)	3623(1)	34(1)
C(8)	-1722(2)	-2734(1)	3601(1)	37(1)	C(28)	1183(2)	3594(1)	4069(1)	36(1)
C(9)	-900(3)	-3292(2)	3493(1)	41(1)	C(29)	732(2)	3132(1)	4411(1)	33(1)
C(10)	316(3)	-3135(2)	3455(1)	41(1)	C(30)	202(2)	2435(1)	4314(1)	27(1)
C(11)	765(2)	-2413(1)	3523(1)	37(1)	C(31)	367(2)	2481(1)	3005(1)	36(1)
C(12)	-75(2)	-1863(1)	3621(1)	31(1)	C(32)	-387(3)	3076(2)	2762(1)	65(1)
C(13)	834(2)	397(1)	3207(1)	28(1)	C(33)	1541(3)	2356(2)	2766(1)	64(1)
C(14)	153(2)	494(1)	2816(1)	36(1)	C(34)	-353(2)	1971(1)	4693(1)	32(1)
C(15)	603(3)	271(2)	2397(1)	44(1)	C(35)	347(3)	1968(2)	5133(1)	49(1)
C(16)	1725(3)	-42(2)	2366(1)	47(1)	C(36)	-1642(2)	2234(2)	4775(1)	49(1)
C(17)	2401(3)	-154(2)	2750(1)	46(1)					

Table A.3: Bond lengths [Å] for $\mathbf{L_1}^{\mathbf{Dipp}}$.

P(1)-N(1)	1.5594(19)	C(11)-H(11)	0.9500	C(26)-C(31)	1.520(3)
P(1)-C(2)	1.801(2)	C(13)-C(14)	1.387(3)	C(27)-C(28)	1.374(3)
P(1)-C(19)	1.811(2)	C(13)-C(18)	1.390(3)	C(27)-H(27)	0.9500
P(1)-C(13)	1.825(2)	C(14)-C(15)	1.385(4)	C(28)-C(29)	1.386(3)
O(1)-C(1)	1.371(3)	C(14)-H(14)	0.9500	C(28)-H(28)	0.9500
O(1)-C(12)	1.389(3)	C(15)-C(16)	1.368(4)	C(29)-C(30)	1.392(3)
N(1)-C(25)	1.409(3)	C(15)-H(15)	0.9500	C(29)-H(29)	0.9500
C(1)-C(2)	1.390(3)	C(16)-C(17)	1.370(4)	C(30)-C(34)	1.514(3)
C(1)-C(6)	1.395(3)	C(16)-H(16)	0.9500	C(31)-C(33)	1.500(4)
C(2)-C(3)	1.389(3)	C(17)-C(18)	1.386(4)	C(31)-C(32)	1.522(4)
C(3)-C(4)	1.394(3)	C(17)-H(17)	0.9500	C(31)-H(31)	1.0000
C(3)-H(3)	0.9500	C(18)-H(18)	0.9500	C(32)-H(32A)	0.9800
C(4)-C(5)	1.381(3)	C(19)-C(24)	1.386(3)	C(32)-H(32B)	0.9800
C(4)-H(4)	0.9500	C(19)-C(20)	1.393(3)	C(32)-H(32C)	0.9800
C(5)-C(6)	1.383(3)	C(20)-C(21)	1.380(4)	C(33)-H(33A)	0.9800
C(5)-H(5)	0.9500	C(20)-H(20)	0.9500	C(33)-H(33B)	0.9800
C(6)-C(7)	1.442(3)	C(21)-C(22)	1.384(4)	C(33)-H(33C)	0.9800
C(7)-C(12)	1.388(3)	C(21)-H(21)	0.9500	C(34)-C(35)	1.509(4)
C(7)-C(8)	1.396(3)	C(22)-C(23)	1.378(4)	C(34)-C(36)	1.526(4)
C(8)-C(9)	1.379(4)	C(22)-H(22)	0.9500	C(34)-H(34)	1.0000
C(8)-H(8)	0.9500	C(23)-C(24)	1.384(4)	C(35)-H(35A)	0.9800
C(9)-C(10)	1.385(4)	C(23)-H(23)	0.9500	C(35)-H(35B)	0.9800
C(9)-H(9)	0.9500	C(24)-H(24)	0.9500	C(35)-H(35C)	0.9800
C(10)-C(11)	1.382(4)	C(25)-C(26)	1.414(3)	C(36)-H(36A)	0.9800
C(10)-H(10)	0.9500	C(25)-C(30)	1.415(3)	C(36)-H(36B)	0.9800
C(11)-C(12)	1.377(3)	C(26)-C(27)	1.391(3)	C(36)-H(36C)	0.9800

Table A.4: Bond angles [°] for $\mathbf{L_1^{Dipp}}$

N(1)-P(1)-C(2)	106.86(11)	C(14)-C(13)-P(1)	117.35(19)	C(27)-C(28)-H(28)	120.5
N(1)-P(1)-C(19)	115.84(10)	C(18)-C(13)-P(1)	123.70(19)	C(29)-C(28)-H(28)	120.5
C(2)-P(1)-C(19)	109.19(10)	C(15)-C(14)-C(13)	120.2(3)	C(28)-C(29)-C(30)	121.6(2)
N(1)-P(1)-C(13)	116.17(11)	C(15)-C(14)-H(14)	119.9	C(28)-C(29)-H(29)	119.2
C(2)-P(1)-C(13)	102.95(10)	C(13)-C(14)-H(14)	119.9	C(30)-C(29)-H(29)	119.2
C(19)-P(1)-C(13)	104.98(11)	C(16)-C(15)-C(14)	120.3(3)	C(29)-C(30)-C(25)	118.8(2)
C(1)-O(1)-C(12)	104.91(18)	C(16)-C(15)-H(15)	119.9	C(29)-C(30)-C(34)	120.0(2)
C(25)-N(1)-P(1)	127.21(16)	C(14)-C(15)-H(15)	119.9	C(25)-C(30)-C(34)	121.1(2)
O(1)-C(1)-C(2)	124.2(2)	C(15)-C(16)-C(17)	120.3(3)	C(33)-C(31)-C(26)	112.4(2)
O(1)-C(1)-C(6)	112.21(19)	C(15)-C(16)-H(16)	119.9	C(33)-C(31)-C(32)	111.1(3)
C(2)-C(1)-C(6)	123.6(2)	C(17)-C(16)-H(16)	119.9	C(26)-C(31)-C(32)	111.0(2)
C(3)-C(2)-C(1)	115.6(2)	C(16)-C(17)-C(18)	120.2(3)	C(33)-C(31)-H(31)	107.4
C(3)-C(2)-P(1)	120.74(18)	C(16)-C(17)-H(17)	119.9	C(26)-C(31)-H(31)	107.4
C(1)-C(2)-P(1)	123.38(18)	C(18)-C(17)-H(17)	119.9	C(32)-C(31)-H(31)	107.4
C(2)-C(3)-C(4)	121.8(2)	C(17)-C(18)-C(13)	120.1(2)	C(31)-C(32)-H(32A)	109.5
C(2)-C(3)-H(3)	119.1	C(17)-C(18)-H(18)	120.0	C(31)-C(32)-H(32B)	109.5
C(4)-C(3)-H(3)	119.1	C(13)-C(18)-H(18)	120.0	H(32A)-C(32)-H(32B)	109.5
C(5)-C(4)-C(3)	121.0(2)	C(24)-C(19)-C(20)	119.1(2)	C(31)-C(32)-H(32C)	109.5
C(5)-C(4)-H(4)	119.5	C(24)-C(19)-P(1)	123.09(19)	H(32A)-C(32)-H(32C)	109.5
C(3)-C(4)-H(4)	119.5	C(20)-C(19)-P(1)	117.59(18)	H(32B)-C(32)-H(32C)	109.5
C(4)-C(5)-C(6)	118.8(2)	C(21)-C(20)-C(19)	120.6(2)	C(31)-C(33)-H(33A)	109.5
C(4)-C(5)-H(5)	120.6	C(21)-C(20)-H(20)	119.7	C(31)-C(33)-H(33B)	109.5
C(6)-C(5)-H(5)	120.6	C(19)-C(20)-H(20)	119.7	H(33A)-C(33)-H(33B)	109.5
C(5)-C(6)-C(1)	119.1(2)	C(20)-C(21)-C(22)	119.7(3)	C(31)-C(33)-H(33C)	109.5
C(5)-C(6)-C(7)	135.5(2)	C(20)-C(21)-H(21)	120.2	H(33A)-C(33)-H(33C)	109.5
C(1)-C(6)-C(7)	105.4(2)	C(22)-C(21)-H(21)	120.2	H(33B)-C(33)-H(33C)	109.5
C(12)-C(7)-C(8)	118.4(2)	C(23)-C(22)-C(21)	120.1(3)	C(35)-C(34)-C(30)	114.9(2)
C(12)-C(7)-C(6)	105.8(2)	C(23)-C(22)-H(22)	119.9	C(35)-C(34)-C(36)	110.6(2)
C(8)-C(7)-C(6)	135.8(2)	C(21)-C(22)-H(22)	119.9	C(30)-C(34)-C(36)	109.6(2)
C(9)-C(8)-C(7)	118.1(2)	C(22)-C(23)-C(24)	120.3(3)	C(35)-C(34)-H(34)	107.1
C(9)-C(8)-H(8)	120.9	C(22)-C(23)-H(23)	119.8	C(30)-C(34)-H(34)	107.1
C(7)-C(8)-H(8)	120.9	C(24)-C(23)-H(23)	119.8	C(36)-C(34)-H(34)	107.1
C(8)-C(9)-C(10)	121.6(2)	C(23)-C(24)-C(19)	120.1(2)	C(34)-C(35)-H(35A)	109.5
C(8)-C(9)-H(9)	119.2	C(23)-C(24)-H(24)	119.9	C(34)-C(35)-H(35B)	109.5
C(10)-C(9)-H(9)	119.2	C(19)-C(24)-H(24)	119.9	H(35A)-C(35)-H(35B)	109.5
C(11)-C(10)-C(9)	121.7(2)	N(1)-C(25)-C(26)	120.4(2)	C(34)-C(35)-H(35C)	109.5
C(11)-C(10)-H(10)	119.1	N(1)-C(25)-C(30)	119.8(2)	H(35A)-C(35)-H(35C)	109.5
C(9)-C(10)-H(10)	119.1	C(26)-C(25)-C(30)	119.7(2)	H(35B)-C(35)-H(35C)	109.5
C(12)-C(11)-C(10)	115.6(2)	C(27)-C(26)-C(25)	118.7(2)	C(34)-C(36)-H(36A)	109.5
C(12)-C(11)-H(11)	122.2	C(27)-C(26)-C(31)	119.8(2)	C(34)-C(36)-H(36B)	109.5
C(10)-C(11)-H(11)	122.2	C(25)-C(26)-C(31)	121.4(2)	H(36A)-C(36)-H(36B)	109.5
C(11)-C(12)-C(7)	124.5(2)	C(28)-C(27)-C(26)	122.0(2)	C(34)-C(36)-H(36C)	109.5

C(11)-C(12)-O(1)	123.8(2)	C(28)-C(27)-H(27)	119.0	H(36A)-C(36)-H(36C)	109.5
C(7)-C(12)-O(1)	111.7(2)	C(26)-C(27)-H(27)	119.0	H(36B)-C(36)-H(36C)	109.5
C(14)-C(13)-C(18)	118.9(2)	C(27)-C(28)-C(29)	119.0(2)		

Table A.5: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_1^{Dipp}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	27(1)	22(1)	26(1)	0(1)	0(1)	-2(1)
O(1)	30(1)	27(1)	40(1)	0(1)	4(1)	-1(1)
N(1)	28(1)	24(1)	33(1)	0(1)	-2(1)	-3(1)
C(1)	28(1)	28(1)	25(1)	1(1)	1(1)	-1(1)
C(2)	31(1)	26(1)	24(1)	0(1)	-2(1)	-5(1)
C(3)	33(1)	30(1)	29(1)	0(1)	0(1)	-1(1)
C(4)	28(1)	40(1)	33(1)	2(1)	3(1)	0(1)
C(5)	31(1)	36(1)	32(1)	2(1)	0(1)	-9(1)
C(6)	35(1)	27(1)	23(1)	1(1)	-2(1)	-4(1)
C(7)	35(1)	31(1)	25(1)	1(1)	1(1)	-3(1)
C(8)	40(2)	33(1)	39(1)	-2(1)	4(1)	-9(1)
C(9)	49(2)	28(1)	46(2)	-4(1)	6(1)	-5(1)
C(10)	43(2)	31(1)	49(2)	-3(1)	1(1)	3(1)
C(11)	36(1)	34(1)	43(2)	0(1)	1(1)	-1(1)
C(12)	37(1)	25(1)	30(1)	0(1)	-1(1)	-3(1)
C(13)	36(1)	21(1)	27(1)	0(1)	3(1)	-6(1)
C(14)	43(2)	30(1)	34(1)	0(1)	-4(1)	0(1)
C(15)	61(2)	41(2)	29(1)	0(1)	-4(1)	-5(1)
C(16)	64(2)	45(2)	33(2)	-3(1)	13(1)	-4(2)
C(17)	47(2)	47(2)	44(2)	2(1)	14(1)	6(1)
C(18)	41(2)	34(1)	34(1)	4(1)	6(1)	5(1)
C(19)	31(1)	26(1)	25(1)	-4(1)	1(1)	1(1)
C(20)	34(1)	37(1)	35(1)	-1(1)	-2(1)	-4(1)
C(21)	35(2)	53(2)	47(2)	-9(1)	-6(1)	-5(1)
C(22)	44(2)	60(2)	35(2)	-7(1)	-14(1)	10(1)
C(23)	51(2)	48(2)	30(1)	3(1)	-2(1)	5(1)
C(24)	38(1)	33(1)	30(1)	-3(1)	1(1)	1(1)
C(25)	21(1)	24(1)	32(1)	-1(1)	-4(1)	2(1)
C(26)	26(1)	24(1)	34(1)	-1(1)	-2(1)	1(1)
C(27)	34(1)	28(1)	40(1)	5(1)	1(1)	-4(1)
C(28)	38(1)	26(1)	45(2)	-4(1)	-6(1)	-6(1)
C(29)	35(1)	34(1)	32(1)	-7(1)	-7(1)	1(1)
C(30)	24(1)	26(1)	32(1)	-1(1)	-1(1)	5(1)
C(31)	48(2)	32(1)	30(1)	1(1)	0(1)	-5(1)
C(32)	83(2)	61(2)	51(2)	1(2)	-27(2)	7(2)
C(33)	62(2)	86(2)	44(2)	-13(2)	7(2)	-7(2)

C(34)	35(1)	31(1)	30(1)	-4(1)	2(1)	2(1)
C(35)	54(2)	56(2)	36(2)	10(1)	-6(1)	-9(2)
C(36)	38(2)	56(2)	53(2)	-2(1)	11(1)	2(1)

Table A.6: Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{34}Cl_2NOPZn$	
Formula weight	663.88	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3247(4) Å	α= 78.32°.
	b = 10.7683(4) Å	β= 83.58°.
	c = 16.9837(7) Å	γ = 75.89°.
Volume	1616.14(11) Å3	
Z	2	
Density (calculated)	1.364 Mg/m3	
Absorption coefficient	1.004 mm-1	
F(000)	688	
Crystal size	0.39 x 0.32 x 0.25 mm3	
Theta range for data collection	2.64 to 26.37°.	
Index ranges	-11<=h<=11, -13<=k<=13, -21<=l<=21	
Reflections collected	17389	
Independent reflections	6576 [R(int) = 0.0115]	
Completeness to theta = 26.37°	99.20%	
Max. and min. transmission	0.7903 and 0.6973	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	6576 / 0 / 383	
Goodness-of-fit on F2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0223, wR2 = 0.0612	
R indices (all data)	R1 = 0.0238, wR2 = 0.0620	
Largest diff. peak and hole	0.394 and -0.251 e.Å-3	

Table A.7: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	858(1)	2789(1)	2819(1)	22(1)	C(16)	7959(2)	-1794(1)	2456(1)	32(1)
P(1)	4138(1)	1819(1)	2102(1)	17(1)	C(17)	7935(2)	-771(2)	2838(1)	31(1)
Cl(1)	422(1)	4861(1)	2254(1)	39(1)	C(18)	6770(2)	325(1)	2745(1)	25(1)
O(1)	2590(1)	2809(1)	3744(1)	22(1)	C(19)	4323(2)	2511(1)	1040(1)	22(1)
C(1)	2208(2)	3392(1)	4428(1)	23(1)	C(20)	5489(2)	1993(2)	529(1)	31(1)
N(1)	2543(1)	1529(1)	2428(1)	19(1)	C(21)	5585(2)	2565(2)	-279(1)	42(1)
Cl(2)	-988(1)	2089(1)	3505(1)	33(1)	C(22)	4537(2)	3647(2)	-576(1)	43(1)
C(2)	1170(2)	3075(1)	5029(1)	28(1)	C(23)	3382(2)	4174(2)	-73(1)	43(1)
C(3)	963(2)	3747(2)	5668(1)	31(1)	C(24)	3268(2)	3617(2)	735(1)	32(1)
C(4)	1764(2)	4676(2)	5686(1)	31(1)	C(25)	2283(1)	260(1)	2419(1)	21(1)

C(5)	2797(2)	4974(1)	5070(1)	28(1)	C(26)	1616(2)	79(1)	1761(1)	27(1)
C(6)	3036(2)	4304(1)	4425(1)	23(1)	C(27)	1425(2)	-1172(2)	1757(1)	37(1)
C(7)	4035(2)	4276(1)	3704(1)	21(1)	C(28)	1856(2)	-2190(2)	2383(1)	41(1)
C(8)	5154(2)	4909(1)	3370(1)	24(1)	C(29)	2443(2)	-1978(1)	3039(1)	36(1)
C(9)	5947(2)	4583(1)	2672(1)	25(1)	C(30)	2670(2)	-759(1)	3078(1)	26(1)
C(10)	5604(2)	3668(1)	2296(1)	23(1)	C(31)	1071(2)	1190(2)	1082(1)	31(1)
C(11)	4470(1)	3023(1)	2608(1)	19(1)	C(32)	1747(2)	916(2)	254(1)	50(1)
C(12)	3724(1)	3346(1)	3322(1)	20(1)	C(33)	-627(2)	1522(2)	1102(1)	44(1)
C(13)	5631(1)	395(1)	2260(1)	21(1)	C(34)	3279(2)	-568(1)	3828(1)	31(1)
C(14)	5664(2)	-644(1)	1873(1)	25(1)	C(35)	2079(2)	-481(2)	4519(1)	51(1)
C(15)	6827(2)	-1735(1)	1975(1)	30(1)	C(36)	4635(2)	-1637(2)	4107(1)	41(1)

Table A.8: Bond lengths [Å] for **1**.

Zn(1)-N(1)	1.9604(11)	C(10)-C(11)	1.4021(18)	C(26)-C(27)	1.403(2)
Zn(1)-Cl(2)	2.1712(4)	C(10)-H(10)	0.9500	C(26)-C(31)	1.514(2)
Zn(1)-Cl(1)	2.2002(4)	C(11)-C(12)	1.3932(18)	C(27)-C(28)	1.379(3)
Zn(1)-O(1)	2.3808(9)	C(13)-C(18)	1.3937(19)	C(27)-H(27)	0.9500
P(1)-N(1)	1.6088(11)	C(13)-C(14)	1.4008(19)	C(28)-C(29)	1.377(3)
P(1)-C(11)	1.7942(13)	C(14)-C(15)	1.387(2)	C(28)-H(28)	0.9500
P(1)-C(13)	1.7988(13)	C(14)-H(14)	0.9500	C(29)-C(30)	1.395(2)
P(1)-C(19)	1.8138(13)	C(15)-C(16)	1.387(2)	C(29)-H(29)	0.9500
O(1)-C(12)	1.3876(16)	C(15)-H(15)	0.9500	C(30)-C(34)	1.520(2)
O(1)-C(1)	1.4021(15)	C(16)-C(17)	1.381(2)	C(31)-C(32)	1.530(2)
C(1)-C(2)	1.376(2)	C(16)-H(16)	0.9500	C(31)-C(33)	1.534(2)
C(1)-C(6)	1.3883(19)	C(17)-C(18)	1.392(2)	C(31)-H(31)	1.0000
N(1)-C(25)	1.4484(16)	C(17)-H(17)	0.9500	C(32)-H(32A)	0.9800
C(2)-C(3)	1.393(2)	C(18)-H(18)	0.9500	C(32)-H(32B)	0.9800
C(2)-H(2)	0.9500	C(19)-C(20)	1.391(2)	C(32)-H(32C)	0.9800
C(3)-C(4)	1.394(2)	C(19)-C(24)	1.395(2)	C(33)-H(33A)	0.9800
C(3)-H(3)	0.9500	C(20)-C(21)	1.388(2)	C(33)-H(33B)	0.9800
C(4)-C(5)	1.383(2)	C(20)-H(20)	0.9500	C(33)-H(33C)	0.9800
C(4)-H(4)	0.9500	C(21)-C(22)	1.373(3)	C(34)-C(35)	1.529(2)
C(5)-C(6)	1.3992(18)	C(21)-H(21)	0.9500	C(34)-C(36)	1.534(2)
C(5)-H(5)	0.9500	C(22)-C(23)	1.380(3)	C(34)-H(34)	1.0000
C(6)-C(7)	1.4543(19)	C(22)-H(22)	0.9500	C(35)-H(35A)	0.9800
C(7)-C(8)	1.3900(19)	C(23)-C(24)	1.386(2)	C(35)-H(35B)	0.9800
C(7)-C(12)	1.3981(18)	C(23)-H(23)	0.9500	C(35)-H(35C)	0.9800
C(8)-C(9)	1.386(2)	C(24)-H(24)	0.9500	C(36)-H(36A)	0.9800
C(8)-H(8)	0.9500	C(25)-C(26)	1.4058(19)	C(36)-H(36B)	0.9800
C(9)-C(10)	1.3914(19)	C(25)-C(30)	1.409(2)	C(36)-H(36C)	0.9800
C(9)-H(9)	0.9500				

Table A.9: Bond angles [°] for **1**

N(1)-Zn(1)-Cl(2)	118.95(3)	C(12)-C(11)-C(10)	115.67(12)	C(28)-C(27)-C(26)	121.31(15)
N(1)-Zn(1)-Cl(1)	120.88(3)	C(12)-C(11)-P(1)	125.14(10)	C(28)-C(27)-H(27)	119.3
Cl(2)-Zn(1)-Cl(1)	116.811(16)	C(10)-C(11)-P(1)	119.13(10)	C(26)-C(27)-H(27)	119.3
N(1)-Zn(1)-O(1)	81.87(4)	O(1)-C(12)-C(11)	125.41(11)	C(29)-C(28)-C(27)	119.91(14)
Cl(2)-Zn(1)-O(1)	108.04(2)	O(1)-C(12)-C(7)	111.33(11)	C(29)-C(28)-H(28)	120.0
Cl(1)-Zn(1)-O(1)	98.59(3)	C(11)-C(12)-C(7)	123.26(12)	C(27)-C(28)-H(28)	120.0
N(1)-P(1)-C(11)	108.47(6)	C(18)-C(13)-C(14)	119.68(12)	C(28)-C(29)-C(30)	121.58(15)
N(1)-P(1)-C(13)	113.23(6)	C(18)-C(13)-P(1)	121.02(10)	C(28)-C(29)-H(29)	119.2
C(11)-P(1)-C(13)	109.10(6)	C(14)-C(13)-P(1)	119.28(10)	C(30)-C(29)-H(29)	119.2
N(1)-P(1)-C(19)	115.62(6)	C(15)-C(14)-C(13)	119.84(13)	C(29)-C(30)-C(25)	117.87(14)
C(11)-P(1)-C(19)	104.40(6)	C(15)-C(14)-H(14)	120.1	C(29)-C(30)-C(34)	119.40(14)
C(13)-P(1)-C(19)	105.54(6)	C(13)-C(14)-H(14)	120.1	C(25)-C(30)-C(34)	122.70(12)
C(12)-O(1)-C(1)	105.58(10)	C(14)-C(15)-C(16)	120.09(14)	C(26)-C(31)-C(32)	112.72(14)
C(12)-O(1)-Zn(1)	108.82(7)	C(14)-C(15)-H(15)	120.0	C(26)-C(31)-C(33)	110.54(13)
C(1)-O(1)-Zn(1)	123.85(8)	C(16)-C(15)-H(15)	120.0	C(32)-C(31)-C(33)	110.85(14)
C(2)-C(1)-C(6)	124.84(13)	C(17)-C(16)-C(15)	120.37(13)	C(26)-C(31)-H(31)	107.5
C(2)-C(1)-O(1)	124.07(12)	C(17)-C(16)-H(16)	119.8	C(32)-C(31)-H(31)	107.5
C(6)-C(1)-O(1)	111.08(11)	C(15)-C(16)-H(16)	119.8	C(33)-C(31)-H(31)	107.5
C(25)-N(1)-P(1)	118.96(8)	C(16)-C(17)-C(18)	120.12(14)	C(31)-C(32)-H(32A)	109.5
C(25)-N(1)-Zn(1)	115.96(8)	C(16)-C(17)-H(17)	119.9	C(31)-C(32)-H(32B)	109.5
P(1)-N(1)-Zn(1)	125.06(6)	C(18)-C(17)-H(17)	119.9	H(32A)-C(32)-H(32B)	109.5
C(1)-C(2)-C(3)	115.59(14)	C(17)-C(18)-C(13)	119.89(13)	C(31)-C(32)-H(32C)	109.5
C(1)-C(2)-H(2)	122.2	C(17)-C(18)-H(18)	120.1	H(32A)-C(32)-H(32C)	109.5
C(3)-C(2)-H(2)	122.2	C(13)-C(18)-H(18)	120.1	H(32B)-C(32)-H(32C)	109.5
C(2)-C(3)-C(4)	121.43(14)	C(20)-C(19)-C(24)	119.45(13)	C(31)-C(33)-H(33A)	109.5
C(2)-C(3)-H(3)	119.3	C(20)-C(19)-P(1)	122.27(11)	C(31)-C(33)-H(33B)	109.5
C(4)-C(3)-H(3)	119.3	C(24)-C(19)-P(1)	118.27(11)	H(33A)-C(33)-H(33B)	109.5
C(5)-C(4)-C(3)	121.48(13)	C(21)-C(20)-C(19)	120.01(15)	C(31)-C(33)-H(33C)	109.5
C(5)-C(4)-H(4)	119.3	C(21)-C(20)-H(20)	120.0	H(33A)-C(33)-H(33C)	109.5
C(3)-C(4)-H(4)	119.3	C(19)-C(20)-H(20)	120.0	H(33B)-C(33)-H(33C)	109.5
C(4)-C(5)-C(6)	118.23(14)	C(22)-C(21)-C(20)	120.25(15)	C(30)-C(34)-C(35)	110.79(14)
C(4)-C(5)-H(5)	120.9	C(22)-C(21)-H(21)	119.9	C(30)-C(34)-C(36)	113.29(13)
C(6)-C(5)-H(5)	120.9	C(20)-C(21)-H(21)	119.9	C(35)-C(34)-C(36)	109.44(13)
C(1)-C(6)-C(5)	118.43(13)	C(21)-C(22)-C(23)	120.22(15)	C(30)-C(34)-H(34)	107.7
C(1)-C(6)-C(7)	106.20(11)	C(21)-C(22)-H(22)	119.9	C(35)-C(34)-H(34)	107.7
C(5)-C(6)-C(7)	135.33(13)	C(23)-C(22)-H(22)	119.9	C(36)-C(34)-H(34)	107.7
C(8)-C(7)-C(12)	119.37(12)	C(22)-C(23)-C(24)	120.36(16)	C(34)-C(35)-H(35A)	109.5
C(8)-C(7)-C(6)	134.84(12)	C(22)-C(23)-H(23)	119.8	C(34)-C(35)-H(35B)	109.5
C(12)-C(7)-C(6)	105.77(12)	C(24)-C(23)-H(23)	119.8	H(35A)-C(35)-H(35B)	109.5
C(9)-C(8)-C(7)	118.84(12)	C(23)-C(24)-C(19)	119.71(15)	C(34)-C(35)-H(35C)	109.5
C(9)-C(8)-H(8)	120.6	C(23)-C(24)-H(24)	120.1	H(35A)-C(35)-H(35C)	109.5
C(7)-C(8)-H(8)	120.6	C(19)-C(24)-H(24)	120.1	H(35B)-C(35)-H(35C)	109.5

C(8)-C(9)-C(10)	120.80(13)	C(26)-C(25)-C(30)	121.38(12)	C(34)-C(36)-H(36A)	109.5
C(8)-C(9)-H(9)	119.6	C(26)-C(25)-N(1)	119.25(12)	C(34)-C(36)-H(36B)	109.5
C(10)-C(9)-H(9)	119.6	C(30)-C(25)-N(1)	119.35(12)	H(36A)-C(36)-H(36B)	109.5
C(9)-C(10)-C(11)	122.02(13)	C(27)-C(26)-C(25)	117.82(14)	C(34)-C(36)-H(36C)	109.5
C(9)-C(10)-H(10)	119.0	C(27)-C(26)-C(31)	120.03(14)	H(36A)-C(36)-H(36C)	109.5
C(11)-C(10)-H(10)	119.0	C(25)-C(26)-C(31)	122.13(12)	H(36B)-C(36)-H(36C)	109.5

Table A.10: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	20(1)	19(1)	28(1)	-8(1)	1(1)	-4(1)
P(1)	19(1)	16(1)	18(1)	-5(1)	0(1)	-4(1)
Cl(1)	42(1)	19(1)	50(1)	-5(1)	7(1)	-2(1)
O(1)	24(1)	24(1)	21(1)	-9(1)	2(1)	-9(1)
C(1)	24(1)	24(1)	20(1)	-8(1)	-4(1)	-1(1)
N(1)	19(1)	15(1)	22(1)	-6(1)	0(1)	-5(1)
Cl(2)	25(1)	38(1)	38(1)	-7(1)	3(1)	-12(1)
C(2)	27(1)	31(1)	25(1)	-6(1)	-2(1)	-6(1)
C(3)	29(1)	39(1)	22(1)	-7(1)	-1(1)	1(1)
C(4)	34(1)	36(1)	24(1)	-13(1)	-7(1)	3(1)
C(5)	31(1)	26(1)	27(1)	-11(1)	-9(1)	-1(1)
C(6)	24(1)	22(1)	22(1)	-6(1)	-7(1)	-1(1)
C(7)	23(1)	19(1)	22(1)	-5(1)	-7(1)	-2(1)
C(8)	28(1)	19(1)	29(1)	-4(1)	-10(1)	-7(1)
C(9)	25(1)	22(1)	30(1)	-1(1)	-5(1)	-10(1)
C(10)	24(1)	20(1)	24(1)	-3(1)	-1(1)	-6(1)
C(11)	21(1)	16(1)	21(1)	-4(1)	-3(1)	-5(1)
C(12)	20(1)	17(1)	22(1)	-3(1)	-4(1)	-4(1)
C(13)	19(1)	19(1)	22(1)	-4(1)	2(1)	-4(1)
C(14)	25(1)	24(1)	28(1)	-8(1)	0(1)	-5(1)
C(15)	31(1)	22(1)	37(1)	-10(1)	4(1)	-4(1)
C(16)	26(1)	24(1)	39(1)	-2(1)	2(1)	2(1)
C(17)	24(1)	30(1)	37(1)	-2(1)	-7(1)	-3(1)
C(18)	24(1)	23(1)	27(1)	-4(1)	-2(1)	-5(1)
C(19)	26(1)	23(1)	19(1)	-4(1)	-2(1)	-9(1)
C(20)	32(1)	33(1)	25(1)	-5(1)	3(1)	-6(1)
C(21)	51(1)	47(1)	25(1)	-7(1)	9(1)	-12(1)
C(22)	65(1)	43(1)	21(1)	2(1)	-2(1)	-19(1)
C(23)	55(1)	34(1)	34(1)	7(1)	-10(1)	-5(1)
C(24)	36(1)	27(1)	29(1)	-2(1)	-1(1)	-3(1)
C(25)	17(1)	19(1)	30(1)	-10(1)	5(1)	-6(1)
C(26)	20(1)	29(1)	36(1)	-17(1)	4(1)	-8(1)
C(27)	26(1)	39(1)	56(1)	-30(1)	5(1)	-13(1)

C(28)	29(1)	23(1)	78(1)	-21(1)	7(1)	-11(1)
C(29)	27(1)	20(1)	58(1)	-5(1)	6(1)	-6(1)
C(30)	21(1)	20(1)	37(1)	-5(1)	6(1)	-5(1)
C(31)	29(1)	41(1)	29(1)	-15(1)	-3(1)	-12(1)
C(32)	49(1)	74(1)	34(1)	-24(1)	4(1)	-19(1)
C(33)	32(1)	56(1)	45(1)	-11(1)	-8(1)	-6(1)
C(34)	35(1)	22(1)	29(1)	2(1)	1(1)	-4(1)
C(35)	48(1)	58(1)	35(1)	-1(1)	6(1)	2(1)
C(36)	38(1)	33(1)	44(1)	4(1)	-5(1)	-3(1)

Table A.11: Crystal data and structure refinement for **2**.

Empirical formula	$C_{66}H_{56}Cl_4N_2O_2P_2Zn_2 \cdot C_7H_8$	
Formula weight	1335.7	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5777(5) Å	α= 114.5680(10)°.
	b = 13.5073(7) Å	β= 92.9570(10)°.
	c = 14.8891(12) Å	γ = 108.8230(10)°.
Volume	1619.06(18) $Å^3$	
Z	2	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	1.003 mm^{-1}	
F(000)	690	
Crystal size	0.24 x 0.17 x 0.12 mm^3	
Theta range for data collection	2.60 to 26.37°.	
Index ranges	-11<=h<=11, -16<=k<=16, -18<=l<=18	
Reflections collected	21637	
Independent reflections	6586 [R(int) = 0.0283]	
Completeness to theta = 26.37°	99.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8925 and 0.7977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6586 / 99 / 407	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0979	
R indices (all data)	R1 = 0.0495, wR2 = 0.1051	
Largest diff. peak and hole	1.531 and -0.359 $e.Å^{-3}$	

Table A.12: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	9800(1)	571(1)	1179(1)	28(1)	C(18)	11573(3)	1279(2)	4172(2)	30(1)
Cl(1)	10839(1)	2472(1)	2214(1)	62(1)	C(19)	8143(3)	753(2)	3824(2)	28(1)
Cl(2)	11544(1)	-163(1)	376(1)	41(1)	C(20)	7467(3)	456(3)	4531(2)	33(1)
N(1)	8431(2)	-414(2)	1711(1)	22(1)	C(21)	7144(3)	1276(3)	5337(2)	42(1)
P(1)	8763(1)	-247(1)	2846(1)	21(1)	C(22)	7511(3)	2396(3)	5450(2)	45(1)
O(1)	5335(2)	-1965(2)	2449(1)	26(1)	C(23)	8171(3)	2703(3)	4752(2)	43(1)
C(1)	3998(3)	-2903(2)	2240(2)	26(1)	C(24)	8496(3)	1889(2)	3935(2)	36(1)
C(2)	2574(3)	-2966(2)	1927(2)	32(1)	C(25)	6971(3)	-1220(2)	1049(2)	25(1)

C(3)	1375(3)	-3976(2)	1772(2)	36(1)	C(26)	6729(3)	-2406(2)	465(2)	30(1)
C(4)	1597(3)	-4860(2)	1922(2)	37(1)	C(27)	5289(3)	-3178(3)	-114(2)	40(1)
C(5)	3033(3)	-4791(2)	2224(2)	32(1)	C(28)	4111(3)	-2801(3)	-159(2)	44(1)
C(6)	4263(3)	-3786(2)	2385(2)	27(1)	C(29)	4417(3)	-1606(3)	366(2)	38(1)
C(7)	5888(3)	-3386(2)	2677(2)	26(1)	C(30)	5830(3)	-803(2)	969(2)	28(1)
C(8)	6868(3)	-3841(2)	2925(2)	31(1)	C(31)	7981(3)	-2863(2)	425(2)	36(1)
C(9)	8404(3)	-3184(2)	3179(2)	32(1)	C(32)	2528(4)	-3662(4)	-753(3)	73(1)
C(10)	8963(3)	-2100(2)	3174(2)	28(1)	C(33)	6106(3)	486(2)	1513(2)	34(1)
C(11)	8008(3)	-1614(2)	2920(2)	24(1)	C(1S)	15258(9)	4578(6)	4357(5)	88(2)
C(12)	6470(3)	-2288(2)	2687(2)	24(1)	C(2S)	14963(7)	3661(5)	3392(5)	82(2)
C(13)	10780(3)	316(2)	3244(2)	23(1)	C(3S)	16150(11)	3443(5)	2957(5)	98(3)
C(14)	11569(3)	-248(2)	2579(2)	26(1)	C(4S)	17633(9)	4142(8)	3489(8)	123(4)
C(15)	13130(3)	165(2)	2838(2)	32(1)	C(5S)	17929(7)	5059(7)	4454(8)	130(5)
C(16)	13913(3)	1134(3)	3750(2)	36(1)	C(6S)	16741(11)	5277(5)	4888(4)	117(4)
C(17)	13138(3)	1689(2)	4420(2)	37(1)	C(7S)	13938(17)	4835(13)	4777(13)	134(5)

Table A.13: Bond lengths [Å] for **2**.

Zn(1)-N(1)	1.9935(19)	C(10)-H(10)	0.9500	C(28)-C(29)	1.388(4)
Zn(1)-Cl(1)	2.2048(9)	C(11)-C(12)	1.392(3)	C(28)-C(32)	1.517(4)
Zn(1)-Cl(2)	2.3436(7)	C(13)-C(18)	1.392(3)	C(29)-C(30)	1.390(4)
Zn(1)-Cl(2)#1	2.3450(7)	C(13)-C(14)	1.398(3)	C(29)-H(29)	0.9500
Cl(2)-Zn(1)#1	2.3450(7)	C(14)-C(15)	1.385(3)	C(30)-C(33)	1.504(4)
N(1)-C(25)	1.448(3)	C(14)-H(14)	0.9500	C(31)-H(31A)	0.9800
N(1)-P(1)	1.6086(19)	C(15)-C(16)	1.379(4)	C(31)-H(31B)	0.9800
P(1)-C(13)	1.794(2)	C(15)-H(15)	0.9500	C(31)-H(31C)	0.9800
P(1)-C(11)	1.806(2)	C(16)-C(17)	1.387(4)	C(32)-H(32A)	0.9800
P(1)-C(19)	1.808(2)	C(16)-H(16)	0.9500	C(32)-H(32B)	0.9800
O(1)-C(12)	1.376(3)	C(17)-C(18)	1.388(4)	C(32)-H(32C)	0.9800
O(1)-C(1)	1.388(3)	C(17)-H(17)	0.9500	C(33)-H(33A)	0.9800
C(1)-C(2)	1.382(4)	C(18)-H(18)	0.9500	C(33)-H(33B)	0.9800
C(1)-C(6)	1.392(4)	C(19)-C(24)	1.393(4)	C(33)-H(33C)	0.9800
C(2)-C(3)	1.390(4)	C(19)-C(20)	1.394(4)	C(1S)-C(2S)	1.3900
C(2)-H(2)	0.9500	C(20)-C(21)	1.385(4)	C(1S)-C(6S)	1.3900
C(3)-C(4)	1.381(4)	C(20)-H(20)	0.9500	C(1S)-C(7S)	1.515(15)
C(3)-H(3)	0.9500	C(21)-C(22)	1.371(5)	C(2S)-C(3S)	1.3900
C(4)-C(5)	1.386(4)	C(21)-H(21)	0.9500	C(2S)-H(2S)	0.9500
C(4)-H(4)	0.9500	C(22)-C(23)	1.383(5)	C(3S)-C(4S)	1.3900
C(5)-C(6)	1.399(3)	C(22)-H(22)	0.9500	C(3S)-H(3S)	0.9500
C(5)-H(5)	0.9500	C(23)-C(24)	1.390(4)	C(4S)-C(5S)	1.3900
C(6)-C(7)	1.448(3)	C(23)-H(23)	0.9500	C(4S)-H(4S)	0.9500
C(7)-C(8)	1.386(4)	C(24)-H(24)	0.9500	C(5S)-C(6S)	1.3900
C(7)-C(12)	1.398(3)	C(25)-C(26)	1.399(4)	C(5S)-H(5S)	0.9500
C(8)-C(9)	1.384(4)	C(25)-C(30)	1.403(3)	C(6S)-H(6S)	0.9500

C(8)-H(8)	0.9500	C(26)-C(27)	1.390(4)	C(7S)-H(7S1)	0.9800
C(9)-C(10)	1.391(4)	C(26)-C(31)	1.509(4)	C(7S)-H(7S2)	0.9800
C(9)-H(9)	0.9500	C(27)-C(28)	1.388(4)	C(7S)-H(7S3)	0.9800
C(10)-C(11)	1.404(3)	C(27)-H(27)	0.9500		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z

Table A.14: Bond angles [°] for **2**

N(1)-Zn(1)-Cl(1)	115.86(6)	C(12)-C(11)-P(1)	123.57(18)	C(28)-C(27)-H(27)	118.9
N(1)-Zn(1)-Cl(2)	115.41(6)	C(10)-C(11)-P(1)	121.21(18)	C(26)-C(27)-H(27)	118.9
Cl(1)-Zn(1)-Cl(2)	112.18(3)	O(1)-C(12)-C(11)	124.9(2)	C(29)-C(28)-C(27)	118.0(3)
N(1)-Zn(1)-Cl(2)#1	107.47(6)	O(1)-C(12)-C(7)	111.5(2)	C(29)-C(28)-C(32)	120.4(3)
Cl(1)-Zn(1)-Cl(2)#1	112.42(4)	C(11)-C(12)-C(7)	123.6(2)	C(27)-C(28)-C(32)	121.6(3)
Cl(2)-Zn(1)-Cl(2)#1	90.63(2)	C(18)-C(13)-C(14)	119.5(2)	C(28)-C(29)-C(30)	121.9(3)
Zn(1)-Cl(2)-Zn(1)#	89.37(2)	C(18)-C(13)-P(1)	122.97(19)	C(28)-C(29)-H(29)	119.0
C(25)-N(1)-P(1)	119.51(15)	C(14)-C(13)-P(1)	117.54(18)	C(30)-C(29)-H(29)	119.0
C(25)-N(1)-Zn(1)	115.55(14)	C(15)-C(14)-C(13)	120.0(2)	C(29)-C(30)-C(25)	118.7(3)
P(1)-N(1)-Zn(1)	124.44(11)	C(15)-C(14)-H(14)	120.0	C(29)-C(30)-C(33)	119.7(2)
N(1)-P(1)-C(13)	106.12(10)	C(13)-C(14)-H(14)	120.0	C(25)-C(30)-C(33)	121.6(2)
N(1)-P(1)-C(11)	112.86(11)	C(16)-C(15)-C(14)	120.3(2)	C(26)-C(31)-H(31A)	109.5
C(13)-P(1)-C(11)	107.51(11)	C(16)-C(15)-H(15)	119.8	C(26)-C(31)-H(31B)	109.5
N(1)-P(1)-C(19)	119.33(11)	C(14)-C(15)-H(15)	119.8	H(31A)-C(31)-H(31B)	109.5
C(13)-P(1)-C(19)	105.63(11)	C(15)-C(16)-C(17)	120.1(2)	C(26)-C(31)-H(31C)	109.5
C(11)-P(1)-C(19)	104.70(11)	C(15)-C(16)-H(16)	119.9	H(31A)-C(31)-H(31C)	109.5
C(12)-O(1)-C(1)	105.62(18)	C(17)-C(16)-H(16)	119.9	H(31B)-C(31)-H(31C)	109.5
C(2)-C(1)-O(1)	124.9(2)	C(16)-C(17)-C(18)	120.1(2)	C(28)-C(32)-H(32A)	109.5
C(2)-C(1)-C(6)	123.6(2)	C(16)-C(17)-H(17)	119.9	C(28)-C(32)-H(32B)	109.5
O(1)-C(1)-C(6)	111.5(2)	C(18)-C(17)-H(17)	119.9	H(32A)-C(32)-H(32B)	109.5
C(1)-C(2)-C(3)	116.0(3)	C(17)-C(18)-C(13)	120.0(2)	C(28)-C(32)-H(32C)	109.5
C(1)-C(2)-H(2)	122.0	C(17)-C(18)-H(18)	120.0	H(32A)-C(32)-H(32C)	109.5
C(3)-C(2)-H(2)	122.0	C(13)-C(18)-H(18)	120.0	H(32B)-C(32)-H(32C)	109.5
C(4)-C(3)-C(2)	121.8(3)	C(24)-C(19)-C(20)	119.4(2)	C(30)-C(33)-H(33A)	109.5
C(4)-C(3)-H(3)	119.1	C(24)-C(19)-P(1)	118.86(19)	C(30)-C(33)-H(33B)	109.5
C(2)-C(3)-H(3)	119.1	C(20)-C(19)-P(1)	121.4(2)	H(33A)-C(33)-H(33B)	109.5
C(3)-C(4)-C(5)	121.5(2)	C(21)-C(20)-C(19)	120.6(3)	C(30)-C(33)-H(33C)	109.5
C(3)-C(4)-H(4)	119.2	C(21)-C(20)-H(20)	119.7	H(33A)-C(33)-H(33C)	109.5
C(5)-C(4)-H(4)	119.2	C(19)-C(20)-H(20)	119.7	H(33B)-C(33)-H(33C)	109.5
C(4)-C(5)-C(6)	118.0(3)	C(22)-C(21)-C(20)	119.8(3)	C(2S)-C(1S)-C(6S)	120.0
C(4)-C(5)-H(5)	121.0	C(22)-C(21)-H(21)	120.1	C(2S)-C(1S)-C(7S)	118.4(10)
C(6)-C(5)-H(5)	121.0	C(20)-C(21)-H(21)	120.1	C(6S)-C(1S)-C(7S)	121.5(10)
C(1)-C(6)-C(5)	119.1(2)	C(21)-C(22)-C(23)	120.3(3)	C(1S)-C(2S)-C(3S)	120.0
C(1)-C(6)-C(7)	105.6(2)	C(21)-C(22)-H(22)	119.8	C(1S)-C(2S)-H(2S)	120.0
C(5)-C(6)-C(7)	135.3(2)	C(23)-C(22)-H(22)	119.8	C(3S)-C(2S)-H(2S)	120.0

C(8)-C(7)-C(12)	119.5(2)	C(22)-C(23)-C(24)	120.6(3)	C(4S)-C(3S)-C(2S)	120.0
C(8)-C(7)-C(6)	134.7(2)	C(22)-C(23)-H(23)	119.7	C(4S)-C(3S)-H(3S)	120.0
C(12)-C(7)-C(6)	105.7(2)	C(24)-C(23)-H(23)	119.7	C(2S)-C(3S)-H(3S)	120.0
C(9)-C(8)-C(7)	118.4(2)	C(23)-C(24)-C(19)	119.3(3)	C(5S)-C(4S)-C(3S)	120.0
C(9)-C(8)-H(8)	120.8	C(23)-C(24)-H(24)	120.4	C(5S)-C(4S)-H(4S)	120.0
C(7)-C(8)-H(8)	120.8	C(19)-C(24)-H(24)	120.4	C(3S)-C(4S)-H(4S)	120.0
C(8)-C(9)-C(10)	121.2(2)	C(26)-C(25)-C(30)	120.5(2)	C(4S)-C(5S)-C(6S)	120.0
C(8)-C(9)-H(9)	119.4	C(26)-C(25)-N(1)	119.5(2)	C(4S)-C(5S)-H(5S)	120.0
C(10)-C(9)-H(9)	119.4	C(30)-C(25)-N(1)	120.0(2)	C(6S)-C(5S)-H(5S)	120.0
C(9)-C(10)-C(11)	122.0(2)	C(27)-C(26)-C(25)	118.4(2)	C(5S)-C(6S)-C(1S)	120.0
C(9)-C(10)-H(10)	119.0	C(27)-C(26)-C(31)	119.3(2)	C(5S)-C(6S)-H(6S)	120.0
C(11)-C(10)-H(10)	119.0	C(25)-C(26)-C(31)	122.2(2)	C(1S)-C(6S)-H(6S)	120.0
C(12)-C(11)-C(10)	115.2(2)	C(28)-C(27)-C(26)	122.2(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z

Table A.15: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	26(1)	31(1)	29(1)	16(1)	10(1)	10(1)
Cl(1)	74(1)	30(1)	63(1)	16(1)	26(1)	1(1)
Cl(2)	34(1)	77(1)	39(1)	39(1)	20(1)	35(1)
N(1)	19(1)	26(1)	19(1)	9(1)	4(1)	7(1)
P(1)	19(1)	25(1)	18(1)	8(1)	5(1)	8(1)
O(1)	20(1)	29(1)	30(1)	15(1)	7(1)	9(1)
C(1)	22(1)	26(1)	23(1)	8(1)	8(1)	5(1)
C(2)	26(1)	33(1)	33(1)	11(1)	8(1)	12(1)
C(3)	21(1)	38(2)	34(1)	6(1)	4(1)	6(1)
C(4)	29(1)	27(1)	36(2)	5(1)	7(1)	0(1)
C(5)	31(1)	24(1)	31(1)	7(1)	8(1)	6(1)
C(6)	27(1)	28(1)	22(1)	8(1)	9(1)	10(1)
C(7)	27(1)	26(1)	22(1)	9(1)	8(1)	8(1)
C(8)	35(1)	29(1)	30(1)	13(1)	9(1)	13(1)
C(9)	32(1)	37(2)	31(1)	17(1)	7(1)	18(1)
C(10)	24(1)	36(1)	24(1)	14(1)	6(1)	11(1)
C(11)	22(1)	29(1)	19(1)	10(1)	6(1)	9(1)
C(12)	24(1)	28(1)	20(1)	10(1)	8(1)	12(1)
C(13)	21(1)	26(1)	21(1)	11(1)	3(1)	6(1)
C(14)	23(1)	27(1)	25(1)	12(1)	4(1)	8(1)
C(15)	24(1)	39(2)	36(1)	21(1)	10(1)	12(1)
C(16)	20(1)	45(2)	41(2)	24(1)	0(1)	4(1)
C(17)	30(1)	36(2)	29(1)	10(1)	-6(1)	2(1)
C(18)	28(1)	32(1)	23(1)	9(1)	2(1)	9(1)

C(19)	23(1)	36(1)	21(1)	8(1)	4(1)	14(1)
C(20)	28(1)	45(2)	23(1)	12(1)	7(1)	16(1)
C(21)	41(2)	63(2)	23(1)	13(1)	10(1)	29(2)
C(22)	39(2)	61(2)	23(1)	1(1)	4(1)	32(2)
C(23)	44(2)	38(2)	36(2)	2(1)	2(1)	23(1)
C(24)	39(2)	35(2)	29(1)	8(1)	7(1)	18(1)
C(25)	22(1)	33(1)	17(1)	12(1)	5(1)	8(1)
C(26)	27(1)	35(1)	20(1)	8(1)	5(1)	9(1)
C(27)	34(2)	38(2)	27(1)	2(1)	4(1)	4(1)
C(28)	25(1)	59(2)	26(1)	6(1)	1(1)	7(1)
C(29)	24(1)	63(2)	28(1)	20(1)	6(1)	18(1)
C(30)	25(1)	42(2)	23(1)	19(1)	10(1)	14(1)
C(31)	38(2)	33(2)	29(1)	5(1)	6(1)	15(1)
C(32)	28(2)	86(3)	51(2)	-3(2)	-5(2)	3(2)
C(33)	31(1)	45(2)	39(2)	26(1)	15(1)	22(1)
C(1S)	145(7)	60(5)	73(5)	49(4)	24(5)	29(5)
C(2S)	100(6)	54(4)	107(6)	62(4)	12(5)	13(4)
C(3S)	195(9)	55(5)	93(6)	58(5)	63(6)	67(6)
C(4S)	136(7)	136(9)	215(11)	157(8)	70(8)	87(7)
C(5S)	99(7)	102(7)	207(11)	126(7)	-43(7)	0(6)
C(6S)	168(9)	76(6)	99(7)	66(6)	-26(7)	10(7)
C(7S)	183(12)	106(10)	159(13)	99(10)	68(11)	53(10)

Table A.16: Crystal data and structure refinement for **3**.

Empirical formula	$C_{48}H_{34}F_{10}NOPZn \cdot C_7H_8$	
Formula weight	1019.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3644(7) Å	α= 70.3270(10)°.
	b = 13.2795(7) Å	β= 70.8490(10)°.
	c = 17.7040(10) Å	γ = 71.9030(10)°.
Volume	2519.4(2) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.595 mm^{-1}	
F(000)	1044	
Crystal size	0.30 x 0.26 x 0.24 mm^3	
Theta range for data collection	2.56 to 25.03°.	
Index ranges	-14<=h<=14, -15<=k<=15, -21<=l<=21	
Reflections collected	24263	
Independent reflections	8863 [R(int) = 0.0219]	
Completeness to theta = 25.03°	99.60%	
Max. and min. transmission	0.8699 and 0.8435	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8863 / 0 / 615	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0998	
R indices (all data)	R1 = 0.0433, wR2 = 0.1033	
Largest diff. peak and hole	0.553 and -0.479 $e.Å^{-3}$	

Table A.17: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn	3020(1)	6404(1)	1884(1)	30(1)	C(22)	2395(2)	10871(2)	772(2)	52(1)
P	3557(1)	7885(1)	2783(1)	26(1)	C(23)	3529(2)	10615(2)	848(2)	53(1)
O	5532(1)	6871(1)	1423(1)	33(1)	C(24)	3907(2)	9692(2)	1441(1)	38(1)
N	3081(1)	6848(1)	2849(1)	26(1)	C(25)	2768(2)	6089(2)	3654(1)	29(1)
F(1)	1481(2)	4675(1)	3224(1)	67(1)	C(26)	3597(2)	5133(2)	3924(1)	35(1)
C(1)	6554(2)	6549(2)	840(1)	36(1)	C(27)	3249(3)	4446(2)	4710(2)	48(1)
C(2)	6584(2)	6201(2)	183(2)	44(1)	C(28)	2139(3)	4675(2)	5205(2)	57(1)
F(2)	1809(2)	2511(2)	3474(1)	101(1)	C(29)	1326(2)	5587(2)	4929(2)	51(1)
C(3)	7693(2)	5928(2)	-333(2)	51(1)	C(30)	1613(2)	6320(2)	4153(1)	36(1)

F(3)	3666(2)	1416(1)	2506(1)	96(1)	C(31)	4847(2)	4828(2)	3423(1)	38(1)
F(4)	5213(2)	2518(2)	1281(1)	82(1)	C(32)	5193(3)	3630(2)	3381(2)	54(1)
C(4)	8698(2)	6004(2)	-186(2)	53(1)	C(33)	5727(2)	5009(2)	3780(2)	45(1)
F(5)	4896(2)	4684(1)	1036(1)	68(1)	C(34)	709(2)	7328(2)	3865(2)	41(1)
C(5)	8644(2)	6356(2)	473(2)	47(1)	C(35)	122(2)	7142(2)	3298(2)	54(1)
F(6)	745(1)	6887(1)	1350(1)	54(1)	C(36)	-231(3)	7752(3)	4568(2)	70(1)
C(6)	7542(2)	6643(2)	1003(1)	37(1)	C(37)	3180(2)	4778(2)	2119(1)	36(1)
F(7)	-144(1)	8419(2)	132(1)	67(1)	C(38)	4098(2)	4176(2)	1651(1)	44(1)
C(7)	7108(2)	7076(2)	1723(1)	36(1)	C(39)	4287(3)	3062(2)	1760(2)	55(1)
F(8)	1132(2)	9857(1)	-1007(1)	64(1)	C(40)	3507(3)	2503(2)	2376(2)	61(1)
C(8)	7613(2)	7391(2)	2181(2)	48(1)	C(41)	2573(3)	3064(2)	2859(2)	62(1)
F(9)	3345(1)	9698(1)	-939(1)	54(1)	C(42)	2428(2)	4179(2)	2721(2)	47(1)
C(9)	6891(2)	7832(2)	2823(2)	50(1)	C(43)	2527(2)	7483(2)	878(1)	33(1)
F(10)	4243(1)	8173(1)	275(1)	44(1)	C(44)	3142(2)	8207(2)	265(1)	33(1)
C(10)	5673(2)	7977(2)	3020(2)	40(1)	C(45)	2707(2)	9000(2)	-366(1)	38(1)
C(11)	5135(2)	7659(2)	2580(1)	31(1)	C(46)	1590(2)	9082(2)	-401(2)	45(1)
C(12)	5888(2)	7211(2)	1941(1)	31(1)	C(47)	947(2)	8358(2)	175(2)	44(1)
C(13)	2961(2)	8369(2)	3714(1)	30(1)	C(48)	1427(2)	7585(2)	792(1)	39(1)
C(14)	2323(2)	9446(2)	3669(2)	42(1)	C(1S)	8257(4)	3628(3)	1830(3)	148(3)
C(15)	1822(3)	9804(2)	4382(2)	59(1)	C(2S)	7892(4)	2816(6)	1709(3)	186(4)
C(16)	1957(3)	9102(2)	5139(2)	59(1)	C(3S)	8284(6)	1720(5)	2097(4)	300(8)
C(17)	2599(2)	8034(2)	5190(2)	49(1)	C(4S)	9040(6)	1435(3)	2605(3)	294(9)
C(18)	3109(2)	7667(2)	4482(1)	37(1)	C(5S)	9405(4)	2247(5)	2726(2)	198(4)
C(19)	3147(2)	9017(2)	1949(1)	28(1)	C(6S)	9014(4)	3343(4)	2339(3)	152(3)
C(20)	2004(2)	9281(2)	1861(1)	34(1)	C(7S)	9346(5)	4206(6)	2510(4)	161(3)
C(21)	1631(2)	10208(2)	1275(2)	44(1)					

Table A.18: Bond lengths [Å] for **3**.

Zn-C(43)	2.012(2)	C(13)-C(14)	1.391(3)	C(33)-H(33A)	0.9800
Zn-C(37)	2.014(2)	C(13)-C(18)	1.399(3)	C(33)-H(33B)	0.9800
Zn-N	2.0158(16)	C(14)-C(15)	1.382(4)	C(33)-H(33C)	0.9800
P-N	1.6136(17)	C(14)-H(14)	0.9500	C(34)-C(36)	1.529(3)
P-C(19)	1.794(2)	C(15)-C(16)	1.380(4)	C(34)-C(35)	1.532(3)
P-C(11)	1.811(2)	C(15)-H(15)	0.9500	C(34)-H(34)	1.0000
P-C(13)	1.815(2)	C(16)-C(17)	1.382(4)	C(35)-H(35A)	0.9800
O-C(12)	1.380(3)	C(16)-H(16)	0.9500	C(35)-H(35B)	0.9800
O-C(1)	1.396(3)	C(17)-C(18)	1.382(3)	C(35)-H(35C)	0.9800
N-C(25)	1.452(3)	C(17)-H(17)	0.9500	C(36)-H(36A)	0.9800
F(1)-C(42)	1.353(3)	C(18)-H(18)	0.9500	C(36)-H(36B)	0.9800
C(1)-C(2)	1.376(3)	C(19)-C(24)	1.386(3)	C(36)-H(36C)	0.9800
C(1)-C(6)	1.393(3)	C(19)-C(20)	1.394(3)	C(37)-C(42)	1.368(3)
C(2)-C(3)	1.393(3)	C(20)-C(21)	1.380(3)	C(37)-C(38)	1.371(3)
C(2)-H(2)	0.9500	C(20)-H(20)	0.9500	C(38)-C(39)	1.379(4)

F(2)-C(41)	1.355(3)	C(21)-C(22)	1.377(4)	C(39)-C(40)	1.371(4)
C(3)-C(4)	1.387(4)	C(21)-H(21)	0.9500	C(40)-C(41)	1.366(4)
C(3)-H(3)	0.9500	C(22)-C(23)	1.377(4)	C(41)-C(42)	1.380(4)
F(3)-C(40)	1.343(3)	C(22)-H(22)	0.9500	C(43)-C(44)	1.376(3)
F(4)-C(39)	1.347(3)	C(23)-C(24)	1.387(3)	C(43)-C(48)	1.378(3)
C(4)-C(5)	1.372(4)	C(23)-H(23)	0.9500	C(44)-C(45)	1.377(3)
C(4)-H(4)	0.9500	C(24)-H(24)	0.9500	C(45)-C(46)	1.371(3)
F(5)-C(38)	1.352(3)	C(25)-C(26)	1.412(3)	C(46)-C(47)	1.371(4)
C(5)-C(6)	1.401(3)	C(25)-C(30)	1.414(3)	C(47)-C(48)	1.375(3)
C(5)-H(5)	0.9500	C(26)-C(27)	1.396(3)	C(1S)-C(2S)	1.3900
F(6)-C(48)	1.367(3)	C(26)-C(31)	1.514(3)	C(1S)-C(6S)	1.3900
C(6)-C(7)	1.448(3)	C(27)-C(28)	1.369(4)	C(1S)-H(1S)	0.9500
F(7)-C(47)	1.351(3)	C(27)-H(27)	0.9500	C(2S)-C(3S)	1.3900
C(7)-C(8)	1.395(3)	C(28)-C(29)	1.372(4)	C(2S)-H(2S)	0.9500
C(7)-C(12)	1.397(3)	C(28)-H(28)	0.9500	C(3S)-C(4S)	1.3900
F(8)-C(46)	1.352(3)	C(29)-C(30)	1.398(3)	C(3S)-H(3S)	0.9500
C(8)-C(9)	1.376(4)	C(29)-H(29)	0.9500	C(4S)-C(5S)	1.3900
C(8)-H(8)	0.9500	C(30)-C(34)	1.512(3)	C(4S)-H(4S)	0.9500
F(9)-C(45)	1.345(3)	C(31)-C(32)	1.535(3)	C(5S)-C(6S)	1.3900
C(9)-C(10)	1.395(3)	C(31)-C(33)	1.535(3)	C(5S)-H(5S)	0.9500
C(9)-H(9)	0.9500	C(31)-H(31)	1.0000	C(6S)-C(7S)	1.478(8)
F(10)-C(44)	1.353(2)	C(32)-H(32A)	0.9800	C(7S)-H(7S1)	0.9800
C(10)-C(11)	1.401(3)	C(32)-H(32B)	0.9800	C(7S)-H(7S2)	0.9800
C(10)-H(10)	0.9500	C(32)-H(32C)	0.9800	C(7S)-H(7S3)	0.9800
C(11)-C(12)	1.386(3)				

Table A.19: Bond angles [°] for **3**

C(43)-Zn-C(37)	122.20(9)	C(24)-C(19)-C(20)	119.4(2)	C(34)-C(36)-H(36A)	109.5
C(43)-Zn-N	123.49(8)	C(24)-C(19)-P	121.25(16)	C(34)-C(36)-H(36B)	109.5
C(37)-Zn-N	113.22(8)	C(20)-C(19)-P	119.04(16)	H(36A)-C(36)-H(36B)	109.5
N-P-C(19)	110.09(9)	C(21)-C(20)-C(19)	120.3(2)	C(34)-C(36)-H(36C)	109.5
N-P-C(11)	115.50(9)	C(21)-C(20)-H(20)	119.8	H(36A)-C(36)-H(36C)	109.5
C(19)-P-C(11)	105.52(10)	C(19)-C(20)-H(20)	119.8	H(36B)-C(36)-H(36C)	109.5
N-P-C(13)	113.02(9)	C(22)-C(21)-C(20)	119.8(2)	C(42)-C(37)-C(38)	114.1(2)
C(19)-P-C(13)	106.80(10)	C(22)-C(21)-H(21)	120.1	C(42)-C(37)-Zn	125.73(18)
C(11)-P-C(13)	105.27(10)	C(20)-C(21)-H(21)	120.1	C(38)-C(37)-Zn	120.16(17)
C(12)-O-C(1)	105.72(16)	C(21)-C(22)-C(23)	120.5(2)	F(5)-C(38)-C(37)	119.3(2)
C(25)-N-P	119.21(13)	C(21)-C(22)-H(22)	119.7	F(5)-C(38)-C(39)	116.0(2)
C(25)-N-Zn	114.96(12)	C(23)-C(22)-H(22)	119.7	C(37)-C(38)-C(39)	124.7(2)
P-N-Zn	125.54(9)	C(22)-C(23)-C(24)	120.1(2)	F(4)-C(39)-C(40)	119.7(2)
C(2)-C(1)-C(6)	124.2(2)	C(22)-C(23)-H(23)	119.9	F(4)-C(39)-C(38)	121.7(3)
C(2)-C(1)-O	124.7(2)	C(24)-C(23)-H(23)	119.9	C(40)-C(39)-C(38)	118.6(3)
C(6)-C(1)-O	111.1(2)	C(19)-C(24)-C(23)	119.8(2)	F(3)-C(40)-C(41)	120.6(3)

C(1)-C(2)-C(3)	115.6(2)	C(19)-C(24)-H(24)	120.1	F(3)-C(40)-C(39)	120.4(3)
C(1)-C(2)-H(2)	122.2	C(23)-C(24)-H(24)	120.1	C(41)-C(40)-C(39)	119.1(2)
C(3)-C(2)-H(2)	122.2	C(26)-C(25)-C(30)	120.85(19)	F(2)-C(41)-C(40)	119.2(3)
C(4)-C(3)-C(2)	121.7(3)	C(26)-C(25)-N	120.62(19)	F(2)-C(41)-C(42)	121.0(3)
C(4)-C(3)-H(3)	119.1	C(30)-C(25)-N	118.53(19)	C(40)-C(41)-C(42)	119.8(3)
C(2)-C(3)-H(3)	119.1	C(27)-C(26)-C(25)	117.9(2)	F(1)-C(42)-C(37)	120.1(2)
C(5)-C(4)-C(3)	121.5(2)	C(27)-C(26)-C(31)	118.2(2)	F(1)-C(42)-C(41)	116.2(2)
C(5)-C(4)-H(4)	119.2	C(25)-C(26)-C(31)	123.89(19)	C(37)-C(42)-C(41)	123.7(3)
C(3)-C(4)-H(4)	119.2	C(28)-C(27)-C(26)	121.7(3)	C(44)-C(43)-C(48)	113.9(2)
C(4)-C(5)-C(6)	118.3(2)	C(28)-C(27)-H(27)	119.2	C(44)-C(43)-Zn	127.20(16)
C(4)-C(5)-H(5)	120.8	C(26)-C(27)-H(27)	119.2	C(48)-C(43)-Zn	118.81(16)
C(6)-C(5)-H(5)	120.8	C(27)-C(28)-C(29)	120.3(2)	F(10)-C(44)-C(43)	119.35(19)
C(1)-C(6)-C(5)	118.6(2)	C(27)-C(28)-H(28)	119.9	F(10)-C(44)-C(45)	116.30(19)
C(1)-C(6)-C(7)	105.78(19)	C(29)-C(28)-H(28)	119.9	C(43)-C(44)-C(45)	124.3(2)
C(5)-C(6)-C(7)	135.6(2)	C(28)-C(29)-C(30)	121.4(2)	F(9)-C(45)-C(46)	119.5(2)
C(8)-C(7)-C(12)	118.7(2)	C(28)-C(29)-H(29)	119.3	F(9)-C(45)-C(44)	121.6(2)
C(8)-C(7)-C(6)	135.3(2)	C(30)-C(29)-H(29)	119.3	C(46)-C(45)-C(44)	118.9(2)
C(12)-C(7)-C(6)	106.03(19)	C(29)-C(30)-C(25)	117.9(2)	F(8)-C(46)-C(47)	120.0(2)
C(9)-C(8)-C(7)	118.7(2)	C(29)-C(30)-C(34)	120.6(2)	F(8)-C(46)-C(45)	120.4(2)
C(9)-C(8)-H(8)	120.6	C(25)-C(30)-C(34)	121.46(19)	C(47)-C(46)-C(45)	119.6(2)
C(7)-C(8)-H(8)	120.6	C(26)-C(31)-C(32)	112.1(2)	F(7)-C(47)-C(46)	119.8(2)
C(8)-C(9)-C(10)	121.6(2)	C(26)-C(31)-C(33)	111.46(19)	F(7)-C(47)-C(48)	121.2(2)
C(8)-C(9)-H(9)	119.2	C(32)-C(31)-C(33)	108.6(2)	C(46)-C(47)-C(48)	118.9(2)
C(10)-C(9)-H(9)	119.2	C(26)-C(31)-H(31)	108.2	F(6)-C(48)-C(47)	116.4(2)
C(9)-C(10)-C(11)	121.3(2)	C(32)-C(31)-H(31)	108.2	F(6)-C(48)-C(43)	119.2(2)
C(9)-C(10)-H(10)	119.3	C(33)-C(31)-H(31)	108.2	C(47)-C(48)-C(43)	124.3(2)
C(11)-C(10)-H(10)	119.3	C(31)-C(32)-H(32A)	109.5	C(2S)-C(1S)-C(6S)	120.0
C(12)-C(11)-C(10)	115.67(19)	C(31)-C(32)-H(32B)	109.5	C(2S)-C(1S)-H(1S)	120.0
C(12)-C(11)-P	121.32(16)	H(32A)-C(32)-H(32E	109.5	C(6S)-C(1S)-H(1S)	120.0
C(10)-C(11)-P	122.92(17)	C(31)-C(32)-H(32C)	109.5	C(1S)-C(2S)-C(3S)	120.0
O-C(12)-C(11)	124.66(18)	H(32A)-C(32)-H(32C	109.5	C(1S)-C(2S)-H(2S)	120.0
O-C(12)-C(7)	111.28(19)	H(32B)-C(32)-H(32C	109.5	C(3S)-C(2S)-H(2S)	120.0
C(11)-C(12)-C(7)	124.0(2)	C(31)-C(33)-H(33A)	109.5	C(4S)-C(3S)-C(2S)	120.0
C(14)-C(13)-C(18)	119.3(2)	C(31)-C(33)-H(33B)	109.5	C(4S)-C(3S)-H(3S)	120.0
C(14)-C(13)-P	119.78(17)	H(33A)-C(33)-H(33E	109.5	C(2S)-C(3S)-H(3S)	120.0
C(18)-C(13)-P	120.91(16)	C(31)-C(33)-H(33C)	109.5	C(3S)-C(4S)-C(5S)	120.0
C(15)-C(14)-C(13)	120.0(2)	H(33A)-C(33)-H(33C	109.5	C(3S)-C(4S)-H(4S)	120.0
C(15)-C(14)-H(14)	120.0	H(33B)-C(33)-H(33C	109.5	C(5S)-C(4S)-H(4S)	120.0
C(13)-C(14)-H(14)	120.0	C(30)-C(34)-C(36)	114.0(2)	C(6S)-C(5S)-C(4S)	120.0
C(16)-C(15)-C(14)	120.4(2)	C(30)-C(34)-C(35)	111.7(2)	C(6S)-C(5S)-H(5S)	120.0
C(16)-C(15)-H(15)	119.8	C(36)-C(34)-C(35)	109.7(2)	C(4S)-C(5S)-H(5S)	120.0
C(14)-C(15)-H(15)	119.8	C(30)-C(34)-H(34)	107.0	C(5S)-C(6S)-C(1S)	120.0
C(15)-C(16)-C(17)	120.2(2)	C(36)-C(34)-H(34)	107.0	C(5S)-C(6S)-C(7S)	119.7(5)

C(15)-C(16)-H(16) 119.9	C(35)-C(34)-H(34) 107.0	C(1S)-C(6S)-C(7S) 120.2(5)
C(17)-C(16)-H(16) 119.9	C(34)-C(35)-H(35A) 109.5	C(6S)-C(7S)-H(7S1) 109.5
C(18)-C(17)-C(16) 120.0(2)	C(34)-C(35)-H(35B) 109.5	C(6S)-C(7S)-H(7S2) 109.5
C(18)-C(17)-H(17) 120.0	H(35A)-C(35)-H(35E 109.5	H(7S1)-C(7S)-H(7S2) 109.5
C(16)-C(17)-H(17) 120.0	C(34)-C(35)-H(35C) 109.5	C(6S)-C(7S)-H(7S3) 109.5
C(17)-C(18)-C(13) 120.1(2)	H(35A)-C(35)-H(35C 109.5	H(7S1)-C(7S)-H(7S3) 109.5
C(17)-C(18)-H(18) 119.9	H(35B)-C(35)-H(35C 109.5	H(7S2)-C(7S)-H(7S3) 109.5
C(13)-C(18)-H(18) 119.9		

Table A.20: Anisotropic displacement parameters ($Å^2$x 10^3)for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Zn	33(1)	34(1)	27(1)	-6(1)	-9(1)	-11(1)
P	24(1)	27(1)	26(1)	-5(1)	-7(1)	-8(1)
O	24(1)	42(1)	30(1)	-8(1)	-6(1)	-6(1)
N	26(1)	30(1)	24(1)	-6(1)	-5(1)	-9(1)
F(1)	64(1)	71(1)	67(1)	-34(1)	15(1)	-32(1)
C(1)	27(1)	36(1)	32(1)	-2(1)	-3(1)	-2(1)
C(2)	37(1)	52(2)	36(1)	-10(1)	-6(1)	-5(1)
F(2)	142(2)	76(1)	78(1)	-18(1)	27(1)	-76(1)
C(3)	46(2)	55(2)	41(1)	-13(1)	-4(1)	-1(1)
F(3)	164(2)	44(1)	86(1)	-24(1)	-16(1)	-40(1)
F(4)	96(1)	69(1)	77(1)	-46(1)	-2(1)	-6(1)
C(4)	36(1)	53(2)	49(2)	-10(1)	2(1)	4(1)
F(5)	72(1)	68(1)	55(1)	-20(1)	14(1)	-30(1)
C(5)	27(1)	42(1)	55(2)	-3(1)	-7(1)	0(1)
F(6)	46(1)	72(1)	50(1)	-4(1)	-15(1)	-30(1)
C(6)	29(1)	31(1)	41(1)	1(1)	-8(1)	-3(1)
F(7)	46(1)	84(1)	79(1)	-7(1)	-39(1)	-18(1)
C(7)	26(1)	33(1)	43(1)	-1(1)	-11(1)	-5(1)
F(8)	71(1)	60(1)	61(1)	4(1)	-44(1)	-6(1)
C(8)	26(1)	52(2)	67(2)	-11(1)	-18(1)	-10(1)
F(9)	60(1)	55(1)	42(1)	6(1)	-16(1)	-23(1)
C(9)	39(1)	60(2)	66(2)	-20(1)	-23(1)	-16(1)
F(10)	31(1)	60(1)	41(1)	-7(1)	-11(1)	-14(1)
C(10)	36(1)	44(1)	48(1)	-14(1)	-14(1)	-11(1)
C(11)	26(1)	31(1)	36(1)	-3(1)	-11(1)	-9(1)
C(12)	29(1)	29(1)	33(1)	0(1)	-11(1)	-7(1)
C(13)	32(1)	31(1)	31(1)	-9(1)	-8(1)	-11(1)
C(14)	56(2)	30(1)	39(1)	-9(1)	-11(1)	-11(1)
C(15)	87(2)	34(1)	51(2)	-19(1)	-12(2)	-4(1)
C(16)	87(2)	50(2)	39(1)	-24(1)	-10(1)	-8(2)
C(17)	68(2)	46(2)	35(1)	-13(1)	-18(1)	-9(1)

C(18)	43(1)	35(1)	35(1)	-11(1)	-14(1)	-6(1)
C(19)	29(1)	27(1)	27(1)	-5(1)	-7(1)	-6(1)
C(20)	31(1)	37(1)	32(1)	-7(1)	-7(1)	-9(1)
C(21)	40(1)	46(1)	39(1)	-6(1)	-16(1)	-2(1)
C(22)	58(2)	39(1)	45(2)	5(1)	-18(1)	-4(1)
C(23)	53(2)	39(1)	52(2)	9(1)	-8(1)	-19(1)
C(24)	33(1)	36(1)	40(1)	-1(1)	-7(1)	-12(1)
C(25)	38(1)	32(1)	22(1)	-7(1)	-6(1)	-16(1)
C(26)	51(1)	32(1)	29(1)	-5(1)	-13(1)	-17(1)
C(27)	67(2)	41(1)	37(1)	4(1)	-17(1)	-23(1)
C(28)	76(2)	59(2)	33(1)	9(1)	-11(1)	-38(2)
C(29)	55(2)	70(2)	32(1)	-11(1)	5(1)	-37(1)
C(30)	40(1)	44(1)	29(1)	-11(1)	-2(1)	-22(1)
C(31)	48(1)	33(1)	33(1)	-5(1)	-18(1)	-4(1)
C(32)	68(2)	39(1)	61(2)	-15(1)	-33(2)	1(1)
C(33)	52(2)	39(1)	45(1)	-4(1)	-22(1)	-7(1)
C(34)	32(1)	53(2)	38(1)	-18(1)	4(1)	-17(1)
C(35)	36(1)	70(2)	63(2)	-24(2)	-11(1)	-16(1)
C(36)	58(2)	82(2)	60(2)	-36(2)	11(2)	-9(2)
C(37)	47(1)	37(1)	31(1)	-10(1)	-13(1)	-14(1)
C(38)	58(2)	48(1)	31(1)	-10(1)	-7(1)	-23(1)
C(39)	74(2)	48(2)	46(2)	-27(1)	-10(1)	-10(1)
C(40)	99(2)	40(2)	52(2)	-18(1)	-15(2)	-27(2)
C(41)	93(2)	54(2)	47(2)	-11(1)	-1(2)	-45(2)
C(42)	59(2)	47(1)	40(1)	-18(1)	-3(1)	-23(1)
C(43)	34(1)	37(1)	29(1)	-11(1)	-11(1)	-5(1)
C(44)	28(1)	43(1)	31(1)	-13(1)	-9(1)	-7(1)
C(45)	44(1)	39(1)	32(1)	-8(1)	-10(1)	-11(1)
C(46)	50(2)	44(1)	41(1)	-6(1)	-27(1)	-2(1)
C(47)	35(1)	56(2)	49(2)	-15(1)	-21(1)	-7(1)
C(48)	38(1)	48(1)	33(1)	-8(1)	-10(1)	-14(1)
C(1S)	69(3)	137(5)	162(6)	21(4)	4(3)	-20(3)
C(2S)	192(7)	152(6)	167(6)	-84(6)	89(5)	-69(6)
C(3S)	550(20)	135(7)	109(6)	-68(5)	86(9)	-68(10)
C(4S)	491(18)	133(6)	82(5)	-50(5)	40(7)	74(9)
C(5S)	231(8)	129(5)	91(4)	-14(4)	35(4)	59(5)
C(6S)	104(4)	131(5)	121(5)	10(4)	49(4)	-18(4)
C(7S)	123(5)	185(7)	164(6)	-18(5)	-43(4)	-43(5)

Table A.21: Crystal data and structure refinement for **4**.

Empirical formula	$C_{45}H_{28}F_{10}NOPZn \cdot C_5H_{12}$	
Formula weight	957.17	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.2741(13) Å	α= 90°.
	b = 14.1963(12) Å	β= 98.3170(10)°.
	c = 21.3107(19) Å	γ = 90°.
Volume	4572.3(7) $Å^3$	
Z	4	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.651 mm^{-1}	
F(000)	1960	
Crystal size	0.30 x 0.26 x 0.18 mm^3	
Theta range for data collection	2.62 to 25.03°.	
Index ranges	-18<=h<=18, -16<=k<=16, -25<=l<=25	
Reflections collected	43393	
Independent reflections	8076 [R(int) = 0.0310]	
Completeness to theta = 25.03°	99.90%	
Max. and min. transmission	0.8941 and 0.8287	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8076 / 0 / 582	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0883	
R indices (all data)	R1 = 0.0513, wR2 = 0.0972	
Largest diff. peak and hole	0.482 and -0.304 $e.Å^{-3}$	

Table A.22: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	10260(1)	8012(1)	2174(1)	34(1)	C(31)	10877(2)	9653(2)	3711(1)	53(1)
P(2)	9436(1)	10054(1)	2202(1)	29(1)	C(33)	8020(2)	8160(2)	2657(1)	45(1)
F(5)	11194(1)	7333(1)	3456(1)	58(1)	C(20)	10137(2)	10752(2)	1159(1)	53(1)
F(1)	8879(1)	6200(1)	1938(1)	54(1)	C(2)	8909(2)	6910(2)	655(1)	50(1)
O(1)	8904(1)	8372(1)	1267(1)	38(1)	F(10)	12208(1)	8080(2)	2571(1)	107(1)
N(2)	9726(1)	9103(1)	2582(1)	30(1)	C(39)	10561(2)	6690(2)	3236(1)	40(1)
F(3)	9757(1)	4523(1)	3815(1)	58(1)	C(18)	9714(2)	11780(2)	2811(1)	45(1)
C(34)	10052(2)	6835(2)	2658(1)	35(1)	C(26)	10018(2)	9154(2)	3741(1)	45(1)
C(13)	9186(2)	10984(2)	2719(1)	31(1)	C(23)	11849(2)	10803(2)	1788(2)	53(1)
C(11)	8476(2)	9935(2)	1608(1)	32(1)	C(5)	7296(2)	7569(2)	-20(1)	51(1)

F(2)	8706(1)	4706(1)	2674(1)	61(1)	F(7)	11743(2)	8814(2)	64(1)	119(1)
C(10)	7839(2)	10642(2)	1480(1)	37(1)	F(9)	13617(1)	8464(2)	1988(1)	123(1)
F(4)	10996(1)	5842(1)	4191(1)	72(1)	C(41)	11146(2)	8433(2)	999(1)	53(1)
C(7)	7633(2)	9028(2)	744(1)	36(1)	C(17)	9555(2)	12453(2)	3246(2)	62(1)
C(12)	8343(2)	9143(2)	1225(1)	32(1)	C(43)	12687(2)	8627(2)	1014(2)	59(1)
C(6)	7760(2)	8112(2)	465(1)	39(1)	C(22)	11669(2)	11108(3)	1172(2)	67(1)
C(19)	10308(2)	10440(2)	1776(1)	34(1)	C(4)	7650(2)	6713(2)	-157(1)	62(1)
C(25)	9451(2)	8905(2)	3194(1)	37(1)	C(45)	12064(2)	8248(2)	1934(2)	59(1)
F(8)	13388(1)	8828(2)	723(1)	83(1)	C(3)	8439(2)	6390(2)	173(1)	61(1)
F(6)	10347(1)	8454(2)	635(1)	100(1)	C(29)	8443(2)	8231(2)	3834(2)	61(1)
C(40)	11210(2)	8239(2)	1630(1)	41(1)	C(21)	10823(2)	11086(3)	861(2)	73(1)
C(37)	9853(2)	5262(2)	3436(1)	43(1)	C(16)	8874(2)	12338(2)	3594(2)	56(1)
C(15)	8337(2)	11554(2)	3506(1)	44(1)	C(42)	11858(2)	8622(3)	684(2)	63(1)
C(9)	7123(2)	10547(2)	999(1)	42(1)	C(44)	12798(2)	8443(3)	1648(2)	68(1)
C(35)	9434(2)	6137(2)	2494(1)	38(1)	C(28)	8987(3)	8472(2)	4382(2)	75(1)
C(38)	10475(2)	5934(2)	3626(1)	45(1)	C(27)	9767(3)	8929(2)	4330(1)	67(1)
C(30)	8653(2)	8436(2)	3233(1)	41(1)	C(32)	8739(4)	8232(3)	5035(2)	133(2)
C(36)	9325(2)	5363(2)	2863(1)	42(1)	C(3S)	415(4)	4534(5)	1235(3)	133(2)
C(14)	8487(2)	10882(2)	3069(1)	37(1)	C(4S)	1344(5)	4833(6)	1577(4)	158(2)
C(8)	7014(2)	9747(2)	631(1)	42(1)	C(5S)	1660(6)	5654(5)	1321(4)	201(4)
C(24)	11174(2)	10462(2)	2091(1)	43(1)	C(1S)	-804(5)	3378(6)	1085(5)	209(4)
C(1)	8536(2)	7759(2)	790(1)	39(1)	C(2S)	86(7)	3689(6)	1435(5)	217(4)

Table A.23: Bond lengths [Å] for **4**.

Zn(1)-N(2)	2.0056(19)	C(37)-C(36)	1.370(4)	C(17)-C(16)	1.373(4)
Zn(1)-C(40)	2.010(3)	C(15)-C(14)	1.376(3)	C(17)-H(17)	0.9500
Zn(1)-C(34)	2.014(2)	C(15)-C(16)	1.379(4)	C(43)-C(42)	1.356(5)
P(2)-N(2)	1.6031(19)	C(15)-H(15)	0.9500	C(43)-C(44)	1.363(5)
P(2)-C(13)	1.797(2)	C(9)-C(8)	1.376(4)	C(22)-C(21)	1.364(5)
P(2)-C(11)	1.802(2)	C(9)-H(9)	0.9500	C(22)-H(22)	0.9500
P(2)-C(19)	1.802(2)	C(35)-C(36)	1.375(4)	C(4)-C(3)	1.383(5)
F(5)-C(39)	1.362(3)	C(38)-C(39)	1.374(4)	C(4)-H(4)	0.9500
F(1)-C(35)	1.356(3)	C(30)-C(29)	1.394(4)	C(45)-C(44)	1.378(4)
O(1)-C(12)	1.384(3)	C(30)-C(33)	1.501(4)	C(3)-H(3)	0.9500
O(1)-C(1)	1.393(3)	C(14)-H(14)	0.9500	C(29)-C(28)	1.375(5)
N(2)-C(25)	1.455(3)	C(8)-H(8)	0.9500	C(29)-H(29)	0.9500
F(3)-C(37)	1.344(3)	C(24)-C(23)	1.382(4)	C(21)-H(21)	0.9500
C(34)-C(39)	1.375(3)	C(24)-H(24)	0.9500	C(16)-H(16)	0.9500
C(34)-C(35)	1.378(3)	C(1)-C(2)	1.381(4)	C(28)-C(27)	1.376(5)
C(13)-C(18)	1.385(3)	C(31)-C(26)	1.500(4)	C(28)-C(32)	1.532(4)
C(13)-C(14)	1.395(3)	C(31)-H(31A)	0.9800	C(27)-H(27)	0.9500
C(11)-C(12)	1.387(3)	C(31)-H(31B)	0.9800	C(32)-H(32A)	0.9800
C(11)-C(10)	1.397(3)	C(31)-H(31C)	0.9800	C(32)-H(32B)	0.9800

F(2)-C(36)	1.348(3)	C(33)-H(33A)	0.9800	C(32)-H(32C)	0.9800
C(10)-C(9)	1.393(3)	C(33)-H(33B)	0.9800	C(3S)-C(2S)	1.392(9)
C(10)-H(10)	0.9500	C(33)-H(33C)	0.9800	C(3S)-C(4S)	1.559(9)
F(4)-C(38)	1.351(3)	C(20)-C(21)	1.386(4)	C(3S)-H(3S1)	0.9900
C(7)-C(8)	1.388(4)	C(20)-H(20)	0.9500	C(3S)-H(3S2)	0.9900
C(7)-C(12)	1.391(3)	C(2)-C(3)	1.379(4)	C(4S)-C(5S)	1.401(9)
C(7)-C(6)	1.455(4)	C(2)-H(2)	0.9500	C(4S)-H(4S1)	0.9900
C(6)-C(1)	1.378(4)	F(10)-C(45)	1.365(4)	C(4S)-H(4S2)	0.9900
C(6)-C(5)	1.397(4)	C(18)-C(17)	1.377(4)	C(5S)-H(5S1)	0.9800
C(19)-C(20)	1.376(4)	C(18)-H(18)	0.9500	C(5S)-H(5S2)	0.9800
C(19)-C(24)	1.394(3)	C(26)-C(27)	1.402(4)	C(5S)-H(5S3)	0.9800
C(25)-C(26)	1.394(4)	C(23)-C(22)	1.372(4)	C(1S)-C(2S)	1.519(11)
C(25)-C(30)	1.401(4)	C(23)-H(23)	0.9500	C(1S)-H(1S1)	0.9800
F(8)-C(43)	1.343(3)	C(5)-C(4)	1.379(4)	C(1S)-H(1S2)	0.9800
F(6)-C(41)	1.349(3)	C(5)-H(5)	0.9500	C(1S)-H(1S3)	0.9800
C(40)-C(41)	1.362(4)	F(7)-C(42)	1.335(4)	C(2S)-H(2S1)	0.9900
C(40)-C(45)	1.370(4)	F(9)-C(44)	1.353(4)	C(2S)-H(2S2)	0.9900
C(37)-C(38)	1.365(4)	C(41)-C(42)	1.386(4)		

Table A.24: Bond angles [°] for **4**

N(2)-Zn(1)-C(40)	119.94(9)	C(37)-C(36)-C(35)	119.3(2)	F(10)-C(45)-C(44)	116.8(3)
N(2)-Zn(1)-C(34)	108.33(9)	C(15)-C(14)-C(13)	120.3(2)	C(40)-C(45)-C(44)	125.0(3)
C(40)-Zn(1)-C(34)	127.50(10)	C(15)-C(14)-H(14)	119.9	C(2)-C(3)-C(4)	121.6(3)
N(2)-P(2)-C(13)	112.16(10)	C(13)-C(14)-H(14)	119.9	C(2)-C(3)-H(3)	119.2
N(2)-P(2)-C(11)	114.42(10)	C(9)-C(8)-C(7)	119.1(2)	C(4)-C(3)-H(3)	119.2
C(13)-P(2)-C(11)	106.01(11)	C(9)-C(8)-H(8)	120.5	C(28)-C(29)-C(30)	122.5(3)
N(2)-P(2)-C(19)	109.89(11)	C(7)-C(8)-H(8)	120.5	C(28)-C(29)-H(29)	118.8
C(13)-P(2)-C(19)	108.87(11)	C(23)-C(24)-C(19)	120.2(3)	C(30)-C(29)-H(29)	118.7
C(11)-P(2)-C(19)	105.11(11)	C(23)-C(24)-H(24)	119.9	C(22)-C(21)-C(20)	120.7(3)
C(12)-O(1)-C(1)	105.50(18)	C(19)-C(24)-H(24)	119.9	C(22)-C(21)-H(21)	119.6
C(25)-N(2)-P(2)	121.40(15)	C(6)-C(1)-C(2)	124.2(2)	C(20)-C(21)-H(21)	119.6
C(25)-N(2)-Zn(1)	115.34(14)	C(6)-C(1)-O(1)	111.5(2)	C(17)-C(16)-C(15)	120.3(3)
P(2)-N(2)-Zn(1)	122.06(11)	C(2)-C(1)-O(1)	124.3(2)	C(17)-C(16)-H(16)	119.9
C(39)-C(34)-C(35)	113.4(2)	C(26)-C(31)-H(31A)	109.5	C(15)-C(16)-H(16)	119.9
C(39)-C(34)-Zn(1)	118.20(18)	C(26)-C(31)-H(31B)	109.5	F(7)-C(42)-C(43)	119.5(3)
C(35)-C(34)-Zn(1)	128.35(19)	H(31A)-C(31)-H(31B)	109.5	F(7)-C(42)-C(41)	121.3(3)
C(18)-C(13)-C(14)	119.0(2)	C(26)-C(31)-H(31C)	109.5	C(43)-C(42)-C(41)	119.3(3)
C(18)-C(13)-P(2)	120.96(18)	H(31A)-C(31)-H(31C)	109.5	F(9)-C(44)-C(43)	120.0(3)
C(14)-C(13)-P(2)	119.87(18)	H(31B)-C(31)-H(31C)	109.5	F(9)-C(44)-C(45)	121.0(3)
C(12)-C(11)-C(10)	115.4(2)	C(30)-C(33)-H(33A)	109.5	C(43)-C(44)-C(45)	119.0(3)
C(12)-C(11)-P(2)	121.57(18)	C(30)-C(33)-H(33B)	109.5	C(29)-C(28)-C(27)	118.2(3)
C(10)-C(11)-P(2)	122.92(18)	H(33A)-C(33)-H(33B)	109.5	C(29)-C(28)-C(32)	121.2(4)
C(9)-C(10)-C(11)	121.6(2)	C(30)-C(33)-H(33C)	109.5	C(27)-C(28)-C(32)	120.6(4)

C(9)-C(10)-H(10)	119.2	H(33A)-C(33)-H(33C)	109.5	C(28)-C(27)-C(26)	122.1(3)
C(11)-C(10)-H(10)	119.2	H(33B)-C(33)-H(33C)	109.5	C(28)-C(27)-H(27)	118.9
C(8)-C(7)-C(12)	118.7(2)	C(19)-C(20)-C(21)	119.8(3)	C(26)-C(27)-H(27)	118.9
C(8)-C(7)-C(6)	135.7(2)	C(19)-C(20)-H(20)	120.1	C(28)-C(32)-H(32A)	109.5
C(12)-C(7)-C(6)	105.6(2)	C(21)-C(20)-H(20)	120.1	C(28)-C(32)-H(32B)	109.5
O(1)-C(12)-C(11)	124.6(2)	C(3)-C(2)-C(1)	115.9(3)	H(32A)-C(32)-H(32B)	109.5
O(1)-C(12)-C(7)	111.4(2)	C(3)-C(2)-H(2)	122.1	C(28)-C(32)-H(32C)	109.5
C(11)-C(12)-C(7)	124.1(2)	C(1)-C(2)-H(2)	122.1	H(32A)-C(32)-H(32C)	109.5
C(1)-C(6)-C(5)	118.6(3)	F(5)-C(39)-C(38)	116.2(2)	H(32B)-C(32)-H(32C)	109.5
C(1)-C(6)-C(7)	106.0(2)	F(5)-C(39)-C(34)	119.3(2)	C(2S)-C(3S)-C(4S)	115.9(8)
C(5)-C(6)-C(7)	135.4(3)	C(38)-C(39)-C(34)	124.5(2)	C(2S)-C(3S)-H(3S1)	108.3
C(20)-C(19)-C(24)	119.2(2)	C(17)-C(18)-C(13)	120.3(2)	C(4S)-C(3S)-H(3S1)	108.3
C(20)-C(19)-P(2)	121.80(19)	C(17)-C(18)-H(18)	119.8	C(2S)-C(3S)-H(3S2)	108.3
C(24)-C(19)-P(2)	118.89(19)	C(13)-C(18)-H(18)	119.8	C(4S)-C(3S)-H(3S2)	108.3
C(26)-C(25)-C(30)	120.8(2)	C(25)-C(26)-C(27)	118.3(3)	H(3S1)-C(3S)-H(3S2)	107.4
C(26)-C(25)-N(2)	118.4(2)	C(25)-C(26)-C(31)	121.7(2)	C(5S)-C(4S)-C(3S)	112.7(7)
C(30)-C(25)-N(2)	120.8(2)	C(27)-C(26)-C(31)	120.0(3)	C(5S)-C(4S)-H(4S1)	109.0
C(41)-C(40)-C(45)	113.1(3)	C(22)-C(23)-C(24)	119.9(3)	C(3S)-C(4S)-H(4S1)	109.0
C(41)-C(40)-Zn(1)	130.2(2)	C(22)-C(23)-H(23)	120.1	C(5S)-C(4S)-H(4S2)	109.0
C(45)-C(40)-Zn(1)	116.6(2)	C(24)-C(23)-H(23)	120.1	C(3S)-C(4S)-H(4S2)	109.0
F(3)-C(37)-C(38)	120.0(2)	C(4)-C(5)-C(6)	118.1(3)	H(4S1)-C(4S)-H(4S2)	107.8
F(3)-C(37)-C(36)	121.0(2)	C(4)-C(5)-H(5)	121.0	C(4S)-C(5S)-H(5S1)	109.5
C(38)-C(37)-C(36)	119.0(2)	C(6)-C(5)-H(5)	121.0	C(4S)-C(5S)-H(5S2)	109.5
C(14)-C(15)-C(16)	119.9(2)	F(6)-C(41)-C(40)	120.2(2)	H(5S1)-C(5S)-H(5S2)	109.5
C(14)-C(15)-H(15)	120.1	F(6)-C(41)-C(42)	115.1(3)	C(4S)-C(5S)-H(5S3)	109.5
C(16)-C(15)-H(15)	120.1	C(40)-C(41)-C(42)	124.6(3)	H(5S1)-C(5S)-H(5S3)	109.5
C(8)-C(9)-C(10)	121.1(2)	C(16)-C(17)-C(18)	120.2(3)	H(5S2)-C(5S)-H(5S3)	109.5
C(8)-C(9)-H(9)	119.5	C(16)-C(17)-H(17)	119.9	C(2S)-C(1S)-H(1S1)	109.5
C(10)-C(9)-H(9)	119.5	C(18)-C(17)-H(17)	119.9	C(2S)-C(1S)-H(1S2)	109.5
F(1)-C(35)-C(36)	116.1(2)	F(8)-C(43)-C(42)	120.6(3)	H(1S1)-C(1S)-H(1S2)	109.5
F(1)-C(35)-C(34)	119.5(2)	F(8)-C(43)-C(44)	120.4(3)	C(2S)-C(1S)-H(1S3)	109.5
C(36)-C(35)-C(34)	124.4(2)	C(42)-C(43)-C(44)	119.1(3)	H(1S1)-C(1S)-H(1S3)	109.5
F(4)-C(38)-C(37)	119.4(2)	C(21)-C(22)-C(23)	120.2(3)	H(1S2)-C(1S)-H(1S3)	109.5
F(4)-C(38)-C(39)	121.2(2)	C(21)-C(22)-H(22)	119.9	C(3S)-C(2S)-C(1S)	116.0(9)
C(37)-C(38)-C(39)	119.4(2)	C(23)-C(22)-H(22)	119.9	C(3S)-C(2S)-H(2S1)	108.3
C(29)-C(30)-C(25)	118.1(3)	C(5)-C(4)-C(3)	121.6(3)	C(1S)-C(2S)-H(2S1)	108.3
C(29)-C(30)-C(33)	119.4(3)	C(5)-C(4)-H(4)	119.2	C(3S)-C(2S)-H(2S2)	108.3
C(25)-C(30)-C(33)	122.5(2)	C(3)-C(4)-H(4)	119.2	C(1S)-C(2S)-H(2S2)	108.3
F(2)-C(36)-C(37)	119.4(2)	F(10)-C(45)-C(40)	118.2(3)	H(2S1)-C(2S)-H(2S2)	107.4
F(2)-C(36)-C(35)	121.3(2)				

Table A.25: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	35(1)	34(1)	33(1)	0(1)	6(1)	1(1)
P(2)	29(1)	30(1)	29(1)	0(1)	4(1)	-1(1)
F(5)	63(1)	43(1)	59(1)	5(1)	-17(1)	-16(1)
F(1)	51(1)	61(1)	46(1)	-4(1)	-8(1)	-5(1)
O(1)	37(1)	39(1)	36(1)	-8(1)	4(1)	0(1)
N(2)	33(1)	30(1)	27(1)	-1(1)	4(1)	0(1)
F(3)	63(1)	40(1)	71(1)	17(1)	9(1)	-2(1)
C(34)	37(1)	32(1)	37(1)	-2(1)	8(1)	4(1)
C(13)	32(1)	29(1)	32(1)	-1(1)	3(1)	2(1)
C(11)	31(1)	35(1)	30(1)	3(1)	6(1)	-1(1)
F(2)	52(1)	50(1)	79(1)	-5(1)	2(1)	-18(1)
C(10)	40(1)	35(1)	35(1)	4(1)	6(1)	0(1)
F(4)	89(1)	58(1)	59(1)	20(1)	-28(1)	-13(1)
C(7)	35(1)	45(1)	27(1)	4(1)	5(1)	-9(1)
C(12)	29(1)	38(1)	30(1)	2(1)	7(1)	-3(1)
C(6)	46(2)	46(2)	26(1)	-1(1)	9(1)	-13(1)
C(19)	36(1)	31(1)	37(1)	2(1)	10(1)	-1(1)
C(25)	51(2)	28(1)	33(1)	2(1)	11(1)	5(1)
F(8)	60(1)	90(1)	110(2)	-9(1)	52(1)	-8(1)
F(6)	55(1)	203(3)	42(1)	13(1)	5(1)	-44(1)
C(40)	41(1)	37(1)	48(2)	-3(1)	13(1)	3(1)
C(37)	47(2)	31(1)	50(2)	6(1)	10(1)	4(1)
C(15)	39(1)	47(2)	48(2)	-5(1)	13(1)	3(1)
C(9)	36(1)	47(2)	43(2)	11(1)	4(1)	5(1)
C(35)	34(1)	39(1)	38(1)	-5(1)	0(1)	3(1)
C(38)	51(2)	38(1)	42(2)	4(1)	-6(1)	2(1)
C(30)	56(2)	30(1)	42(2)	3(1)	20(1)	1(1)
C(36)	36(1)	33(1)	56(2)	-7(1)	8(1)	-4(1)
C(14)	34(1)	36(1)	43(1)	0(1)	7(1)	-1(1)
C(8)	38(1)	55(2)	32(1)	7(1)	-1(1)	-7(1)
C(24)	38(1)	46(2)	45(2)	0(1)	9(1)	-2(1)
C(1)	43(1)	44(2)	30(1)	-6(1)	9(1)	-10(1)
C(31)	65(2)	47(2)	42(2)	-3(1)	-15(1)	0(1)
C(33)	40(2)	42(2)	56(2)	5(1)	17(1)	-3(1)
C(20)	43(2)	69(2)	48(2)	17(1)	9(1)	-3(1)
C(2)	57(2)	52(2)	43(2)	-10(1)	14(1)	-3(1)
F(10)	48(1)	201(3)	73(1)	40(2)	7(1)	25(1)
C(39)	41(1)	31(1)	45(2)	-1(1)	-2(1)	-3(1)
C(18)	38(1)	37(1)	64(2)	-11(1)	18(1)	-5(1)
C(26)	67(2)	36(1)	31(1)	-1(1)	-1(1)	4(1)

C(23)	37(2)	61(2)	63(2)	2(2)	13(1)	-4(1)
C(5)	59(2)	62(2)	32(1)	-1(1)	2(1)	-20(2)
F(7)	88(2)	218(3)	56(1)	15(2)	30(1)	-52(2)
F(9)	36(1)	219(3)	114(2)	18(2)	14(1)	24(2)
C(41)	46(2)	68(2)	46(2)	-6(1)	11(1)	-16(1)
C(17)	45(2)	48(2)	96(2)	-32(2)	25(2)	-15(1)
C(43)	49(2)	58(2)	77(2)	-8(2)	35(2)	-1(1)
C(22)	51(2)	80(2)	75(2)	22(2)	27(2)	-8(2)
C(4)	87(2)	60(2)	39(2)	-16(1)	6(2)	-23(2)
C(45)	46(2)	78(2)	55(2)	10(2)	13(1)	19(2)
C(3)	84(2)	54(2)	48(2)	-18(2)	16(2)	-8(2)
C(29)	93(2)	43(2)	54(2)	0(1)	35(2)	-11(2)
C(21)	62(2)	104(3)	56(2)	36(2)	18(2)	-7(2)
C(16)	47(2)	53(2)	68(2)	-29(2)	14(1)	-1(1)
C(42)	64(2)	78(2)	51(2)	-3(2)	23(2)	-19(2)
C(44)	32(2)	85(2)	88(3)	0(2)	15(2)	16(2)
C(28)	139(3)	51(2)	42(2)	-1(2)	35(2)	-17(2)
C(27)	119(3)	47(2)	33(2)	-1(1)	5(2)	-5(2)
C(32)	247(7)	112(4)	54(2)	-1(2)	66(3)	-57(4)
C(3S)	140(5)	117(5)	158(5)	-28(4)	70(5)	19(4)
C(4S)	146(6)	162(7)	173(7)	-7(6)	48(5)	18(5)
C(5S)	234(9)	99(5)	282(11)	-30(6)	79(8)	19(5)
C(1S)	118(6)	157(7)	343(13)	-22(7)	5(7)	-16(5)
C(2S)	241(11)	150(8)	279(12)	18(8)	105(10)	30(8)

Table A.26: Crystal data and structure refinement for **5b**.

Empirical formula	$C_{40}H_{38}F_3NO_4PS$	
Formula weight	716.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2135(5) Å	α= 77.0560(10)°.
	b = 10.9472(6) Å	β= 88.6580(10)°.
	c = 18.2092(10) Å	γ = 87.1610(10)°.
Volume	1787.61(17) $Å^3$	
Z	2	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	750	
Crystal size	0.50 x 0.39 x 0.29 mm^3	
Theta range for data collection	1.91 to 25.03°.	
Index ranges	-10<=h<=10, -13<=k<=13, -21<=l<=21	
Reflections collected	17259	
Independent reflections	6284 [R(int) = 0.0146]	
Completeness to theta = 25.03°	99.70%	
Max. and min. transmission	0.9464 and 0.9103	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6284 / 6 / 472	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1128	
R indices (all data)	R1 = 0.0463, wR2 = 0.1166	
Largest diff. peak and hole	0.796 and -0.487 $e.Å^{-3}$	

Table A.27: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **5b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	8569(1)	5541(1)	2303(1)	23(1)	C(22)	9383(3)	3423(2)	4730(1)	49(1)
N(1)	6973(2)	6260(1)	2149(1)	24(1)	C(23)	8069(3)	3361(2)	4405(1)	43(1)
C(12)	9769(2)	8841(2)	3241(1)	29(1)	C(24)	7822(2)	3976(2)	3663(1)	34(1)
C(1S)	3544(3)	-53(3)	4887(1)	55(1)	C(25)	6557(2)	7511(2)	2246(1)	24(1)
O(1)	9273(1)	7777(1)	3047(1)	29(1)	C(26)	5856(2)	7676(2)	2908(1)	28(1)
C(11)	9155(2)	9379(2)	3797(1)	36(1)	C(27)	5529(2)	8900(2)	2983(1)	36(1)
C(2S)	4373(2)	718(2)	4353(1)	48(1)	C(28)	5885(2)	9918(2)	2426(1)	41(1)
C(10)	9784(2)	10453(2)	3896(1)	39(1)	C(29)	6513(2)	9738(2)	1762(1)	38(1)
C(3S)	5833(3)	765(3)	4467(1)	51(1)	C(30)	6840(2)	8538(2)	1649(1)	28(1)
C(9)	10969(2)	10950(2)	3459(1)	38(1)	C(31)	5428(2)	6595(2)	3543(1)	32(1)

C(8)	11574(2)	10387(2)	2911(1)	36(1)	C(32)	6179(3)	6625(2)	4279(1)	47(1)
C(7)	10953(2)	9307(2)	2792(1)	29(1)	C(33)	3776(2)	6582(2)	3647(1)	48(1)
C(6)	11192(2)	8492(2)	2270(1)	29(1)	C(34)	7358(2)	8349(2)	882(1)	32(1)
C(5)	12181(2)	8415(2)	1689(1)	36(1)	C(35)	8233(3)	9416(2)	433(1)	55(1)
C(4)	12053(2)	7472(2)	1304(1)	39(1)	C(36)	6049(3)	8121(3)	438(1)	52(1)
C(3)	10970(2)	6610(2)	1483(1)	33(1)	S(1)	4056(1)	3820(1)	2278(1)	42(1)
C(2)	9961(2)	6660(2)	2062(1)	26(1)	O(2)	2664(3)	3617(3)	2608(1)	85(1)
C(1)	10124(2)	7605(2)	2449(1)	26(1)	O(3)	5250(3)	3063(2)	2636(1)	89(1)
C(13)	8702(2)	4451(2)	1700(1)	26(1)	O(4)	4385(2)	5109(2)	2025(1)	70(1)
C(14)	9396(3)	3284(2)	1940(1)	44(1)	O(2B)	2920(40)	4850(30)	2290(20)	85(13)
C(15)	9528(3)	2473(2)	1455(1)	55(1)	O(3B)	3590(30)	2650(20)	2674(16)	51(8)
C(16)	8981(2)	2812(2)	742(1)	42(1)	O(4B)	5380(30)	4150(20)	2468(15)	43(8)
C(17)	8281(3)	3964(2)	504(1)	44(1)	C(37)	3910(3)	3326(3)	1397(1)	52(1)
C(18)	8135(3)	4787(2)	978(1)	40(1)	F(1)	2861(3)	3943(2)	978(1)	100(1)
C(19)	8905(2)	4696(2)	3257(1)	27(1)	F(2)	5108(3)	3373(3)	1019(1)	138(1)
C(20)	10247(2)	4734(2)	3585(1)	37(1)	F(3)	3560(2)	2126(2)	1505(1)	77(1)
C(21)	10477(3)	4084(2)	4321(1)	49(1)					

Table A.28: Bond lengths [Å] for **5b**.

P(1)-N(1)	1.6333(15)	C(3)-C(2)	1.398(3)	C(28)-H(28)	0.9500
P(1)-C(13)	1.7910(18)	C(3)-H(3)	0.9500	C(29)-C(30)	1.392(3)
P(1)-C(2)	1.7959(18)	C(2)-C(1)	1.391(3)	C(29)-H(29)	0.9500
P(1)-C(19)	1.8021(18)	C(13)-C(14)	1.384(3)	C(30)-C(34)	1.519(3)
N(1)-C(25)	1.451(2)	C(13)-C(18)	1.390(3)	C(31)-C(33)	1.530(3)
N(1)-H(1N)	0.82(2)	C(14)-C(15)	1.384(3)	C(31)-C(32)	1.530(3)
C(12)-C(11)	1.379(3)	C(14)-H(14)	0.9500	C(31)-H(31)	1.0000
C(12)-O(1)	1.391(2)	C(15)-C(16)	1.369(3)	C(32)-H(32A)	0.9800
C(12)-C(7)	1.395(3)	C(15)-H(15)	0.9500	C(32)-H(32B)	0.9800
C(1S)-C(3S)#1	1.378(4)	C(16)-C(17)	1.371(3)	C(32)-H(32C)	0.9800
C(1S)-C(2S)	1.380(4)	C(16)-H(16)	0.9500	C(33)-H(33A)	0.9800
C(1S)-H(1S)	0.9500	C(17)-C(18)	1.381(3)	C(33)-H(33B)	0.9800
O(1)-C(1)	1.369(2)	C(17)-H(17)	0.9500	C(33)-H(33C)	0.9800
C(11)-C(10)	1.385(3)	C(18)-H(18)	0.9500	C(34)-C(35)	1.523(3)
C(11)-H(11)	0.9500	C(19)-C(20)	1.391(3)	C(34)-C(36)	1.528(3)
C(2S)-C(3S)	1.371(3)	C(19)-C(24)	1.395(3)	C(34)-H(34)	1.0000
C(2S)-H(2S)	0.9500	C(20)-C(21)	1.385(3)	C(35)-H(35A)	0.9800
C(10)-C(9)	1.394(3)	C(20)-H(20)	0.9500	C(35)-H(35B)	0.9800
C(10)-H(10)	0.9500	C(21)-C(22)	1.375(4)	C(35)-H(35C)	0.9800
C(3S)-C(1S)#1	1.378(4)	C(21)-H(21)	0.9500	C(36)-H(36A)	0.9800
C(3S)-H(3S)	0.9500	C(22)-C(23)	1.372(3)	C(36)-H(36B)	0.9800
C(9)-C(8)	1.379(3)	C(22)-H(22)	0.9500	C(36)-H(36C)	0.9800
C(9)-H(9)	0.9500	C(23)-C(24)	1.386(3)	S(1)-O(4B)	1.36(2)
C(8)-C(7)	1.400(3)	C(23)-H(23)	0.9500	S(1)-O(3B)	1.40(2)

C(8)-H(8)	0.9500	C(24)-H(24)	0.9500	S(1)-O(2)	1.410(2)
C(7)-C(6)	1.448(3)	C(25)-C(26)	1.398(3)	S(1)-O(3)	1.423(2)
C(6)-C(5)	1.395(3)	C(25)-C(30)	1.408(3)	S(1)-O(4)	1.4276(19)
C(6)-C(1)	1.399(3)	C(26)-C(27)	1.395(3)	S(1)-O(2B)	1.50(3)
C(5)-C(4)	1.382(3)	C(26)-C(31)	1.518(3)	S(1)-C(37)	1.814(3)
C(5)-H(5)	0.9500	C(27)-C(28)	1.376(3)	C(37)-F(2)	1.285(3)
C(4)-C(3)	1.390(3)	C(27)-H(27)	0.9500	C(37)-F(1)	1.308(3)
C(4)-H(4)	0.9500	C(28)-C(29)	1.378(3)	C(37)-F(3)	1.339(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table A.29: Bond angles [°] for **5b**

N(1)-P(1)-C(13)	105.90(8)	C(13)-C(14)-C(15)	119.60(19)	C(31)-C(32)-H(32A)	109.5
N(1)-P(1)-C(2)	109.59(8)	C(13)-C(14)-H(14)	120.2	C(31)-C(32)-H(32B)	109.5
C(13)-P(1)-C(2)	110.16(8)	C(15)-C(14)-H(14)	120.2	H(32A)-C(32)-H(32B)	109.5
N(1)-P(1)-C(19)	115.96(8)	C(16)-C(15)-C(14)	120.8(2)	C(31)-C(32)-H(32C)	109.5
C(13)-P(1)-C(19)	108.61(8)	C(16)-C(15)-H(15)	119.6	H(32A)-C(32)-H(32C)	109.5
C(2)-P(1)-C(19)	106.57(8)	C(14)-C(15)-H(15)	119.6	H(32B)-C(32)-H(32C)	109.5
C(25)-N(1)-P(1)	126.83(13)	C(15)-C(16)-C(17)	119.87(19)	C(31)-C(33)-H(33A)	109.5
C(25)-N(1)-H(1N)	115.7(16)	C(15)-C(16)-H(16)	120.1	C(31)-C(33)-H(33B)	109.5
P(1)-N(1)-H(1N)	115.6(15)	C(17)-C(16)-H(16)	120.1	H(33A)-C(33)-H(33B)	109.5
C(11)-C(12)-O(1)	124.39(17)	C(16)-C(17)-C(18)	120.3(2)	C(31)-C(33)-H(33C)	109.5
C(11)-C(12)-C(7)	124.27(18)	C(16)-C(17)-H(17)	119.8	H(33A)-C(33)-H(33C)	109.5
O(1)-C(12)-C(7)	111.33(16)	C(18)-C(17)-H(17)	119.8	H(33B)-C(33)-H(33C)	109.5
C(3S)#1-C(1S)-C(2	120.7(2)	C(17)-C(18)-C(13)	120.01(18)	C(30)-C(34)-C(35)	114.01(17)
C(3S)#1-C(1S)-H(1	119.7	C(17)-C(18)-H(18)	120.0	C(30)-C(34)-C(36)	109.01(16)
C(2S)-C(1S)-H(1S)	119.7	C(13)-C(18)-H(18)	120.0	C(35)-C(34)-C(36)	111.18(19)
C(1)-O(1)-C(12)	105.52(14)	C(20)-C(19)-C(24)	119.91(18)	C(30)-C(34)-H(34)	107.5
C(12)-C(11)-C(10)	115.87(19)	C(20)-C(19)-P(1)	120.47(15)	C(35)-C(34)-H(34)	107.5
C(12)-C(11)-H(11)	122.1	C(24)-C(19)-P(1)	119.60(14)	C(36)-C(34)-H(34)	107.5
C(10)-C(11)-H(11)	122.1	C(21)-C(20)-C(19)	119.5(2)	C(34)-C(35)-H(35A)	109.5
C(3S)-C(2S)-C(1S)	119.4(2)	C(21)-C(20)-H(20)	120.3	C(34)-C(35)-H(35B)	109.5
C(3S)-C(2S)-H(2S)	120.3	C(19)-C(20)-H(20)	120.3	H(35A)-C(35)-H(35B)	109.5
C(1S)-C(2S)-H(2S)	120.3	C(22)-C(21)-C(20)	120.4(2)	C(34)-C(35)-H(35C)	109.5
C(11)-C(10)-C(9)	121.7(2)	C(22)-C(21)-H(21)	119.8	H(35A)-C(35)-H(35C)	109.5
C(11)-C(10)-H(10)	119.2	C(20)-C(21)-H(21)	119.8	H(35B)-C(35)-H(35C)	109.5
C(9)-C(10)-H(10)	119.2	C(23)-C(22)-C(21)	120.3(2)	C(34)-C(36)-H(36A)	109.5
C(2S)-C(3S)-C(1S)	120.0(2)	C(23)-C(22)-H(22)	119.9	C(34)-C(36)-H(36B)	109.5
C(2S)-C(3S)-H(3S)	120.0	C(21)-C(22)-H(22)	119.9	H(36A)-C(36)-H(36B)	109.5
C(1S)#1-C(3S)-H(3	120.0	C(22)-C(23)-C(24)	120.5(2)	C(34)-C(36)-H(36C)	109.5
C(8)-C(9)-C(10)	121.40(18)	C(22)-C(23)-H(23)	119.8	H(36A)-C(36)-H(36C)	109.5
C(8)-C(9)-H(9)	119.3	C(24)-C(23)-H(23)	119.8	H(36B)-C(36)-H(36C)	109.5
C(10)-C(9)-H(9)	119.3	C(23)-C(24)-C(19)	119.3(2)	O(4B)-S(1)-O(3B)	116.3(15)

C(9)-C(8)-C(7)	118.32(19)	C(23)-C(24)-H(24)	120.3	O(4B)-S(1)-O(2)	138.4(11)
C(9)-C(8)-H(8)	120.8	C(19)-C(24)-H(24)	120.3	O(3B)-S(1)-O(2)	55.5(12)
C(7)-C(8)-H(8)	120.8	C(26)-C(25)-C(30)	121.46(16)	O(4B)-S(1)-O(3)	49.7(11)
C(12)-C(7)-C(8)	118.47(18)	C(26)-C(25)-N(1)	120.31(15)	O(3B)-S(1)-O(3)	69.6(12)
C(12)-C(7)-C(6)	105.68(16)	C(30)-C(25)-N(1)	118.21(15)	O(2)-S(1)-O(3)	118.01(18)
C(8)-C(7)-C(6)	135.81(18)	C(27)-C(26)-C(25)	117.92(17)	O(4B)-S(1)-O(4)	63.4(11)
C(5)-C(6)-C(1)	118.91(18)	C(27)-C(26)-C(31)	118.68(17)	O(3B)-S(1)-O(4)	166.4(12)
C(5)-C(6)-C(7)	135.66(18)	C(25)-C(26)-C(31)	123.40(16)	O(2)-S(1)-O(4)	114.73(15)
C(1)-C(6)-C(7)	105.43(16)	C(28)-C(27)-C(26)	121.36(18)	O(3)-S(1)-O(4)	112.84(14)
C(4)-C(5)-C(6)	118.53(18)	C(28)-C(27)-H(27)	119.3	O(4B)-S(1)-O(2B)	111.1(18)
C(4)-C(5)-H(5)	120.7	C(26)-C(27)-H(27)	119.3	O(3B)-S(1)-O(2B)	111.7(18)
C(6)-C(5)-H(5)	120.7	C(27)-C(28)-C(29)	119.93(18)	O(2)-S(1)-O(2B)	56.3(15)
C(5)-C(4)-C(3)	121.68(18)	C(27)-C(28)-H(28)	120.0	O(3)-S(1)-O(2B)	148.8(16)
C(5)-C(4)-H(4)	119.2	C(29)-C(28)-H(28)	120.0	O(4)-S(1)-O(2B)	58.8(15)
C(3)-C(4)-H(4)	119.2	C(28)-C(29)-C(30)	121.25(18)	O(4B)-S(1)-C(37)	118.1(11)
C(4)-C(3)-C(2)	121.30(18)	C(28)-C(29)-H(29)	119.4	O(3B)-S(1)-C(37)	90.0(12)
C(4)-C(3)-H(3)	119.4	C(30)-C(29)-H(29)	119.4	O(2)-S(1)-C(37)	103.14(12)
C(2)-C(3)-H(3)	119.4	C(29)-C(30)-C(25)	117.83(17)	O(3)-S(1)-C(37)	103.27(13)
C(1)-C(2)-C(3)	116.03(17)	C(29)-C(30)-C(34)	120.64(17)	O(4)-S(1)-C(37)	102.10(13)
C(1)-C(2)-P(1)	122.35(13)	C(25)-C(30)-C(34)	121.31(16)	O(2B)-S(1)-C(37)	107.9(16)
C(3)-C(2)-P(1)	121.60(14)	C(26)-C(31)-C(33)	110.85(16)	F(2)-C(37)-F(1)	110.6(3)
O(1)-C(1)-C(2)	124.49(16)	C(26)-C(31)-C(32)	111.61(17)	F(2)-C(37)-F(3)	104.0(3)
O(1)-C(1)-C(6)	111.99(16)	C(33)-C(31)-C(32)	111.34(17)	F(1)-C(37)-F(3)	103.8(2)
C(2)-C(1)-C(6)	123.52(17)	C(26)-C(31)-H(31)	107.6	F(2)-C(37)-S(1)	113.35(19)
C(14)-C(13)-C(18)	119.40(17)	C(33)-C(31)-H(31)	107.6	F(1)-C(37)-S(1)	112.2(2)
C(14)-C(13)-P(1)	120.58(15)	C(32)-C(31)-H(31)	107.6	F(3)-C(37)-S(1)	112.17(17)
C(18)-C(13)-P(1)	120.00(14)				

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table A.30: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **5b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	25(1)	21(1)	23(1)	-5(1)	0(1)	0(1)
N(1)	24(1)	21(1)	27(1)	-5(1)	0(1)	-2(1)
C(12)	28(1)	24(1)	34(1)	-6(1)	-5(1)	-2(1)
C(1S)	36(1)	84(2)	49(1)	-26(1)	-1(1)	-6(1)
O(1)	28(1)	28(1)	33(1)	-11(1)	5(1)	-6(1)
C(11)	34(1)	35(1)	40(1)	-11(1)	0(1)	-3(1)
C(2S)	44(1)	61(2)	43(1)	-23(1)	-1(1)	2(1)
C(10)	44(1)	34(1)	44(1)	-16(1)	-7(1)	3(1)
C(3S)	46(1)	67(2)	46(1)	-23(1)	3(1)	-12(1)
C(9)	42(1)	27(1)	46(1)	-8(1)	-14(1)	-4(1)

C(8)	34(1)	31(1)	40(1)	-1(1)	-8(1)	-8(1)
C(7)	27(1)	27(1)	31(1)	-2(1)	-6(1)	-1(1)
C(6)	26(1)	28(1)	30(1)	-1(1)	-4(1)	-2(1)
C(5)	29(1)	41(1)	36(1)	-3(1)	4(1)	-10(1)
C(4)	32(1)	49(1)	35(1)	-9(1)	11(1)	-5(1)
C(3)	31(1)	37(1)	33(1)	-10(1)	4(1)	-1(1)
C(2)	24(1)	26(1)	28(1)	-4(1)	0(1)	0(1)
C(1)	23(1)	27(1)	27(1)	-3(1)	0(1)	-1(1)
C(13)	28(1)	24(1)	29(1)	-8(1)	1(1)	0(1)
C(14)	59(1)	33(1)	43(1)	-14(1)	-21(1)	13(1)
C(15)	76(2)	34(1)	59(2)	-21(1)	-26(1)	22(1)
C(16)	52(1)	35(1)	44(1)	-21(1)	-5(1)	5(1)
C(17)	66(2)	40(1)	29(1)	-12(1)	-6(1)	10(1)
C(18)	60(1)	29(1)	29(1)	-7(1)	-4(1)	12(1)
C(19)	34(1)	23(1)	24(1)	-7(1)	-2(1)	3(1)
C(20)	40(1)	33(1)	38(1)	-9(1)	-9(1)	0(1)
C(21)	59(2)	46(1)	41(1)	-8(1)	-23(1)	1(1)
C(22)	82(2)	37(1)	27(1)	-4(1)	-12(1)	5(1)
C(23)	64(2)	30(1)	33(1)	-1(1)	6(1)	-1(1)
C(24)	39(1)	27(1)	34(1)	-3(1)	0(1)	0(1)
C(25)	23(1)	23(1)	28(1)	-6(1)	-2(1)	2(1)
C(26)	25(1)	29(1)	29(1)	-7(1)	-2(1)	2(1)
C(27)	38(1)	37(1)	36(1)	-15(1)	2(1)	6(1)
C(28)	50(1)	27(1)	48(1)	-14(1)	-1(1)	7(1)
C(29)	45(1)	24(1)	41(1)	-1(1)	1(1)	0(1)
C(30)	26(1)	26(1)	30(1)	-4(1)	0(1)	0(1)
C(31)	31(1)	36(1)	26(1)	-5(1)	3(1)	0(1)
C(32)	53(1)	55(1)	30(1)	-3(1)	-5(1)	-5(1)
C(33)	36(1)	60(2)	41(1)	2(1)	7(1)	-4(1)
C(34)	36(1)	28(1)	29(1)	0(1)	4(1)	1(1)
C(35)	65(2)	45(1)	48(1)	0(1)	23(1)	-11(1)
C(36)	54(1)	68(2)	37(1)	-16(1)	-5(1)	2(1)
S(1)	43(1)	37(1)	50(1)	-15(1)	-4(1)	-2(1)
O(2)	77(2)	109(2)	91(2)	-63(2)	38(1)	-52(1)
O(3)	115(2)	78(2)	83(2)	-40(1)	-58(2)	40(1)
O(4)	55(1)	42(1)	116(2)	-21(1)	-18(1)	-13(1)
C(37)	53(1)	60(2)	41(1)	-4(1)	-3(1)	-8(1)
F(1)	139(2)	76(1)	80(1)	-5(1)	-64(1)	13(1)
F(2)	100(2)	246(3)	105(2)	-106(2)	53(1)	-76(2)
F(3)	124(2)	54(1)	60(1)	-22(1)	-13(1)	-5(1)

Table A.31: Crystal data and structure refinement for **6b**.

Empirical formula	$C_{39}H_{39}F_3NO_4PSZn$	
Formula weight	771.11	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6030(9) Å	α= 75.1590(10)°.
	b = 12.3790(12) Å	β= 83.3150(10)°.
	c = 16.7009(16) Å	γ = 74.0350(10)°.
Volume	1842.8(3) $Å^3$	
Z	2	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.823 mm^{-1}	
F(000)	800	
Crystal size	0.32 x 0.16 x 0.11 mm^3	
Theta range for data collection	2.60 to 25.03°.	
Index ranges	-11<=h<=11, -14<=k<=14, -19<=l<=19	
Reflections collected	17771	
Independent reflections	6479 [R(int) = 0.0313]	
Completeness to theta = 25.03°	99.60%	
Max. and min. transmission	0.9179 and 0.7776	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6479 / 1200 / 591	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0806	
R indices (all data)	R1 = 0.0570, wR2 = 0.0891	
Largest diff. peak and hole	0.347 and -0.295 e.$Å^{-3}$	

Table A.32: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **6b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn	5981(4)	7374(3)	7835(2)	32(1)	C(11)	6742(9)	8282(7)	9859(5)	78(2)
ZnB	6164(8)	7501(7)	7936(5)	42(1)	C(11B)	6275(14)	7885(10)	9965(7)	38(2)
P	9224(1)	6597(1)	7029(1)	29(1)	C(12)	7717(10)	8430(8)	9187(5)	58(2)
S	5268(1)	10162(1)	7134(1)	37(1)	C(12B)	7296(15)	8140(12)	9337(9)	31(2)
N	7699(2)	6366(1)	7433(1)	27(1)	C(13)	10728(2)	5340(2)	7283(2)	35(1)
O(1)	7954(11)	7779(8)	8579(6)	42(2)	C(14)	11775(2)	5300(2)	7808(2)	42(1)
C(1B)	9022(12)	8153(11)	8021(6)	40(2)	C(15)	12925(3)	4324(2)	7992(2)	52(1)
O(1B)	7720(20)	7528(16)	8695(12)	32(2)	C(16)	13034(3)	3404(2)	7657(2)	55(1)
C(1)	8720(20)	8037(18)	8219(11)	27(3)	C(17)	12004(3)	3426(2)	7143(2)	51(1)
F(1)	7464(2)	10769(2)	6250(1)	91(1)	C(18)	10845(3)	4394(2)	6952(2)	44(1)

C(2B)	9607(19)	7718(14)	7337(8)	36(2)	C(19)	9313(2)	7097(2)	5915(1)	35(1)
C(2)	9470(40)	7790(30)	7479(17)	30(3)	C(20)	8182(3)	8005(2)	5549(2)	40(1)
F(2)	5480(2)	12096(1)	6125(1)	76(1)	C(21)	8219(3)	8461(2)	4704(2)	49(1)
O(2)	3770(2)	10437(2)	6989(1)	59(1)	C(22)	9397(3)	8019(2)	4214(2)	58(1)
C(3)	10682(12)	8266(10)	6853(6)	45(2)	C(23)	10524(3)	7139(2)	4567(2)	62(1)
C(3B)	10440(20)	8370(19)	7098(11)	34(3)	C(24)	10490(3)	6672(2)	5412(2)	49(1)
F(3)	5807(2)	10699(1)	5532(1)	76(1)	C(25)	7447(2)	5233(2)	7523(1)	29(1)
O(3)	5649(2)	10535(2)	7799(1)	60(1)	C(26)	6731(2)	5026(2)	6916(1)	33(1)
C(4)	11078(13)	9130(10)	7092(6)	67(2)	C(27)	6528(3)	3922(2)	7026(2)	44(1)
C(4B)	10750(20)	9253(17)	7384(10)	40(3)	C(28)	6992(3)	3060(2)	7720(2)	50(1)
O(4)	6067(2)	8981(1)	7103(1)	46(1)	C(29)	7630(3)	3293(2)	8328(2)	47(1)
C(5)	10460(10)	9516(7)	7783(6)	67(3)	C(30)	7875(2)	4370(2)	8257(2)	35(1)
C(5B)	9973(16)	9524(15)	8105(9)	43(3)	C(31)	6134(2)	5958(2)	6159(1)	36(1)
C(6)	9422(11)	9034(8)	8266(6)	58(2)	C(32)	6852(3)	5663(2)	5350(2)	51(1)
C(6B)	8976(16)	8929(15)	8510(10)	34(2)	C(33)	4482(3)	6200(2)	6148(2)	51(1)
C(7)	8575(10)	9188(6)	9007(6)	69(2)	C(34)	8510(3)	4605(2)	8967(2)	41(1)
C(7B)	8011(13)	8998(12)	9255(8)	36(2)	C(35)	9728(3)	3604(2)	9380(2)	56(1)
C(8)	8482(11)	9908(7)	9554(5)	104(2)	C(36)	7297(3)	4923(3)	9618(2)	62(1)
C(8B)	7742(15)	9641(11)	9823(8)	53(3)	C(37)	4107(5)	7104(4)	8314(3)	41(1)
C(9)	7570(13)	9776(9)	10217(6)	118(3)	C(37B)	4357(9)	7549(9)	8611(6)	62(2)
C(9B)	6722(18)	9462(12)	10477(10)	54(3)	C(38)	3276(5)	7868(4)	8897(3)	52(1)
C(10)	6695(14)	9019(9)	10401(6)	101(3)	C(38B)	3496(13)	6855(12)	8529(8)	107(5)
C(10B)	6015(12)	8569(9)	10536(7)	45(2)	C(39)	6050(3)	10970(2)	6215(2)	51(1)

Table A.33: Bond lengths [Å] for **6b**.

Zn-N	1.942(4)	C(6)-C(7)	1.424(11)	C(24)-H(24)	0.9500
Zn-C(37)	1.962(6)	C(6B)-C(7B)	1.468(16)	C(25)-C(26)	1.399(3)
Zn-O(4)	2.069(4)	C(7)-C(12)	1.369(10)	C(25)-C(30)	1.419(3)
Zn-O(1)	2.602(10)	C(7)-C(8)	1.412(10)	C(26)-C(27)	1.397(3)
ZnB-C(37B)	1.951(11)	C(7B)-C(8B)	1.348(17)	C(26)-C(31)	1.522(3)
ZnB-O(4)	1.983(8)	C(7B)-C(12B)	1.387(16)	C(27)-C(28)	1.381(4)
ZnB-N	2.008(8)	C(8)-C(9)	1.335(13)	C(27)-H(27)	0.9500
ZnB-O(1B)	2.08(2)	C(8)-H(8)	0.9500	C(28)-C(29)	1.371(4)
P-N	1.6065(18)	C(8B)-C(9B)	1.40(2)	C(28)-H(28)	0.9500
P-C(2B)	1.736(14)	C(8B)-H(8B)	0.9500	C(29)-C(30)	1.389(3)
P-C(13)	1.804(2)	C(9)-C(10)	1.379(15)	C(29)-H(29)	0.9500
P-C(19)	1.805(2)	C(9)-H(9)	0.9500	C(30)-C(34)	1.519(3)
P-C(2)	1.89(3)	C(9B)-C(10B)	1.426(19)	C(31)-C(32)	1.527(3)
S-O(2)	1.4189(18)	C(9B)-H(9B)	0.9500	C(31)-C(33)	1.533(3)
S-O(3)	1.4245(19)	C(10)-C(11)	1.430(12)	C(31)-H(31)	1.0000
S-O(4)	1.4634(16)	C(10)-H(10)	0.9500	C(32)-H(32A)	0.9800
S-C(39)	1.811(3)	C(10B)-C(11B)	1.389(15)	C(32)-H(32B)	0.9800
N-C(25)	1.456(3)	C(10B)-H(10B)	0.9500	C(32)-H(32C)	0.9800

O(1)-C(1B)	1.398(8)	C(11)-C(12)	1.384(10)	C(33)-H(33A)	0.9800
O(1)-C(12)	1.412(12)	C(11)-H(11)	0.9500	C(33)-H(33B)	0.9800
C(1B)-C(2B)	1.382(13)	C(11B)-C(12B)	1.386(16)	C(33)-H(33C)	0.9800
C(1B)-C(6)	1.415(13)	C(11B)-H(11B)	0.9500	C(34)-C(35)	1.527(3)
O(1B)-C(1)	1.359(17)	C(13)-C(18)	1.391(3)	C(34)-C(36)	1.538(3)
O(1B)-C(12B)	1.43(2)	C(13)-C(14)	1.392(3)	C(34)-H(34)	1.0000
C(1)-C(6B)	1.40(2)	C(14)-C(15)	1.389(3)	C(35)-H(35A)	0.9800
C(1)-C(2)	1.42(2)	C(14)-H(14)	0.9500	C(35)-H(35B)	0.9800
F(1)-C(39)	1.316(3)	C(15)-C(16)	1.366(4)	C(35)-H(35C)	0.9800
C(2B)-C(3)	1.445(18)	C(15)-H(15)	0.9500	C(36)-H(36A)	0.9800
C(2)-C(3B)	1.34(3)	C(16)-C(17)	1.374(4)	C(36)-H(36B)	0.9800
F(2)-C(39)	1.326(3)	C(16)-H(16)	0.9500	C(36)-H(36C)	0.9800
C(3)-C(4)	1.388(13)	C(17)-C(18)	1.389(3)	C(37)-C(38)	1.534(6)
C(3)-H(3)	0.9500	C(17)-H(17)	0.9500	C(37)-H(37A)	0.9900
C(3B)-C(4B)	1.41(2)	C(18)-H(18)	0.9500	C(37)-H(37B)	0.9900
C(3B)-H(3B)	0.9500	C(19)-C(24)	1.392(3)	C(37B)-C(38B)	1.384(16)
F(3)-C(39)	1.329(3)	C(19)-C(20)	1.396(3)	C(37B)-H(37C)	0.9900
C(4)-C(5)	1.371(10)	C(20)-C(21)	1.379(3)	C(37B)-H(37D)	0.9900
C(4)-H(4)	0.9500	C(20)-H(20)	0.9500	C(38)-H(38A)	0.9800
C(4B)-C(5B)	1.406(16)	C(21)-C(22)	1.386(4)	C(38)-H(38B)	0.9800
C(4B)-H(4B)	0.9500	C(21)-H(21)	0.9500	C(38)-H(38C)	0.9800
C(5)-C(6)	1.376(11)	C(22)-C(23)	1.370(4)	C(38B)-H(38D)	0.9800
C(5)-H(5)	0.9500	C(22)-H(22)	0.9500	C(38B)-H(38E)	0.9800
C(5B)-C(6B)	1.378(16)	C(23)-C(24)	1.382(4)	C(38B)-H(38F)	0.9800
C(5B)-H(5B)	0.9500	C(23)-H(23)	0.9500		

Table A.34: Bond angles [°] for **6b**

N-Zn-C(37)	131.6(2)	C(5B)-C(6B)-C(7B)	133.8(14)	C(30)-C(25)-N	118.6(2)
N-Zn-O(4)	102.12(19)	C(1)-C(6B)-C(7B)	105.1(10)	C(27)-C(26)-C(25)	118.2(2)
C(37)-Zn-O(4)	119.6(2)	C(12)-C(7)-C(8)	118.1(9)	C(27)-C(26)-C(31)	118.9(2)
N-Zn-O(1)	80.3(3)	C(12)-C(7)-C(6)	108.0(8)	C(25)-C(26)-C(31)	122.9(2)
C(37)-Zn-O(1)	127.3(3)	C(8)-C(7)-C(6)	134.0(8)	C(28)-C(27)-C(26)	121.2(2)
O(4)-Zn-O(1)	80.4(2)	C(8B)-C(7B)-C(12B)	119.5(10)	C(28)-C(27)-H(27)	119.4
C(37B)-ZnB-O(4)	111.2(5)	C(8B)-C(7B)-C(6B)	135.6(13)	C(26)-C(27)-H(27)	119.4
C(37B)-ZnB-N	138.8(5)	C(12B)-C(7B)-C(6B)	104.9(11)	C(29)-C(28)-C(27)	119.8(2)
O(4)-ZnB-N	102.9(4)	C(9)-C(8)-C(7)	116.6(10)	C(29)-C(28)-H(28)	120.1
C(37B)-ZnB-O(1B)	106.9(7)	C(9)-C(8)-H(8)	121.7	C(27)-C(28)-H(28)	120.1
O(4)-ZnB-O(1B)	100.7(5)	C(7)-C(8)-H(8)	121.7	C(28)-C(29)-C(30)	122.0(2)
N-ZnB-O(1B)	88.2(6)	C(7B)-C(8B)-C(9B)	120.1(11)	C(28)-C(29)-H(29)	119.0
N-P-C(2B)	111.8(5)	C(7B)-C(8B)-H(8B)	120.0	C(30)-C(29)-H(29)	119.0
N-P-C(13)	112.94(10)	C(9B)-C(8B)-H(8B)	120.0	C(29)-C(30)-C(25)	117.6(2)
C(2B)-P-C(13)	108.0(6)	C(8)-C(9)-C(10)	125.7(10)	C(29)-C(30)-C(34)	119.9(2)
N-P-C(19)	115.43(10)	C(8)-C(9)-H(9)	117.2	C(25)-C(30)-C(34)	122.4(2)

C(2B)-P-C(19)	101.5(5)	C(10)-C(9)-H(9)	117.2	C(26)-C(31)-C(32)	112.2(2)
C(13)-P-C(19)	106.36(11)	C(8B)-C(9B)-C(10B)	118.3(10)	C(26)-C(31)-C(33)	111.59(19)
N-P-C(2)	104.9(9)	C(8B)-C(9B)-H(9B)	120.8	C(32)-C(31)-C(33)	110.4(2)
C(2B)-P-C(2)	7.3(13)	C(10B)-C(9B)-H(9B)	120.8	C(26)-C(31)-H(31)	107.5
C(13)-P-C(2)	109.7(11)	C(9)-C(10)-C(11)	119.6(10)	C(32)-C(31)-H(31)	107.5
C(19)-P-C(2)	107.3(9)	C(9)-C(10)-H(10)	120.2	C(33)-C(31)-H(31)	107.5
O(2)-S-O(3)	116.91(13)	C(11)-C(10)-H(10)	120.2	C(31)-C(32)-H(32A)	109.5
O(2)-S-O(4)	114.66(11)	C(11B)-C(10B)-C(9B	123.1(10)	C(31)-C(32)-H(32B)	109.5
O(3)-S-O(4)	113.37(11)	C(11B)-C(10B)-H(10	118.5	H(32A)-C(32)-H(32B)	109.5
O(2)-S-C(39)	104.74(13)	C(9B)-C(10B)-H(10B	118.5	C(31)-C(32)-H(32C)	109.5
O(3)-S-C(39)	104.27(13)	C(12)-C(11)-C(10)	113.0(9)	H(32A)-C(32)-H(32C)	109.5
O(4)-S-C(39)	100.32(11)	C(12)-C(11)-H(11)	123.5	H(32B)-C(32)-H(32C)	109.5
C(25)-N-P	119.28(13)	C(10)-C(11)-H(11)	123.5	C(31)-C(33)-H(33A)	109.5
C(25)-N-Zn	109.39(16)	C(12B)-C(11B)-C(10	114.0(10)	C(31)-C(33)-H(33B)	109.5
P-N-Zn	131.32(14)	C(12B)-C(11B)-H(11	123.0	H(33A)-C(33)-H(33B)	109.5
C(25)-N-ZnB	116.6(2)	C(10B)-C(11B)-H(11	123.0	C(31)-C(33)-H(33C)	109.5
P-N-ZnB	123.8(2)	C(7)-C(12)-C(11)	127.0(9)	H(33A)-C(33)-H(33C)	109.5
Zn-N-ZnB	9.8(2)	C(7)-C(12)-O(1)	110.4(6)	H(33B)-C(33)-H(33C)	109.5
C(1B)-O(1)-C(12)	105.7(7)	C(11)-C(12)-O(1)	122.6(9)	C(30)-C(34)-C(35)	113.9(2)
C(1B)-O(1)-Zn	112.1(7)	C(11B)-C(12B)-C(7B	125.0(12)	C(30)-C(34)-C(36)	109.6(2)
C(12)-O(1)-Zn	126.7(7)	C(11B)-C(12B)-O(1B	122.4(10)	C(35)-C(34)-C(36)	109.9(2)
C(2B)-C(1B)-O(1)	124.9(11)	C(7B)-C(12B)-O(1B)	112.6(10)	C(30)-C(34)-H(34)	107.7
C(2B)-C(1B)-C(6)	125.3(9)	C(18)-C(13)-C(14)	119.3(2)	C(35)-C(34)-H(34)	107.7
O(1)-C(1B)-C(6)	109.8(8)	C(18)-C(13)-P	119.69(19)	C(36)-C(34)-H(34)	107.7
C(1)-O(1B)-C(12B)	103.6(12)	C(14)-C(13)-P	120.97(18)	C(34)-C(35)-H(35A)	109.5
C(1)-O(1B)-ZnB	108.9(15)	C(15)-C(14)-C(13)	119.9(3)	C(34)-C(35)-H(35B)	109.5
C(12B)-O(1B)-ZnB	119.7(14)	C(15)-C(14)-H(14)	120.0	H(35A)-C(35)-H(35B)	109.5
O(1B)-C(1)-C(6B)	113.8(14)	C(13)-C(14)-H(14)	120.0	C(34)-C(35)-H(35C)	109.5
O(1B)-C(1)-C(2)	127.8(19)	C(16)-C(15)-C(14)	120.2(3)	H(35A)-C(35)-H(35C)	109.5
C(6B)-C(1)-C(2)	118.4(16)	C(16)-C(15)-H(15)	119.9	H(35B)-C(35)-H(35C)	109.5
C(1B)-C(2B)-C(3)	114.0(11)	C(14)-C(15)-H(15)	119.9	C(34)-C(36)-H(36A)	109.5
C(1B)-C(2B)-P	127.5(12)	C(15)-C(16)-C(17)	120.6(2)	C(34)-C(36)-H(36B)	109.5
C(3)-C(2B)-P	118.5(7)	C(15)-C(16)-H(16)	119.7	H(36A)-C(36)-H(36B)	109.5
C(3B)-C(2)-C(1)	120(2)	C(17)-C(16)-H(16)	119.7	C(34)-C(36)-H(36C)	109.5
C(3B)-C(2)-P	118.0(15)	C(16)-C(17)-C(18)	120.1(3)	H(36A)-C(36)-H(36C)	109.5
C(1)-C(2)-P	122(2)	C(16)-C(17)-H(17)	120.0	H(36B)-C(36)-H(36C)	109.5
C(4)-C(3)-C(2B)	120.9(8)	C(18)-C(17)-H(17)	120.0	C(38)-C(37)-Zn	116.4(4)
C(4)-C(3)-H(3)	119.5	C(17)-C(18)-C(13)	119.9(3)	C(38)-C(37)-H(37A)	108.2
C(2B)-C(3)-H(3)	119.5	C(17)-C(18)-H(18)	120.1	Zn-C(37)-H(37A)	108.2
C(2)-C(3B)-C(4B)	123.5(13)	C(13)-C(18)-H(18)	120.1	C(38)-C(37)-H(37B)	108.2
C(2)-C(3B)-H(3B)	118.3	C(24)-C(19)-C(20)	118.7(2)	Zn-C(37)-H(37B)	108.2
C(4B)-C(3B)-H(3B	118.3	C(24)-C(19)-P	123.29(18)	H(37A)-C(37)-H(37B)	107.3
C(5)-C(4)-C(3)	122.0(9)	C(20)-C(19)-P	117.91(17)	C(38B)-C(37B)-ZnB	118.6(10)

C(5)-C(4)-H(4)	119.0	C(21)-C(20)-C(19)	120.7(2)	C(38B)-C(37B)-H(37C)	107.7
C(3)-C(4)-H(4)	119.0	C(21)-C(20)-H(20)	119.7	ZnB-C(37B)-H(37C)	107.7
C(5B)-C(4B)-C(3B)	117.0(13)	C(19)-C(20)-H(20)	119.7	C(38B)-C(37B)-H(37D	107.7
C(5B)-C(4B)-H(4B	121.5	C(20)-C(21)-C(22)	119.7(2)	ZnB-C(37B)-H(37D)	107.7
C(3B)-C(4B)-H(4B	121.5	C(20)-C(21)-H(21)	120.1	H(37C)-C(37B)-H(37D	107.1
S-O(4)-ZnB	130.3(3)	C(22)-C(21)-H(21)	120.1	C(37B)-C(38B)-H(38D	109.5
S-O(4)-Zn	133.16(16)	C(23)-C(22)-C(21)	120.2(3)	C(37B)-C(38B)-H(38E)	109.5
ZnB-O(4)-Zn	9.5(2)	C(23)-C(22)-H(22)	119.9	H(38D)-C(38B)-H(38E	109.5
C(4)-C(5)-C(6)	119.8(8)	C(21)-C(22)-H(22)	119.9	C(37B)-C(38B)-H(38F)	109.5
C(4)-C(5)-H(5)	120.1	C(22)-C(23)-C(24)	120.4(3)	H(38D)-C(38B)-H(38F	109.5
C(6)-C(5)-H(5)	120.1	C(22)-C(23)-H(23)	119.8	H(38E)-C(38B)-H(38F)	109.5
C(6B)-C(5B)-C(4B)	120.4(14)	C(24)-C(23)-H(23)	119.8	F(1)-C(39)-F(2)	108.0(2)
C(6B)-C(5B)-H(5B	119.8	C(23)-C(24)-C(19)	120.3(2)	F(1)-C(39)-F(3)	107.4(3)
C(4B)-C(5B)-H(5B	119.8	C(23)-C(24)-H(24)	119.9	F(2)-C(39)-F(3)	107.2(2)
C(5)-C(6)-C(1B)	117.9(7)	C(19)-C(24)-H(24)	119.9	F(1)-C(39)-S	111.66(19)
C(5)-C(6)-C(7)	135.9(9)	C(26)-C(25)-C(30)	121.2(2)	F(2)-C(39)-S	110.7(2)
C(1B)-C(6)-C(7)	106.1(7)	C(26)-C(25)-N	120.19(19)	F(3)-C(39)-S	111.64(19)
C(5B)-C(6B)-C(1)	121.1(13)				

Table A.35: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **6b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn	28(1)	26(1)	37(1)	-6(1)	5(1)	-2(1)
ZnB	32(2)	41(2)	47(2)	-7(1)	5(1)	-1(1)
P	24(1)	24(1)	36(1)	-3(1)	0(1)	-5(1)
S	37(1)	26(1)	44(1)	-7(1)	-8(1)	1(1)
N	24(1)	22(1)	32(1)	-4(1)	1(1)	-4(1)
O(1)	50(5)	36(5)	36(4)	-9(3)	-11(3)	0(2)
C(1B)	39(5)	29(3)	48(5)	2(3)	-16(3)	-6(3)
O(1B)	38(4)	23(6)	34(4)	-7(4)	5(3)	-10(3)
C(1)	34(7)	19(6)	29(7)	-6(6)	-4(4)	-6(5)
F(1)	61(1)	85(1)	115(2)	9(1)	7(1)	-32(1)
C(2B)	27(4)	25(3)	52(5)	-5(3)	-11(4)	2(3)
C(2)	29(7)	27(6)	40(6)	-12(5)	4(5)	-15(5)
F(2)	111(2)	29(1)	77(1)	1(1)	-8(1)	-11(1)
O(2)	37(1)	50(1)	81(1)	-7(1)	-13(1)	-1(1)
C(3)	36(4)	33(3)	63(6)	1(3)	-7(3)	-14(3)
C(3B)	31(6)	31(5)	37(7)	-11(5)	15(4)	-5(4)
F(3)	116(2)	58(1)	46(1)	-10(1)	-2(1)	-12(1)
O(3)	78(1)	51(1)	52(1)	-20(1)	-16(1)	-8(1)
C(4)	65(6)	42(4)	92(7)	9(4)	-29(4)	-23(4)
C(4B)	43(7)	37(7)	49(10)	-11(6)	0(6)	-24(6)
O(4)	51(1)	25(1)	53(1)	-5(1)	2(1)	1(1)

C(5)	88(8)	38(4)	82(8)	1(5)	-48(5)	-23(5)
C(5B)	43(7)	38(6)	56(8)	-19(6)	-2(4)	-18(4)
C(6)	71(7)	30(3)	75(5)	-9(4)	-37(3)	-6(4)
C(6B)	28(6)	32(5)	42(7)	-6(5)	-10(4)	-9(4)
C(7)	89(6)	45(3)	68(5)	-17(3)	-46(4)	12(3)
C(7B)	38(6)	32(6)	38(5)	-14(4)	-9(4)	-3(4)
C(8)	147(8)	66(4)	97(5)	-32(4)	-66(5)	11(4)
C(8B)	77(7)	47(6)	44(6)	-27(5)	-18(5)	-10(5)
C(9)	162(9)	94(6)	84(6)	-47(5)	-56(6)	33(5)
C(9B)	72(7)	45(8)	51(6)	-35(6)	-9(5)	3(6)
C(10)	133(8)	89(9)	53(4)	-38(5)	-30(5)	47(5)
C(10B)	54(6)	46(6)	32(5)	-17(4)	-14(4)	2(4)
C(11)	83(6)	78(5)	50(4)	-19(4)	-21(3)	28(3)
C(11B)	46(6)	41(6)	21(4)	-8(4)	-6(3)	0(4)
C(12)	76(6)	46(5)	40(3)	-14(4)	-30(3)	19(3)
C(12B)	35(6)	25(5)	32(5)	-7(4)	-6(3)	-2(3)
C(13)	27(1)	29(1)	42(1)	-1(1)	6(1)	-5(1)
C(14)	31(1)	38(1)	49(2)	0(1)	-1(1)	-6(1)
C(15)	30(1)	49(2)	60(2)	2(1)	-6(1)	2(1)
C(16)	36(2)	38(2)	70(2)	4(1)	7(1)	6(1)
C(17)	44(2)	33(1)	67(2)	-12(1)	13(1)	-1(1)
C(18)	36(1)	37(1)	53(2)	-8(1)	5(1)	-5(1)
C(19)	31(1)	30(1)	38(1)	-2(1)	5(1)	-6(1)
C(20)	36(1)	35(1)	42(1)	-4(1)	5(1)	-7(1)
C(21)	54(2)	38(1)	45(2)	5(1)	-3(1)	-6(1)
C(22)	71(2)	49(2)	39(2)	3(1)	11(1)	-10(2)
C(23)	62(2)	54(2)	50(2)	-2(1)	23(1)	-2(2)
C(24)	39(2)	45(2)	50(2)	1(1)	12(1)	-2(1)
C(25)	23(1)	25(1)	37(1)	-5(1)	6(1)	-6(1)
C(26)	25(1)	33(1)	42(1)	-10(1)	4(1)	-8(1)
C(27)	34(1)	41(1)	62(2)	-17(1)	-2(1)	-13(1)
C(28)	41(2)	28(1)	80(2)	-6(1)	-1(1)	-12(1)
C(29)	41(2)	32(1)	59(2)	7(1)	-2(1)	-11(1)
C(30)	24(1)	34(1)	41(1)	0(1)	2(1)	-6(1)
C(31)	32(1)	39(1)	39(1)	-11(1)	-2(1)	-9(1)
C(32)	50(2)	60(2)	41(2)	-15(1)	-5(1)	-6(1)
C(33)	36(1)	59(2)	56(2)	-9(1)	-7(1)	-8(1)
C(34)	40(1)	40(1)	37(1)	3(1)	-3(1)	-8(1)
C(35)	48(2)	53(2)	52(2)	6(1)	-12(1)	-4(1)
C(36)	59(2)	70(2)	43(2)	-6(1)	4(1)	-3(2)
C(37B)	29(4)	88(7)	50(5)	-14(5)	14(4)	7(4)
C(38B)	65(7)	143(11)	95(9)	28(8)	-6(6)	-49(7)
C(39)	56(2)	34(1)	57(2)	-2(1)	-8(1)	-7(1)

Table A.36: Crystal data and structure refinement for **7**.

Empirical formula	$C_{78}H_{74}F_{12}N_2O_{16}P_2S_4Zn_3$	
Formula weight	1909.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7291(15) Å	α= 86.3080(10)°.
	b = 13.8611(16) Å	β= 89.1350(10)°.
	c = 14.2257(17) Å	γ = 84.4560(10)°.
Volume	2492.9(5) $Å^3$	
Z	2	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.908 mm^{-1}	
F(000)	976	
Crystal size	0.28 x 0.26 x 0.13 mm^3	
Theta range for data collection	2.59 to 25.03°.	
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	
Reflections collected	23701	
Independent reflections	8770 [R(int) = 0.0381]	
Completeness to theta = 25.03°	99.60%	
Max. and min. transmission	0.8879 and 0.7869	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8770 / 0 / 534	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1026	
R indices (all data)	R1 = 0.0664, wR2 = 0.1102	
Largest diff. peak and hole	0.645 and -0.329 $e.Å^{-3}$	

Table A.37: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	10000	5000	5000	31(1)	C(11)	7880(2)	7510(2)	8294(2)	30(1)
S(1)	10417(1)	7200(1)	5692(1)	38(1)	C(12)	7685(2)	6659(2)	8793(2)	30(1)
O(1)	8564(2)	5345(2)	7343(1)	34(1)	C(13)	5715(3)	8299(2)	7802(2)	37(1)
P(1)	7032(1)	8056(1)	7357(1)	31(1)	C(14)	4886(3)	8626(3)	7181(3)	47(1)
N(1)	7099(2)	7321(2)	6514(2)	29(1)	C(15)	3872(3)	8806(3)	7518(3)	61(1)
C(1)	6932(3)	5356(2)	9304(2)	37(1)	C(16)	3660(3)	8700(3)	8471(3)	71(1)
F(1)	8208(2)	3442(2)	6766(2)	70(1)	C(17)	4462(4)	8409(3)	9093(3)	68(1)
Zn(2)	8286(1)	6371(1)	6284(1)	27(1)	C(18)	5485(3)	8203(3)	8769(3)	52(1)
S(2)	9479(1)	4619(1)	7386(1)	34(1)	C(19)	7472(3)	9243(2)	7056(2)	37(1)
O(2)	9605(2)	7055(2)	6415(2)	36(1)	C(20)	8432(3)	9305(2)	6572(2)	41(1)

F(2)	9587(2)	2741(2)	7464(2)	84(1)	C(21)	8772(3)	10194(3)	6307(3)	53(1)
C(2)	6220(3)	4688(3)	9431(3)	49(1)	C(22)	8173(4)	11040(3)	6526(3)	66(1)
O(3)	10071(2)	4582(2)	6518(2)	39(1)	C(23)	7245(4)	10984(3)	7020(3)	78(2)
F(3)	8322(2)	3409(2)	8279(2)	97(1)	C(24)	6890(3)	10089(3)	7284(3)	58(1)
C(3)	6458(3)	3931(3)	10098(3)	60(1)	C(25)	6270(3)	7336(2)	5813(2)	33(1)
O(4)	10765(2)	6330(2)	5234(2)	43(1)	C(26)	6315(3)	7927(3)	4971(2)	43(1)
F(4)	11749(2)	6627(3)	7014(2)	105(1)	C(27)	5507(4)	7900(3)	4329(3)	63(1)
C(4)	7372(3)	3884(3)	10620(3)	54(1)	C(28)	4720(3)	7302(3)	4472(3)	65(1)
O(5)	6816(2)	6169(2)	8678(1)	34(1)	C(29)	4707(3)	6711(3)	5282(3)	51(1)
F(5)	11281(2)	8172(3)	6900(2)	123(1)	C(30)	5475(2)	6710(2)	5962(2)	35(1)
C(5)	8073(3)	4569(3)	10498(2)	46(1)	C(31)	7176(3)	8584(3)	4746(3)	58(1)
O(6)	8597(2)	5697(2)	5174(1)	32(1)	C(32)	7775(4)	8306(4)	3840(3)	104(2)
C(6)	7857(3)	5336(2)	9825(2)	36(1)	C(33)	6738(4)	9654(3)	4703(4)	96(2)
F(6)	12359(2)	7541(2)	5890(2)	103(1)	C(34)	5446(3)	6017(3)	6827(2)	40(1)
O(7)	10237(2)	8067(2)	5111(2)	67(1)	C(35)	5879(3)	4999(3)	6591(3)	62(1)
C(7)	8351(3)	6188(2)	9488(2)	33(1)	C(36)	4342(3)	5999(3)	7265(3)	65(1)
O(8)	10082(2)	4603(2)	8223(2)	53(1)	C(37)	7772(3)	5532(3)	4537(3)	52(1)
C(8)	9262(3)	6604(3)	9699(2)	45(1)	C(38)	8865(4)	3485(3)	7477(3)	56(1)
C(9)	9479(3)	7460(3)	9227(3)	51(1)	C(39)	11514(3)	7379(4)	6422(4)	74(2)
C(10)	8799(3)	7909(3)	8537(2)	42(1)					

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Table A.39: Bond angles [°] for **7**

O(6)#1-Zn(1)-O(6)	180.000(1)	C(5)-C(6)-C(1)	117.8(3)	C(26)-C(27)-H(27)	118.7
O(6)#1-Zn(1)-O(3)	89.86(8)	C(5)-C(6)-C(7)	136.6(3)	C(27)-C(28)-C(29)	119.4(4)
O(6)-Zn(1)-O(3)	90.14(8)	C(1)-C(6)-C(7)	105.6(3)	C(27)-C(28)-H(28)	120.3
O(6)#1-Zn(1)-O(3)#1	90.14(8)	C(8)-C(7)-C(12)	118.4(3)	C(29)-C(28)-H(28)	120.3
O(6)-Zn(1)-O(3)#1	89.86(8)	C(8)-C(7)-C(6)	135.7(3)	C(28)-C(29)-C(30)	121.4(4)
O(3)-Zn(1)-O(3)#1	180.0	C(12)-C(7)-C(6)	105.9(3)	C(28)-C(29)-H(29)	119.3
O(6)#1-Zn(1)-O(4)#1	90.77(8)	C(9)-C(8)-C(7)	119.4(3)	C(30)-C(29)-H(29)	119.3
O(6)-Zn(1)-O(4)#1	89.23(8)	C(9)-C(8)-H(8)	120.3	C(29)-C(30)-C(25)	118.6(3)
O(3)-Zn(1)-O(4)#1	89.74(9)	C(7)-C(8)-H(8)	120.3	C(29)-C(30)-C(34)	119.2(3)
O(3)#1-Zn(1)-O(4)#1	90.26(9)	C(8)-C(9)-C(10)	120.7(3)	C(25)-C(30)-C(34)	122.1(3)
O(6)#1-Zn(1)-O(4)	89.23(8)	C(8)-C(9)-H(9)	119.6	C(26)-C(31)-C(33)	111.2(4)
O(6)-Zn(1)-O(4)	90.77(8)	C(10)-C(9)-H(9)	119.6	C(26)-C(31)-C(32)	110.9(3)
O(3)-Zn(1)-O(4)	90.26(9)	C(9)-C(10)-C(11)	121.8(3)	C(33)-C(31)-C(32)	112.5(4)
O(3)#1-Zn(1)-O(4)	89.74(9)	C(9)-C(10)-H(10)	119.1	C(26)-C(31)-H(31)	107.3
O(4)#1-Zn(1)-O(4)	180.0	C(11)-C(10)-H(10)	119.1	C(33)-C(31)-H(31)	107.3
O(7)-S(1)-O(4)	117.00(16)	C(12)-C(11)-C(10)	115.6(3)	C(32)-C(31)-H(31)	107.3
O(7)-S(1)-O(2)	114.80(15)	C(12)-C(11)-P(1)	122.4(2)	C(31)-C(32)-H(32A)	109.5
O(4)-S(1)-O(2)	113.18(13)	C(10)-C(11)-P(1)	121.9(2)	C(31)-C(32)-H(32B)	109.5
O(7)-S(1)-C(39)	105.4(2)	O(5)-C(12)-C(11)	124.6(3)	H(32A)-C(32)-H(32B)	109.5

O(4)-S(1)-C(39)	103.57(19)	O(5)-C(12)-C(7)	111.3(3)	C(31)-C(32)-H(32C)	109.5
O(2)-S(1)-C(39)	100.28(19)	C(11)-C(12)-C(7)	124.1(3)	H(32A)-C(32)-H(32C)	109.5
S(2)-O(1)-Zn(2)	124.38(12)	C(18)-C(13)-C(14)	118.2(3)	H(32B)-C(32)-H(32C)	109.5
N(1)-P(1)-C(13)	112.59(15)	C(18)-C(13)-P(1)	121.6(3)	C(31)-C(33)-H(33A)	109.5
N(1)-P(1)-C(11)	107.79(13)	C(14)-C(13)-P(1)	120.1(3)	C(31)-C(33)-H(33B)	109.5
C(13)-P(1)-C(11)	109.61(15)	C(15)-C(14)-C(13)	120.4(4)	H(33A)-C(33)-H(33B)	109.5
N(1)-P(1)-C(19)	115.60(14)	C(15)-C(14)-H(14)	119.8	C(31)-C(33)-H(33C)	109.5
C(13)-P(1)-C(19)	104.80(16)	C(13)-C(14)-H(14)	119.8	H(33A)-C(33)-H(33C)	109.5
C(11)-P(1)-C(19)	106.18(15)	C(14)-C(15)-C(16)	120.5(4)	H(33B)-C(33)-H(33C)	109.5
C(25)-N(1)-P(1)	122.5(2)	C(14)-C(15)-H(15)	119.8	C(30)-C(34)-C(35)	110.2(3)
C(25)-N(1)-Zn(2)	112.61(19)	C(16)-C(15)-H(15)	119.8	C(30)-C(34)-C(36)	113.0(3)
P(1)-N(1)-Zn(2)	124.86(14)	C(17)-C(16)-C(15)	120.1(4)	C(35)-C(34)-C(36)	110.1(3)
C(2)-C(1)-O(5)	124.8(3)	C(17)-C(16)-H(16)	119.9	C(30)-C(34)-H(34)	107.8
C(2)-C(1)-C(6)	124.0(3)	C(15)-C(16)-H(16)	119.9	C(35)-C(34)-H(34)	107.8
O(5)-C(1)-C(6)	111.1(3)	C(16)-C(17)-C(18)	120.5(4)	C(36)-C(34)-H(34)	107.8
O(6)-Zn(2)-N(1)	127.91(10)	C(16)-C(17)-H(17)	119.8	C(34)-C(35)-H(35A)	109.5
O(6)-Zn(2)-O(1)	104.20(9)	C(18)-C(17)-H(17)	119.8	C(34)-C(35)-H(35B)	109.5
N(1)-Zn(2)-O(1)	114.05(9)	C(17)-C(18)-C(13)	120.3(4)	H(35A)-C(35)-H(35B)	109.5
O(6)-Zn(2)-O(2)	101.65(9)	C(17)-C(18)-H(18)	119.9	C(34)-C(35)-H(35C)	109.5
N(1)-Zn(2)-O(2)	106.43(10)	C(13)-C(18)-H(18)	119.9	H(35A)-C(35)-H(35C)	109.5
O(1)-Zn(2)-O(2)	97.88(9)	C(24)-C(19)-C(20)	118.8(3)	H(35B)-C(35)-H(35C)	109.5
O(8)-S(2)-O(3)	115.99(15)	C(24)-C(19)-P(1)	122.2(3)	C(34)-C(36)-H(36A)	109.5
O(8)-S(2)-O(1)	114.31(14)	C(20)-C(19)-P(1)	119.0(3)	C(34)-C(36)-H(36B)	109.5
O(3)-S(2)-O(1)	113.36(13)	C(21)-C(20)-C(19)	120.5(3)	H(36A)-C(36)-H(36B)	109.5
O(8)-S(2)-C(38)	104.72(19)	C(21)-C(20)-H(20)	119.8	C(34)-C(36)-H(36C)	109.5
O(3)-S(2)-C(38)	104.13(17)	C(19)-C(20)-H(20)	119.8	H(36A)-C(36)-H(36C)	109.5
O(1)-S(2)-C(38)	102.26(17)	C(20)-C(21)-C(22)	120.2(4)	H(36B)-C(36)-H(36C)	109.5
S(1)-O(2)-Zn(2)	126.86(13)	C(20)-C(21)-H(21)	119.9	O(6)-C(37)-H(37A)	109.5
C(1)-C(2)-C(3)	116.9(4)	C(22)-C(21)-H(21)	119.9	O(6)-C(37)-H(37B)	109.5
C(1)-C(2)-H(2)	121.5	C(23)-C(22)-C(21)	119.5(4)	H(37A)-C(37)-H(37B)	109.5
C(3)-C(2)-H(2)	121.5	C(23)-C(22)-H(22)	120.2	O(6)-C(37)-H(37C)	109.5
S(2)-O(3)-Zn(1)	143.65(14)	C(21)-C(22)-H(22)	120.2	H(37A)-C(37)-H(37C)	109.5
C(2)-C(3)-C(4)	120.5(4)	C(22)-C(23)-C(24)	120.7(4)	H(37B)-C(37)-H(37C)	109.5
C(2)-C(3)-H(3)	119.7	C(22)-C(23)-H(23)	119.7	F(2)-C(38)-F(3)	108.3(3)
C(4)-C(3)-H(3)	119.7	C(24)-C(23)-H(23)	119.7	F(2)-C(38)-F(1)	108.6(3)
S(1)-O(4)-Zn(1)	132.64(14)	C(19)-C(24)-C(23)	120.2(4)	F(3)-C(38)-F(1)	108.4(4)
C(5)-C(4)-C(3)	122.0(3)	C(19)-C(24)-H(24)	119.9	F(2)-C(38)-S(2)	110.4(3)
C(5)-C(4)-H(4)	119.0	C(23)-C(24)-H(24)	119.9	F(3)-C(38)-S(2)	110.2(3)
C(3)-C(4)-H(4)	119.0	C(30)-C(25)-C(26)	120.8(3)	F(1)-C(38)-S(2)	110.8(3)
C(12)-O(5)-C(1)	106.0(2)	C(30)-C(25)-N(1)	119.0(3)	F(4)-C(39)-F(6)	109.4(4)
C(4)-C(5)-C(6)	118.7(4)	C(26)-C(25)-N(1)	120.1(3)	F(4)-C(39)-F(5)	109.5(5)
C(4)-C(5)-H(5)	120.7	C(27)-C(26)-C(25)	117.1(3)	F(6)-C(39)-F(5)	106.6(4)
C(6)-C(5)-H(5)	120.7	C(27)-C(26)-C(31)	119.3(3)	F(4)-C(39)-S(1)	111.6(3)

C(37)-O(6)-Zn(2)	121.02(18)	C(25)-C(26)-C(31)	123.5(3)	F(6)-C(39)-S(1)	110.3(4)
C(37)-O(6)-Zn(1)	117.98(18)	C(28)-C(27)-C(26)	122.6(4)	F(5)-C(39)-S(1)	109.4(3)
Zn(2)-O(6)-Zn(1)	119.99(10)	C(28)-C(27)-H(27)	118.7		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table A.40: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	32(1)	35(1)	25(1)	-4(1)	3(1)	-1(1)
S(1)	35(1)	37(1)	44(1)	-3(1)	5(1)	-9(1)
O(1)	47(1)	30(1)	24(1)	2(1)	8(1)	3(1)
P(1)	37(1)	28(1)	25(1)	1(1)	-1(1)	2(1)
N(1)	32(2)	33(2)	23(1)	2(1)	-1(1)	-2(1)
C(1)	41(2)	41(2)	26(2)	5(2)	3(2)	3(2)
F(1)	73(2)	51(1)	92(2)	-22(1)	3(2)	-19(1)
Zn(2)	30(1)	29(1)	23(1)	-1(1)	1(1)	-2(1)
S(2)	46(1)	30(1)	24(1)	1(1)	1(1)	0(1)
O(2)	34(1)	40(1)	37(1)	-7(1)	5(1)	-7(1)
F(2)	107(2)	30(1)	109(2)	1(1)	7(2)	11(1)
C(2)	43(2)	63(3)	41(2)	9(2)	-1(2)	-11(2)
O(3)	41(1)	46(1)	26(1)	1(1)	4(1)	5(1)
F(3)	149(3)	58(2)	84(2)	5(1)	62(2)	-31(2)
C(3)	65(3)	61(3)	53(3)	16(2)	6(2)	-21(2)
O(4)	42(1)	39(1)	48(2)	-13(1)	13(1)	-8(1)
F(4)	63(2)	176(3)	72(2)	-7(2)	-26(2)	11(2)
C(4)	63(3)	53(3)	42(2)	21(2)	0(2)	-1(2)
O(5)	32(1)	43(1)	27(1)	6(1)	-4(1)	-1(1)
F(5)	62(2)	166(3)	161(3)	-121(3)	20(2)	-45(2)
C(5)	55(2)	48(2)	32(2)	4(2)	-4(2)	4(2)
O(6)	29(1)	42(1)	26(1)	-8(1)	-3(1)	0(1)
C(6)	39(2)	41(2)	25(2)	1(2)	2(2)	3(2)
F(6)	45(2)	145(3)	130(3)	-58(2)	24(2)	-41(2)
O(7)	79(2)	46(2)	71(2)	21(1)	21(2)	1(2)
C(7)	38(2)	39(2)	21(2)	-3(2)	-1(1)	3(2)
O(8)	67(2)	62(2)	28(1)	-2(1)	-13(1)	9(1)
C(8)	48(2)	54(2)	31(2)	2(2)	-14(2)	0(2)
C(9)	48(2)	61(3)	45(2)	2(2)	-16(2)	-15(2)
C(10)	56(2)	39(2)	31(2)	0(2)	-7(2)	-8(2)
C(11)	34(2)	32(2)	23(2)	-5(1)	-3(1)	1(2)
C(12)	30(2)	37(2)	22(2)	-7(2)	2(1)	0(2)
C(13)	40(2)	32(2)	37(2)	1(2)	4(2)	8(2)
C(14)	47(2)	44(2)	47(2)	1(2)	2(2)	8(2)

C(15)	41(2)	61(3)	76(3)	7(2)	4(2)	10(2)
C(16)	50(3)	69(3)	86(4)	20(3)	27(3)	18(2)
C(17)	79(3)	67(3)	47(3)	17(2)	27(2)	24(2)
C(18)	63(3)	51(2)	38(2)	4(2)	11(2)	16(2)
C(19)	51(2)	30(2)	31(2)	0(2)	0(2)	-2(2)
C(20)	56(2)	29(2)	37(2)	-1(2)	-2(2)	-5(2)
C(21)	74(3)	40(2)	45(2)	1(2)	4(2)	-12(2)
C(22)	105(4)	35(2)	60(3)	0(2)	6(3)	-15(2)
C(23)	110(4)	32(2)	87(4)	0(2)	10(3)	9(3)
C(24)	69(3)	36(2)	68(3)	0(2)	14(2)	5(2)
C(25)	34(2)	42(2)	22(2)	0(2)	-6(1)	6(2)
C(26)	51(2)	49(2)	28(2)	3(2)	-7(2)	-4(2)
C(27)	82(3)	73(3)	34(2)	17(2)	-22(2)	-15(3)
C(28)	63(3)	89(3)	45(3)	5(2)	-27(2)	-16(3)
C(29)	40(2)	70(3)	44(2)	1(2)	-11(2)	-10(2)
C(30)	32(2)	45(2)	27(2)	-1(2)	-5(2)	0(2)
C(31)	82(3)	63(3)	30(2)	11(2)	-9(2)	-21(2)
C(32)	114(4)	173(6)	36(3)	-2(3)	9(3)	-80(4)
C(33)	130(5)	62(3)	95(4)	43(3)	-56(4)	-28(3)
C(34)	40(2)	52(2)	29(2)	2(2)	-2(2)	-12(2)
C(35)	69(3)	60(3)	53(3)	11(2)	14(2)	-2(2)
C(36)	56(3)	72(3)	64(3)	9(2)	14(2)	-7(2)
C(37)	36(2)	81(3)	40(2)	-20(2)	-7(2)	4(2)
C(38)	74(3)	32(2)	60(3)	-3(2)	20(2)	-4(2)
C(39)	36(3)	103(4)	90(4)	-43(3)	11(3)	-18(3)

Table A.41: Crystal data and structure refinement for $\mathbf{L_2^{Mes}}$.

Empirical formula	$C_{54}H_{48}N_2OP_2$	
Formula weight	802.88	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.0464(6) Å	α= 90°.
	b = 16.3859(11) Å	β= 95.4910(10)°.
	c = 28.9463(19) Å	γ = 90°.
Volume	4271.1(5) $Å^3$	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.144 mm^{-1}	
F(000)	1696	
Crystal size	0.44 x 0.40 x 0.36 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-10<=h<=10, -19<=k<=19, -34<=l<=34	
Reflections collected	40610	
Independent reflections	7537 [R(int) = 0.0256]	
Completeness to theta = 25.03°	99.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6810	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7537 / 0 / 538	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0863	
R indices (all data)	R1 = 0.0420, wR2 = 0.0912	
Largest diff. peak and hole	0.279 and -0.318 $e.Å^{-3}$	

Table A.42: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_2^{Mes}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	2173(1)	2263(1)	1392(1)	27(1)	C(26)	-1164(2)	3344(1)	1152(1)	36(1)
O(1)	1127(1)	1622(1)	2324(1)	26(1)	C(27)	-2114(2)	3859(1)	882(1)	46(1)
C(1)	780(2)	1140(1)	1933(1)	27(1)	C(28)	-1626(2)	4556(1)	675(1)	52(1)
N(1)	1366(2)	3062(1)	1506(1)	32(1)	C(29)	-133(2)	4737(1)	749(1)	51(1)
P(2)	1402(1)	2447(1)	3359(1)	25(1)	C(30)	868(2)	4249(1)	1018(1)	39(1)
N(2)	677(2)	2630(1)	3818(1)	32(1)	C(31)	-1759(2)	2584(1)	1361(1)	47(1)
C(2)	1207(2)	1313(1)	1495(1)	29(1)	C(32)	-2689(3)	5105(2)	378(1)	83(1)
C(3)	782(2)	732(1)	1156(1)	36(1)	C(33)	2483(2)	4474(1)	1092(1)	57(1)
C(4)	-37(2)	41(1)	1253(1)	40(1)	C(34)	1056(2)	3197(1)	2900(1)	27(1)

C(5)	-468(2)	-100(1)	1689(1)	36(1)	C(35)	2051(2)	3804(1)	2807(1)	36(1)
C(6)	-39(2)	457(1)	2038(1)	29(1)	C(36)	1632(2)	4414(1)	2490(1)	44(1)
C(7)	-218(2)	516(1)	2528(1)	29(1)	C(37)	246(2)	4415(1)	2254(1)	40(1)
C(8)	-900(2)	38(1)	2842(1)	36(1)	C(38)	-741(2)	3803(1)	2334(1)	37(1)
C(9)	-861(2)	292(1)	3297(1)	38(1)	C(39)	-354(2)	3209(1)	2660(1)	34(1)
C(10)	-153(2)	1015(1)	3441(1)	32(1)	C(40)	3392(2)	2294(1)	3440(1)	26(1)
C(11)	550(2)	1512(1)	3136(1)	27(1)	C(41)	4054(2)	1544(1)	3368(1)	34(1)
C(12)	501(2)	1235(1)	2681(1)	25(1)	C(42)	5562(2)	1436(1)	3487(1)	39(1)
C(13)	2661(2)	2205(1)	801(1)	32(1)	C(43)	6424(2)	2070(1)	3675(1)	36(1)
C(14)	1567(2)	2373(1)	443(1)	39(1)	C(44)	5777(2)	2814(1)	3752(1)	31(1)
C(15)	1917(2)	2442(1)	-10(1)	49(1)	C(45)	4269(2)	2926(1)	3638(1)	28(1)
C(16)	3363(2)	2340(1)	-111(1)	56(1)	C(46)	1216(2)	3239(1)	4137(1)	31(1)
C(17)	4450(2)	2164(2)	241(1)	62(1)	C(47)	2248(2)	3030(1)	4515(1)	37(1)
C(18)	4110(2)	2098(1)	695(1)	47(1)	C(48)	2771(2)	3636(1)	4823(1)	44(1)
C(19)	3842(2)	2131(1)	1778(1)	30(1)	C(49)	2276(2)	4437(1)	4786(1)	46(1)
C(20)	4564(2)	1379(1)	1798(1)	38(1)	C(50)	1197(2)	4620(1)	4428(1)	41(1)
C(21)	5816(2)	1258(1)	2102(1)	43(1)	C(51)	661(2)	4041(1)	4105(1)	34(1)
C(22)	6330(2)	1876(1)	2396(1)	41(1)	C(52)	2715(2)	2154(1)	4596(1)	47(1)
C(23)	5615(2)	2621(1)	2383(1)	41(1)	C(53)	2831(3)	5081(2)	5131(1)	67(1)
C(24)	4372(2)	2756(1)	2070(1)	34(1)	C(54)	-538(2)	4275(1)	3731(1)	40(1)
C(25)	359(2)	3537(1)	1220(1)	32(1)					

Table A.43: Bond lengths [Å] for $\mathbf{L_2^{Mes}}$.

P(1)-N(1)	1.5491(14)	C(17)-C(18)	1.383(3)	C(36)-C(37)	1.370(3)
P(1)-C(19)	1.8035(16)	C(17)-H(17)	0.9500	C(36)-H(36)	0.9500
P(1)-C(13)	1.8089(17)	C(18)-H(18)	0.9500	C(37)-C(38)	1.377(3)
P(1)-C(2)	1.8241(16)	C(19)-C(24)	1.383(2)	C(37)-H(37)	0.9500
O(1)-C(12)	1.3797(18)	C(19)-C(20)	1.394(2)	C(38)-C(39)	1.378(2)
O(1)-C(1)	1.3884(18)	C(20)-C(21)	1.380(2)	C(38)-H(38)	0.9500
C(1)-C(2)	1.392(2)	C(20)-H(20)	0.9500	C(39)-H(39)	0.9500
C(1)-C(6)	1.393(2)	C(21)-C(22)	1.376(3)	C(40)-C(41)	1.391(2)
N(1)-C(25)	1.405(2)	C(21)-H(21)	0.9500	C(40)-C(45)	1.395(2)
P(2)-N(2)	1.5651(13)	C(22)-C(23)	1.379(3)	C(41)-C(42)	1.386(2)
P(2)-C(11)	1.8067(16)	C(22)-H(22)	0.9500	C(41)-H(41)	0.9500
P(2)-C(40)	1.8111(15)	C(23)-C(24)	1.394(2)	C(42)-C(43)	1.379(2)
P(2)-C(34)	1.8150(16)	C(23)-H(23)	0.9500	C(42)-H(42)	0.9500
N(2)-C(46)	1.413(2)	C(24)-H(24)	0.9500	C(43)-C(44)	1.379(2)
C(2)-C(3)	1.393(2)	C(25)-C(30)	1.402(2)	C(43)-H(43)	0.9500
C(3)-C(4)	1.395(2)	C(25)-C(26)	1.408(2)	C(44)-C(45)	1.384(2)
C(3)-H(3)	0.9500	C(26)-C(27)	1.391(2)	C(44)-H(44)	0.9500
C(4)-C(5)	1.376(3)	C(26)-C(31)	1.506(3)	C(45)-H(45)	0.9500
C(4)-H(4)	0.9500	C(27)-C(28)	1.381(3)	C(46)-C(51)	1.408(2)
C(5)-C(6)	1.390(2)	C(27)-H(27)	0.9500	C(46)-C(47)	1.411(2)

C(5)-H(5)	0.9500	C(28)-C(29)	1.379(3)	C(47)-C(48)	1.387(3)
C(6)-C(7)	1.444(2)	C(28)-C(32)	1.520(3)	C(47)-C(52)	1.508(3)
C(7)-C(8)	1.389(2)	C(29)-C(30)	1.390(3)	C(48)-C(49)	1.388(3)
C(7)-C(12)	1.397(2)	C(29)-H(29)	0.9500	C(48)-H(48)	0.9500
C(8)-C(9)	1.376(3)	C(30)-C(33)	1.502(3)	C(49)-C(50)	1.388(3)
C(8)-H(8)	0.9500	C(31)-H(31A)	0.9800	C(49)-C(53)	1.505(3)
C(9)-C(10)	1.392(2)	C(31)-H(31B)	0.9800	C(50)-C(51)	1.386(2)
C(9)-H(9)	0.9500	C(31)-H(31C)	0.9800	C(50)-H(50)	0.9500
C(10)-C(11)	1.398(2)	C(32)-H(32A)	0.9800	C(51)-C(54)	1.506(2)
C(10)-H(10)	0.9500	C(32)-H(32B)	0.9800	C(52)-H(52A)	0.9800
C(11)-C(12)	1.391(2)	C(32)-H(32C)	0.9800	C(52)-H(52B)	0.9800
C(13)-C(18)	1.387(2)	C(33)-H(33A)	0.9800	C(52)-H(52C)	0.9800
C(13)-C(14)	1.391(2)	C(33)-H(33B)	0.9800	C(53)-H(53A)	0.9800
C(14)-C(15)	1.383(2)	C(33)-H(33C)	0.9800	C(53)-H(53B)	0.9800
C(14)-H(14)	0.9500	C(34)-C(35)	1.387(2)	C(53)-H(53C)	0.9800
C(15)-C(16)	1.377(3)	C(34)-C(39)	1.393(2)	C(54)-H(54A)	0.9800
C(15)-H(15)	0.9500	C(35)-C(36)	1.384(2)	C(54)-H(54B)	0.9800
C(16)-C(17)	1.377(3)	C(35)-H(35)	0.9500	C(54)-H(54C)	0.9800
C(16)-H(16)	0.9500				

Table A.44: Bond angles [°] for $\mathbf{L_2^{Mes}}$

N(1)-P(1)-C(19)	110.70(7)	C(18)-C(17)-H(17)	119.6	C(37)-C(36)-H(36)	119.6
N(1)-P(1)-C(13)	114.06(8)	C(17)-C(18)-C(13)	120.15(18)	C(35)-C(36)-H(36)	119.6
C(19)-P(1)-C(13)	108.34(7)	C(17)-C(18)-H(18)	119.9	C(36)-C(37)-C(38)	119.52(16)
N(1)-P(1)-C(2)	116.31(7)	C(13)-C(18)-H(18)	119.9	C(36)-C(37)-H(37)	120.2
C(19)-P(1)-C(2)	100.54(7)	C(24)-C(19)-C(20)	119.81(15)	C(38)-C(37)-H(37)	120.2
C(13)-P(1)-C(2)	105.81(7)	C(24)-C(19)-P(1)	120.68(13)	C(37)-C(38)-C(39)	120.23(16)
C(12)-O(1)-C(1)	105.76(11)	C(20)-C(19)-P(1)	119.45(13)	C(37)-C(38)-H(38)	119.9
O(1)-C(1)-C(2)	124.50(13)	C(21)-C(20)-C(19)	120.30(17)	C(39)-C(38)-H(38)	119.9
O(1)-C(1)-C(6)	111.28(13)	C(21)-C(20)-H(20)	119.8	C(38)-C(39)-C(34)	120.84(16)
C(2)-C(1)-C(6)	124.22(14)	C(19)-C(20)-H(20)	119.8	C(38)-C(39)-H(39)	119.6
C(25)-N(1)-P(1)	129.52(11)	C(22)-C(21)-C(20)	119.82(17)	C(34)-C(39)-H(39)	119.6
N(2)-P(2)-C(11)	105.47(7)	C(22)-C(21)-H(21)	120.1	C(41)-C(40)-C(45)	118.78(14)
N(2)-P(2)-C(40)	114.21(7)	C(20)-C(21)-H(21)	120.1	C(41)-C(40)-P(2)	122.72(12)
C(11)-P(2)-C(40)	108.23(7)	C(21)-C(22)-C(23)	120.38(16)	C(45)-C(40)-P(2)	117.97(11)
N(2)-P(2)-C(34)	115.79(7)	C(21)-C(22)-H(22)	119.8	C(42)-C(41)-C(40)	120.18(16)
C(11)-P(2)-C(34)	105.92(7)	C(23)-C(22)-H(22)	119.8	C(42)-C(41)-H(41)	119.9
C(40)-P(2)-C(34)	106.70(7)	C(22)-C(23)-C(24)	120.30(17)	C(40)-C(41)-H(41)	119.9
C(46)-N(2)-P(2)	122.88(11)	C(22)-C(23)-H(23)	119.9	C(43)-C(42)-C(41)	120.54(16)
C(1)-C(2)-C(3)	114.90(15)	C(24)-C(23)-H(23)	119.9	C(43)-C(42)-H(42)	119.7
C(1)-C(2)-P(1)	120.04(12)	C(19)-C(24)-C(23)	119.37(16)	C(41)-C(42)-H(42)	119.7
C(3)-C(2)-P(1)	125.00(13)	C(19)-C(24)-H(24)	120.3	C(42)-C(43)-C(44)	119.79(15)
C(2)-C(3)-C(4)	122.00(16)	C(23)-C(24)-H(24)	120.3	C(42)-C(43)-H(43)	120.1

C(2)-C(3)-H(3)	119.0	C(30)-C(25)-N(1)	119.10(15)	C(44)-C(43)-H(43)	120.1
C(4)-C(3)-H(3)	119.0	C(30)-C(25)-C(26)	118.95(16)	C(43)-C(44)-C(45)	120.14(15)
C(5)-C(4)-C(3)	121.48(16)	N(1)-C(25)-C(26)	121.86(15)	C(43)-C(44)-H(44)	119.9
C(5)-C(4)-H(4)	119.3	C(27)-C(26)-C(25)	119.10(17)	C(45)-C(44)-H(44)	119.9
C(3)-C(4)-H(4)	119.3	C(27)-C(26)-C(31)	120.08(17)	C(44)-C(45)-C(40)	120.56(15)
C(4)-C(5)-C(6)	118.30(16)	C(25)-C(26)-C(31)	120.81(15)	C(44)-C(45)-H(45)	119.7
C(4)-C(5)-H(5)	120.8	C(28)-C(27)-C(26)	122.62(19)	C(40)-C(45)-H(45)	119.7
C(6)-C(5)-H(5)	120.8	C(28)-C(27)-H(27)	118.7	C(51)-C(46)-C(47)	118.88(15)
C(5)-C(6)-C(1)	119.08(15)	C(26)-C(27)-H(27)	118.7	C(51)-C(46)-N(2)	121.16(14)
C(5)-C(6)-C(7)	135.13(15)	C(29)-C(28)-C(27)	117.33(18)	C(47)-C(46)-N(2)	119.79(15)
C(1)-C(6)-C(7)	105.79(13)	C(29)-C(28)-C(32)	121.2(2)	C(48)-C(47)-C(46)	118.99(17)
C(8)-C(7)-C(12)	119.29(15)	C(27)-C(28)-C(32)	121.5(2)	C(48)-C(47)-C(52)	120.57(16)
C(8)-C(7)-C(6)	134.72(15)	C(28)-C(29)-C(30)	122.65(19)	C(46)-C(47)-C(52)	120.36(16)
C(12)-C(7)-C(6)	105.98(13)	C(28)-C(29)-H(29)	118.7	C(47)-C(48)-C(49)	122.67(17)
C(9)-C(8)-C(7)	118.96(15)	C(30)-C(29)-H(29)	118.7	C(47)-C(48)-H(48)	118.7
C(9)-C(8)-H(8)	120.5	C(29)-C(30)-C(25)	119.34(18)	C(49)-C(48)-H(48)	118.7
C(7)-C(8)-H(8)	120.5	C(29)-C(30)-C(33)	120.77(18)	C(50)-C(49)-C(48)	117.46(17)
C(8)-C(9)-C(10)	120.87(15)	C(25)-C(30)-C(33)	119.89(16)	C(50)-C(49)-C(53)	120.71(19)
C(8)-C(9)-H(9)	119.6	C(26)-C(31)-H(31A)	109.5	C(48)-C(49)-C(53)	121.79(19)
C(10)-C(9)-H(9)	119.6	C(26)-C(31)-H(31B)	109.5	C(51)-C(50)-C(49)	122.14(18)
C(9)-C(10)-C(11)	122.01(16)	H(31A)-C(31)-H(31E	109.5	C(51)-C(50)-H(50)	118.9
C(9)-C(10)-H(10)	119.0	C(26)-C(31)-H(31C)	109.5	C(49)-C(50)-H(50)	118.9
C(11)-C(10)-H(10)	119.0	H(31A)-C(31)-H(31C	109.5	C(50)-C(51)-C(46)	119.68(16)
C(12)-C(11)-C(10)	115.68(14)	H(31B)-C(31)-H(31C	109.5	C(50)-C(51)-C(54)	119.46(16)
C(12)-C(11)-P(2)	126.09(12)	C(28)-C(32)-H(32A)	109.5	C(46)-C(51)-C(54)	120.84(15)
C(10)-C(11)-P(2)	118.22(12)	C(28)-C(32)-H(32B)	109.5	C(47)-C(52)-H(52A)	109.5
O(1)-C(12)-C(11)	125.64(13)	H(32A)-C(32)-H(32E	109.5	C(47)-C(52)-H(52B)	109.5
O(1)-C(12)-C(7)	111.18(13)	C(28)-C(32)-H(32C)	109.5	H(52A)-C(52)-H(52B)	109.5
C(11)-C(12)-C(7)	123.18(14)	H(32A)-C(32)-H(32C	109.5	C(47)-C(52)-H(52C)	109.5
C(18)-C(13)-C(14)	118.67(16)	H(32B)-C(32)-H(32C	109.5	H(52A)-C(52)-H(52C)	109.5
C(18)-C(13)-P(1)	122.53(13)	C(30)-C(33)-H(33A)	109.5	H(52B)-C(52)-H(52C)	109.5
C(14)-C(13)-P(1)	118.32(12)	C(30)-C(33)-H(33B)	109.5	C(49)-C(53)-H(53A)	109.5
C(15)-C(14)-C(13)	120.82(17)	H(33A)-C(33)-H(33E	109.5	C(49)-C(53)-H(53B)	109.5
C(15)-C(14)-H(14)	119.6	C(30)-C(33)-H(33C)	109.5	H(53A)-C(53)-H(53B)	109.5
C(13)-C(14)-H(14)	119.6	H(33A)-C(33)-H(33C	109.5	C(49)-C(53)-H(53C)	109.5
C(16)-C(15)-C(14)	119.99(18)	H(33B)-C(33)-H(33C	109.5	H(53A)-C(53)-H(53C)	109.5
C(16)-C(15)-H(15)	120.0	C(35)-C(34)-C(39)	118.22(15)	H(53B)-C(53)-H(53C)	109.5
C(14)-C(15)-H(15)	120.0	C(35)-C(34)-P(2)	124.01(12)	C(51)-C(54)-H(54A)	109.5
C(17)-C(16)-C(15)	119.61(18)	C(39)-C(34)-P(2)	117.45(12)	C(51)-C(54)-H(54B)	109.5
C(17)-C(16)-H(16)	120.2	C(36)-C(35)-C(34)	120.41(16)	H(54A)-C(54)-H(54B)	109.5
C(15)-C(16)-H(16)	120.2	C(36)-C(35)-H(35)	119.8	C(51)-C(54)-H(54C)	109.5
C(16)-C(17)-C(18)	120.76(19)	C(34)-C(35)-H(35)	119.8	H(54A)-C(54)-H(54C)	109.5
C(16)-C(17)-H(17)	119.6	C(37)-C(36)-C(35)	120.71(17)	H(54B)-C(54)-H(54C)	109.5

Table A.45: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_2^{Mes}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	25(1)	30(1)	27(1)	-1(1)	2(1)	0(1)
O(1)	26(1)	24(1)	30(1)	-2(1)	4(1)	-5(1)
C(1)	22(1)	25(1)	33(1)	-3(1)	-2(1)	1(1)
N(1)	32(1)	32(1)	32(1)	-1(1)	2(1)	2(1)
P(2)	22(1)	25(1)	29(1)	0(1)	4(1)	1(1)
N(2)	28(1)	35(1)	33(1)	-2(1)	7(1)	1(1)
C(2)	26(1)	28(1)	33(1)	-2(1)	-1(1)	2(1)
C(3)	39(1)	34(1)	33(1)	-3(1)	-4(1)	3(1)
C(4)	49(1)	29(1)	40(1)	-7(1)	-12(1)	0(1)
C(5)	35(1)	26(1)	47(1)	-2(1)	-8(1)	-4(1)
C(6)	21(1)	24(1)	42(1)	0(1)	-2(1)	1(1)
C(7)	20(1)	23(1)	42(1)	1(1)	1(1)	1(1)
C(8)	27(1)	25(1)	56(1)	4(1)	5(1)	-4(1)
C(9)	32(1)	32(1)	52(1)	12(1)	13(1)	-1(1)
C(10)	27(1)	32(1)	39(1)	6(1)	10(1)	4(1)
C(11)	20(1)	25(1)	36(1)	3(1)	5(1)	3(1)
C(12)	19(1)	24(1)	34(1)	4(1)	5(1)	1(1)
C(13)	32(1)	34(1)	31(1)	-1(1)	5(1)	1(1)
C(14)	36(1)	50(1)	32(1)	-3(1)	3(1)	7(1)
C(15)	54(1)	60(1)	32(1)	1(1)	2(1)	14(1)
C(16)	61(1)	73(2)	35(1)	8(1)	17(1)	9(1)
C(17)	44(1)	96(2)	49(1)	9(1)	21(1)	11(1)
C(18)	34(1)	67(1)	40(1)	6(1)	7(1)	6(1)
C(19)	26(1)	37(1)	28(1)	4(1)	4(1)	-2(1)
C(20)	34(1)	36(1)	43(1)	1(1)	-1(1)	0(1)
C(21)	33(1)	41(1)	54(1)	9(1)	-2(1)	2(1)
C(22)	28(1)	53(1)	42(1)	12(1)	-3(1)	-6(1)
C(23)	36(1)	49(1)	37(1)	-2(1)	-1(1)	-11(1)
C(24)	30(1)	38(1)	35(1)	1(1)	3(1)	-4(1)
C(25)	36(1)	32(1)	28(1)	-5(1)	4(1)	5(1)
C(26)	33(1)	40(1)	35(1)	-7(1)	5(1)	6(1)
C(27)	39(1)	55(1)	42(1)	-10(1)	-1(1)	16(1)
C(28)	65(1)	49(1)	40(1)	-1(1)	-4(1)	22(1)
C(29)	73(2)	36(1)	43(1)	6(1)	5(1)	8(1)
C(30)	50(1)	32(1)	36(1)	-1(1)	4(1)	1(1)
C(31)	31(1)	51(1)	60(1)	-1(1)	7(1)	-1(1)
C(32)	96(2)	81(2)	69(2)	14(1)	-12(1)	41(2)
C(33)	59(1)	44(1)	68(1)	9(1)	5(1)	-16(1)
C(34)	27(1)	25(1)	31(1)	-2(1)	2(1)	3(1)

C(35)	30(1)	37(1)	39(1)	6(1)	-1(1)	-3(1)
C(36)	43(1)	38(1)	49(1)	11(1)	0(1)	-6(1)
C(37)	47(1)	31(1)	42(1)	6(1)	0(1)	7(1)
C(38)	31(1)	36(1)	43(1)	-2(1)	-3(1)	10(1)
C(39)	26(1)	31(1)	45(1)	-1(1)	3(1)	2(1)
C(40)	24(1)	31(1)	25(1)	4(1)	4(1)	2(1)
C(41)	31(1)	31(1)	39(1)	-4(1)	2(1)	2(1)
C(42)	34(1)	36(1)	47(1)	-5(1)	2(1)	11(1)
C(43)	25(1)	46(1)	37(1)	0(1)	1(1)	6(1)
C(44)	29(1)	35(1)	30(1)	2(1)	1(1)	-2(1)
C(45)	29(1)	28(1)	29(1)	2(1)	5(1)	2(1)
C(46)	26(1)	40(1)	29(1)	0(1)	10(1)	0(1)
C(47)	31(1)	50(1)	30(1)	3(1)	9(1)	4(1)
C(48)	35(1)	68(1)	30(1)	-1(1)	2(1)	2(1)
C(49)	41(1)	59(1)	37(1)	-12(1)	6(1)	-3(1)
C(50)	40(1)	41(1)	44(1)	-7(1)	9(1)	-1(1)
C(51)	29(1)	39(1)	34(1)	-2(1)	8(1)	1(1)
C(52)	48(1)	57(1)	37(1)	11(1)	7(1)	11(1)
C(53)	66(2)	77(2)	56(1)	-25(1)	-5(1)	-4(1)
C(54)	37(1)	37(1)	46(1)	-3(1)	3(1)	8(1)

Table A.46: Crystal data and structure refinement for **9**.

Empirical formula	$C_{105}H_{96}B_2N_2O_2P_2$	
Formula weight	1501.4	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 17.2935(9) Å	α= 90°.
	b = 20.5469(11) Å	β= 90°.
	c = 23.7107(13) Å	γ = 90°.
Volume	8425.1(8) $Å^3$	
Z	4	
Density (calculated)	1.184 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	3184	
Crystal size	0.42 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.08 to 25.03°.	
Index ranges	-20<=h<=20, -24<=k<=24, -28<=l<=28	
Reflections collected	97914	
Independent reflections	7433 [R(int) = 0.1083]	
Completeness to theta = 25.03°	99.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6912	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7433 / 0 / 516	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1008	
R indices (all data)	R1 = 0.0838, wR2 = 0.1183	
Largest diff. peak and hole	0.196 and -0.317 $e.Å^{-3}$	

Table A.47: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **9**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	4461(1)	2083(1)	6448(1)	31(1)	C(27)	3338(2)	3648(1)	6466(1)	58(1)
O(1)	5000	1405(1)	7500	32(1)	C(40)	8234(1)	446(1)	5898(1)	38(1)
C(2)	4782(1)	994(1)	7060(1)	30(1)	C(46)	7813(1)	-432(1)	5117(1)	37(1)
N(1)	3906(1)	2431(1)	6920(1)	36(1)	C(33)	7179(1)	-342(1)	6689(1)	42(1)
C(13)	5413(1)	2400(1)	6540(1)	33(1)	C(29)	6559(1)	-900(1)	5949(1)	41(1)
C(20)	2573(1)	2039(1)	7067(1)	36(1)	C(39)	6885(1)	576(1)	5356(1)	37(1)
C(18)	6037(1)	2069(1)	6301(1)	38(1)	C(30)	6169(1)	-1288(1)	6334(1)	48(1)
C(1)	4516(1)	1218(1)	6545(1)	31(1)	C(28)	7075(1)	-404(1)	6107(1)	36(1)
C(3)	4853(1)	342(1)	7211(1)	33(1)	C(45)	9014(1)	316(1)	5778(1)	49(1)

C(19)	3073(1)	2523(1)	6873(1)	34(1)	C(34)	6083(1)	481(1)	5331(1)	44(1)
C(14)	5524(1)	3008(1)	6786(1)	40(1)	C(38)	7146(2)	1146(1)	5090(1)	46(1)
C(21)	1779(1)	2156(1)	7022(1)	41(1)	C(51)	7706(1)	-318(1)	4543(1)	46(1)
C(7)	4133(1)	2280(1)	5758(1)	34(1)	C(35)	5586(2)	908(1)	5054(1)	50(1)
C(8)	3443(1)	2034(1)	5542(1)	40(1)	C(47)	8249(1)	-990(1)	5249(1)	46(1)
C(4)	4636(1)	-124(1)	6816(1)	40(1)	B(1)	7499(2)	47(1)	5623(1)	36(1)
C(25)	2856(1)	1412(1)	7320(1)	46(1)	C(41)	8109(2)	961(1)	6274(1)	45(1)
C(11)	4335(1)	2888(1)	4903(1)	47(1)	C(32)	6797(2)	-732(1)	7081(1)	52(1)
C(12)	4575(1)	2709(1)	5436(1)	43(1)	C(36)	5872(2)	1462(1)	4802(1)	54(1)
C(5)	4356(1)	79(1)	6299(1)	41(1)	C(37)	6656(2)	1581(1)	4823(1)	53(1)
C(22)	1489(1)	2724(1)	6788(1)	43(1)	C(43)	9464(2)	1175(1)	6380(1)	62(1)
C(23)	2003(1)	3194(1)	6610(1)	45(1)	C(48)	8552(2)	-1398(1)	4841(1)	58(1)
C(10)	3658(2)	2636(1)	4688(1)	48(1)	C(31)	6291(2)	-1205(1)	6905(1)	52(1)
C(24)	2804(1)	3109(1)	6651(1)	40(1)	C(44)	9616(2)	671(1)	6015(1)	59(1)
C(17)	6762(1)	2350(1)	6316(1)	47(1)	C(50)	8013(2)	-729(2)	4129(1)	60(1)
C(6)	4296(1)	736(1)	6162(1)	37(1)	C(42)	8707(2)	1323(1)	6510(1)	56(1)
C(15)	6260(1)	3275(1)	6804(1)	47(1)	C(49)	8439(2)	-1268(2)	4279(1)	63(1)
C(9)	3215(1)	2214(1)	5003(1)	46(1)	O(1S)	5000	4206(1)	7500	86(1)
C(26)	629(1)	2820(1)	6724(1)	58(1)	C(2S)	5000	4793(2)	7500	59(1)
C(16)	6875(1)	2946(1)	6570(1)	48(1)	C(3S)	4279(2)	5166(1)	7373(1)	75(1)

Table A.48: Bond lengths [Å] for **9**.

P(1)-N(1)	1.6393(18)	C(5)-C(6)	1.392(3)	C(30)-H(30)	0.9500
P(1)-C(7)	1.777(2)	C(5)-H(5)	0.9500	C(28)-B(1)	1.646(3)
P(1)-C(13)	1.784(2)	C(22)-C(23)	1.379(3)	C(45)-C(44)	1.388(3)
P(1)-C(1)	1.794(2)	C(22)-C(26)	1.509(3)	C(45)-H(45)	0.9500
O(1)-C(2)	1.393(2)	C(23)-C(24)	1.398(3)	C(34)-C(35)	1.391(3)
O(1)-C(2)#1	1.393(2)	C(23)-H(23)	0.9500	C(34)-H(34)	0.9500
C(2)-C(1)	1.385(3)	C(10)-C(9)	1.376(3)	C(38)-C(37)	1.384(3)
C(2)-C(3)	1.393(3)	C(10)-H(10)	0.9500	C(38)-H(38)	0.9500
N(1)-C(19)	1.457(3)	C(24)-C(27)	1.509(3)	C(51)-C(50)	1.400(3)
N(1)-H(1N)	0.8934	C(17)-C(16)	1.379(3)	C(51)-H(51)	0.9500
C(13)-C(14)	1.393(3)	C(17)-H(17)	0.9500	C(35)-C(36)	1.377(4)
C(13)-C(18)	1.395(3)	C(6)-H(6)	0.9500	C(35)-H(35)	0.9500
C(20)-C(19)	1.396(3)	C(15)-C(16)	1.378(3)	C(47)-C(48)	1.385(3)
C(20)-C(21)	1.397(3)	C(15)-H(15)	0.9500	C(47)-H(47)	0.9500
C(20)-C(25)	1.504(3)	C(9)-H(9)	0.9500	C(41)-C(42)	1.391(3)
C(18)-C(17)	1.381(3)	C(26)-H(26A)	0.9800	C(41)-H(41)	0.9500
C(18)-H(18)	0.9500	C(26)-H(26B)	0.9800	C(32)-C(31)	1.374(4)
C(1)-C(6)	1.396(3)	C(26)-H(26C)	0.9800	C(32)-H(32)	0.9500
C(3)-C(4)	1.391(3)	C(16)-H(16)	0.9500	C(36)-C(37)	1.380(4)
C(3)-C(3)#1	1.462(4)	C(27)-H(27A)	0.9800	C(36)-H(36)	0.9500
C(19)-C(24)	1.394(3)	C(27)-H(27B)	0.9800	C(37)-H(37)	0.9500

C(14)-C(15)	1.385(3)	C(27)-H(27C)	0.9800	C(43)-C(44)	1.374(4)
C(14)-H(14)	0.9500	C(40)-C(41)	1.400(3)	C(43)-C(42)	1.381(4)
C(21)-C(22)	1.386(3)	C(40)-C(45)	1.404(3)	C(43)-H(43)	0.9500
C(21)-H(21)	0.9500	C(40)-B(1)	1.648(3)	C(48)-C(49)	1.372(4)
C(7)-C(8)	1.394(3)	C(46)-C(51)	1.393(3)	C(48)-H(48)	0.9500
C(7)-C(12)	1.397(3)	C(46)-C(47)	1.407(3)	C(31)-H(31)	0.9500
C(8)-C(9)	1.388(3)	C(46)-B(1)	1.644(3)	C(44)-H(44)	0.9500
C(8)-H(8)	0.9500	C(33)-C(32)	1.393(3)	C(50)-C(49)	1.377(4)
C(4)-C(5)	1.382(3)	C(33)-C(28)	1.399(3)	C(50)-H(50)	0.9500
C(4)-H(4)	0.9500	C(33)-H(33)	0.9500	C(42)-H(42)	0.9500
C(25)-H(25A)	0.9800	C(29)-C(30)	1.388(3)	C(49)-H(49)	0.9500
C(25)-H(25B)	0.9800	C(29)-C(28)	1.404(3)	O(1S)-C(2S)	1.206(4)
C(25)-H(25C)	0.9800	C(29)-H(29)	0.9500	C(2S)-C(3S)#1	1.494(3)
C(11)-C(12)	1.378(3)	C(39)-C(34)	1.401(3)	C(2S)-C(3S)	1.494(3)
C(11)-C(10)	1.379(3)	C(39)-C(38)	1.406(3)	C(3S)-H(3S1)	0.9800
C(11)-H(11)	0.9500	C(39)-B(1)	1.648(3)	C(3S)-H(3S2)	0.9800
C(12)-H(12)	0.9500	C(30)-C(31)	1.380(3)	C(3S)-H(3S3)	0.9800

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table A.49: Bond angles [°] for **9**

N(1)-P(1)-C(7)	110.00(10)	C(21)-C(22)-C(26)	120.5(2)	C(35)-C(34)-H(34)	118.5
N(1)-P(1)-C(13)	107.28(10)	C(22)-C(23)-C(24)	121.9(2)	C(39)-C(34)-H(34)	118.5
C(7)-P(1)-C(13)	108.95(10)	C(22)-C(23)-H(23)	119.0	C(37)-C(38)-C(39)	123.0(2)
N(1)-P(1)-C(1)	112.08(10)	C(24)-C(23)-H(23)	119.0	C(37)-C(38)-H(38)	118.5
C(7)-P(1)-C(1)	111.12(10)	C(9)-C(10)-C(11)	120.6(2)	C(39)-C(38)-H(38)	118.5
C(13)-P(1)-C(1)	107.24(10)	C(9)-C(10)-H(10)	119.7	C(46)-C(51)-C(50)	122.2(3)
C(2)-O(1)-C(2)#1	105.5(2)	C(11)-C(10)-H(10)	119.7	C(46)-C(51)-H(51)	118.9
C(1)-C(2)-O(1)	123.35(18)	C(19)-C(24)-C(23)	117.8(2)	C(50)-C(51)-H(51)	118.9
C(1)-C(2)-C(3)	125.13(19)	C(19)-C(24)-C(27)	122.6(2)	C(36)-C(35)-C(34)	120.3(3)
O(1)-C(2)-C(3)	111.51(18)	C(23)-C(24)-C(27)	119.6(2)	C(36)-C(35)-H(35)	119.9
C(19)-N(1)-P(1)	125.62(15)	C(16)-C(17)-C(18)	120.8(2)	C(34)-C(35)-H(35)	119.9
C(19)-N(1)-H(1N)	117.2	C(16)-C(17)-H(17)	119.6	C(48)-C(47)-C(46)	122.7(2)
P(1)-N(1)-H(1N)	115.0	C(18)-C(17)-H(17)	119.6	C(48)-C(47)-H(47)	118.6
C(14)-C(13)-C(18)	120.0(2)	C(5)-C(6)-C(1)	121.1(2)	C(46)-C(47)-H(47)	118.6
C(14)-C(13)-P(1)	120.41(17)	C(5)-C(6)-H(6)	119.4	C(46)-B(1)-C(28)	108.63(18)
C(18)-C(13)-P(1)	119.08(16)	C(1)-C(6)-H(6)	119.4	C(46)-B(1)-C(40)	109.39(19)
C(19)-C(20)-C(21)	117.5(2)	C(16)-C(15)-C(14)	120.2(2)	C(28)-B(1)-C(40)	110.44(18)
C(19)-C(20)-C(25)	122.7(2)	C(16)-C(15)-H(15)	119.9	C(46)-B(1)-C(39)	109.02(18)
C(21)-C(20)-C(25)	119.8(2)	C(14)-C(15)-H(15)	119.9	C(28)-B(1)-C(39)	110.62(19)
C(17)-C(18)-C(13)	119.2(2)	C(10)-C(9)-C(8)	120.6(2)	C(40)-B(1)-C(39)	108.73(18)
C(17)-C(18)-H(18)	120.4	C(10)-C(9)-H(9)	119.7	C(42)-C(41)-C(40)	123.1(3)
C(13)-C(18)-H(18)	120.4	C(8)-C(9)-H(9)	119.7	C(42)-C(41)-H(41)	118.4

C(2)-C(1)-C(6)	115.35(19)	C(22)-C(26)-H(26A)	109.5	C(40)-C(41)-H(41)	118.4
C(2)-C(1)-P(1)	117.37(16)	C(22)-C(26)-H(26B)	109.5	C(31)-C(32)-C(33)	120.5(2)
C(6)-C(1)-P(1)	127.24(17)	H(26A)-C(26)-H(26E	109.5	C(31)-C(32)-H(32)	119.7
C(4)-C(3)-C(2)	117.75(19)	C(22)-C(26)-H(26C)	109.5	C(33)-C(32)-H(32)	119.7
C(4)-C(3)-C(3)#1	136.50(13)	H(26A)-C(26)-H(26C	109.5	C(35)-C(36)-C(37)	118.9(2)
C(2)-C(3)-C(3)#1	105.73(12)	H(26B)-C(26)-H(26C	109.5	C(35)-C(36)-H(36)	120.5
C(24)-C(19)-C(20)	122.1(2)	C(15)-C(16)-C(17)	120.1(2)	C(37)-C(36)-H(36)	120.5
C(24)-C(19)-N(1)	118.1(2)	C(15)-C(16)-H(16)	119.9	C(36)-C(37)-C(38)	120.3(2)
C(20)-C(19)-N(1)	119.72(19)	C(17)-C(16)-H(16)	119.9	C(36)-C(37)-H(37)	119.9
C(15)-C(14)-C(13)	119.6(2)	C(24)-C(27)-H(27A)	109.5	C(38)-C(37)-H(37)	119.9
C(15)-C(14)-H(14)	120.2	C(24)-C(27)-H(27B)	109.5	C(44)-C(43)-C(42)	119.3(3)
C(13)-C(14)-H(14)	120.2	H(27A)-C(27)-H(27E	109.5	C(44)-C(43)-H(43)	120.4
C(22)-C(21)-C(20)	122.0(2)	C(24)-C(27)-H(27C)	109.5	C(42)-C(43)-H(43)	120.4
C(22)-C(21)-H(21)	119.0	H(27A)-C(27)-H(27C	109.5	C(49)-C(48)-C(47)	120.5(3)
C(20)-C(21)-H(21)	119.0	H(27B)-C(27)-H(27C	109.5	C(49)-C(48)-H(48)	119.8
C(8)-C(7)-C(12)	119.7(2)	C(41)-C(40)-C(45)	114.9(2)	C(47)-C(48)-H(48)	119.8
C(8)-C(7)-P(1)	122.03(17)	C(41)-C(40)-B(1)	120.6(2)	C(32)-C(31)-C(30)	118.8(2)
C(12)-C(7)-P(1)	118.24(17)	C(45)-C(40)-B(1)	124.6(2)	C(32)-C(31)-H(31)	120.6
C(9)-C(8)-C(7)	119.1(2)	C(51)-C(46)-C(47)	115.2(2)	C(30)-C(31)-H(31)	120.6
C(9)-C(8)-H(8)	120.5	C(51)-C(46)-B(1)	124.7(2)	C(43)-C(44)-C(45)	120.4(3)
C(7)-C(8)-H(8)	120.5	C(47)-C(46)-B(1)	120.0(2)	C(43)-C(44)-H(44)	119.8
C(5)-C(4)-C(3)	119.0(2)	C(32)-C(33)-C(28)	123.0(2)	C(45)-C(44)-H(44)	119.8
C(5)-C(4)-H(4)	120.5	C(32)-C(33)-H(33)	118.5	C(49)-C(50)-C(51)	120.5(3)
C(3)-C(4)-H(4)	120.5	C(28)-C(33)-H(33)	118.5	C(49)-C(50)-H(50)	119.7
C(20)-C(25)-H(25A	109.5	C(30)-C(29)-C(28)	123.4(2)	C(51)-C(50)-H(50)	119.7
C(20)-C(25)-H(25B	109.5	C(30)-C(29)-H(29)	118.3	C(43)-C(42)-C(41)	119.7(3)
H(25A)-C(25)-H(25	109.5	C(28)-C(29)-H(29)	118.3	C(43)-C(42)-H(42)	120.1
C(20)-C(25)-H(25C	109.5	C(34)-C(39)-C(38)	114.6(2)	C(41)-C(42)-H(42)	120.1
H(25A)-C(25)-H(25	109.5	C(34)-C(39)-B(1)	124.2(2)	C(48)-C(49)-C(50)	118.9(3)
H(25B)-C(25)-H(25	109.5	C(38)-C(39)-B(1)	121.0(2)	C(48)-C(49)-H(49)	120.5
C(12)-C(11)-C(10)	119.6(2)	C(31)-C(30)-C(29)	120.0(2)	C(50)-C(49)-H(49)	120.5
C(12)-C(11)-H(11)	120.2	C(31)-C(30)-H(30)	120.0	O(1S)-C(2S)-C(3S)#1	120.89(17)
C(10)-C(11)-H(11)	120.2	C(29)-C(30)-H(30)	120.0	O(1S)-C(2S)-C(3S)	120.89(17)
C(11)-C(12)-C(7)	120.4(2)	C(33)-C(28)-C(29)	114.3(2)	C(3S)#1-C(2S)-C(3S)	118.2(3)
C(11)-C(12)-H(12)	119.8	C(33)-C(28)-B(1)	125.3(2)	C(2S)-C(3S)-H(3S1)	109.5
C(7)-C(12)-H(12)	119.8	C(29)-C(28)-B(1)	120.4(2)	C(2S)-C(3S)-H(3S2)	109.5
C(4)-C(5)-C(6)	121.6(2)	C(44)-C(45)-C(40)	122.6(3)	H(3S1)-C(3S)-H(3S2)	109.5
C(4)-C(5)-H(5)	119.2	C(44)-C(45)-H(45)	118.7	C(2S)-C(3S)-H(3S3)	109.5
C(6)-C(5)-H(5)	119.2	C(40)-C(45)-H(45)	118.7	H(3S1)-C(3S)-H(3S3)	109.5
C(23)-C(22)-C(21)	118.6(2)	C(35)-C(34)-C(39)	122.9(2)	H(3S2)-C(3S)-H(3S3)	109.5
C(23)-C(22)-C(26)	120.8(2)				

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table A.50: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	30(1)	31(1)	34(1)	1(1)	-2(1)	-2(1)
O(1)	34(1)	26(1)	36(1)	0	-4(1)	0
C(2)	28(1)	29(1)	34(1)	-7(1)	1(1)	-1(1)
N(1)	32(1)	37(1)	38(1)	-3(1)	-4(1)	2(1)
C(13)	32(1)	32(1)	35(1)	5(1)	-4(1)	-3(1)
C(20)	36(1)	42(1)	30(1)	-3(1)	1(1)	1(1)
C(18)	35(1)	33(1)	45(1)	2(1)	-1(1)	-4(1)
C(1)	30(1)	29(1)	35(1)	-1(1)	2(1)	-2(1)
C(3)	31(1)	29(1)	38(1)	0(1)	4(1)	0(1)
C(19)	30(1)	39(1)	34(1)	-6(1)	-3(1)	4(1)
C(14)	36(1)	39(1)	46(1)	-2(1)	0(1)	-5(1)
C(21)	35(1)	52(2)	36(1)	-9(1)	5(1)	-3(1)
C(7)	31(1)	31(1)	39(1)	0(1)	-2(1)	1(1)
C(8)	38(1)	37(1)	44(1)	0(1)	-3(1)	-3(1)
C(4)	46(2)	29(1)	44(1)	-5(1)	4(1)	0(1)
C(25)	42(2)	48(2)	48(2)	7(1)	5(1)	-3(1)
C(11)	46(2)	47(2)	48(2)	16(1)	-5(1)	-1(1)
C(12)	38(1)	43(1)	46(1)	8(1)	-5(1)	-5(1)
C(5)	46(2)	35(1)	43(1)	-10(1)	1(1)	-5(1)
C(22)	35(1)	55(2)	39(1)	-17(1)	-5(1)	9(1)
C(23)	45(2)	45(1)	44(1)	-8(1)	-7(1)	12(1)
C(10)	52(2)	49(2)	42(1)	8(1)	-10(1)	7(1)
C(24)	41(2)	38(1)	42(1)	-5(1)	-4(1)	5(1)
C(17)	33(1)	49(2)	58(2)	6(1)	2(1)	0(1)
C(6)	37(1)	39(1)	36(1)	-4(1)	1(1)	-3(1)
C(15)	49(2)	40(1)	52(2)	-2(1)	-4(1)	-15(1)
C(9)	42(2)	45(1)	51(2)	-1(1)	-16(1)	-2(1)
C(26)	40(2)	72(2)	62(2)	-18(2)	-7(1)	12(1)
C(16)	37(2)	50(2)	59(2)	9(1)	-6(1)	-11(1)
C(27)	56(2)	37(1)	81(2)	6(1)	-3(2)	5(1)
C(40)	41(2)	39(1)	34(1)	7(1)	0(1)	-7(1)
C(46)	32(1)	40(1)	40(1)	-3(1)	6(1)	-11(1)
C(33)	41(2)	46(1)	39(1)	3(1)	3(1)	2(1)
C(29)	35(1)	45(1)	45(1)	2(1)	5(1)	0(1)
C(39)	41(1)	39(1)	30(1)	-4(1)	4(1)	-3(1)
C(30)	33(1)	47(2)	64(2)	7(1)	11(1)	-2(1)
C(28)	34(1)	36(1)	38(1)	1(1)	4(1)	5(1)

C(45)	43(2)	54(2)	49(2)	4(1)	-3(1)	-12(1)
C(34)	42(2)	48(1)	41(1)	0(1)	3(1)	1(1)
C(38)	50(2)	45(1)	43(1)	5(1)	0(1)	-4(1)
C(51)	40(2)	57(2)	40(1)	-6(1)	4(1)	-11(1)
C(35)	42(2)	70(2)	39(1)	-5(1)	-1(1)	8(1)
C(47)	40(2)	46(1)	52(2)	-6(1)	9(1)	-4(1)
B(1)	35(2)	40(2)	34(1)	0(1)	1(1)	-5(1)
C(41)	58(2)	41(1)	35(1)	3(1)	-4(1)	-7(1)
C(32)	56(2)	60(2)	39(1)	12(1)	10(1)	10(1)
C(36)	65(2)	57(2)	39(2)	2(1)	-7(1)	14(1)
C(37)	71(2)	45(2)	43(2)	5(1)	-4(1)	1(1)
C(43)	69(2)	63(2)	55(2)	15(2)	-23(2)	-33(2)
C(48)	41(2)	55(2)	77(2)	-18(2)	14(2)	-4(1)
C(31)	43(2)	54(2)	59(2)	18(1)	17(1)	5(1)
C(44)	49(2)	68(2)	60(2)	11(2)	-9(1)	-18(2)
C(50)	49(2)	87(2)	44(2)	-16(2)	10(1)	-23(2)
C(42)	83(2)	45(2)	40(2)	5(1)	-13(2)	-17(2)
C(49)	40(2)	77(2)	73(2)	-35(2)	17(2)	-12(2)
O(1S)	118(3)	40(2)	99(2)	0	22(2)	0
C(2S)	84(3)	45(2)	47(2)	0	18(2)	0
C(3S)	80(2)	59(2)	87(2)	-12(2)	3(2)	1(2)

Table A.51: Crystal data and structure refinement for **10b**.

Empirical formula	$C_{81}H_{72}BN_2OP_2Zn$	
Formula weight	1227.53	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4348(10) Å	α= 86.6850(10)°.
	b = 15.8183(14) Å	β= 75.8230(10)°.
	c = 19.2062(17) Å	γ = 82.7630(10)°.
Volume	3340.0(5) $Å^3$	
Z	2	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.463 mm^{-1}	
F(000)	1290	
Crystal size	0.26 x 0.15 x 0.13 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-13<=h<=13, -18<=k<=18, -22<=l<=22	
Reflections collected	40680	
Independent reflections	11774 [R(int) = 0.0712]	
Completeness to theta = 25.03°	99.70%	
Max. and min. transmission	0.9418 and 0.8902	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11774 / 1475 / 822	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.1571	
R indices (all data)	R1 = 0.1200, wR2 = 0.1777	
Largest diff. peak and hole	0.557 and -0.895 e.$Å^{-3}$	

Table A.52: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **10b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	3275(1)	7259(1)	3419(1)	68(1)	C(41)	1309(5)	4735(3)	4071(2)	64(1)
B(1)	1893(5)	7847(3)	8506(3)	55(1)	C(42)	1457(4)	5492(3)	3666(2)	47(1)
P(1)	2576(1)	6454(1)	2029(1)	35(1)	C(43)	4842(4)	5063(3)	2784(2)	62(1)
O(1)	5187(2)	6946(2)	1881(1)	36(1)	C(44)	2101(6)	3287(3)	4535(3)	109(2)
N(1)	2824(3)	6379(2)	2821(2)	37(1)	C(45)	385(3)	6156(3)	3693(2)	54(1)
C(1)	4959(3)	6637(2)	1278(2)	33(1)	C(46)	4162(4)	8958(3)	3191(2)	53(1)
P(2)	6042(1)	7771(1)	3038(1)	40(1)	C(47)	3958(4)	9404(4)	3820(3)	76(2)
N(2)	4606(3)	8044(2)	3188(2)	43(1)	C(48)	3559(7)	10267(5)	3797(4)	134(3)
C(2)	3886(3)	6322(2)	1272(2)	34(1)	C(49)	3365(9)	10692(5)	3178(4)	165(4)

C(3)	3826(3)	6037(2)	605(2)	39(1)	C(50)	3551(6)	10229(4)	2579(3)	111(2)
C(4)	4783(4)	6080(2)	0(2)	42(1)	C(51)	3936(4)	9363(3)	2565(2)	57(1)
C(5)	5821(4)	6419(2)	23(2)	40(1)	C(52)	4168(4)	8992(4)	4519(2)	79(2)
C(6)	5923(3)	6701(2)	675(2)	35(1)	C(53)	2991(12)	11673(5)	3143(5)	289(8)
C(7)	6825(3)	7100(2)	927(2)	34(1)	C(54)	4104(4)	8909(3)	1876(2)	46(1)
C(8)	7953(3)	7369(2)	623(2)	40(1)	C(55)	2716(4)	8429(3)	8821(2)	47(1)
C(9)	8507(3)	7760(3)	1059(2)	45(1)	C(56)	2653(4)	9310(2)	8676(2)	50(1)
C(10)	7977(3)	7887(2)	1781(2)	41(1)	C(57)	3338(4)	9824(3)	8922(3)	61(1)
C(11)	6825(3)	7636(2)	2111(2)	38(1)	C(58)	4150(4)	9483(3)	9328(3)	67(1)
C(12)	6313(3)	7239(2)	1656(2)	35(1)	C(59)	4243(4)	8622(3)	9479(3)	71(1)
C(13)	1861(3)	7511(2)	1884(2)	37(1)	C(60)	3551(4)	8115(3)	9222(2)	62(1)
C(14)	1194(4)	7985(3)	2471(2)	49(1)	C(61)	481(5)	8282(3)	8684(3)	61(1)
C(15)	657(4)	8800(3)	2364(3)	62(1)	C(62)	-21(4)	8785(3)	9271(2)	56(1)
C(16)	765(4)	9151(3)	1685(3)	59(1)	C(63)	-1234(5)	9092(3)	9492(3)	76(2)
C(17)	1416(4)	8684(3)	1096(2)	50(1)	C(64)	-2030(6)	8907(4)	9119(5)	127(3)
C(18)	1953(4)	7874(3)	1195(2)	45(1)	C(65)	-1593(8)	8403(5)	8533(6)	184(4)
C(19)	1643(4)	5680(3)	1890(2)	41(1)	C(66)	-375(8)	8106(4)	8338(5)	164(4)
C(20)	470(4)	5922(3)	1808(2)	47(1)	C(67)	1921(4)	6891(2)	8887(2)	44(1)
C(21)	-232(4)	5314(4)	1702(2)	65(1)	C(68)	1100(3)	6702(2)	9526(2)	42(1)
C(22)	214(5)	4478(4)	1682(2)	74(2)	C(69)	1087(3)	5900(3)	9851(2)	41(1)
C(23)	1379(5)	4212(3)	1764(3)	75(1)	C(70)	1913(4)	5242(3)	9552(2)	44(1)
C(24)	2093(4)	4823(3)	1870(2)	58(1)	C(71)	2758(4)	5398(3)	8941(2)	59(1)
C(25)	6862(3)	8497(3)	3363(2)	42(1)	C(72)	2772(4)	6197(3)	8619(2)	69(1)
C(26)	7465(4)	8240(3)	3900(2)	53(1)	C(73)	2684(5)	7688(3)	7621(2)	65(2)
C(27)	8067(4)	8813(3)	4160(2)	63(1)	C(74)	2255(5)	7115(3)	7248(3)	86(2)
C(28)	8049(4)	9639(3)	3896(2)	62(1)	C(75)	2780(6)	6993(3)	6522(3)	112(3)
C(29)	7463(4)	9897(3)	3365(2)	59(1)	C(76)	3734(6)	7443(4)	6169(2)	112(4)
C(30)	6875(4)	9329(3)	3091(2)	49(1)	C(77)	4162(5)	8016(4)	6542(3)	120(4)
C(31)	6293(4)	6756(3)	3468(2)	45(1)	C(78)	3637(5)	8138(3)	7268(3)	86(3)
C(32)	7231(4)	6156(3)	3171(3)	64(1)	C(79)	2051(9)	7500(9)	4378(4)	163(6)
C(33)	7470(5)	5394(3)	3542(3)	82(2)	C(73B)	2102(11)	7870(7)	7605(4)	51(3)
C(34)	6766(6)	5258(4)	4219(3)	87(2)	C(74B)	1274(9)	7912(8)	7178(6)	78(4)
C(35)	5838(6)	5850(4)	4526(3)	90(2)	C(75B)	1686(11)	7827(8)	6439(5)	98(5)
C(36)	5597(5)	6591(3)	4160(2)	63(1)	C(76B)	2925(12)	7701(8)	6127(4)	77(5)
C(37)	2614(3)	5596(3)	3241(2)	43(1)	C(77B)	3752(9)	7659(9)	6555(6)	83(5)
C(38)	3591(4)	4964(3)	3243(2)	50(1)	C(78B)	3341(10)	7744(8)	7294(6)	75(5)
C(39)	3395(5)	4232(3)	3655(2)	67(1)	C(79B)	2700(20)	6748(10)	4500(9)	70(6)
C(40)	2268(5)	4091(3)	4074(2)	70(1)					

Table A.53: Bond lengths [Å] for **10b**.

Zn(1)-C(79)	2.045(9)	C(25)-C(30)	1.388(5)	C(55)-C(60)	1.396(6)
Zn(1)-N(2)	2.034(3)	C(25)-C(26)	1.392(5)	C(55)-C(56)	1.402(5)
Zn(1)-N(1)	2.046(3)	C(26)-C(27)	1.386(6)	C(56)-C(57)	1.372(6)

Zn(1)-C(79B)	2.160(16)	C(26)-H(26)	0.9500	C(56)-H(56)	0.9500
B(1)-C(55)	1.632(7)	C(27)-C(28)	1.373(6)	C(57)-C(58)	1.394(6)
B(1)-C(61)	1.635(7)	C(27)-H(27)	0.9500	C(57)-H(57)	0.9500
B(1)-C(67)	1.642(6)	C(28)-C(29)	1.371(6)	C(58)-C(59)	1.372(6)
B(1)-C(73B)	1.686(9)	C(28)-H(28)	0.9500	C(58)-H(58)	0.9500
B(1)-C(73)	1.735(6)	C(29)-C(30)	1.384(5)	C(59)-C(60)	1.381(6)
P(1)-N(1)	1.609(3)	C(29)-H(29)	0.9500	C(59)-H(59)	0.9500
P(1)-C(19)	1.793(4)	C(30)-H(30)	0.9500	C(60)-H(60)	0.9500
P(1)-C(13)	1.804(4)	C(31)-C(32)	1.372(6)	C(61)-C(62)	1.381(6)
P(1)-C(2)	1.815(4)	C(31)-C(36)	1.400(6)	C(61)-C(66)	1.374(7)
O(1)-C(1)	1.376(4)	C(32)-C(33)	1.396(6)	C(62)-C(63)	1.380(6)
O(1)-C(12)	1.383(4)	C(32)-H(32)	0.9500	C(62)-H(62)	0.9500
N(1)-C(37)	1.451(5)	C(33)-C(34)	1.373(7)	C(63)-C(64)	1.356(8)
C(1)-C(2)	1.384(5)	C(33)-H(33)	0.9500	C(63)-H(63)	0.9500
C(1)-C(6)	1.398(5)	C(34)-C(35)	1.363(8)	C(64)-C(65)	1.370(11)
P(2)-N(2)	1.603(3)	C(34)-H(34)	0.9500	C(64)-H(64)	0.9500
P(2)-C(31)	1.787(4)	C(35)-C(36)	1.364(7)	C(65)-C(66)	1.378(11)
P(2)-C(25)	1.798(4)	C(35)-H(35)	0.9500	C(65)-H(65)	0.9500
P(2)-C(11)	1.798(4)	C(36)-H(36)	0.9500	C(66)-H(66)	0.9500
N(2)-C(46)	1.471(5)	C(37)-C(42)	1.398(5)	C(67)-C(68)	1.393(5)
C(2)-C(3)	1.402(5)	C(37)-C(38)	1.403(5)	C(67)-C(72)	1.402(5)
C(3)-C(4)	1.393(5)	C(38)-C(39)	1.375(6)	C(68)-C(69)	1.381(5)
C(3)-H(3)	0.9500	C(38)-C(43)	1.507(6)	C(68)-H(68)	0.9500
C(4)-C(5)	1.375(5)	C(39)-C(40)	1.379(7)	C(69)-C(70)	1.363(5)
C(4)-H(4)	0.9500	C(39)-H(39)	0.9500	C(69)-H(69)	0.9500
C(5)-C(6)	1.389(5)	C(40)-C(41)	1.400(6)	C(70)-C(71)	1.357(5)
C(5)-H(5)	0.9500	C(40)-C(44)	1.512(6)	C(70)-H(70)	0.9500
C(6)-C(7)	1.463(5)	C(41)-C(42)	1.396(6)	C(71)-C(72)	1.375(6)
C(7)-C(8)	1.388(5)	C(41)-H(41)	0.9500	C(71)-H(71)	0.9500
C(7)-C(12)	1.397(5)	C(42)-C(45)	1.503(6)	C(72)-H(72)	0.9500
C(8)-C(9)	1.380(5)	C(43)-H(43A)	0.9800	C(73)-C(74)	1.3900
C(8)-H(8)	0.9500	C(43)-H(43B)	0.9800	C(73)-C(78)	1.3900
C(9)-C(10)	1.386(5)	C(43)-H(43C)	0.9800	C(74)-C(75)	1.3900
C(9)-H(9)	0.9500	C(44)-H(44A)	0.9800	C(74)-H(74)	0.9500
C(10)-C(11)	1.411(5)	C(44)-H(44B)	0.9800	C(75)-C(76)	1.3900
C(10)-H(10)	0.9500	C(44)-H(44C)	0.9800	C(75)-H(75)	0.9500
C(11)-C(12)	1.380(5)	C(45)-H(45A)	0.9800	C(76)-C(77)	1.3900
C(13)-C(14)	1.394(5)	C(45)-H(45B)	0.9800	C(76)-H(76)	0.9500
C(13)-C(18)	1.396(5)	C(45)-H(45C)	0.9800	C(77)-C(78)	1.3900
C(14)-C(15)	1.384(6)	C(46)-C(47)	1.389(6)	C(77)-H(77)	0.9500
C(14)-H(14)	0.9500	C(46)-C(51)	1.394(6)	C(78)-H(78)	0.9500
C(15)-C(16)	1.371(6)	C(47)-C(48)	1.385(8)	C(79)-H(79A)	0.9800
C(15)-H(15)	0.9500	C(47)-C(52)	1.518(7)	C(79)-H(79B)	0.9800

C(16)-C(17)	1.387(6)	C(48)-C(49)	1.382(9)	C(79)-H(79C)	0.9800
C(16)-H(16)	0.9500	C(48)-H(48)	0.9500	C(73B)-C(74B)	1.3900
C(17)-C(18)	1.373(5)	C(49)-C(50)	1.357(8)	C(73B)-C(78B)	1.3900
C(17)-H(17)	0.9500	C(49)-C(53)	1.560(9)	C(74B)-C(75B)	1.3900
C(18)-H(18)	0.9500	C(50)-C(51)	1.384(7)	C(74B)-H(74B)	0.9500
C(19)-C(24)	1.388(6)	C(50)-H(50)	0.9500	C(75B)-C(76B)	1.3900
C(19)-C(20)	1.392(5)	C(51)-C(54)	1.502(6)	C(75B)-H(75B)	0.9500
C(20)-C(21)	1.382(5)	C(52)-H(52A)	0.9800	C(76B)-C(77B)	1.3900
C(20)-H(20)	0.9500	C(52)-H(52B)	0.9800	C(76B)-H(76B)	0.9500
C(21)-C(22)	1.354(7)	C(52)-H(52C)	0.9800	C(77B)-C(78B)	1.3900
C(21)-H(21)	0.9500	C(53)-H(53A)	0.9800	C(77B)-H(77B)	0.9500
C(22)-C(23)	1.390(7)	C(53)-H(53B)	0.9800	C(78B)-H(78B)	0.9500
C(22)-H(22)	0.9500	C(53)-H(53C)	0.9800	C(79B)-H(79D)	0.9802
C(23)-C(24)	1.394(6)	C(54)-H(54A)	0.9800	C(79B)-H(79E)	0.9802
C(23)-H(23)	0.9500	C(54)-H(54B)	0.9800	C(79B)-H(79F)	0.9802
C(24)-H(24)	0.9500	C(54)-H(54C)	0.9800		

Table A.54: Bond angles [°] for **10b**

C(79)-Zn(1)-N(2)	113.5(3)	C(19)-C(24)-H(24)	119.9	C(51)-C(54)-H(54B)	109.5
C(79)-Zn(1)-N(1)	114.3(2)	C(23)-C(24)-H(24)	119.9	H(54A)-C(54)-H(54B)	109.5
N(2)-Zn(1)-N(1)	131.75(12)	C(30)-C(25)-C(26)	119.3(4)	C(51)-C(54)-H(54C)	109.5
C(79)-Zn(1)-C(79B	37.6(6)	C(30)-C(25)-P(2)	120.1(3)	H(54A)-C(54)-H(54C)	109.5
N(2)-Zn(1)-C(79B)	119.7(5)	C(26)-C(25)-P(2)	120.6(3)	H(54B)-C(54)-H(54C)	109.5
N(1)-Zn(1)-C(79B)	102.3(4)	C(27)-C(26)-C(25)	120.0(4)	C(60)-C(55)-C(56)	114.5(4)
C(55)-B(1)-C(61)	109.8(3)	C(27)-C(26)-H(26)	120.0	C(60)-C(55)-B(1)	124.9(4)
C(55)-B(1)-C(67)	110.4(4)	C(25)-C(26)-H(26)	120.0	C(56)-C(55)-B(1)	120.6(4)
C(61)-B(1)-C(67)	107.7(4)	C(28)-C(27)-C(26)	120.1(4)	C(57)-C(56)-C(55)	122.7(4)
C(55)-B(1)-C(73B)	116.1(5)	C(28)-C(27)-H(27)	120.0	C(57)-C(56)-H(56)	118.6
C(61)-B(1)-C(73B)	96.3(5)	C(26)-C(27)-H(27)	120.0	C(55)-C(56)-H(56)	118.7
C(67)-B(1)-C(73B)	115.2(5)	C(29)-C(28)-C(27)	120.4(4)	C(56)-C(57)-C(58)	120.7(4)
C(55)-B(1)-C(73)	104.1(4)	C(29)-C(28)-H(28)	119.8	C(56)-C(57)-H(57)	119.6
C(61)-B(1)-C(73)	119.8(4)	C(27)-C(28)-H(28)	119.8	C(58)-C(57)-H(57)	119.6
C(67)-B(1)-C(73)	104.7(3)	C(28)-C(29)-C(30)	120.3(4)	C(59)-C(58)-C(57)	118.4(5)
C(73B)-B(1)-C(73)	23.5(4)	C(28)-C(29)-H(29)	119.9	C(59)-C(58)-H(58)	120.8
N(1)-P(1)-C(19)	112.68(17)	C(30)-C(29)-H(29)	119.9	C(57)-C(58)-H(58)	120.8
N(1)-P(1)-C(13)	109.27(17)	C(29)-C(30)-C(25)	120.0(4)	C(60)-C(59)-C(58)	120.0(5)
C(19)-P(1)-C(13)	109.48(18)	C(29)-C(30)-H(30)	120.0	C(60)-C(59)-H(59)	120.0
N(1)-P(1)-C(2)	117.39(16)	C(25)-C(30)-H(30)	120.0	C(58)-C(59)-H(59)	120.0
C(19)-P(1)-C(2)	103.66(17)	C(32)-C(31)-C(36)	118.3(4)	C(59)-C(60)-C(55)	123.7(4)
C(13)-P(1)-C(2)	103.80(17)	C(32)-C(31)-P(2)	121.8(3)	C(59)-C(60)-H(60)	118.2
C(1)-O(1)-C(12)	105.6(3)	C(36)-C(31)-P(2)	119.6(4)	C(55)-C(60)-H(60)	118.1
C(37)-N(1)-P(1)	118.7(2)	C(31)-C(32)-C(33)	120.9(5)	C(62)-C(61)-C(66)	112.1(5)
C(37)-N(1)-Zn(1)	110.2(2)	C(31)-C(32)-H(32)	119.6	C(62)-C(61)-B(1)	122.6(4)

P(1)-N(1)-Zn(1)	130.96(18)	C(33)-C(32)-H(32)	119.6	C(66)-C(61)-B(1)	124.8(5)
O(1)-C(1)-C(2)	123.5(3)	C(34)-C(33)-C(32)	119.0(5)	C(63)-C(62)-C(61)	125.1(5)
O(1)-C(1)-C(6)	112.0(3)	C(34)-C(33)-H(33)	120.5	C(63)-C(62)-H(62)	117.5
C(2)-C(1)-C(6)	124.5(3)	C(32)-C(33)-H(33)	120.5	C(61)-C(62)-H(62)	117.5
N(2)-P(2)-C(31)	108.30(18)	C(33)-C(34)-C(35)	120.9(5)	C(64)-C(63)-C(62)	119.9(6)
N(2)-P(2)-C(25)	114.59(18)	C(33)-C(34)-H(34)	119.5	C(64)-C(63)-H(63)	120.0
C(31)-P(2)-C(25)	107.67(18)	C(35)-C(34)-H(34)	119.6	C(62)-C(63)-H(63)	120.0
N(2)-P(2)-C(11)	115.78(16)	C(36)-C(35)-C(34)	120.1(5)	C(63)-C(64)-C(65)	118.0(7)
C(31)-P(2)-C(11)	105.36(19)	C(36)-C(35)-H(35)	120.0	C(63)-C(64)-H(64)	121.0
C(25)-P(2)-C(11)	104.50(17)	C(34)-C(35)-H(35)	119.9	C(65)-C(64)-H(64)	121.0
C(46)-N(2)-P(2)	118.4(3)	C(35)-C(36)-C(31)	120.9(5)	C(66)-C(65)-C(64)	119.9(7)
C(46)-N(2)-Zn(1)	114.5(2)	C(35)-C(36)-H(36)	119.6	C(66)-C(65)-H(65)	120.0
P(2)-N(2)-Zn(1)	127.1(2)	C(31)-C(36)-H(36)	119.6	C(64)-C(65)-H(65)	120.0
C(1)-C(2)-C(3)	115.0(3)	C(42)-C(37)-C(38)	120.4(4)	C(65)-C(66)-C(61)	125.0(7)
C(1)-C(2)-P(1)	121.3(3)	C(42)-C(37)-N(1)	120.1(4)	C(65)-C(66)-H(66)	117.5
C(3)-C(2)-P(1)	122.8(3)	C(38)-C(37)-N(1)	119.5(3)	C(61)-C(66)-H(66)	117.5
C(4)-C(3)-C(2)	121.5(4)	C(39)-C(38)-C(37)	119.4(4)	C(68)-C(67)-C(72)	113.6(4)
C(4)-C(3)-H(3)	119.2	C(39)-C(38)-C(43)	119.5(4)	C(68)-C(67)-B(1)	122.3(4)
C(2)-C(3)-H(3)	119.3	C(37)-C(38)-C(43)	121.0(4)	C(72)-C(67)-B(1)	124.1(4)
C(5)-C(4)-C(3)	121.7(3)	C(38)-C(39)-C(40)	122.5(5)	C(69)-C(68)-C(67)	123.4(4)
C(5)-C(4)-H(4)	119.1	C(38)-C(39)-H(39)	118.7	C(69)-C(68)-H(68)	118.3
C(3)-C(4)-H(4)	119.1	C(40)-C(39)-H(39)	118.8	C(67)-C(68)-H(68)	118.3
C(4)-C(5)-C(6)	118.6(4)	C(39)-C(40)-C(41)	117.2(4)	C(70)-C(69)-C(68)	120.3(4)
C(4)-C(5)-H(5)	120.7	C(39)-C(40)-C(44)	120.7(5)	C(70)-C(69)-H(69)	119.8
C(6)-C(5)-H(5)	120.7	C(41)-C(40)-C(44)	122.1(5)	C(68)-C(69)-H(69)	119.8
C(5)-C(6)-C(1)	118.6(3)	C(42)-C(41)-C(40)	122.7(4)	C(71)-C(70)-C(69)	118.7(4)
C(5)-C(6)-C(7)	136.1(3)	C(42)-C(41)-H(41)	118.6	C(71)-C(70)-H(70)	120.7
C(1)-C(6)-C(7)	105.3(3)	C(40)-C(41)-H(41)	118.6	C(69)-C(70)-H(70)	120.7
C(8)-C(7)-C(12)	118.4(3)	C(41)-C(42)-C(37)	117.8(4)	C(70)-C(71)-C(72)	121.0(4)
C(8)-C(7)-C(6)	136.4(4)	C(41)-C(42)-C(45)	119.7(4)	C(70)-C(71)-H(71)	119.5
C(12)-C(7)-C(6)	105.2(3)	C(37)-C(42)-C(45)	122.5(4)	C(72)-C(71)-H(71)	119.5
C(9)-C(8)-C(7)	118.0(4)	C(38)-C(43)-H(43A)	109.5	C(71)-C(72)-C(67)	122.9(4)
C(9)-C(8)-H(8)	121.0	C(38)-C(43)-H(43B)	109.5	C(71)-C(72)-H(72)	118.5
C(7)-C(8)-H(8)	121.0	H(43A)-C(43)-H(43E	109.5	C(67)-C(72)-H(72)	118.5
C(10)-C(9)-C(8)	122.3(4)	C(38)-C(43)-H(43C)	109.5	C(74)-C(73)-C(78)	120.0
C(10)-C(9)-H(9)	118.9	H(43A)-C(43)-H(43C	109.5	C(74)-C(73)-B(1)	116.1(4)
C(8)-C(9)-H(9)	118.9	H(43B)-C(43)-H(43C	109.5	C(78)-C(73)-B(1)	123.8(4)
C(9)-C(10)-C(11)	121.7(4)	C(40)-C(44)-H(44A)	109.5	C(73)-C(74)-C(75)	120.0
C(9)-C(10)-H(10)	119.2	C(40)-C(44)-H(44B)	109.5	C(73)-C(74)-H(74)	120.0
C(11)-C(10)-H(10)	119.2	H(44A)-C(44)-H(44E	109.5	C(75)-C(74)-H(74)	120.0
C(12)-C(11)-C(10)	113.9(3)	C(40)-C(44)-H(44C)	109.5	C(76)-C(75)-C(74)	120.0
C(12)-C(11)-P(2)	120.2(3)	H(44A)-C(44)-H(44C	109.5	C(76)-C(75)-H(75)	120.0
C(10)-C(11)-P(2)	125.8(3)	H(44B)-C(44)-H(44C	109.5	C(74)-C(75)-H(75)	120.0

O(1)-C(12)-C(11)	122.5(3)	C(42)-C(45)-H(45A)	109.5	C(77)-C(76)-C(75)	120.0
O(1)-C(12)-C(7)	111.8(3)	C(42)-C(45)-H(45B)	109.5	C(77)-C(76)-H(76)	120.0
C(11)-C(12)-C(7)	125.7(3)	H(45A)-C(45)-H(45E	109.5	C(75)-C(76)-H(76)	120.0
C(14)-C(13)-C(18)	118.6(4)	C(42)-C(45)-H(45C)	109.5	C(76)-C(77)-C(78)	120.0
C(14)-C(13)-P(1)	119.7(3)	H(45A)-C(45)-H(45C	109.5	C(76)-C(77)-H(77)	120.0
C(18)-C(13)-P(1)	121.7(3)	H(45B)-C(45)-H(45C	109.5	C(78)-C(77)-H(77)	120.0
C(15)-C(14)-C(13)	120.0(4)	C(47)-C(46)-C(51)	120.9(5)	C(77)-C(78)-C(73)	120.0
C(15)-C(14)-H(14)	120.0	C(47)-C(46)-N(2)	119.5(4)	C(77)-C(78)-H(78)	120.0
C(13)-C(14)-H(14)	120.0	C(51)-C(46)-N(2)	119.6(4)	C(73)-C(78)-H(78)	120.0
C(16)-C(15)-C(14)	120.8(4)	C(48)-C(47)-C(46)	117.7(5)	Zn(1)-C(79)-H(79A)	109.5
C(16)-C(15)-H(15)	119.6	C(48)-C(47)-C(52)	119.2(5)	Zn(1)-C(79)-H(79B)	109.5
C(14)-C(15)-H(15)	119.6	C(46)-C(47)-C(52)	123.1(5)	Zn(1)-C(79)-H(79C)	109.4
C(15)-C(16)-C(17)	119.8(4)	C(49)-C(48)-C(47)	122.7(6)	C(74B)-C(73B)-C(78B)	120.0
C(15)-C(16)-H(16)	120.1	C(49)-C(48)-H(48)	118.6	C(74B)-C(73B)-B(1)	131.0(7)
C(17)-C(16)-H(16)	120.1	C(47)-C(48)-H(48)	118.7	C(78B)-C(73B)-B(1)	108.6(7)
C(18)-C(17)-C(16)	120.0(4)	C(50)-C(49)-C(48)	117.7(6)	C(73B)-C(74B)-C(75B)	120.0
C(18)-C(17)-H(17)	120.0	C(50)-C(49)-C(53)	119.8(7)	C(73B)-C(74B)-H(74B)	120.0
C(16)-C(17)-H(17)	120.0	C(48)-C(49)-C(53)	122.5(6)	C(75B)-C(74B)-H(74B)	120.0
C(17)-C(18)-C(13)	120.9(4)	C(49)-C(50)-C(51)	122.8(6)	C(74B)-C(75B)-C(76B)	120.0
C(17)-C(18)-H(18)	119.6	C(49)-C(50)-H(50)	118.6	C(74B)-C(75B)-H(75B)	120.0
C(13)-C(18)-H(18)	119.6	C(51)-C(50)-H(50)	118.6	C(76B)-C(75B)-H(75B)	120.0
C(24)-C(19)-C(20)	119.3(4)	C(50)-C(51)-C(46)	118.2(4)	C(77B)-C(76B)-C(75B)	120.0
C(24)-C(19)-P(1)	119.5(3)	C(50)-C(51)-C(54)	118.5(4)	C(77B)-C(76B)-H(76B)	120.0
C(20)-C(19)-P(1)	121.2(3)	C(46)-C(51)-C(54)	123.3(4)	C(75B)-C(76B)-H(76B)	120.0
C(19)-C(20)-C(21)	120.1(4)	C(47)-C(52)-H(52A)	109.5	C(76B)-C(77B)-C(78B)	120.0
C(19)-C(20)-H(20)	119.9	C(47)-C(52)-H(52B)	109.5	C(76B)-C(77B)-H(77B)	120.0
C(21)-C(20)-H(20)	119.9	H(52A)-C(52)-H(52E	109.5	C(78B)-C(77B)-H(77B)	120.0
C(22)-C(21)-C(20)	120.3(5)	C(47)-C(52)-H(52C)	109.5	C(77B)-C(78B)-C(73B)	120.0
C(22)-C(21)-H(21)	119.9	H(52A)-C(52)-H(52C	109.5	C(77B)-C(78B)-H(78B)	120.0
C(20)-C(21)-H(21)	119.9	H(52B)-C(52)-H(52C	109.5	C(73B)-C(78B)-H(78B)	120.0
C(21)-C(22)-C(23)	121.2(5)	C(49)-C(53)-H(53A)	109.5	Zn(1)-C(79B)-H(79D)	109.6
C(21)-C(22)-H(22)	119.4	C(49)-C(53)-H(53B)	109.5	Zn(1)-C(79B)-H(79E)	109.6
C(23)-C(22)-H(22)	119.4	H(53A)-C(53)-H(53E	109.5	H(79D)-C(79B)-H(79E	109.5
C(22)-C(23)-C(24)	118.8(5)	C(49)-C(53)-H(53C)	109.4	Zn(1)-C(79B)-H(79F)	109.3
C(22)-C(23)-H(23)	120.6	H(53A)-C(53)-H(53C	109.5	H(79D)-C(79B)-H(79F)	109.5
C(24)-C(23)-H(23)	120.6	H(53B)-C(53)-H(53C	109.5	H(79E)-C(79B)-H(79F)	109.5
C(19)-C(24)-C(23)	120.2(5)	C(51)-C(54)-H(54A)	109.5		

Table A.55: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **10b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	52(1)	124(1)	34(1)	-19(1)	1(1)	-49(1)
B(1)	87(4)	36(3)	39(3)	1(2)	-8(2)	-4(2)

P(1)	28(1)	47(1)	31(1)	-4(1)	-8(1)	-5(1)
O(1)	28(1)	57(2)	24(1)	-1(1)	-5(1)	-10(1)
N(1)	28(2)	52(2)	32(2)	-1(1)	-6(1)	-7(2)
C(1)	30(2)	37(2)	28(2)	-1(2)	-6(2)	3(2)
P(2)	33(1)	59(1)	32(1)	6(1)	-11(1)	-14(1)
N(2)	30(2)	69(2)	33(2)	-3(2)	-8(1)	-13(2)
C(2)	34(2)	41(2)	27(2)	2(2)	-9(2)	-1(2)
C(3)	41(2)	38(2)	37(2)	-7(2)	-11(2)	4(2)
C(4)	52(3)	43(2)	29(2)	-10(2)	-11(2)	6(2)
C(5)	42(2)	41(2)	32(2)	-1(2)	-2(2)	5(2)
C(6)	31(2)	38(2)	32(2)	3(2)	-2(2)	5(2)
C(7)	27(2)	35(2)	36(2)	7(2)	-6(2)	5(2)
C(8)	34(2)	45(2)	36(2)	5(2)	0(2)	-1(2)
C(9)	27(2)	54(3)	48(2)	8(2)	2(2)	-6(2)
C(10)	29(2)	51(3)	44(2)	10(2)	-11(2)	-8(2)
C(11)	30(2)	48(2)	36(2)	7(2)	-7(2)	-6(2)
C(12)	23(2)	43(2)	36(2)	7(2)	-7(2)	-4(2)
C(13)	25(2)	45(2)	43(2)	-3(2)	-13(2)	-6(2)
C(14)	45(3)	50(3)	48(3)	-5(2)	-3(2)	-10(2)
C(15)	55(3)	51(3)	72(3)	-12(2)	1(3)	-1(2)
C(16)	47(3)	44(3)	82(3)	-1(2)	-13(2)	-1(2)
C(17)	49(3)	46(3)	60(3)	5(2)	-22(2)	-8(2)
C(18)	44(2)	48(3)	46(2)	-6(2)	-17(2)	-6(2)
C(19)	43(2)	49(2)	32(2)	-5(2)	-5(2)	-11(2)
C(20)	42(2)	66(3)	39(2)	-7(2)	-13(2)	-17(2)
C(21)	60(3)	98(4)	44(3)	-10(3)	-11(2)	-35(3)
C(22)	91(4)	92(4)	48(3)	-9(3)	-10(3)	-57(3)
C(23)	110(4)	57(3)	56(3)	-6(2)	-8(3)	-29(3)
C(24)	74(3)	58(3)	45(3)	-6(2)	-12(2)	-18(2)
C(25)	34(2)	59(3)	36(2)	6(2)	-11(2)	-20(2)
C(26)	49(3)	78(3)	39(2)	9(2)	-17(2)	-24(2)
C(27)	60(3)	94(4)	46(3)	3(3)	-23(2)	-29(3)
C(28)	61(3)	77(3)	53(3)	-20(3)	-10(2)	-19(3)
C(29)	65(3)	51(3)	59(3)	-13(2)	-7(2)	-8(2)
C(30)	44(3)	58(3)	47(3)	-6(2)	-12(2)	-7(2)
C(31)	38(2)	60(3)	44(2)	11(2)	-17(2)	-20(2)
C(32)	42(3)	73(3)	74(3)	33(3)	-14(2)	-9(2)
C(33)	59(3)	78(4)	110(4)	45(3)	-28(3)	-19(3)
C(34)	101(5)	80(4)	94(4)	54(3)	-48(4)	-38(3)
C(35)	121(5)	90(4)	67(4)	30(3)	-28(3)	-51(3)
C(36)	85(3)	70(3)	43(3)	11(2)	-17(2)	-40(3)
C(37)	37(2)	62(3)	28(2)	2(2)	-7(2)	-9(2)
C(38)	57(3)	63(3)	27(2)	0(2)	-12(2)	3(2)

C(39)	89(3)	66(3)	37(3)	0(2)	-6(2)	9(3)
C(40)	102(4)	56(3)	44(3)	-2(2)	-3(3)	-11(3)
C(41)	71(3)	76(3)	36(3)	-3(2)	11(2)	-25(3)
C(42)	41(2)	62(3)	37(2)	-5(2)	-3(2)	-15(2)
C(43)	47(3)	82(3)	51(3)	2(2)	-12(2)	11(2)
C(44)	171(6)	69(4)	63(4)	10(3)	16(4)	-21(4)
C(45)	31(2)	88(3)	43(3)	-7(2)	1(2)	-19(2)
C(46)	34(2)	76(3)	46(2)	-12(2)	-7(2)	0(2)
C(47)	59(3)	112(4)	53(3)	-27(3)	-14(3)	20(3)
C(48)	169(7)	135(5)	95(4)	-72(4)	-59(5)	87(5)
C(49)	254(9)	123(5)	120(6)	-65(4)	-107(6)	117(6)
C(50)	158(6)	87(4)	94(4)	-34(3)	-70(4)	60(4)
C(51)	48(3)	69(3)	54(3)	-9(2)	-17(2)	6(2)
C(52)	59(3)	129(5)	50(3)	-29(3)	-13(2)	-8(3)
C(53)	530(20)	146(6)	214(10)	-122(6)	-229(12)	211(11)
C(54)	40(2)	61(3)	44(2)	6(2)	-19(2)	-13(2)
C(55)	55(3)	38(2)	40(2)	1(2)	4(2)	-2(2)
C(56)	45(3)	40(2)	60(3)	10(2)	-2(2)	-10(2)
C(57)	46(3)	46(3)	83(4)	6(2)	-4(2)	-10(2)
C(58)	62(3)	66(3)	77(4)	4(3)	-14(3)	-26(3)
C(59)	69(3)	77(3)	70(3)	16(3)	-26(3)	-14(3)
C(60)	82(4)	45(3)	57(3)	7(2)	-19(3)	-3(2)
C(61)	91(3)	35(2)	73(3)	3(2)	-54(3)	-3(2)
C(62)	46(3)	67(3)	55(3)	18(2)	-14(2)	-17(2)
C(63)	56(3)	74(4)	93(4)	36(3)	-14(3)	-11(3)
C(64)	83(4)	69(4)	251(9)	38(4)	-93(5)	-4(3)
C(65)	176(7)	97(6)	351(12)	-61(6)	-212(8)	38(5)
C(66)	204(6)	94(5)	254(8)	-87(5)	-194(7)	77(5)
C(67)	55(3)	34(2)	37(2)	-3(2)	-2(2)	-4(2)
C(68)	39(2)	41(2)	43(2)	-7(2)	-6(2)	-6(2)
C(69)	37(2)	52(3)	35(2)	5(2)	-6(2)	-13(2)
C(70)	41(2)	40(2)	53(3)	8(2)	-17(2)	-8(2)
C(71)	55(3)	35(2)	70(3)	-3(2)	10(2)	4(2)
C(72)	80(3)	41(3)	62(3)	0(2)	27(3)	-3(2)
C(73)	124(7)	35(4)	36(3)	13(3)	-24(4)	2(4)
C(74)	163(7)	52(4)	38(4)	-6(3)	-11(4)	-13(4)
C(75)	224(10)	49(5)	50(4)	-15(4)	-19(5)	11(5)
C(76)	195(10)	70(6)	36(4)	4(4)	7(5)	39(6)
C(77)	191(9)	51(6)	75(5)	-2(4)	44(6)	5(5)
C(78)	139(7)	46(5)	51(4)	11(4)	12(4)	-5(4)
C(79)	124(9)	345(17)	49(5)	-57(7)	4(4)	-169(11)
C(73B)	83(8)	21(7)	51(5)	10(5)	-19(5)	-14(7)
C(74B)	103(9)	95(11)	46(6)	2(8)	-22(6)	-45(10)

C(75B)	124(10)	139(15)	47(7)	-6(10)	-13(8)	-84(12)
C(76B)	117(11)	66(10)	47(8)	15(8)	-9(7)	-43(10)
C(77B)	129(10)	65(11)	42(7)	-14(9)	-8(7)	15(10)
C(78B)	92(8)	77(12)	47(7)	-11(9)	7(6)	-15(10)
C(79B)	129(17)	56(10)	51(6)	9(7)	-59(9)	-40(10)

Table A.56: Crystal data and structure refinement for **11**.

Empirical formula	$C_{84}H_{73}BN_2OP_2Zn \cdot C_6H_5Br$	
Formula weight	1421.57	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.7836(9) Å	α= 90°.
	b = 21.8185(11) Å	β= 100.5040(10)°.
	c = 19.8868(10) Å	γ = 90°.
Volume	7587.0(7) $Å^3$	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.941 mm^{-1}	
F(000)	2960	
Crystal size	0.56 x 0.52 x 0.39 mm^3	
Theta range for data collection	2.08 to 25.03°.	
Index ranges	-21<=h<=21, -25<=k<=25, -23<=l<=23	
Reflections collected	90924	
Independent reflections	13399 [R(int) = 0.0398]	
Completeness to theta = 25.03°	100%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6530	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13399 / 0 / 877	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1337	
R indices (all data)	R1 = 0.0634, wR2 = 0.1410	
Largest diff. peak and hole	1.017 and -0.767 $e.Å^{-3}$	

Table A.57: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **11**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	7521(1)	6803(1)	5673(1)	38(1)	C(43)	10560(2)	6033(2)	8570(2)	56(1)
P(1)	5687(1)	7102(1)	5495(1)	25(1)	C(44)	10286(2)	5569(2)	8135(2)	53(1)
O(1)	6544(1)	6607(1)	6861(1)	29(1)	C(45)	9582(2)	5627(2)	7700(2)	44(1)
N(1)	6389(1)	6706(1)	5333(1)	28(1)	C(46)	8695(2)	7292(1)	6717(2)	34(1)
C(1)	5769(2)	6699(1)	6820(1)	28(1)	C(47)	9415(2)	7255(2)	6526(2)	40(1)
B(1)	2749(2)	5946(2)	274(2)	29(1)	C(48)	9876(2)	7768(2)	6595(2)	53(1)
P(2)	8231(1)	6244(1)	7180(1)	31(1)	C(49)	9651(2)	8313(2)	6844(2)	61(1)
N(2)	8179(1)	6766(1)	6610(1)	31(1)	C(50)	8942(2)	8341(2)	7033(2)	53(1)

C(2)	5286(2)	6867(1)	6223(1)	28(1)	C(51)	8452(2)	7833(1)	6978(2)	39(1)
C(3)	4519(2)	6936(1)	6279(2)	33(1)	C(52)	9706(2)	6680(2)	6247(2)	49(1)
C(4)	4279(2)	6853(1)	6902(2)	37(1)	C(53)	10163(3)	8873(2)	6893(4)	103(2)
C(5)	4785(2)	6705(1)	7490(2)	36(1)	C(54)	7707(2)	7885(2)	7224(2)	44(1)
C(6)	5553(2)	6625(1)	7454(1)	30(1)	C(55)	8132(2)	6914(2)	4965(2)	60(1)
C(7)	6253(2)	6481(1)	7928(1)	31(1)	C(56)	8498(3)	7426(2)	4917(2)	69(1)
C(8)	6460(2)	6354(1)	8624(2)	40(1)	C(57)	9004(3)	7512(3)	4447(3)	84(2)
C(9)	7217(2)	6229(1)	8890(2)	44(1)	C(58)	9099(3)	7027(3)	4012(3)	96(2)
C(10)	7771(2)	6210(1)	8475(2)	39(1)	C(59)	8707(3)	6472(3)	4032(3)	89(2)
C(11)	7585(2)	6329(1)	7778(1)	32(1)	C(60)	8222(3)	6423(2)	4521(2)	73(1)
C(12)	6825(2)	6471(1)	7535(1)	30(1)	C(61)	3268(2)	5921(1)	1048(1)	29(1)
C(13)	4895(2)	7113(1)	4793(1)	29(1)	C(62)	3573(2)	6431(1)	1426(2)	34(1)
C(14)	4573(2)	6557(1)	4546(2)	38(1)	C(63)	4047(2)	6386(2)	2061(2)	39(1)
C(15)	4016(2)	6543(2)	3964(2)	49(1)	C(64)	4239(2)	5817(2)	2346(2)	40(1)
C(16)	3760(2)	7080(2)	3644(2)	52(1)	C(65)	3954(2)	5303(2)	1992(2)	42(1)
C(17)	4050(2)	7632(2)	3897(2)	46(1)	C(66)	3478(2)	5353(1)	1357(2)	38(1)
C(18)	4632(2)	7652(1)	4464(2)	35(1)	C(67)	3309(2)	5839(1)	-289(1)	28(1)
C(19)	5994(2)	7873(1)	5715(1)	28(1)	C(68)	4081(2)	5684(1)	-117(2)	33(1)
C(20)	6623(2)	8118(1)	5476(2)	37(1)	C(69)	4540(2)	5580(1)	-606(2)	40(1)
C(21)	6845(2)	8716(2)	5639(2)	45(1)	C(70)	4235(2)	5622(1)	-1293(2)	42(1)
C(22)	6436(2)	9078(1)	6016(2)	44(1)	C(71)	3468(2)	5782(1)	-1484(2)	40(1)
C(23)	5808(2)	8840(1)	6239(2)	44(1)	C(72)	3027(2)	5892(1)	-993(2)	35(1)
C(24)	5592(2)	8240(1)	6099(2)	36(1)	C(73)	2093(2)	5409(1)	207(1)	30(1)
C(25)	6266(2)	6237(1)	4807(1)	29(1)	C(74)	1932(2)	4984(1)	-326(2)	35(1)
C(26)	6278(2)	6389(1)	4122(2)	32(1)	C(75)	1350(2)	4550(2)	-371(2)	45(1)
C(27)	6173(2)	5921(2)	3639(2)	41(1)	C(76)	890(2)	4532(2)	118(2)	50(1)
C(28)	6055(2)	5317(2)	3808(2)	46(1)	C(77)	1032(2)	4936(2)	656(2)	48(1)
C(29)	6041(2)	5181(1)	4480(2)	43(1)	C(78)	1624(2)	5357(2)	705(2)	40(1)
C(30)	6140(2)	5628(1)	4991(2)	34(1)	C(79)	2335(2)	6624(1)	129(1)	31(1)
C(31)	6064(2)	5459(1)	5706(2)	42(1)	C(80)	1569(2)	6755(2)	137(2)	38(1)
C(32)	6383(2)	7031(1)	3893(2)	39(1)	C(81)	1260(2)	7344(2)	14(2)	51(1)
C(33)	5923(3)	4820(2)	3260(2)	69(1)	C(82)	1710(2)	7823(2)	-122(2)	52(1)
C(34)	7981(2)	5517(1)	6770(2)	34(1)	C(83)	2471(2)	7713(2)	-131(2)	50(1)
C(35)	7696(2)	5049(1)	7132(2)	39(1)	C(84)	2770(2)	7130(1)	-11(2)	40(1)
C(36)	7559(2)	4478(2)	6836(2)	51(1)	C(1S)	1799(2)	8254(1)	2595(1)	68(1)
C(37)	7698(2)	4377(2)	6184(2)	64(1)	C(2S)	1701(2)	7740(1)	2982(1)	75(1)
C(38)	7986(2)	4836(2)	5826(2)	64(1)	C(3S)	1817(2)	7158(1)	2736(1)	65(1)
C(39)	8131(2)	5410(2)	6123(2)	48(1)	C(4S)	2033(1)	7090(1)	2103(1)	55(1)
C(40)	9159(2)	6157(1)	7705(2)	37(1)	C(5S)	2132(1)	7604(1)	1715(1)	51(1)
C(41)	9451(2)	6632(2)	8135(2)	48(1)	C(6S)	2015(1)	8186(1)	1961(1)	56(1)
C(42)	10154(2)	6562(2)	8565(2)	55(1)	Br(1)	2134(1)	8878(1)	1447(1)	85(1)

Table A.58: Bond lengths [Å] for **11**.

Zn(1)-C(55)	1.943(4)	C(26)-C(32)	1.497(4)	C(57)-C(58)	1.398(8)
Zn(1)-N(2)	2.012(2)	C(27)-C(28)	1.386(5)	C(57)-H(57)	0.9500
Zn(1)-N(1)	2.016(2)	C(27)-H(27)	0.9500	C(58)-C(59)	1.402(8)
P(1)-N(1)	1.598(2)	C(28)-C(29)	1.373(5)	C(58)-H(58)	0.9500
P(1)-C(13)	1.795(3)	C(28)-C(33)	1.525(4)	C(59)-C(60)	1.415(6)
P(1)-C(19)	1.798(3)	C(29)-C(30)	1.395(4)	C(59)-H(59)	0.9500
P(1)-C(2)	1.801(3)	C(29)-H(29)	0.9500	C(60)-H(60)	0.9500
O(1)-C(12)	1.374(3)	C(30)-C(31)	1.498(4)	C(61)-C(62)	1.396(4)
O(1)-C(1)	1.380(3)	C(31)-H(31A)	0.9800	C(61)-C(66)	1.402(4)
N(1)-C(25)	1.451(3)	C(31)-H(31B)	0.9800	C(62)-C(63)	1.388(4)
C(1)-C(2)	1.382(4)	C(31)-H(31C)	0.9800	C(62)-H(62)	0.9500
C(1)-C(6)	1.393(4)	C(32)-H(32A)	0.9800	C(63)-C(64)	1.381(5)
B(1)-C(73)	1.642(4)	C(32)-H(32B)	0.9800	C(63)-H(63)	0.9500
B(1)-C(67)	1.645(4)	C(32)-H(32C)	0.9800	C(64)-C(65)	1.372(5)
B(1)-C(61)	1.646(4)	C(33)-H(33A)	0.9800	C(64)-H(64)	0.9500
B(1)-C(79)	1.655(4)	C(33)-H(33B)	0.9800	C(65)-C(66)	1.390(4)
P(2)-N(2)	1.599(2)	C(33)-H(33C)	0.9800	C(65)-H(65)	0.9500
P(2)-C(40)	1.795(3)	C(34)-C(39)	1.381(5)	C(66)-H(66)	0.9500
P(2)-C(34)	1.801(3)	C(34)-C(35)	1.395(4)	C(67)-C(68)	1.395(4)
P(2)-C(11)	1.807(3)	C(35)-C(36)	1.381(4)	C(67)-C(72)	1.402(4)
N(2)-C(46)	1.460(4)	C(35)-H(35)	0.9500	C(68)-C(69)	1.396(4)
C(2)-C(3)	1.397(4)	C(36)-C(37)	1.381(6)	C(68)-H(68)	0.9500
C(3)-C(4)	1.393(4)	C(36)-H(36)	0.9500	C(69)-C(70)	1.379(5)
C(3)-H(3)	0.9500	C(37)-C(38)	1.381(6)	C(69)-H(69)	0.9500
C(4)-C(5)	1.378(4)	C(37)-H(37)	0.9500	C(70)-C(71)	1.392(5)
C(4)-H(4)	0.9500	C(38)-C(39)	1.388(5)	C(70)-H(70)	0.9500
C(5)-C(6)	1.391(4)	C(38)-H(38)	0.9500	C(71)-C(72)	1.381(4)
C(5)-H(5)	0.9500	C(39)-H(39)	0.9500	C(71)-H(71)	0.9500
C(6)-C(7)	1.452(4)	C(40)-C(45)	1.381(4)	C(72)-H(72)	0.9500
C(7)-C(12)	1.391(4)	C(40)-C(41)	1.382(5)	C(73)-C(74)	1.396(4)
C(7)-C(8)	1.394(4)	C(41)-C(42)	1.388(5)	C(73)-C(78)	1.410(4)
C(8)-C(9)	1.380(5)	C(41)-H(41)	0.9500	C(74)-C(75)	1.394(4)
C(8)-H(8)	0.9500	C(42)-C(43)	1.362(5)	C(74)-H(74)	0.9500
C(9)-C(10)	1.396(5)	C(42)-H(42)	0.9500	C(75)-C(76)	1.381(5)
C(9)-H(9)	0.9500	C(43)-C(44)	1.363(6)	C(75)-H(75)	0.9500
C(10)-C(11)	1.390(4)	C(43)-H(43)	0.9500	C(76)-C(77)	1.374(5)
C(10)-H(10)	0.9500	C(44)-C(45)	1.391(5)	C(76)-H(76)	0.9500
C(11)-C(12)	1.384(4)	C(44)-H(44)	0.9500	C(77)-C(78)	1.387(5)
C(13)-C(18)	1.386(4)	C(45)-H(45)	0.9500	C(77)-H(77)	0.9500
C(13)-C(14)	1.390(4)	C(46)-C(51)	1.390(4)	C(78)-H(78)	0.9500
C(14)-C(15)	1.380(4)	C(46)-C(47)	1.403(4)	C(79)-C(80)	1.395(4)
C(14)-H(14)	0.9500	C(47)-C(48)	1.379(5)	C(79)-C(84)	1.404(4)

C(15)-C(16)	1.371(5)	C(47)-C(52)	1.501(5)	C(80)-C(81)	1.403(5)
C(15)-H(15)	0.9500	C(48)-C(49)	1.375(6)	C(80)-H(80)	0.9500
C(16)-C(17)	1.369(5)	C(48)-H(48)	0.9500	C(81)-C(82)	1.371(5)
C(16)-H(16)	0.9500	C(49)-C(50)	1.382(6)	C(81)-H(81)	0.9500
C(17)-C(18)	1.386(5)	C(49)-C(53)	1.517(5)	C(82)-C(83)	1.377(5)
C(17)-H(17)	0.9500	C(50)-C(51)	1.400(5)	C(82)-H(82)	0.9500
C(18)-H(18)	0.9500	C(50)-H(50)	0.9500	C(83)-C(84)	1.383(4)
C(19)-C(24)	1.391(4)	C(51)-C(54)	1.499(5)	C(83)-H(83)	0.9500
C(19)-C(20)	1.398(4)	C(52)-H(52A)	0.9800	C(84)-H(84)	0.9500
C(20)-C(21)	1.383(4)	C(52)-H(52B)	0.9800	C(1S)-C(2S)	1.3900
C(20)-H(20)	0.9500	C(52)-H(52C)	0.9800	C(1S)-C(6S)	1.3900
C(21)-C(22)	1.384(5)	C(53)-H(53A)	0.9800	C(1S)-H(1S)	0.9500
C(21)-H(21)	0.9500	C(53)-H(53B)	0.9800	C(2S)-C(3S)	1.3900
C(22)-C(23)	1.376(5)	C(53)-H(53C)	0.9800	C(2S)-H(2S)	0.9500
C(22)-H(22)	0.9500	C(54)-H(54A)	0.9800	C(3S)-C(4S)	1.3900
C(23)-C(24)	1.378(4)	C(54)-H(54B)	0.9800	C(3S)-H(3S)	0.9500
C(23)-H(23)	0.9500	C(54)-H(54C)	0.9800	C(4S)-C(5S)	1.3900
C(24)-H(24)	0.9500	C(55)-C(56)	1.306(6)	C(4S)-H(4S)	0.9500
C(25)-C(26)	1.405(4)	C(55)-C(60)	1.417(6)	C(5S)-C(6S)	1.3900
C(25)-C(30)	1.407(4)	C(56)-C(57)	1.422(6)	C(5S)-H(5S)	0.9500
C(26)-C(27)	1.389(4)	C(56)-H(56)	0.9500	C(6S)-Br(1)	1.858(2)

Table A.59: Bond angles [°] for **11**

C(55)-Zn(1)-N(2)	111.58(13)	C(28)-C(27)-C(26)	122.5(3)	C(55)-C(56)-C(57)	123.0(5)
C(55)-Zn(1)-N(1)	115.21(12)	C(28)-C(27)-H(27)	118.7	C(55)-C(56)-H(56)	118.5
N(2)-Zn(1)-N(1)	133.12(10)	C(26)-C(27)-H(27)	118.7	C(57)-C(56)-H(56)	118.5
N(1)-P(1)-C(13)	112.37(12)	C(29)-C(28)-C(27)	118.1(3)	C(58)-C(57)-C(56)	118.0(5)
N(1)-P(1)-C(19)	109.99(13)	C(29)-C(28)-C(33)	121.0(3)	C(58)-C(57)-H(57)	121.0
C(13)-P(1)-C(19)	109.73(13)	C(27)-C(28)-C(33)	120.9(3)	C(56)-C(57)-H(57)	121.0
N(1)-P(1)-C(2)	116.52(13)	C(28)-C(29)-C(30)	122.5(3)	C(57)-C(58)-C(59)	121.2(5)
C(13)-P(1)-C(2)	105.04(13)	C(28)-C(29)-H(29)	118.8	C(57)-C(58)-H(58)	119.4
C(19)-P(1)-C(2)	102.61(13)	C(30)-C(29)-H(29)	118.8	C(59)-C(58)-H(58)	119.4
C(12)-O(1)-C(1)	105.8(2)	C(29)-C(30)-C(25)	118.3(3)	C(58)-C(59)-C(60)	117.1(5)
C(25)-N(1)-P(1)	120.44(18)	C(29)-C(30)-C(31)	120.0(3)	C(58)-C(59)-H(59)	121.5
C(25)-N(1)-Zn(1)	109.01(17)	C(25)-C(30)-C(31)	121.6(3)	C(60)-C(59)-H(59)	121.5
P(1)-N(1)-Zn(1)	130.13(13)	C(30)-C(31)-H(31A)	109.5	C(59)-C(60)-C(55)	121.6(5)
O(1)-C(1)-C(2)	123.2(2)	C(30)-C(31)-H(31B)	109.5	C(59)-C(60)-H(60)	119.2
O(1)-C(1)-C(6)	111.5(2)	H(31A)-C(31)-H(31B)	109.5	C(55)-C(60)-H(60)	119.2
C(2)-C(1)-C(6)	125.2(3)	C(30)-C(31)-H(31C)	109.5	C(62)-C(61)-C(66)	114.9(3)
C(73)-B(1)-C(67)	110.6(2)	H(31A)-C(31)-H(31C)	109.5	C(62)-C(61)-B(1)	125.0(3)
C(73)-B(1)-C(61)	108.7(2)	H(31B)-C(31)-H(31C)	109.5	C(66)-C(61)-B(1)	119.9(2)
C(67)-B(1)-C(61)	109.0(2)	C(26)-C(32)-H(32A)	109.5	C(63)-C(62)-C(61)	123.1(3)
C(73)-B(1)-C(79)	109.8(2)	C(26)-C(32)-H(32B)	109.5	C(63)-C(62)-H(62)	118.5

C(67)-B(1)-C(79)	108.3(2)	H(32A)-C(32)-H(32B)	109.5	C(61)-C(62)-H(62)	118.5
C(61)-B(1)-C(79)	110.4(2)	C(26)-C(32)-H(32C)	109.5	C(64)-C(63)-C(62)	120.1(3)
N(2)-P(2)-C(40)	114.55(13)	H(32A)-C(32)-H(32C)	109.5	C(64)-C(63)-H(63)	120.0
N(2)-P(2)-C(34)	109.24(13)	H(32B)-C(32)-H(32C)	109.5	C(62)-C(63)-H(63)	120.0
C(40)-P(2)-C(34)	107.18(14)	C(28)-C(33)-H(33A)	109.5	C(65)-C(64)-C(63)	118.9(3)
N(2)-P(2)-C(11)	115.59(13)	C(28)-C(33)-H(33B)	109.5	C(65)-C(64)-H(64)	120.6
C(40)-P(2)-C(11)	104.82(14)	H(33A)-C(33)-H(33B)	109.5	C(63)-C(64)-H(64)	120.6
C(34)-P(2)-C(11)	104.72(14)	C(28)-C(33)-H(33C)	109.5	C(64)-C(65)-C(66)	120.6(3)
C(46)-N(2)-P(2)	120.21(18)	H(33A)-C(33)-H(33C)	109.5	C(64)-C(65)-H(65)	119.7
C(46)-N(2)-Zn(1)	110.37(17)	H(33B)-C(33)-H(33C)	109.5	C(66)-C(65)-H(65)	119.7
P(2)-N(2)-Zn(1)	129.29(13)	C(39)-C(34)-C(35)	120.5(3)	C(65)-C(66)-C(61)	122.5(3)
C(1)-C(2)-C(3)	115.0(3)	C(39)-C(34)-P(2)	119.8(2)	C(65)-C(66)-H(66)	118.8
C(1)-C(2)-P(1)	119.4(2)	C(35)-C(34)-P(2)	119.6(2)	C(61)-C(66)-H(66)	118.8
C(3)-C(2)-P(1)	124.7(2)	C(36)-C(35)-C(34)	119.5(3)	C(68)-C(67)-C(72)	114.9(3)
C(4)-C(3)-C(2)	121.3(3)	C(36)-C(35)-H(35)	120.3	C(68)-C(67)-B(1)	123.9(2)
C(4)-C(3)-H(3)	119.4	C(34)-C(35)-H(35)	120.3	C(72)-C(67)-B(1)	121.1(3)
C(2)-C(3)-H(3)	119.4	C(37)-C(36)-C(35)	119.8(3)	C(67)-C(68)-C(69)	122.8(3)
C(5)-C(4)-C(3)	121.7(3)	C(37)-C(36)-H(36)	120.1	C(67)-C(68)-H(68)	118.6
C(5)-C(4)-H(4)	119.2	C(35)-C(36)-H(36)	120.1	C(69)-C(68)-H(68)	118.6
C(3)-C(4)-H(4)	119.2	C(38)-C(37)-C(36)	120.9(3)	C(70)-C(69)-C(68)	120.4(3)
C(4)-C(5)-C(6)	118.8(3)	C(38)-C(37)-H(37)	119.5	C(70)-C(69)-H(69)	119.8
C(4)-C(5)-H(5)	120.6	C(36)-C(37)-H(37)	119.5	C(68)-C(69)-H(69)	119.8
C(6)-C(5)-H(5)	120.6	C(37)-C(38)-C(39)	119.6(4)	C(69)-C(70)-C(71)	118.5(3)
C(5)-C(6)-C(1)	117.9(3)	C(37)-C(38)-H(38)	120.2	C(69)-C(70)-H(70)	120.8
C(5)-C(6)-C(7)	136.7(3)	C(39)-C(38)-H(38)	120.2	C(71)-C(70)-H(70)	120.8
C(1)-C(6)-C(7)	105.5(3)	C(34)-C(39)-C(38)	119.7(3)	C(72)-C(71)-C(70)	120.3(3)
C(12)-C(7)-C(8)	117.8(3)	C(34)-C(39)-H(39)	120.1	C(72)-C(71)-H(71)	119.9
C(12)-C(7)-C(6)	105.5(2)	C(38)-C(39)-H(39)	120.1	C(70)-C(71)-H(71)	119.9
C(8)-C(7)-C(6)	136.7(3)	C(45)-C(40)-C(41)	119.2(3)	C(71)-C(72)-C(67)	123.1(3)
C(9)-C(8)-C(7)	118.9(3)	C(45)-C(40)-P(2)	121.9(2)	C(71)-C(72)-H(72)	118.4
C(9)-C(8)-H(8)	120.6	C(41)-C(40)-P(2)	118.9(2)	C(67)-C(72)-H(72)	118.4
C(7)-C(8)-H(8)	120.6	C(40)-C(41)-C(42)	119.6(3)	C(74)-C(73)-C(78)	114.4(3)
C(8)-C(9)-C(10)	121.5(3)	C(40)-C(41)-H(41)	120.2	C(74)-C(73)-B(1)	125.4(3)
C(8)-C(9)-H(9)	119.2	C(42)-C(41)-H(41)	120.2	C(78)-C(73)-B(1)	120.2(3)
C(10)-C(9)-H(9)	119.2	C(43)-C(42)-C(41)	121.0(4)	C(75)-C(74)-C(73)	123.2(3)
C(11)-C(10)-C(9)	121.2(3)	C(43)-C(42)-H(42)	119.5	C(75)-C(74)-H(74)	118.4
C(11)-C(10)-H(10)	119.4	C(41)-C(42)-H(42)	119.5	C(73)-C(74)-H(74)	118.4
C(9)-C(10)-H(10)	119.4	C(42)-C(43)-C(44)	119.8(3)	C(76)-C(75)-C(74)	120.1(3)
C(12)-C(11)-C(10)	115.5(3)	C(42)-C(43)-H(43)	120.1	C(76)-C(75)-H(75)	120.0
C(12)-C(11)-P(2)	119.4(2)	C(44)-C(43)-H(43)	120.1	C(74)-C(75)-H(75)	120.0
C(10)-C(11)-P(2)	124.9(2)	C(43)-C(44)-C(45)	120.3(3)	C(77)-C(76)-C(75)	118.8(3)
O(1)-C(12)-C(11)	123.2(3)	C(43)-C(44)-H(44)	119.9	C(77)-C(76)-H(76)	120.6
O(1)-C(12)-C(7)	111.7(2)	C(45)-C(44)-H(44)	119.9	C(75)-C(76)-H(76)	120.6

C(11)-C(12)-C(7)	125.0(3)	C(40)-C(45)-C(44)	120.1(3)	C(76)-C(77)-C(78)	120.6(3)
C(18)-C(13)-C(14)	119.6(3)	C(40)-C(45)-H(45)	119.9	C(76)-C(77)-H(77)	119.7
C(18)-C(13)-P(1)	121.8(2)	C(44)-C(45)-H(45)	119.9	C(78)-C(77)-H(77)	119.7
C(14)-C(13)-P(1)	118.5(2)	C(51)-C(46)-C(47)	120.8(3)	C(77)-C(78)-C(73)	122.9(3)
C(15)-C(14)-C(13)	120.0(3)	C(51)-C(46)-N(2)	119.5(3)	C(77)-C(78)-H(78)	118.6
C(15)-C(14)-H(14)	120.0	C(47)-C(46)-N(2)	119.7(3)	C(73)-C(78)-H(78)	118.6
C(13)-C(14)-H(14)	120.0	C(48)-C(47)-C(46)	118.8(3)	C(80)-C(79)-C(84)	114.6(3)
C(16)-C(15)-C(14)	119.9(3)	C(48)-C(47)-C(52)	118.4(3)	C(80)-C(79)-B(1)	125.8(3)
C(16)-C(15)-H(15)	120.1	C(46)-C(47)-C(52)	122.8(3)	C(84)-C(79)-B(1)	119.6(3)
C(14)-C(15)-H(15)	120.1	C(49)-C(48)-C(47)	122.0(4)	C(79)-C(80)-C(81)	122.5(3)
C(17)-C(16)-C(15)	120.6(3)	C(49)-C(48)-H(48)	119.0	C(79)-C(80)-H(80)	118.8
C(17)-C(16)-H(16)	119.7	C(47)-C(48)-H(48)	119.0	C(81)-C(80)-H(80)	118.8
C(15)-C(16)-H(16)	119.7	C(48)-C(49)-C(50)	118.4(3)	C(82)-C(81)-C(80)	120.6(3)
C(16)-C(17)-C(18)	120.2(3)	C(48)-C(49)-C(53)	120.6(4)	C(82)-C(81)-H(81)	119.7
C(16)-C(17)-H(17)	119.9	C(50)-C(49)-C(53)	121.0(4)	C(80)-C(81)-H(81)	119.7
C(18)-C(17)-H(17)	119.9	C(49)-C(50)-C(51)	122.0(3)	C(81)-C(82)-C(83)	118.7(3)
C(13)-C(18)-C(17)	119.6(3)	C(49)-C(50)-H(50)	119.0	C(81)-C(82)-H(82)	120.7
C(13)-C(18)-H(18)	120.2	C(51)-C(50)-H(50)	119.0	C(83)-C(82)-H(82)	120.7
C(17)-C(18)-H(18)	120.2	C(46)-C(51)-C(50)	118.0(3)	C(82)-C(83)-C(84)	120.4(3)
C(24)-C(19)-C(20)	119.3(3)	C(46)-C(51)-C(54)	122.6(3)	C(82)-C(83)-H(83)	119.8
C(24)-C(19)-P(1)	120.5(2)	C(50)-C(51)-C(54)	119.3(3)	C(84)-C(83)-H(83)	119.8
C(20)-C(19)-P(1)	120.1(2)	C(47)-C(52)-H(52A)	109.5	C(83)-C(84)-C(79)	123.3(3)
C(21)-C(20)-C(19)	119.6(3)	C(47)-C(52)-H(52B)	109.5	C(83)-C(84)-H(84)	118.4
C(21)-C(20)-H(20)	120.2	H(52A)-C(52)-H(52B)	109.5	C(79)-C(84)-H(84)	118.4
C(19)-C(20)-H(20)	120.2	C(47)-C(52)-H(52C)	109.5	C(2S)-C(1S)-C(6S)	120.0
C(20)-C(21)-C(22)	120.6(3)	H(52A)-C(52)-H(52C)	109.5	C(2S)-C(1S)-H(1S)	120.0
C(20)-C(21)-H(21)	119.7	H(52B)-C(52)-H(52C)	109.5	C(6S)-C(1S)-H(1S)	120.0
C(22)-C(21)-H(21)	119.7	C(49)-C(53)-H(53A)	109.5	C(3S)-C(2S)-C(1S)	120.0
C(23)-C(22)-C(21)	119.7(3)	C(49)-C(53)-H(53B)	109.5	C(3S)-C(2S)-H(2S)	120.0
C(23)-C(22)-H(22)	120.1	H(53A)-C(53)-H(53B)	109.5	C(1S)-C(2S)-H(2S)	120.0
C(21)-C(22)-H(22)	120.1	C(49)-C(53)-H(53C)	109.5	C(2S)-C(3S)-C(4S)	120.0
C(22)-C(23)-C(24)	120.5(3)	H(53A)-C(53)-H(53C)	109.5	C(2S)-C(3S)-H(3S)	120.0
C(22)-C(23)-H(23)	119.8	H(53B)-C(53)-H(53C)	109.5	C(4S)-C(3S)-H(3S)	120.0
C(24)-C(23)-H(23)	119.8	C(51)-C(54)-H(54A)	109.5	C(3S)-C(4S)-C(5S)	120.0
C(23)-C(24)-C(19)	120.3(3)	C(51)-C(54)-H(54B)	109.5	C(3S)-C(4S)-H(4S)	120.0
C(23)-C(24)-H(24)	119.9	H(54A)-C(54)-H(54B)	109.5	C(5S)-C(4S)-H(4S)	120.0
C(19)-C(24)-H(24)	119.9	C(51)-C(54)-H(54C)	109.5	C(6S)-C(5S)-C(4S)	120.0
C(26)-C(25)-C(30)	120.4(3)	H(54A)-C(54)-H(54C)	109.5	C(6S)-C(5S)-H(5S)	120.0
C(26)-C(25)-N(1)	120.4(2)	H(54B)-C(54)-H(54C)	109.5	C(4S)-C(5S)-H(5S)	120.0
C(30)-C(25)-N(1)	119.2(3)	C(56)-C(55)-C(60)	119.1(4)	C(5S)-C(6S)-C(1S)	120.0
C(27)-C(26)-C(25)	118.2(3)	C(56)-C(55)-Zn(1)	120.8(4)	C(5S)-C(6S)-Br(1)	120.65(15)
C(27)-C(26)-C(32)	119.1(3)	C(60)-C(55)-Zn(1)	120.0(3)	C(1S)-C(6S)-Br(1)	119.35(15)
C(25)-C(26)-C(32)	122.7(3)				

Table A.60: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	30(1)	50(1)	33(1)	-7(1)	2(1)	-6(1)
P(1)	27(1)	22(1)	26(1)	-1(1)	2(1)	-4(1)
O(1)	27(1)	35(1)	24(1)	2(1)	3(1)	-2(1)
N(1)	30(1)	25(1)	27(1)	-4(1)	2(1)	-2(1)
C(1)	27(2)	23(1)	33(2)	-2(1)	7(1)	-3(1)
B(1)	31(2)	27(2)	29(2)	1(1)	7(1)	4(1)
P(2)	28(1)	26(1)	34(1)	-1(1)	-2(1)	-2(1)
N(2)	27(1)	31(1)	33(1)	-2(1)	-1(1)	-5(1)
C(2)	29(2)	22(1)	32(2)	0(1)	7(1)	-5(1)
C(3)	29(2)	26(1)	43(2)	3(1)	5(1)	-1(1)
C(4)	33(2)	30(2)	53(2)	3(1)	19(2)	1(1)
C(5)	43(2)	26(2)	43(2)	2(1)	21(1)	2(1)
C(6)	42(2)	19(1)	32(2)	1(1)	11(1)	0(1)
C(7)	44(2)	20(1)	29(2)	-1(1)	8(1)	-1(1)
C(8)	64(2)	26(2)	31(2)	1(1)	14(2)	2(2)
C(9)	67(2)	36(2)	26(2)	3(1)	3(2)	3(2)
C(10)	50(2)	31(2)	31(2)	-1(1)	-4(1)	1(1)
C(11)	39(2)	24(1)	30(2)	-2(1)	2(1)	-3(1)
C(12)	40(2)	24(1)	23(1)	-1(1)	2(1)	-3(1)
C(13)	29(2)	30(2)	27(1)	0(1)	5(1)	2(1)
C(14)	29(2)	36(2)	45(2)	-5(1)	1(1)	1(1)
C(15)	34(2)	64(2)	46(2)	-18(2)	-5(2)	2(2)
C(16)	33(2)	88(3)	31(2)	-5(2)	-1(1)	14(2)
C(17)	37(2)	66(2)	36(2)	20(2)	14(1)	22(2)
C(18)	38(2)	36(2)	36(2)	6(1)	14(1)	9(1)
C(19)	34(2)	23(1)	27(1)	-2(1)	4(1)	-4(1)
C(20)	47(2)	33(2)	35(2)	-7(1)	15(1)	-9(1)
C(21)	60(2)	36(2)	44(2)	-7(1)	21(2)	-22(2)
C(22)	62(2)	25(2)	45(2)	-5(1)	11(2)	-12(2)
C(23)	54(2)	30(2)	48(2)	-11(1)	13(2)	-1(2)
C(24)	35(2)	33(2)	42(2)	-5(1)	11(1)	-3(1)
C(25)	24(1)	26(1)	32(2)	-6(1)	-1(1)	0(1)
C(26)	30(2)	30(2)	33(2)	-4(1)	0(1)	3(1)
C(27)	39(2)	49(2)	34(2)	-13(1)	0(1)	5(2)
C(28)	45(2)	35(2)	52(2)	-19(2)	-6(2)	8(2)
C(29)	42(2)	24(2)	55(2)	-6(1)	-7(2)	3(1)
C(30)	29(2)	27(2)	40(2)	-2(1)	-4(1)	1(1)
C(31)	45(2)	30(2)	47(2)	7(1)	1(2)	-5(1)
C(32)	46(2)	41(2)	29(2)	1(1)	8(1)	3(1)

C(33)	81(3)	48(2)	69(3)	-32(2)	-10(2)	13(2)
C(34)	28(2)	29(2)	43(2)	-6(1)	0(1)	-2(1)
C(35)	38(2)	29(2)	47(2)	0(1)	2(1)	-4(1)
C(36)	49(2)	31(2)	71(3)	-5(2)	8(2)	-7(2)
C(37)	74(3)	34(2)	88(3)	-23(2)	23(2)	-13(2)
C(38)	75(3)	57(2)	64(2)	-29(2)	26(2)	-15(2)
C(39)	49(2)	41(2)	56(2)	-10(2)	16(2)	-8(2)
C(40)	30(2)	35(2)	42(2)	9(1)	-3(1)	-5(1)
C(41)	44(2)	44(2)	50(2)	2(2)	-9(2)	1(2)
C(42)	44(2)	60(2)	53(2)	2(2)	-12(2)	-13(2)
C(43)	29(2)	71(3)	63(2)	31(2)	-4(2)	-2(2)
C(44)	32(2)	51(2)	74(3)	23(2)	4(2)	1(2)
C(45)	32(2)	38(2)	61(2)	10(2)	5(2)	-1(1)
C(46)	29(2)	31(2)	36(2)	7(1)	-6(1)	-5(1)
C(47)	27(2)	44(2)	46(2)	11(2)	-4(1)	-2(1)
C(48)	32(2)	50(2)	71(2)	25(2)	-5(2)	-7(2)
C(49)	40(2)	39(2)	96(3)	22(2)	-14(2)	-10(2)
C(50)	48(2)	30(2)	70(2)	6(2)	-14(2)	-4(2)
C(51)	38(2)	34(2)	40(2)	5(1)	-9(1)	-3(1)
C(52)	31(2)	59(2)	57(2)	8(2)	8(2)	2(2)
C(53)	55(3)	44(2)	195(6)	26(3)	-13(3)	-19(2)
C(54)	45(2)	34(2)	50(2)	-7(2)	0(2)	0(1)
C(55)	34(2)	106(3)	40(2)	0(2)	4(2)	-8(2)
C(56)	81(3)	80(3)	46(2)	19(2)	9(2)	10(3)
C(57)	70(3)	99(4)	91(4)	28(3)	32(3)	8(3)
C(58)	97(4)	104(4)	101(4)	36(3)	54(3)	24(3)
C(59)	95(4)	103(4)	72(3)	21(3)	27(3)	16(3)
C(60)	59(3)	98(3)	64(3)	13(3)	16(2)	8(2)
C(61)	28(2)	31(2)	28(1)	1(1)	10(1)	1(1)
C(62)	37(2)	33(2)	33(2)	0(1)	11(1)	3(1)
C(63)	40(2)	43(2)	35(2)	-10(1)	7(1)	-1(1)
C(64)	41(2)	49(2)	29(2)	0(1)	1(1)	2(2)
C(65)	44(2)	39(2)	40(2)	10(1)	1(1)	-1(1)
C(66)	43(2)	31(2)	37(2)	1(1)	0(1)	0(1)
C(67)	33(2)	21(1)	31(2)	0(1)	8(1)	1(1)
C(68)	36(2)	29(2)	34(2)	1(1)	8(1)	2(1)
C(69)	35(2)	33(2)	56(2)	7(1)	19(2)	8(1)
C(70)	56(2)	31(2)	47(2)	6(1)	30(2)	7(2)
C(71)	58(2)	33(2)	31(2)	6(1)	14(2)	5(2)
C(72)	38(2)	32(2)	34(2)	2(1)	5(1)	6(1)
C(73)	26(2)	28(1)	34(2)	6(1)	3(1)	6(1)
C(74)	31(2)	32(2)	41(2)	5(1)	0(1)	6(1)
C(75)	35(2)	36(2)	57(2)	3(2)	-8(2)	0(1)

C(76)	27(2)	43(2)	74(3)	20(2)	-4(2)	-3(1)
C(77)	31(2)	57(2)	59(2)	21(2)	13(2)	4(2)
C(78)	35(2)	46(2)	40(2)	6(1)	9(1)	5(1)
C(79)	37(2)	33(2)	23(1)	-2(1)	5(1)	6(1)
C(80)	32(2)	41(2)	38(2)	-6(1)	0(1)	7(1)
C(81)	43(2)	58(2)	46(2)	-11(2)	-5(2)	23(2)
C(82)	76(3)	35(2)	41(2)	1(2)	2(2)	23(2)
C(83)	74(3)	33(2)	47(2)	8(2)	24(2)	10(2)
C(84)	47(2)	35(2)	41(2)	5(1)	20(2)	7(1)
C(1S)	61(3)	85(3)	54(2)	-26(2)	1(2)	20(2)
C(2S)	64(3)	105(4)	55(3)	-11(3)	13(2)	29(3)
C(3S)	45(2)	86(3)	60(3)	1(2)	2(2)	15(2)
C(4S)	39(2)	70(3)	56(2)	-15(2)	4(2)	7(2)
C(5S)	33(2)	70(3)	50(2)	-19(2)	2(2)	4(2)
C(6S)	36(2)	69(3)	57(2)	-16(2)	-8(2)	1(2)
Br(1)	84(1)	72(1)	93(1)	-3(1)	1(1)	-7(1)

Table A.61: Crystal data and structure refinement for **12**.

Empirical formula	$C_{86}H_{77}BN_2O_3P_2Zn$	
Formula weight	1324.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.8781(11) Å	α= 90°.
	b = 21.6874(13) Å	β= 101.0830(10)°.
	c = 19.8464(12) Å	γ = 90°.
Volume	7551.5(8) $Å^3$	
Z	4	
Density (calculated)	1.165 Mg/m^3	
Absorption coefficient	0.416 mm^{-1}	
F(000)	2784	
Crystal size	0.42 x 0.20 x 0.03 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-21<=h<=21, -25<=k<=25, -23<=l<=23	
Reflections collected	90217	
Independent reflections	13330 [R(int) = 0.1224]	
Completeness to theta = 25.03°	99.80%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6748	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13330 / 48 / 755	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1378	
R indices (all data)	R1 = 0.1138, wR2 = 0.1544	
Largest diff. peak and hole	0.880 and -0.434 $e.Å^{-3}$	

Table A.62: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **12**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	2515(1)	6888(1)	4237(1)	33(1)	C(42)	6003(1)	6456(1)	5971(1)	44(1)
P(1)	1733(1)	6314(1)	2772(1)	28(1)	C(43)	6282(1)	6978(1)	6342(1)	45(1)
O(1)	3436(1)	6646(1)	3114(1)	28(1)	C(44)	5979(1)	7554(1)	6142(1)	40(1)
N(1)	1796(2)	6840(1)	3350(1)	27(1)	C(45)	5397(1)	7609(1)	5570(1)	30(1)
C(1)	3146(2)	6515(2)	2434(2)	26(1)	C(46)	3715(2)	6260(2)	5158(2)	28(1)
B(1)	2787(3)	4032(2)	290(2)	32(1)	C(47)	3704(2)	6402(2)	5850(2)	35(1)
P(2)	4326(1)	7128(1)	4496(1)	26(1)	C(48)	3823(2)	5925(2)	6327(2)	44(1)
N(2)	3596(2)	6757(1)	4653(1)	26(1)	C(49)	3936(3)	5318(2)	6142(2)	49(1)

C(2)	2386(2)	6390(2)	2187(2)	26(1)	C(50)	3934(2)	5196(2)	5457(2)	42(1)
C(3)	2199(2)	6265(2)	1483(2)	32(1)	C(51)	3835(2)	5655(2)	4964(2)	32(1)
C(4)	2747(2)	6263(2)	1075(2)	40(1)	C(52)	3589(2)	7040(2)	6094(2)	41(1)
C(5)	3513(2)	6377(2)	1348(2)	34(1)	C(53)	4052(3)	4809(2)	6682(2)	73(2)
C(6)	3714(2)	6505(2)	2047(2)	29(1)	C(54)	3887(2)	5492(2)	4235(2)	38(1)
C(7)	4421(2)	6643(2)	2522(2)	26(1)	C(57)	2111(1)	4585(1)	189(1)	35(1)
C(8)	5185(2)	6716(2)	2489(2)	32(1)	C(58)	1647(2)	4617(1)	676(1)	43(1)
C(9)	5698(2)	6852(2)	3077(2)	36(1)	C(59)	1067(1)	5052(1)	608(1)	55(1)
C(10)	5464(2)	6930(2)	3704(2)	32(1)	C(60)	950(1)	5455(1)	54(2)	56(1)
C(11)	4700(2)	6871(2)	3761(2)	25(1)	C(61)	1413(2)	5424(1)	-433(1)	47(1)
C(12)	4210(2)	6723(2)	3160(2)	26(1)	C(62)	1993(1)	4988(1)	-366(1)	38(1)
C(13)	1959(2)	5579(1)	3173(1)	30(1)	C(63)	3372(1)	4125(1)	-280(1)	32(1)
C(14)	1793(2)	5467(1)	3818(1)	41(1)	C(64)	3070(1)	4053(1)	-975(1)	38(1)
C(15)	1921(2)	4886(1)	4113(1)	53(1)	C(65)	3527(2)	4148(1)	-1458(1)	44(1)
C(16)	2215(2)	4417(1)	3763(2)	57(1)	C(66)	4287(2)	4313(1)	-1246(1)	47(1)
C(17)	2381(2)	4529(1)	3118(1)	46(1)	C(67)	4590(1)	4385(1)	-551(1)	41(1)
C(18)	2253(2)	5110(1)	2823(1)	37(1)	C(68)	4132(1)	4290(1)	-68(1)	37(1)
C(19)	812(1)	6255(1)	2223(1)	30(1)	C(69)	2378(1)	3322(1)	165(1)	34(1)
C(20)	533(1)	6750(1)	1804(1)	37(1)	C(70)	1620(1)	3215(1)	200(1)	39(1)
C(21)	-151(1)	6693(1)	1337(1)	44(1)	C(71)	1324(1)	2622(1)	115(1)	52(1)
C(22)	-554(1)	6142(1)	1288(1)	47(1)	C(72)	1786(2)	2134(1)	-4(1)	56(1)
C(23)	-275(1)	5647(1)	1707(1)	42(1)	C(73)	2545(2)	2240(1)	-39(1)	53(1)
C(24)	409(1)	5704(1)	2174(1)	36(1)	C(74)	2841(1)	2834(1)	46(1)	42(1)
C(25)	1293(2)	7376(2)	3217(2)	32(1)	C(75)	3309(1)	4088(1)	1095(1)	31(1)
C(26)	1546(2)	7913(2)	2942(2)	39(1)	C(76)	3478(2)	4674(1)	1366(1)	41(1)
C(27)	1060(3)	8420(2)	2846(2)	56(1)	C(77)	3938(2)	4743(1)	2011(1)	45(1)
C(28)	346(3)	8405(2)	3014(3)	67(2)	C(78)	4231(1)	4226(1)	2384(1)	46(1)
C(29)	110(3)	7873(2)	3277(2)	55(1)	C(79)	4063(1)	3640(1)	2114(1)	42(1)
C(30)	570(2)	7350(2)	3395(2)	37(1)	C(80)	3602(1)	3571(1)	1469(1)	36(1)
C(31)	2315(3)	7959(2)	2761(2)	48(1)	C(1S)	2043(2)	2949(1)	2181(2)	64(1)
C(32)	-178(3)	8964(2)	2883(4)	106(2)	C(2S)	1815(2)	2868(2)	2807(2)	71(2)
C(33)	272(2)	6789(2)	3685(2)	48(1)	C(3S)	1713(2)	2276(2)	3044(1)	71(2)
C(34)	4077(1)	7918(1)	4283(1)	27(1)	C(4S)	1837(2)	1767(1)	2656(2)	75(2)
C(35)	4445(1)	8245(1)	3840(1)	34(1)	C(5S)	2065(2)	1848(2)	2030(2)	68(2)
C(36)	4251(2)	8856(1)	3682(1)	40(1)	C(6S)	2167(2)	2439(2)	1793(1)	61(1)
C(37)	3687(2)	9140(1)	3967(1)	43(1)	O(2)	1890(2)	6592(2)	4963(2)	67(1)
C(38)	3319(1)	8812(1)	4410(1)	46(1)	O(3)	2030(2)	7577(2)	4744(2)	62(1)
C(39)	3514(1)	8202(1)	4568(1)	36(1)	C(55)	1741(3)	7160(4)	5060(3)	78(2)
C(40)	5117(1)	7087(1)	5198(1)	26(1)	C(56)	1241(4)	7321(4)	5555(4)	148(4)
C(41)	5420(1)	6510(1)	5399(1)	36(1)					

Table A.63: Bond lengths [Å] for **12**.

Zn(1)-N(2)	1.971(3)	C(25)-C(26)	1.398(5)	C(57)-C(58)	1.3900

Zn(1)-N(1)	1.972(3)	C(25)-C(30)	1.406(5)	C(57)-C(62)	1.3900
Zn(1)-O(3)	2.082(3)	C(26)-C(27)	1.391(6)	C(58)-C(59)	1.3900
Zn(1)-O(2)	2.089(3)	C(26)-C(31)	1.490(6)	C(58)-H(58)	0.9500
Zn(1)-C(55)	2.410(6)	C(27)-C(28)	1.381(7)	C(59)-C(60)	1.3900
P(1)-N(1)	1.606(3)	C(27)-H(27)	0.9500	C(59)-H(59)	0.9500
P(1)-C(13)	1.793(2)	C(28)-C(29)	1.367(7)	C(60)-C(61)	1.3900
P(1)-C(19)	1.7962(19)	C(28)-C(32)	1.522(6)	C(60)-H(60)	0.9500
P(1)-C(2)	1.803(4)	C(29)-C(30)	1.395(5)	C(61)-C(62)	1.3900
O(1)-C(12)	1.379(4)	C(29)-H(29)	0.9500	C(61)-H(61)	0.9500
O(1)-C(1)	1.379(4)	C(30)-C(33)	1.487(6)	C(62)-H(62)	0.9500
N(1)-C(25)	1.463(4)	C(31)-H(31A)	0.9800	C(63)-C(64)	1.3900
C(1)-C(2)	1.380(5)	C(31)-H(31B)	0.9800	C(63)-C(68)	1.3900
C(1)-C(6)	1.387(5)	C(31)-H(31C)	0.9800	C(64)-C(65)	1.3900
B(1)-C(57)	1.689(5)	C(32)-H(32A)	0.9800	C(64)-H(64)	0.9500
B(1)-C(75)	1.693(5)	C(32)-H(32B)	0.9800	C(65)-C(66)	1.3900
B(1)-C(63)	1.693(5)	C(32)-H(32C)	0.9800	C(65)-H(65)	0.9500
B(1)-C(69)	1.702(5)	C(33)-H(33A)	0.9800	C(66)-C(67)	1.3900
P(2)-N(2)	1.614(3)	C(33)-H(33B)	0.9800	C(66)-H(66)	0.9500
P(2)-C(40)	1.7873(19)	C(33)-H(33C)	0.9800	C(67)-C(68)	1.3900
P(2)-C(34)	1.7998(19)	C(34)-C(35)	1.3900	C(67)-H(67)	0.9500
P(2)-C(11)	1.804(4)	C(34)-C(39)	1.3900	C(68)-H(68)	0.9500
N(2)-C(46)	1.459(4)	C(35)-C(36)	1.3900	C(69)-C(70)	1.3900
C(2)-C(3)	1.400(5)	C(35)-H(35)	0.9500	C(69)-C(74)	1.3900
C(3)-C(4)	1.387(5)	C(36)-C(37)	1.3900	C(70)-C(71)	1.3900
C(3)-H(3)	0.9500	C(36)-H(36)	0.9500	C(70)-H(70)	0.9500
C(4)-C(5)	1.394(5)	C(37)-C(38)	1.3900	C(71)-C(72)	1.3900
C(4)-H(4)	0.9500	C(37)-H(37)	0.9500	C(71)-H(71)	0.9500
C(5)-C(6)	1.392(5)	C(38)-C(39)	1.3900	C(72)-C(73)	1.3900
C(5)-H(5)	0.9500	C(38)-H(38)	0.9500	C(72)-H(72)	0.9500
C(6)-C(7)	1.455(5)	C(39)-H(39)	0.9500	C(73)-C(74)	1.3900
C(7)-C(8)	1.389(5)	C(40)-C(41)	1.3900	C(73)-H(73)	0.9500
C(7)-C(12)	1.400(5)	C(40)-C(45)	1.3900	C(74)-H(74)	0.9500
C(8)-C(9)	1.370(5)	C(41)-C(42)	1.3900	C(75)-C(76)	1.3900
C(8)-H(8)	0.9500	C(41)-H(41)	0.9500	C(75)-C(80)	1.3900
C(9)-C(10)	1.398(5)	C(42)-C(43)	1.3900	C(76)-C(77)	1.3900
C(9)-H(9)	0.9500	C(42)-H(42)	0.9500	C(76)-H(76)	0.9500
C(10)-C(11)	1.399(5)	C(43)-C(44)	1.3900	C(77)-C(78)	1.3900
C(10)-H(10)	0.9500	C(43)-H(43)	0.9500	C(77)-H(77)	0.9500
C(11)-C(12)	1.376(5)	C(44)-C(45)	1.3900	C(78)-C(79)	1.3900
C(13)-C(14)	1.3900	C(44)-H(44)	0.9500	C(78)-H(78)	0.9500
C(13)-C(18)	1.3900	C(45)-H(45)	0.9500	C(79)-C(80)	1.3900
C(14)-C(15)	1.3900	C(46)-C(51)	1.396(5)	C(79)-H(79)	0.9500
C(14)-H(14)	0.9500	C(46)-C(47)	1.410(5)	C(80)-H(80)	0.9500

C(15)-C(16)	1.3900	C(47)-C(48)	1.391(5)	C(1S)-C(2S)	1.3900
C(15)-H(15)	0.9500	C(47)-C(52)	1.494(5)	C(1S)-C(6S)	1.3900
C(16)-C(17)	1.3900	C(48)-C(49)	1.392(6)	C(1S)-H(1S)	0.9500
C(16)-H(16)	0.9500	C(48)-H(48)	0.9500	C(2S)-C(3S)	1.3900
C(17)-C(18)	1.3900	C(49)-C(50)	1.385(6)	C(2S)-H(2S)	0.9500
C(17)-H(17)	0.9500	C(49)-C(53)	1.524(5)	C(3S)-C(4S)	1.3900
C(18)-H(18)	0.9500	C(50)-C(51)	1.383(5)	C(3S)-H(3S)	0.9500
C(19)-C(20)	1.3900	C(50)-H(50)	0.9500	C(4S)-C(5S)	1.3900
C(19)-C(24)	1.3900	C(51)-C(54)	1.510(5)	C(4S)-H(4S)	0.9500
C(20)-C(21)	1.3900	C(52)-H(52A)	0.9800	C(5S)-C(6S)	1.3900
C(20)-H(20)	0.9500	C(52)-H(52B)	0.9800	C(5S)-H(5S)	0.9500
C(21)-C(22)	1.3900	C(52)-H(52C)	0.9800	C(6S)-H(6S)	0.9500
C(21)-H(21)	0.9500	C(53)-H(53A)	0.9800	O(2)-C(55)	1.282(7)
C(22)-C(23)	1.3900	C(53)-H(53B)	0.9800	O(3)-C(55)	1.267(7)
C(22)-H(22)	0.9500	C(53)-H(53C)	0.9800	C(55)-C(56)	1.491(7)
C(23)-C(24)	1.3900	C(54)-H(54A)	0.9800	C(56)-H(56A)	0.9800
C(23)-H(23)	0.9500	C(54)-H(54B)	0.9800	C(56)-H(56B)	0.9800
C(24)-H(24)	0.9500	C(54)-H(54C)	0.9800	C(56)-H(56C)	0.9800

Table A.64: Bond angles [°] for **12**

N(2)-Zn(1)-N(1)	141.73(12)	C(26)-C(25)-C(30)	120.9(4)	H(54A)-C(54)-H(54C)	109.5
N(2)-Zn(1)-O(3)	111.54(12)	C(26)-C(25)-N(1)	120.0(4)	H(54B)-C(54)-H(54C)	109.5
N(1)-Zn(1)-O(3)	102.04(12)	C(30)-C(25)-N(1)	119.0(3)	C(58)-C(57)-C(62)	120.0
N(2)-Zn(1)-O(2)	106.14(12)	C(27)-C(26)-C(25)	118.2(4)	C(58)-C(57)-B(1)	117.4(2)
N(1)-Zn(1)-O(2)	104.80(12)	C(27)-C(26)-C(31)	119.7(4)	C(62)-C(57)-B(1)	122.5(2)
O(3)-Zn(1)-O(2)	63.79(15)	C(25)-C(26)-C(31)	122.2(4)	C(57)-C(58)-C(59)	120.0
N(2)-Zn(1)-C(55)	113.30(16)	C(28)-C(27)-C(26)	122.1(4)	C(57)-C(58)-H(58)	120.0
N(1)-Zn(1)-C(55)	104.89(16)	C(28)-C(27)-H(27)	119.0	C(59)-C(58)-H(58)	120.0
O(3)-Zn(1)-C(55)	31.71(18)	C(26)-C(27)-H(27)	119.0	C(60)-C(59)-C(58)	120.0
O(2)-Zn(1)-C(55)	32.11(19)	C(29)-C(28)-C(27)	118.6(4)	C(60)-C(59)-H(59)	120.0
N(1)-P(1)-C(13)	109.57(14)	C(29)-C(28)-C(32)	120.8(5)	C(58)-C(59)-H(59)	120.0
N(1)-P(1)-C(19)	114.45(14)	C(27)-C(28)-C(32)	120.6(5)	C(59)-C(60)-C(61)	120.0
C(13)-P(1)-C(19)	107.93(12)	C(28)-C(29)-C(30)	122.5(5)	C(59)-C(60)-H(60)	120.0
N(1)-P(1)-C(2)	115.49(16)	C(28)-C(29)-H(29)	118.8	C(61)-C(60)-H(60)	120.0
C(13)-P(1)-C(2)	104.36(14)	C(30)-C(29)-H(29)	118.8	C(60)-C(61)-C(62)	120.0
C(19)-P(1)-C(2)	104.31(15)	C(29)-C(30)-C(25)	117.7(4)	C(60)-C(61)-H(61)	120.0
C(12)-O(1)-C(1)	105.9(3)	C(29)-C(30)-C(33)	119.2(4)	C(62)-C(61)-H(61)	120.0
C(25)-N(1)-P(1)	118.6(2)	C(25)-C(30)-C(33)	123.1(4)	C(61)-C(62)-C(57)	120.0
C(25)-N(1)-Zn(1)	113.1(2)	C(26)-C(31)-H(31A)	109.5	C(61)-C(62)-H(62)	120.0
P(1)-N(1)-Zn(1)	128.24(16)	C(26)-C(31)-H(31B)	109.5	C(57)-C(62)-H(62)	120.0
O(1)-C(1)-C(2)	123.2(3)	H(31A)-C(31)-H(31B)	109.5	C(64)-C(63)-C(68)	120.0
O(1)-C(1)-C(6)	111.5(3)	C(26)-C(31)-H(31C)	109.5	C(64)-C(63)-B(1)	118.5(2)
C(2)-C(1)-C(6)	125.2(3)	H(31A)-C(31)-H(31C)	109.5	C(68)-C(63)-B(1)	121.4(2)

C(57)-B(1)-C(75)	108.3(3)	H(31B)-C(31)-H(31C)	109.5	C(65)-C(64)-C(63)	120.0
C(57)-B(1)-C(63)	110.8(3)	C(28)-C(32)-H(32A)	109.5	C(65)-C(64)-H(64)	120.0
C(75)-B(1)-C(63)	108.8(3)	C(28)-C(32)-H(32B)	109.5	C(63)-C(64)-H(64)	120.0
C(57)-B(1)-C(69)	110.3(3)	H(32A)-C(32)-H(32B)	109.5	C(64)-C(65)-C(66)	120.0
C(75)-B(1)-C(69)	110.3(3)	C(28)-C(32)-H(32C)	109.5	C(64)-C(65)-H(65)	120.0
C(63)-B(1)-C(69)	108.3(3)	H(32A)-C(32)-H(32C)	109.5	C(66)-C(65)-H(65)	120.0
N(2)-P(2)-C(40)	111.86(14)	H(32B)-C(32)-H(32C)	109.5	C(67)-C(66)-C(65)	120.0
N(2)-P(2)-C(34)	110.32(14)	C(30)-C(33)-H(33A)	109.5	C(67)-C(66)-H(66)	120.0
C(40)-P(2)-C(34)	110.75(12)	C(30)-C(33)-H(33B)	109.5	C(65)-C(66)-H(66)	120.0
N(2)-P(2)-C(11)	116.17(16)	H(33A)-C(33)-H(33B)	109.5	C(66)-C(67)-C(68)	120.0
C(40)-P(2)-C(11)	104.74(14)	C(30)-C(33)-H(33C)	109.5	C(66)-C(67)-H(67)	120.0
C(34)-P(2)-C(11)	102.53(14)	H(33A)-C(33)-H(33C)	109.5	C(68)-C(67)-H(67)	120.0
C(46)-N(2)-P(2)	119.0(2)	H(33B)-C(33)-H(33C)	109.5	C(67)-C(68)-C(63)	120.0
C(46)-N(2)-Zn(1)	113.4(2)	C(35)-C(34)-C(39)	120.0	C(67)-C(68)-H(68)	120.0
P(2)-N(2)-Zn(1)	127.66(16)	C(35)-C(34)-P(2)	120.57(13)	C(63)-C(68)-H(68)	120.0
C(1)-C(2)-C(3)	115.0(3)	C(39)-C(34)-P(2)	119.43(13)	C(70)-C(69)-C(74)	120.0
C(1)-C(2)-P(1)	120.3(3)	C(34)-C(35)-C(36)	120.0	C(70)-C(69)-B(1)	122.6(2)
C(3)-C(2)-P(1)	124.4(3)	C(34)-C(35)-H(35)	120.0	C(74)-C(69)-B(1)	117.4(2)
C(4)-C(3)-C(2)	121.6(4)	C(36)-C(35)-H(35)	120.0	C(71)-C(70)-C(69)	120.0
C(4)-C(3)-H(3)	119.2	C(37)-C(36)-C(35)	120.0	C(71)-C(70)-H(70)	120.0
C(2)-C(3)-H(3)	119.2	C(37)-C(36)-H(36)	120.0	C(69)-C(70)-H(70)	120.0
C(3)-C(4)-C(5)	121.6(4)	C(35)-C(36)-H(36)	120.0	C(70)-C(71)-C(72)	120.0
C(3)-C(4)-H(4)	119.2	C(38)-C(37)-C(36)	120.0	C(70)-C(71)-H(71)	120.0
C(5)-C(4)-H(4)	119.2	C(38)-C(37)-H(37)	120.0	C(72)-C(71)-H(71)	120.0
C(6)-C(5)-C(4)	118.0(4)	C(36)-C(37)-H(37)	120.0	C(71)-C(72)-C(73)	120.0
C(6)-C(5)-H(5)	121.0	C(37)-C(38)-C(39)	120.0	C(71)-C(72)-H(72)	120.0
C(4)-C(5)-H(5)	121.0	C(37)-C(38)-H(38)	120.0	C(73)-C(72)-H(72)	120.0
C(1)-C(6)-C(5)	118.6(4)	C(39)-C(38)-H(38)	120.0	C(74)-C(73)-C(72)	120.0
C(1)-C(6)-C(7)	106.0(3)	C(38)-C(39)-C(34)	120.0	C(74)-C(73)-H(73)	120.0
C(5)-C(6)-C(7)	135.4(4)	C(38)-C(39)-H(39)	120.0	C(72)-C(73)-H(73)	120.0
C(8)-C(7)-C(12)	117.8(3)	C(34)-C(39)-H(39)	120.0	C(73)-C(74)-C(69)	120.0
C(8)-C(7)-C(6)	137.1(3)	C(41)-C(40)-C(45)	120.0	C(73)-C(74)-H(74)	120.0
C(12)-C(7)-C(6)	105.1(3)	C(41)-C(40)-P(2)	118.35(13)	C(69)-C(74)-H(74)	120.0
C(9)-C(8)-C(7)	119.3(4)	C(45)-C(40)-P(2)	121.51(13)	C(76)-C(75)-C(80)	120.0
C(9)-C(8)-H(8)	120.4	C(42)-C(41)-C(40)	120.0	C(76)-C(75)-B(1)	118.0(2)
C(7)-C(8)-H(8)	120.4	C(42)-C(41)-H(41)	120.0	C(80)-C(75)-B(1)	121.9(2)
C(8)-C(9)-C(10)	121.1(4)	C(40)-C(41)-H(41)	120.0	C(75)-C(76)-C(77)	120.0
C(8)-C(9)-H(9)	119.4	C(41)-C(42)-C(43)	120.0	C(75)-C(76)-H(76)	120.0
C(10)-C(9)-H(9)	119.4	C(41)-C(42)-H(42)	120.0	C(77)-C(76)-H(76)	120.0
C(9)-C(10)-C(11)	121.8(4)	C(43)-C(42)-H(42)	120.0	C(76)-C(77)-C(78)	120.0
C(9)-C(10)-H(10)	119.1	C(44)-C(43)-C(42)	120.0	C(76)-C(77)-H(77)	120.0
C(11)-C(10)-H(10)	119.1	C(44)-C(43)-H(43)	120.0	C(78)-C(77)-H(77)	120.0
C(12)-C(11)-C(10)	114.8(3)	C(42)-C(43)-H(43)	120.0	C(79)-C(78)-C(77)	120.0

C(12)-C(11)-P(2)	120.0(3)	C(45)-C(44)-C(43)	120.0	C(79)-C(78)-H(78)	120.0
C(10)-C(11)-P(2)	123.8(3)	C(45)-C(44)-H(44)	120.0	C(77)-C(78)-H(78)	120.0
C(11)-C(12)-O(1)	123.3(3)	C(43)-C(44)-H(44)	120.0	C(78)-C(79)-C(80)	120.0
C(11)-C(12)-C(7)	125.2(3)	C(44)-C(45)-C(40)	120.0	C(78)-C(79)-H(79)	120.0
O(1)-C(12)-C(7)	111.5(3)	C(44)-C(45)-H(45)	120.0	C(80)-C(79)-H(79)	120.0
C(14)-C(13)-C(18)	120.0	C(40)-C(45)-H(45)	120.0	C(79)-C(80)-C(75)	120.0
C(14)-C(13)-P(1)	119.65(14)	C(51)-C(46)-C(47)	120.4(3)	C(79)-C(80)-H(80)	120.0
C(18)-C(13)-P(1)	120.22(14)	C(51)-C(46)-N(2)	120.9(3)	C(75)-C(80)-H(80)	120.0
C(15)-C(14)-C(13)	120.0	C(47)-C(46)-N(2)	118.7(3)	C(2S)-C(1S)-C(6S)	120.0
C(15)-C(14)-H(14)	120.0	C(48)-C(47)-C(46)	118.1(4)	C(2S)-C(1S)-H(1S)	120.0
C(13)-C(14)-H(14)	120.0	C(48)-C(47)-C(52)	118.8(4)	C(6S)-C(1S)-H(1S)	120.0
C(14)-C(15)-C(16)	120.0	C(46)-C(47)-C(52)	123.0(3)	C(3S)-C(2S)-C(1S)	120.0
C(14)-C(15)-H(15)	120.0	C(47)-C(48)-C(49)	122.4(4)	C(3S)-C(2S)-H(2S)	120.0
C(16)-C(15)-H(15)	120.0	C(47)-C(48)-H(48)	118.8	C(1S)-C(2S)-H(2S)	120.0
C(17)-C(16)-C(15)	120.0	C(49)-C(48)-H(48)	118.8	C(2S)-C(3S)-C(4S)	120.0
C(17)-C(16)-H(16)	120.0	C(50)-C(49)-C(48)	117.7(4)	C(2S)-C(3S)-H(3S)	120.0
C(15)-C(16)-H(16)	120.0	C(50)-C(49)-C(53)	121.9(4)	C(4S)-C(3S)-H(3S)	120.0
C(18)-C(17)-C(16)	120.0	C(48)-C(49)-C(53)	120.4(4)	C(3S)-C(4S)-C(5S)	120.0
C(18)-C(17)-H(17)	120.0	C(51)-C(50)-C(49)	122.3(4)	C(3S)-C(4S)-H(4S)	120.0
C(16)-C(17)-H(17)	120.0	C(51)-C(50)-H(50)	118.8	C(5S)-C(4S)-H(4S)	120.0
C(17)-C(18)-C(13)	120.0	C(49)-C(50)-H(50)	118.8	C(6S)-C(5S)-C(4S)	120.0
C(17)-C(18)-H(18)	120.0	C(50)-C(51)-C(46)	119.1(4)	C(6S)-C(5S)-H(5S)	120.0
C(13)-C(18)-H(18)	120.0	C(50)-C(51)-C(54)	119.1(3)	C(4S)-C(5S)-H(5S)	120.0
C(20)-C(19)-C(24)	120.0	C(46)-C(51)-C(54)	121.8(3)	C(5S)-C(6S)-C(1S)	120.0
C(20)-C(19)-P(1)	119.34(14)	C(47)-C(52)-H(52A)	109.5	C(5S)-C(6S)-H(6S)	120.0
C(24)-C(19)-P(1)	120.46(14)	C(47)-C(52)-H(52B)	109.5	C(1S)-C(6S)-H(6S)	120.0
C(19)-C(20)-C(21)	120.0	H(52A)-C(52)-H(52B)	109.5	C(55)-O(2)-Zn(1)	87.9(4)
C(19)-C(20)-H(20)	120.0	C(47)-C(52)-H(52C)	109.5	C(55)-O(3)-Zn(1)	88.5(3)
C(21)-C(20)-H(20)	120.0	H(52A)-C(52)-H(52C)	109.5	O(3)-C(55)-O(2)	119.7(5)
C(22)-C(21)-C(20)	120.0	H(52B)-C(52)-H(52C)	109.5	O(3)-C(55)-C(56)	120.8(7)
C(22)-C(21)-H(21)	120.0	C(49)-C(53)-H(53A)	109.5	O(2)-C(55)-C(56)	119.5(7)
C(20)-C(21)-H(21)	120.0	C(49)-C(53)-H(53B)	109.5	O(3)-C(55)-Zn(1)	59.7(3)
C(21)-C(22)-C(23)	120.0	H(53A)-C(53)-H(53B)	109.5	O(2)-C(55)-Zn(1)	60.0(3)
C(21)-C(22)-H(22)	120.0	C(49)-C(53)-H(53C)	109.5	C(56)-C(55)-Zn(1)	178.2(4)
C(23)-C(22)-H(22)	120.0	H(53A)-C(53)-H(53C)	109.5	C(55)-C(56)-H(56A)	109.5
C(24)-C(23)-C(22)	120.0	H(53B)-C(53)-H(53C)	109.5	C(55)-C(56)-H(56B)	109.5
C(24)-C(23)-H(23)	120.0	C(51)-C(54)-H(54A)	109.5	H(56A)-C(56)-H(56B)	109.5
C(22)-C(23)-H(23)	120.0	C(51)-C(54)-H(54B)	109.5	C(55)-C(56)-H(56C)	109.5
C(23)-C(24)-C(19)	120.0	H(54A)-C(54)-H(54B)	109.5	H(56A)-C(56)-H(56C)	109.5
C(23)-C(24)-H(24)	120.0	C(51)-C(54)-H(54C)	109.5	H(56B)-C(56)-H(56C)	109.5
C(19)-C(24)-H(24)	120.0				

Table A.65: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **12**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	29(1)	40(1)	29(1)	-3(1)	3(1)	4(1)
P(1)	28(1)	27(1)	27(1)	0(1)	3(1)	-1(1)
O(1)	23(2)	38(2)	24(1)	-4(1)	5(1)	-2(1)
N(1)	22(2)	28(2)	29(2)	-1(1)	0(1)	2(1)
C(1)	31(2)	25(2)	23(2)	2(2)	5(2)	-2(2)
B(1)	33(3)	28(3)	35(3)	-2(2)	12(2)	-4(2)
P(2)	27(1)	23(1)	27(1)	0(1)	3(1)	1(1)
N(2)	30(2)	24(2)	26(2)	3(1)	7(1)	1(1)
C(2)	30(2)	21(2)	29(2)	0(2)	9(2)	3(2)
C(3)	37(2)	32(2)	28(2)	-3(2)	5(2)	-2(2)
C(4)	55(3)	40(3)	23(2)	-2(2)	7(2)	-1(2)
C(5)	49(3)	28(2)	30(2)	-1(2)	17(2)	-1(2)
C(6)	36(2)	22(2)	29(2)	2(2)	7(2)	1(2)
C(7)	38(2)	15(2)	29(2)	-4(2)	13(2)	3(2)
C(8)	40(3)	25(2)	36(2)	-4(2)	19(2)	-2(2)
C(9)	31(2)	33(2)	48(3)	-2(2)	16(2)	2(2)
C(10)	32(2)	25(2)	39(2)	-6(2)	6(2)	-2(2)
C(11)	26(2)	20(2)	30(2)	-1(2)	6(2)	2(2)
C(12)	25(2)	22(2)	31(2)	0(2)	5(2)	3(2)
C(13)	25(2)	28(2)	37(2)	-1(2)	3(2)	1(2)
C(14)	45(3)	36(3)	42(3)	6(2)	13(2)	3(2)
C(15)	64(3)	48(3)	50(3)	13(2)	19(2)	7(2)
C(16)	58(3)	35(3)	76(4)	16(3)	7(3)	3(2)
C(17)	44(3)	32(3)	61(3)	0(2)	5(2)	3(2)
C(18)	33(2)	38(3)	37(2)	-1(2)	0(2)	-1(2)
C(19)	29(2)	33(2)	26(2)	-4(2)	2(2)	1(2)
C(20)	35(3)	41(3)	34(2)	1(2)	1(2)	-4(2)
C(21)	35(3)	56(3)	40(3)	4(2)	0(2)	9(2)
C(22)	32(3)	62(3)	44(3)	-9(2)	0(2)	-3(2)
C(23)	32(3)	43(3)	49(3)	-10(2)	4(2)	-9(2)
C(24)	33(2)	33(2)	40(2)	-1(2)	3(2)	-3(2)
C(25)	37(3)	27(2)	30(2)	-5(2)	-1(2)	5(2)
C(26)	41(3)	28(2)	41(2)	-6(2)	-6(2)	-2(2)
C(27)	49(3)	26(2)	83(4)	0(2)	-14(3)	2(2)
C(28)	52(4)	37(3)	103(4)	-13(3)	-11(3)	11(3)
C(29)	36(3)	49(3)	77(3)	-22(3)	2(2)	8(2)
C(30)	28(2)	39(3)	43(2)	-6(2)	2(2)	7(2)
C(31)	55(3)	37(3)	50(3)	8(2)	5(2)	-4(2)
C(32)	70(4)	39(3)	193(7)	-12(4)	-18(4)	26(3)
C(33)	33(3)	61(3)	51(3)	-7(2)	14(2)	1(2)

C(34)	30(2)	25(2)	23(2)	-2(2)	1(2)	1(2)
C(35)	36(2)	28(2)	41(2)	4(2)	16(2)	0(2)
C(36)	46(3)	34(2)	42(2)	11(2)	14(2)	-1(2)
C(37)	60(3)	31(2)	38(2)	9(2)	10(2)	7(2)
C(38)	61(3)	36(3)	47(3)	4(2)	23(2)	13(2)
C(39)	51(3)	27(2)	34(2)	8(2)	17(2)	9(2)
C(40)	26(2)	30(2)	24(2)	-2(2)	5(2)	-4(2)
C(41)	26(2)	29(2)	49(3)	-1(2)	-2(2)	2(2)
C(42)	31(3)	44(3)	53(3)	16(2)	-1(2)	5(2)
C(43)	32(3)	65(3)	36(2)	6(2)	-1(2)	-4(2)
C(44)	35(3)	51(3)	32(2)	-15(2)	6(2)	-10(2)
C(45)	34(2)	27(2)	33(2)	-4(2)	11(2)	-2(2)
C(46)	20(2)	32(2)	32(2)	4(2)	2(2)	-2(2)
C(47)	35(2)	35(2)	33(2)	6(2)	7(2)	-3(2)
C(48)	51(3)	44(3)	35(2)	8(2)	4(2)	3(2)
C(49)	57(3)	37(3)	49(3)	17(2)	4(2)	-1(2)
C(50)	48(3)	23(2)	53(3)	3(2)	3(2)	0(2)
C(51)	31(2)	23(2)	41(2)	1(2)	3(2)	-2(2)
C(52)	54(3)	37(3)	35(2)	-2(2)	15(2)	1(2)
C(53)	97(4)	44(3)	72(4)	29(3)	5(3)	3(3)
C(54)	39(3)	32(2)	43(2)	-9(2)	4(2)	9(2)
C(57)	31(2)	36(2)	37(2)	-10(2)	1(2)	-7(2)
C(58)	35(3)	45(3)	50(3)	-7(2)	12(2)	4(2)
C(59)	38(3)	64(3)	64(3)	-25(3)	16(2)	-7(2)
C(60)	38(3)	43(3)	77(4)	-24(3)	-10(3)	5(2)
C(61)	40(3)	39(3)	56(3)	-6(2)	-7(2)	-2(2)
C(62)	33(2)	32(2)	45(3)	1(2)	-2(2)	1(2)
C(63)	41(3)	19(2)	35(2)	1(2)	6(2)	2(2)
C(64)	42(3)	35(2)	39(2)	-8(2)	13(2)	-4(2)
C(65)	63(3)	34(2)	38(2)	-6(2)	16(2)	0(2)
C(66)	65(3)	28(2)	58(3)	-2(2)	36(3)	-3(2)
C(67)	37(3)	31(2)	57(3)	-2(2)	20(2)	-3(2)
C(68)	39(3)	30(2)	41(2)	0(2)	10(2)	-2(2)
C(69)	43(3)	40(2)	19(2)	4(2)	6(2)	-2(2)
C(70)	34(3)	42(3)	38(2)	5(2)	2(2)	-2(2)
C(71)	47(3)	60(3)	45(3)	14(2)	-4(2)	-14(3)
C(72)	84(4)	41(3)	40(3)	2(2)	2(3)	-17(3)
C(73)	72(4)	44(3)	47(3)	-8(2)	22(3)	-8(3)
C(74)	49(3)	34(2)	46(3)	-5(2)	19(2)	-6(2)
C(75)	30(2)	32(2)	32(2)	0(2)	13(2)	-1(2)
C(76)	46(3)	37(3)	38(2)	1(2)	1(2)	8(2)
C(77)	49(3)	35(3)	48(3)	-11(2)	6(2)	2(2)
C(78)	40(3)	65(3)	32(2)	-4(2)	7(2)	-1(2)

C(79)	40(3)	45(3)	40(3)	12(2)	8(2)	7(2)
C(80)	38(3)	33(2)	41(2)	5(2)	15(2)	-3(2)
C(1S)	54(3)	77(4)	56(3)	12(3)	0(3)	-17(3)
C(2S)	50(3)	80(4)	83(4)	-14(3)	12(3)	-16(3)
C(3S)	64(4)	97(5)	54(3)	3(3)	13(3)	-27(3)
C(4S)	87(4)	79(4)	56(3)	19(3)	8(3)	-8(3)
C(5S)	65(4)	77(4)	60(3)	7(3)	6(3)	7(3)
C(6S)	43(3)	90(4)	50(3)	22(3)	4(2)	-8(3)
O(2)	48(2)	115(3)	40(2)	-12(2)	16(2)	-22(2)
O(3)	41(2)	79(2)	62(2)	-36(2)	3(2)	11(2)
C(55)	40(3)	135(5)	60(4)	-51(4)	10(3)	-19(4)
C(56)	81(5)	247(9)	134(6)	-128(6)	67(4)	-52(5)

Table A.66: Crystal data and structure refinement for **15b**.

Empirical formula	$C_{84}H_{70}BF_{3.10}N_2O_{1.62}P_2Zn \cdot 1.38\ CHCl_3$	
Formula weight	1494.99	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.4192(12) Å	α= 90°.
	b = 21.5109(15) Å	β= 99.3290(10)°.
	c = 20.0888(14) Å	γ = 90°.
Volume	7427.8(9) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	3095	
Crystal size	0.93 x 0.41 x 0.17 mm^3	
Theta range for data collection	1.72 to 26.37°.	
Index ranges	-21<=h<=21, -26<=k<=26, -25<=l<=25	
Reflections collected	98561	
Independent reflections	15188 [R(int) = 0.0256]	
Completeness to theta = 26.37°	100%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9088 and 0.6151	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15188 / 48 / 994	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1294	
R indices (all data)	R1 = 0.0578, wR2 = 0.1371	
Largest diff. peak and hole	1.388 and -0.645 e.$Å^{-3}$	

Table A.67: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **15b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	2566(1)	8321(1)	733(1)	36(1)	C(50)	4916(2)	7276(1)	1518(1)	44(1)
P(1)	735(1)	7961(1)	491(1)	27(1)	C(51)	4462(1)	7812(1)	1477(1)	37(1)
O(1)	1555(1)	8462(1)	1857(1)	30(1)	C(52)	2739(2)	7179(1)	2236(2)	44(1)
N(1)	1456(1)	8369(1)	333(1)	28(1)	C(53)	5212(2)	6157(2)	1835(2)	72(1)
C(1)	765(1)	8358(1)	1805(1)	28(1)	C(54)	4760(2)	8396(1)	1201(2)	44(1)
B(1)	2213(2)	4019(1)	9685(1)	26(1)	O(2)	3165(4)	8159(3)	62(3)	56(2)
P(2)	3275(1)	8822(1)	2228(1)	30(1)	C(55)	3506(7)	8464(6)	-332(5)	60(3)
N(2)	3233(1)	8328(1)	1622(1)	32(1)	C(56)	4026(4)	8176(5)	-712(3)	65(2)

C(2)	296(1)	8198(1)	1206(1)	30(1)
C(3)	-491(1)	8106(1)	1247(1)	35(1)
C(4)	-764(2)	8166(1)	1859(2)	39(1)
C(5)	-272(2)	8303(1)	2449(1)	37(1)
C(6)	515(1)	8403(1)	2428(1)	30(1)
C(7)	1211(2)	8535(1)	2911(1)	31(1)
C(8)	1387(2)	8632(1)	3607(1)	36(1)
C(9)	2150(2)	8751(1)	3884(1)	40(1)
C(10)	2740(2)	8791(1)	3492(1)	35(1)
C(11)	2581(1)	8700(1)	2793(1)	30(1)
C(12)	1811(1)	8570(1)	2533(1)	29(1)
C(13)	1055(2)	7181(1)	713(1)	32(1)
C(14)	618(2)	6803(1)	1076(1)	39(1)
C(15)	844(2)	6191(1)	1223(2)	45(1)
C(16)	1509(2)	5962(1)	1023(1)	47(1)
C(17)	1953(2)	6337(1)	673(1)	47(1)
C(18)	1723(2)	6946(1)	508(1)	39(1)
C(19)	-51(1)	7948(1)	-206(1)	30(1)
C(20)	-389(1)	8511(1)	-444(1)	35(1)
C(21)	-956(2)	8523(1)	-1009(1)	41(1)
C(22)	-1213(2)	7973(1)	-1326(1)	42(1)
C(23)	-904(2)	7414(1)	-1078(1)	41(1)
C(24)	-316(2)	7395(1)	-523(1)	34(1)
C(25)	1346(1)	8823(1)	-209(1)	29(1)
C(26)	1216(1)	9448(1)	-56(1)	36(1)
C(27)	1131(2)	9878(1)	-577(2)	50(1)
C(28)	1169(2)	9713(1)	-1236(2)	57(1)
C(29)	1294(2)	9095(1)	-1371(2)	47(1)
C(30)	1388(2)	8642(1)	-871(1)	35(1)
C(31)	1146(2)	9649(1)	649(2)	47(1)
C(32)	1066(3)	10192(2)	-1800(2)	92(2)
C(33)	1512(2)	7980(1)	-1064(1)	41(1)
C(34)	4212(1)	8858(1)	2751(1)	35(1)
C(35)	4472(2)	8356(1)	3163(1)	45(1)
C(36)	5188(2)	8390(2)	3587(2)	54(1)
C(37)	5636(2)	8915(2)	3600(2)	54(1)
C(38)	5394(2)	9402(2)	3184(2)	53(1)
C(39)	4679(2)	9381(1)	2757(2)	43(1)
C(40)	3060(1)	9585(1)	1890(1)	35(1)
C(41)	2720(2)	10026(1)	2257(1)	38(1)
C(42)	2640(2)	10633(1)	2033(2)	50(1)
C(43)	2899(2)	10808(2)	1450(2)	62(1)
C(44)	3229(2)	10374(2)	1082(2)	73(1)
C(57)	4432(4)	8518(5)	-1141(3)	81(2)
C(58)	4327(4)	9131(4)	-1242(4)	83(2)
C(59)	3820(5)	9439(4)	-899(4)	88(2)
C(60)	3433(3)	9112(4)	-451(3)	70(2)
F(1)	2956(2)	9430(2)	-103(2)	94(1)
F(2)	3719(4)	10062(3)	-970(4)	137(2)
F(3)	4710(3)	9455(3)	-1663(3)	131(2)
F(4)	4935(3)	8209(3)	-1464(2)	109(2)
F(5)	4139(2)	7553(3)	-599(2)	72(1)
C(61)	3194(6)	8083(4)	-13(5)	36(4)
C(62)	3563(3)	7513(3)	-36(3)	34(2)
C(63)	4081(4)	7421(3)	-486(4)	201(19)
C(64)	4229(5)	7900(4)	-913(4)	58(3)
C(65)	3859(7)	8470(3)	-890(5)	72(4)
C(66)	3341(8)	8562(3)	-440(6)	43(4)
C(92)	3911(9)	10454(10)	-987(8)	173(7)
Cl(4)	4576(5)	10302(6)	-275(4)	266(5)
Cl(5)	3027(5)	10297(3)	-914(3)	177(2)
Cl(6)	4238(8)	10043(4)	-1626(4)	285(6)
C(67)	1690(1)	4054(1)	8925(1)	28(1)
C(68)	1451(1)	4633(1)	8640(1)	33(1)
C(69)	969(2)	4696(1)	8022(1)	37(1)
C(70)	700(2)	4173(1)	7653(1)	40(1)
C(71)	920(2)	3592(1)	7915(1)	40(1)
C(72)	1404(2)	3538(1)	8535(1)	33(1)
C(73)	1641(1)	4126(1)	10251(1)	26(1)
C(74)	1925(1)	4077(1)	10944(1)	31(1)
C(75)	1477(2)	4202(1)	11438(1)	36(1)
C(76)	701(2)	4366(1)	11258(1)	37(1)
C(77)	386(2)	4398(1)	10584(1)	37(1)
C(78)	854(1)	4283(1)	10094(1)	31(1)
C(79)	2630(1)	3329(1)	9808(1)	28(1)
C(80)	2181(2)	2806(1)	9907(1)	35(1)
C(81)	2481(2)	2207(1)	9981(1)	42(1)
C(82)	3267(2)	2107(1)	9968(1)	44(1)
C(83)	3732(2)	2608(1)	9885(1)	40(1)
C(84)	3419(1)	3205(1)	9804(1)	32(1)
C(85)	2885(1)	4565(1)	9744(1)	28(1)
C(86)	3357(2)	4618(1)	9241(1)	36(1)
C(87)	3966(2)	5038(1)	9282(2)	44(1)
C(88)	4123(2)	5443(1)	9819(2)	44(1)
C(89)	3660(2)	5419(1)	10316(2)	41(1)
C(90)	3057(1)	4987(1)	10277(1)	33(1)

C(45)	3318(2)	9766(2)	1300(2)	60(1)	C(91)	3349(2)	2221(2)	7503(2)	56(1)
C(46)	3738(1)	7782(1)	1702(1)	32(1)	Cl(1)	2883(1)	2750(1)	7971(1)	68(1)
C(47)	3494(2)	7229(1)	1969(1)	37(1)	Cl(2)	3079(1)	2342(1)	6635(1)	71(1)
C(48)	3980(2)	6710(1)	2005(2)	46(1)	Cl(3)	3137(1)	1452(1)	7716(1)	90(1)
C(49)	4690(2)	6727(1)	1782(2)	48(1)					

Table A.68: Bond lengths [Å] for **15b**.

Zn(1)-O(2)	1.866(6)	C(28)-C(29)	1.382(4)	C(59)-C(60)	1.399(10)
Zn(1)-N(2)	1.968(2)	C(28)-C(32)	1.519(4)	C(60)-F(1)	1.356(7)
Zn(1)-N(1)	1.9724(19)	C(29)-C(30)	1.391(4)	C(61)-C(62)	1.3900
Zn(1)-C(61)	2.058(6)	C(29)-H(29)	0.9500	C(61)-C(66)	1.3900
P(1)-N(1)	1.606(2)	C(30)-C(33)	1.501(4)	C(62)-C(63)	1.3900
P(1)-C(19)	1.793(2)	C(31)-H(31A)	0.9800	C(62)-H(62)	0.9500
P(1)-C(13)	1.802(2)	C(31)-H(31B)	0.9800	C(63)-C(64)	1.3900
P(1)-C(2)	1.805(2)	C(31)-H(31C)	0.9800	C(63)-H(63)	0.9500
O(1)-C(12)	1.378(3)	C(32)-H(32A)	0.9800	C(64)-C(65)	1.3900
O(1)-C(1)	1.380(3)	C(32)-H(32B)	0.9800	C(64)-H(64)	0.9500
N(1)-C(25)	1.451(3)	C(32)-H(32C)	0.9800	C(65)-C(66)	1.3900
C(1)-C(2)	1.385(3)	C(33)-H(33A)	0.9800	C(65)-H(65)	0.9500
C(1)-C(6)	1.394(3)	C(33)-H(33B)	0.9800	C(66)-H(66)	0.9500
B(1)-C(73)	1.644(3)	C(33)-H(33C)	0.9800	C(92)-Cl(5)	1.606(15)
B(1)-C(85)	1.649(3)	C(34)-C(39)	1.387(4)	C(92)-Cl(4)	1.719(16)
B(1)-C(67)	1.649(3)	C(34)-C(35)	1.391(4)	C(92)-Cl(6)	1.730(16)
B(1)-C(79)	1.654(3)	C(35)-C(36)	1.394(4)	C(92)-H(92)	1.0000
P(2)-N(2)	1.608(2)	C(35)-H(35)	0.9500	Cl(4)-Cl(4)#1	2.14(2)
P(2)-C(40)	1.792(3)	C(36)-C(37)	1.370(5)	C(67)-C(72)	1.403(3)
P(2)-C(34)	1.794(2)	C(36)-H(36)	0.9500	C(67)-C(68)	1.405(3)
P(2)-C(11)	1.808(3)	C(37)-C(38)	1.365(5)	C(68)-C(69)	1.389(4)
N(2)-C(46)	1.459(3)	C(37)-H(37)	0.9500	C(68)-H(68)	0.9500
C(2)-C(3)	1.401(3)	C(38)-C(39)	1.394(4)	C(69)-C(70)	1.386(4)
C(3)-C(4)	1.393(4)	C(38)-H(38)	0.9500	C(69)-H(69)	0.9500
C(3)-H(3)	0.9500	C(39)-H(39)	0.9500	C(70)-C(71)	1.385(4)
C(4)-C(5)	1.378(4)	C(40)-C(45)	1.390(4)	C(70)-H(70)	0.9500
C(4)-H(4)	0.9500	C(40)-C(41)	1.390(4)	C(71)-C(72)	1.390(4)
C(5)-C(6)	1.395(4)	C(41)-C(42)	1.382(4)	C(71)-H(71)	0.9500
C(5)-H(5)	0.9500	C(41)-H(41)	0.9500	C(72)-H(72)	0.9500
C(6)-C(7)	1.454(4)	C(42)-C(43)	1.375(5)	C(73)-C(78)	1.398(3)
C(7)-C(12)	1.390(3)	C(42)-H(42)	0.9500	C(73)-C(74)	1.405(3)
C(7)-C(8)	1.398(3)	C(43)-C(44)	1.372(5)	C(74)-C(75)	1.383(3)
C(8)-C(9)	1.378(4)	C(43)-H(43)	0.9500	C(74)-H(74)	0.9500
C(8)-H(8)	0.9500	C(44)-C(45)	1.381(5)	C(75)-C(76)	1.387(4)
C(9)-C(10)	1.395(4)	C(44)-H(44)	0.9500	C(75)-H(75)	0.9500
C(9)-H(9)	0.9500	C(45)-H(45)	0.9500	C(76)-C(77)	1.377(4)

C(10)-C(11)	1.399(3)	C(46)-C(47)	1.399(4)	C(76)-H(76)	0.9500
C(10)-H(10)	0.9500	C(46)-C(51)	1.408(4)	C(77)-C(78)	1.397(3)
C(11)-C(12)	1.388(3)	C(47)-C(48)	1.395(4)	C(77)-H(77)	0.9500
C(13)-C(18)	1.390(4)	C(47)-C(52)	1.504(4)	C(78)-H(78)	0.9500
C(13)-C(14)	1.396(4)	C(48)-C(49)	1.382(4)	C(79)-C(84)	1.402(3)
C(14)-C(15)	1.391(4)	C(48)-H(48)	0.9500	C(79)-C(80)	1.403(3)
C(14)-H(14)	0.9500	C(49)-C(50)	1.379(5)	C(80)-C(81)	1.388(4)
C(15)-C(16)	1.379(4)	C(49)-C(53)	1.520(4)	C(80)-H(80)	0.9500
C(15)-H(15)	0.9500	C(50)-C(51)	1.392(4)	C(81)-C(82)	1.391(4)
C(16)-C(17)	1.386(4)	C(50)-H(50)	0.9500	C(81)-H(81)	0.9500
C(16)-H(16)	0.9500	C(51)-C(54)	1.499(4)	C(82)-C(83)	1.374(4)
C(17)-C(18)	1.393(4)	C(52)-H(52A)	0.9800	C(82)-H(82)	0.9500
C(17)-H(17)	0.9500	C(52)-H(52B)	0.9800	C(83)-C(84)	1.393(4)
C(18)-H(18)	0.9500	C(52)-H(52C)	0.9800	C(83)-H(83)	0.9500
C(19)-C(24)	1.392(3)	C(53)-H(53A)	0.9800	C(84)-H(84)	0.9500
C(19)-C(20)	1.396(3)	C(53)-H(53B)	0.9800	C(85)-C(90)	1.397(3)
C(20)-C(21)	1.379(4)	C(53)-H(53C)	0.9800	C(85)-C(86)	1.407(3)
C(20)-H(20)	0.9500	C(54)-H(54A)	0.9800	C(86)-C(87)	1.386(4)
C(21)-C(22)	1.382(4)	C(54)-H(54B)	0.9800	C(86)-H(86)	0.9500
C(21)-H(21)	0.9500	C(54)-H(54C)	0.9800	C(87)-C(88)	1.378(4)
C(22)-C(23)	1.378(4)	O(2)-C(55)	1.250(10)	C(87)-H(87)	0.9500
C(22)-H(22)	0.9500	C(55)-C(60)	1.415(13)	C(88)-C(89)	1.383(4)
C(23)-C(24)	1.386(4)	C(55)-C(56)	1.418(12)	C(88)-H(88)	0.9500
C(23)-H(23)	0.9500	C(56)-F(5)	1.369(10)	C(89)-C(90)	1.395(4)
C(24)-H(24)	0.9500	C(56)-C(57)	1.408(10)	C(89)-H(89)	0.9500
C(25)-C(30)	1.400(4)	C(57)-C(58)	1.341(11)	C(90)-H(90)	0.9500
C(25)-C(26)	1.405(3)	C(57)-F(4)	1.349(8)	C(91)-Cl(2)	1.750(3)
C(26)-C(27)	1.387(4)	C(58)-F(3)	1.353(8)	C(91)-Cl(1)	1.756(3)
C(26)-C(31)	1.504(4)	C(58)-C(59)	1.376(11)	C(91)-Cl(3)	1.763(4)
C(27)-C(28)	1.384(5)	C(59)-F(2)	1.355(10)	C(91)-H(91)	1.0000
C(27)-H(27)	0.9500				

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z

Table A.69: Bond angles [°] for **15b**

O(2)-Zn(1)-N(2)	109.8(2)	C(26)-C(27)-H(27)	118.8	C(57)-C(58)-C(59)	118.7(7)
O(2)-Zn(1)-N(1)	110.0(2)	C(29)-C(28)-C(27)	117.9(3)	F(3)-C(58)-C(59)	119.1(8)
N(2)-Zn(1)-N(1)	139.97(8)	C(29)-C(28)-C(32)	120.7(3)	F(2)-C(59)-C(58)	120.4(8)
O(2)-Zn(1)-C(61)	3.9(5)	C(27)-C(28)-C(32)	121.4(3)	F(2)-C(59)-C(60)	119.9(8)
N(2)-Zn(1)-C(61)	110.9(3)	C(28)-C(29)-C(30)	122.4(3)	C(58)-C(59)-C(60)	119.6(8)
N(1)-Zn(1)-C(61)	108.5(3)	C(28)-C(29)-H(29)	118.8	F(1)-C(60)-C(59)	118.5(7)
N(1)-P(1)-C(19)	112.07(11)	C(30)-C(29)-H(29)	118.8	F(1)-C(60)-C(55)	117.1(7)
N(1)-P(1)-C(13)	109.72(11)	C(29)-C(30)-C(25)	118.3(2)	C(59)-C(60)-C(55)	124.4(7)

C(19)-P(1)-C(13)	110.18(11)	C(29)-C(30)-C(33)	118.9(2)	C(62)-C(61)-C(66)	120.0
N(1)-P(1)-C(2)	116.70(11)	C(25)-C(30)-C(33)	122.8(2)	C(62)-C(61)-Zn(1)	123.2(4)
C(19)-P(1)-C(2)	104.95(11)	C(26)-C(31)-H(31A)	109.5	C(66)-C(61)-Zn(1)	116.0(4)
C(13)-P(1)-C(2)	102.72(11)	C(26)-C(31)-H(31B)	109.5	C(61)-C(62)-C(63)	120.0
C(12)-O(1)-C(1)	105.12(18)	H(31A)-C(31)-H(31E	109.5	C(61)-C(62)-H(62)	120.0
C(25)-N(1)-P(1)	120.28(15)	C(26)-C(31)-H(31C)	109.5	C(63)-C(62)-H(62)	120.0
C(25)-N(1)-Zn(1)	109.99(15)	H(31A)-C(31)-H(31C	109.5	C(64)-C(63)-C(62)	120.0
P(1)-N(1)-Zn(1)	129.58(11)	H(31B)-C(31)-H(31C	109.5	C(64)-C(63)-H(63)	120.0
O(1)-C(1)-C(2)	123.1(2)	C(28)-C(32)-H(32A)	109.5	C(62)-C(63)-H(63)	120.0
O(1)-C(1)-C(6)	112.0(2)	C(28)-C(32)-H(32B)	109.5	C(63)-C(64)-C(65)	120.0
C(2)-C(1)-C(6)	124.8(2)	H(32A)-C(32)-H(32E	109.5	C(63)-C(64)-H(64)	120.0
C(73)-B(1)-C(85)	110.70(18)	C(28)-C(32)-H(32C)	109.5	C(65)-C(64)-H(64)	120.0
C(73)-B(1)-C(67)	109.12(18)	H(32A)-C(32)-H(32C	109.5	C(64)-C(65)-C(66)	120.0
C(85)-B(1)-C(67)	108.32(19)	H(32B)-C(32)-H(32C	109.5	C(64)-C(65)-H(65)	120.0
C(73)-B(1)-C(79)	108.81(18)	C(30)-C(33)-H(33A)	109.5	C(66)-C(65)-H(65)	120.0
C(85)-B(1)-C(79)	109.82(18)	C(30)-C(33)-H(33B)	109.5	C(65)-C(66)-C(61)	120.0
C(67)-B(1)-C(79)	110.06(18)	H(33A)-C(33)-H(33E	109.5	C(65)-C(66)-H(66)	120.0
N(2)-P(2)-C(40)	109.78(12)	C(30)-C(33)-H(33C)	109.5	C(61)-C(66)-H(66)	120.0
N(2)-P(2)-C(34)	113.38(11)	H(33A)-C(33)-H(33C	109.5	Cl(5)-C(92)-Cl(4)	114.3(11)
C(40)-P(2)-C(34)	107.28(12)	H(33B)-C(33)-H(33C	109.5	Cl(5)-C(92)-Cl(6)	113.3(11)
N(2)-P(2)-C(11)	115.28(11)	C(39)-C(34)-C(35)	119.4(2)	Cl(4)-C(92)-Cl(6)	105.2(11)
C(40)-P(2)-C(11)	104.49(11)	C(39)-C(34)-P(2)	121.1(2)	Cl(5)-C(92)-H(92)	107.9
C(34)-P(2)-C(11)	105.97(12)	C(35)-C(34)-P(2)	119.5(2)	Cl(4)-C(92)-H(92)	107.9
C(46)-N(2)-P(2)	119.76(16)	C(34)-C(35)-C(36)	119.7(3)	Cl(6)-C(92)-H(92)	107.9
C(46)-N(2)-Zn(1)	110.52(14)	C(34)-C(35)-H(35)	120.1	C(92)-Cl(4)-Cl(4)#1	149.5(12)
P(2)-N(2)-Zn(1)	129.71(12)	C(36)-C(35)-H(35)	120.1	C(72)-C(67)-C(68)	114.8(2)
C(1)-C(2)-C(3)	115.4(2)	C(37)-C(36)-C(35)	120.3(3)	C(72)-C(67)-B(1)	125.1(2)
C(1)-C(2)-P(1)	119.65(18)	C(37)-C(36)-H(36)	119.8	C(68)-C(67)-B(1)	120.0(2)
C(3)-C(2)-P(1)	123.49(19)	C(35)-C(36)-H(36)	119.8	C(69)-C(68)-C(67)	123.0(2)
C(4)-C(3)-C(2)	121.1(2)	C(38)-C(37)-C(36)	120.3(3)	C(69)-C(68)-H(68)	118.5
C(4)-C(3)-H(3)	119.5	C(38)-C(37)-H(37)	119.9	C(67)-C(68)-H(68)	118.5
C(2)-C(3)-H(3)	119.5	C(36)-C(37)-H(37)	119.9	C(70)-C(69)-C(68)	120.2(2)
C(5)-C(4)-C(3)	121.7(2)	C(37)-C(38)-C(39)	120.5(3)	C(70)-C(69)-H(69)	119.9
C(5)-C(4)-H(4)	119.1	C(37)-C(38)-H(38)	119.8	C(68)-C(69)-H(69)	119.9
C(3)-C(4)-H(4)	119.1	C(39)-C(38)-H(38)	119.8	C(71)-C(70)-C(69)	118.6(2)
C(4)-C(5)-C(6)	118.9(2)	C(34)-C(39)-C(38)	119.8(3)	C(71)-C(70)-H(70)	120.7
C(4)-C(5)-H(5)	120.5	C(34)-C(39)-H(39)	120.1	C(69)-C(70)-H(70)	120.7
C(6)-C(5)-H(5)	120.5	C(38)-C(39)-H(39)	120.1	C(70)-C(71)-C(72)	120.4(2)
C(1)-C(6)-C(5)	118.0(2)	C(45)-C(40)-C(41)	119.1(3)	C(70)-C(71)-H(71)	119.8
C(1)-C(6)-C(7)	105.3(2)	C(45)-C(40)-P(2)	120.1(2)	C(72)-C(71)-H(71)	119.8
C(5)-C(6)-C(7)	136.7(2)	C(41)-C(40)-P(2)	120.3(2)	C(71)-C(72)-C(67)	122.9(2)
C(12)-C(7)-C(8)	118.4(2)	C(42)-C(41)-C(40)	120.1(3)	C(71)-C(72)-H(72)	118.6
C(12)-C(7)-C(6)	105.4(2)	C(42)-C(41)-H(41)	119.9	C(67)-C(72)-H(72)	118.6

C(8)-C(7)-C(6)	136.2(2)	C(40)-C(41)-H(41)	119.9	C(78)-C(73)-C(74)	114.6(2)
C(9)-C(8)-C(7)	118.2(2)	C(43)-C(42)-C(41)	120.3(3)	C(78)-C(73)-B(1)	124.1(2)
C(9)-C(8)-H(8)	120.9	C(43)-C(42)-H(42)	119.8	C(74)-C(73)-B(1)	121.3(2)
C(7)-C(8)-H(8)	120.9	C(41)-C(42)-H(42)	119.8	C(75)-C(74)-C(73)	123.2(2)
C(8)-C(9)-C(10)	122.3(2)	C(44)-C(43)-C(42)	119.8(3)	C(75)-C(74)-H(74)	118.4
C(8)-C(9)-H(9)	118.9	C(44)-C(43)-H(43)	120.1	C(73)-C(74)-H(74)	118.4
C(10)-C(9)-H(9)	118.9	C(42)-C(43)-H(43)	120.1	C(74)-C(75)-C(76)	120.1(2)
C(9)-C(10)-C(11)	121.0(2)	C(43)-C(44)-C(45)	120.6(3)	C(74)-C(75)-H(75)	119.9
C(9)-C(10)-H(10)	119.5	C(43)-C(44)-H(44)	119.7	C(76)-C(75)-H(75)	119.9
C(11)-C(10)-H(10)	119.5	C(45)-C(44)-H(44)	119.7	C(77)-C(76)-C(75)	119.0(2)
C(12)-C(11)-C(10)	115.3(2)	C(44)-C(45)-C(40)	120.0(3)	C(77)-C(76)-H(76)	120.5
C(12)-C(11)-P(2)	119.76(18)	C(44)-C(45)-H(45)	120.0	C(75)-C(76)-H(76)	120.5
C(10)-C(11)-P(2)	124.6(2)	C(40)-C(45)-H(45)	120.0	C(76)-C(77)-C(78)	120.0(2)
O(1)-C(12)-C(11)	123.0(2)	C(47)-C(46)-C(51)	120.3(2)	C(76)-C(77)-H(77)	120.0
O(1)-C(12)-C(7)	112.2(2)	C(47)-C(46)-N(2)	120.7(2)	C(78)-C(77)-H(77)	120.0
C(11)-C(12)-C(7)	124.8(2)	C(51)-C(46)-N(2)	119.0(2)	C(77)-C(78)-C(73)	123.1(2)
C(18)-C(13)-C(14)	119.8(2)	C(48)-C(47)-C(46)	118.8(3)	C(77)-C(78)-H(78)	118.5
C(18)-C(13)-P(1)	120.3(2)	C(48)-C(47)-C(52)	118.8(3)	C(73)-C(78)-H(78)	118.5
C(14)-C(13)-P(1)	119.88(19)	C(46)-C(47)-C(52)	122.4(2)	C(84)-C(79)-C(80)	114.7(2)
C(15)-C(14)-C(13)	120.1(3)	C(49)-C(48)-C(47)	121.9(3)	C(84)-C(79)-B(1)	125.3(2)
C(15)-C(14)-H(14)	119.9	C(49)-C(48)-H(48)	119.1	C(80)-C(79)-B(1)	120.0(2)
C(13)-C(14)-H(14)	119.9	C(47)-C(48)-H(48)	119.1	C(81)-C(80)-C(79)	123.4(2)
C(16)-C(15)-C(14)	119.9(3)	C(50)-C(49)-C(48)	118.3(3)	C(81)-C(80)-H(80)	118.3
C(16)-C(15)-H(15)	120.0	C(50)-C(49)-C(53)	120.9(3)	C(79)-C(80)-H(80)	118.3
C(14)-C(15)-H(15)	120.0	C(48)-C(49)-C(53)	120.9(3)	C(80)-C(81)-C(82)	119.7(3)
C(15)-C(16)-C(17)	120.2(2)	C(49)-C(50)-C(51)	122.5(3)	C(80)-C(81)-H(81)	120.1
C(15)-C(16)-H(16)	119.9	C(49)-C(50)-H(50)	118.8	C(82)-C(81)-H(81)	120.1
C(17)-C(16)-H(16)	119.9	C(51)-C(50)-H(50)	118.8	C(83)-C(82)-C(81)	118.9(2)
C(16)-C(17)-C(18)	120.4(3)	C(50)-C(51)-C(46)	118.3(3)	C(83)-C(82)-H(82)	120.6
C(16)-C(17)-H(17)	119.8	C(50)-C(51)-C(54)	119.2(2)	C(81)-C(82)-H(82)	120.6
C(18)-C(17)-H(17)	119.8	C(46)-C(51)-C(54)	122.5(2)	C(82)-C(83)-C(84)	120.6(3)
C(13)-C(18)-C(17)	119.5(3)	C(47)-C(52)-H(52A)	109.5	C(82)-C(83)-H(83)	119.7
C(13)-C(18)-H(18)	120.2	C(47)-C(52)-H(52B)	109.5	C(84)-C(83)-H(83)	119.7
C(17)-C(18)-H(18)	120.2	H(52A)-C(52)-H(52E	109.5	C(83)-C(84)-C(79)	122.7(2)
C(24)-C(19)-C(20)	119.6(2)	C(47)-C(52)-H(52C)	109.5	C(83)-C(84)-H(84)	118.6
C(24)-C(19)-P(1)	121.72(19)	H(52A)-C(52)-H(52C	109.5	C(79)-C(84)-H(84)	118.6
C(20)-C(19)-P(1)	118.69(18)	H(52B)-C(52)-H(52C	109.5	C(90)-C(85)-C(86)	114.9(2)
C(21)-C(20)-C(19)	120.3(2)	C(49)-C(53)-H(53A)	109.5	C(90)-C(85)-B(1)	125.4(2)
C(21)-C(20)-H(20)	119.8	C(49)-C(53)-H(53B)	109.5	C(86)-C(85)-B(1)	119.7(2)
C(19)-C(20)-H(20)	119.8	H(53A)-C(53)-H(53E	109.5	C(87)-C(86)-C(85)	122.7(3)
C(20)-C(21)-C(22)	119.8(3)	C(49)-C(53)-H(53C)	109.5	C(87)-C(86)-H(86)	118.6
C(20)-C(21)-H(21)	120.1	H(53A)-C(53)-H(53C	109.5	C(85)-C(86)-H(86)	118.6
C(22)-C(21)-H(21)	120.1	H(53B)-C(53)-H(53C	109.5	C(88)-C(87)-C(86)	120.7(3)

C(23)-C(22)-C(21)	120.1(2)	C(51)-C(54)-H(54A)	109.5	C(88)-C(87)-H(87)	119.7
C(23)-C(22)-H(22)	119.9	C(51)-C(54)-H(54B)	109.5	C(86)-C(87)-H(87)	119.7
C(21)-C(22)-H(22)	119.9	H(54A)-C(54)-H(54E	109.5	C(87)-C(88)-C(89)	118.5(2)
C(22)-C(23)-C(24)	120.7(2)	C(51)-C(54)-H(54C)	109.5	C(87)-C(88)-H(88)	120.7
C(22)-C(23)-H(23)	119.7	H(54A)-C(54)-H(54C	109.5	C(89)-C(88)-H(88)	120.7
C(24)-C(23)-H(23)	119.7	H(54B)-C(54)-H(54C	109.5	C(88)-C(89)-C(90)	120.3(3)
C(23)-C(24)-C(19)	119.3(2)	C(55)-O(2)-Zn(1)	137.6(7)	C(88)-C(89)-H(89)	119.8
C(23)-C(24)-H(24)	120.3	O(2)-C(55)-C(60)	125.8(9)	C(90)-C(89)-H(89)	119.8
C(19)-C(24)-H(24)	120.3	O(2)-C(55)-C(56)	121.4(10)	C(89)-C(90)-C(85)	122.8(2)
C(30)-C(25)-C(26)	120.6(2)	C(60)-C(55)-C(56)	112.8(9)	C(89)-C(90)-H(90)	118.6
C(30)-C(25)-N(1)	120.2(2)	F(5)-C(56)-C(57)	122.8(7)	C(85)-C(90)-H(90)	118.6
C(26)-C(25)-N(1)	119.1(2)	F(5)-C(56)-C(55)	115.2(7)	Cl(2)-C(91)-Cl(1)	111.35(18)
C(27)-C(26)-C(25)	118.4(3)	C(57)-C(56)-C(55)	121.9(9)	Cl(2)-C(91)-Cl(3)	110.42(18)
C(27)-C(26)-C(31)	120.2(2)	C(58)-C(57)-F(4)	119.7(7)	Cl(1)-C(91)-Cl(3)	110.2(2)
C(25)-C(26)-C(31)	121.4(2)	C(58)-C(57)-C(56)	122.5(7)	Cl(2)-C(91)-H(91)	108.3
C(28)-C(27)-C(26)	122.4(3)	F(4)-C(57)-C(56)	117.8(8)	Cl(1)-C(91)-H(91)	108.3
C(28)-C(27)-H(27)	118.8	C(57)-C(58)-F(3)	122.2(7)	Cl(3)-C(91)-H(91)	108.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z

Table A.70: Anisotropic displacement parameters ($Å^2$x 10^3)for **15b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	26(1)	55(1)	28(1)	8(1)	3(1)	6(1)
P(1)	29(1)	22(1)	27(1)	-3(1)	2(1)	6(1)
O(1)	26(1)	38(1)	24(1)	-4(1)	3(1)	6(1)
N(1)	29(1)	25(1)	27(1)	-1(1)	0(1)	6(1)
C(1)	28(1)	25(1)	33(1)	-2(1)	7(1)	5(1)
B(1)	25(1)	26(1)	29(1)	-2(1)	6(1)	2(1)
P(2)	29(1)	33(1)	27(1)	-2(1)	2(1)	6(1)
N(2)	28(1)	39(1)	28(1)	-4(1)	1(1)	11(1)
C(2)	30(1)	26(1)	34(1)	-3(1)	4(1)	5(1)
C(3)	31(1)	27(1)	45(1)	-7(1)	5(1)	1(1)
C(4)	33(1)	31(1)	57(2)	-6(1)	16(1)	-2(1)
C(5)	44(1)	26(1)	45(1)	-4(1)	22(1)	-2(1)
C(6)	39(1)	19(1)	33(1)	-2(1)	12(1)	2(1)
C(7)	41(1)	21(1)	31(1)	-1(1)	11(1)	3(1)
C(8)	56(2)	26(1)	29(1)	0(1)	16(1)	-1(1)
C(9)	63(2)	33(1)	24(1)	0(1)	6(1)	-2(1)
C(10)	45(1)	30(1)	26(1)	-2(1)	1(1)	0(1)
C(11)	36(1)	28(1)	27(1)	-1(1)	3(1)	4(1)
C(12)	37(1)	27(1)	22(1)	-2(1)	4(1)	5(1)
C(13)	41(1)	25(1)	28(1)	0(1)	3(1)	7(1)

C(14)	40(1)	31(1)	46(2)	3(1)	9(1)	5(1)
C(15)	55(2)	31(1)	51(2)	8(1)	12(1)	4(1)
C(16)	71(2)	28(1)	42(2)	7(1)	11(1)	15(1)
C(17)	65(2)	39(2)	39(2)	6(1)	19(1)	25(1)
C(18)	55(2)	33(1)	31(1)	6(1)	14(1)	16(1)
C(19)	31(1)	27(1)	29(1)	-3(1)	1(1)	-1(1)
C(20)	31(1)	28(1)	41(1)	-3(1)	-4(1)	-1(1)
C(21)	32(1)	42(1)	45(2)	7(1)	-5(1)	-1(1)
C(22)	35(1)	58(2)	32(1)	0(1)	-2(1)	-13(1)
C(23)	43(2)	45(2)	35(1)	-15(1)	11(1)	-18(1)
C(24)	40(1)	27(1)	36(1)	-6(1)	13(1)	-4(1)
C(25)	28(1)	23(1)	33(1)	1(1)	-4(1)	2(1)
C(26)	30(1)	25(1)	51(2)	-4(1)	-4(1)	1(1)
C(27)	50(2)	21(1)	75(2)	5(1)	-6(2)	1(1)
C(28)	69(2)	37(2)	58(2)	18(1)	-11(2)	-5(1)
C(29)	58(2)	43(2)	37(1)	11(1)	-4(1)	-7(1)
C(30)	38(1)	30(1)	33(1)	3(1)	-3(1)	-2(1)
C(31)	44(2)	31(1)	63(2)	-17(1)	-1(1)	6(1)
C(32)	129(4)	53(2)	83(3)	38(2)	-17(3)	-8(2)
C(33)	63(2)	34(1)	28(1)	-2(1)	10(1)	-2(1)
C(34)	31(1)	41(1)	33(1)	-8(1)	1(1)	7(1)
C(35)	41(2)	47(2)	41(2)	-3(1)	-7(1)	6(1)
C(36)	43(2)	69(2)	44(2)	-5(2)	-8(1)	15(2)
C(37)	31(1)	75(2)	53(2)	-22(2)	-4(1)	10(1)
C(38)	32(1)	62(2)	65(2)	-21(2)	4(1)	-2(1)
C(39)	35(1)	45(2)	50(2)	-11(1)	6(1)	4(1)
C(40)	29(1)	37(1)	39(1)	4(1)	3(1)	7(1)
C(41)	32(1)	37(1)	43(1)	-1(1)	2(1)	4(1)
C(42)	43(2)	38(2)	65(2)	1(1)	2(1)	8(1)
C(43)	55(2)	45(2)	86(3)	24(2)	12(2)	11(2)
C(44)	80(3)	70(2)	78(3)	38(2)	37(2)	23(2)
C(45)	67(2)	58(2)	59(2)	20(2)	29(2)	24(2)
C(46)	29(1)	37(1)	28(1)	-8(1)	-2(1)	9(1)
C(47)	33(1)	41(1)	33(1)	-7(1)	-2(1)	7(1)
C(48)	44(2)	40(2)	51(2)	-8(1)	-4(1)	8(1)
C(49)	38(2)	47(2)	55(2)	-20(1)	-6(1)	14(1)
C(50)	28(1)	56(2)	45(2)	-20(1)	0(1)	10(1)
C(51)	28(1)	49(2)	32(1)	-14(1)	-2(1)	7(1)
C(52)	43(2)	41(2)	47(2)	2(1)	7(1)	5(1)
C(53)	53(2)	52(2)	109(3)	-21(2)	4(2)	21(2)
C(54)	30(1)	57(2)	47(2)	-10(1)	7(1)	1(1)
O(2)	36(4)	98(5)	36(3)	-8(3)	10(2)	5(3)
C(55)	45(4)	95(6)	37(4)	-7(4)	0(3)	15(4)

C(56)	45(3)	108(7)	44(4)	-6(5)	14(3)	-4(4)
C(57)	57(4)	144(7)	48(3)	-4(4)	20(3)	3(4)
C(58)	73(4)	106(6)	77(5)	6(4)	32(4)	-13(4)
C(59)	83(5)	88(5)	94(5)	5(4)	13(4)	-14(4)
C(60)	43(3)	106(6)	64(4)	-22(4)	14(3)	-6(3)
F(1)	64(2)	107(3)	114(3)	-40(3)	25(2)	-5(2)
F(2)	110(4)	105(4)	205(7)	19(4)	54(4)	-18(4)
F(3)	106(4)	176(6)	124(4)	40(4)	59(3)	-22(4)
F(4)	84(3)	174(5)	82(3)	4(3)	54(2)	16(3)
F(5)	50(2)	104(3)	64(2)	-17(2)	21(2)	32(2)
C(61)	29(7)	48(6)	32(7)	4(5)	5(5)	-2(5)
C(62)	23(3)	51(4)	31(3)	-4(3)	9(3)	0(3)
C(63)	240(30)	85(13)	230(30)	-10(15)	-110(20)	-85(16)
C(64)	61(6)	63(6)	62(7)	-18(5)	46(5)	-19(5)
C(65)	108(11)	55(7)	71(9)	2(5)	65(8)	-10(6)
C(66)	51(9)	42(6)	42(7)	14(4)	21(7)	4(5)
C(92)	244(13)	176(19)	99(11)	-19(11)	26(8)	-111(15)
Cl(4)	161(6)	442(16)	195(6)	65(8)	33(5)	-32(8)
Cl(5)	188(5)	181(6)	150(5)	34(4)	-12(4)	-29(5)
Cl(6)	527(16)	166(6)	223(7)	-33(6)	248(9)	-131(8)
C(67)	27(1)	31(1)	28(1)	-1(1)	10(1)	1(1)
C(68)	35(1)	30(1)	35(1)	-1(1)	5(1)	-1(1)
C(69)	38(1)	36(1)	37(1)	6(1)	5(1)	5(1)
C(70)	38(1)	51(2)	31(1)	1(1)	3(1)	1(1)
C(71)	45(2)	40(1)	34(1)	-9(1)	6(1)	-4(1)
C(72)	37(1)	30(1)	32(1)	-2(1)	9(1)	2(1)
C(73)	28(1)	19(1)	33(1)	-2(1)	8(1)	-1(1)
C(74)	30(1)	28(1)	34(1)	1(1)	7(1)	1(1)
C(75)	48(2)	31(1)	31(1)	2(1)	12(1)	2(1)
C(76)	46(2)	28(1)	43(1)	3(1)	24(1)	5(1)
C(77)	31(1)	34(1)	50(2)	7(1)	16(1)	7(1)
C(78)	28(1)	32(1)	35(1)	0(1)	7(1)	2(1)
C(79)	30(1)	30(1)	24(1)	-1(1)	6(1)	3(1)
C(80)	36(1)	33(1)	38(1)	2(1)	9(1)	3(1)
C(81)	51(2)	32(1)	45(2)	6(1)	10(1)	0(1)
C(82)	56(2)	34(1)	42(2)	5(1)	7(1)	15(1)
C(83)	37(1)	47(2)	36(1)	1(1)	5(1)	14(1)
C(84)	31(1)	35(1)	31(1)	0(1)	5(1)	4(1)
C(85)	23(1)	27(1)	35(1)	3(1)	5(1)	4(1)
C(86)	35(1)	36(1)	39(1)	5(1)	11(1)	5(1)
C(87)	30(1)	44(2)	60(2)	18(1)	17(1)	5(1)
C(88)	26(1)	36(1)	69(2)	15(1)	1(1)	-2(1)
C(89)	33(1)	33(1)	54(2)	0(1)	-3(1)	0(1)

C(90)	29(1)	29(1)	41(1)	0(1)	5(1)	2(1)
C(91)	38(2)	73(2)	52(2)	-18(2)	-5(1)	11(2)
Cl(1)	59(1)	83(1)	62(1)	-25(1)	8(1)	13(1)
Cl(2)	61(1)	93(1)	54(1)	-18(1)	-4(1)	30(1)
Cl(3)	96(1)	78(1)	91(1)	-11(1)	4(1)	6(1)

Table A.71: Crystal data and structure refinement for $\mathbf{L_2^{Mipp}}$.

Empirical formula	$C_{54}H_{48}N_2OP_2 \cdot 0.2\ CH_2Cl_2$	
Formula weight	819.87	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.5434(11) Å	α= 62.3130(10)°.
	b = 14.8956(15) Å	β= 86.1340(10)°.
	c = 15.1659(15) Å	γ = 78.1150(10)°.
Volume	2258.4(4) $Å^3$	
Z	2	
Density (calculated)	1.206 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	865	
Crystal size	0.58 x 0.22 x 0.13 mm^3	
Theta range for data collection	2.60 to 25.03°.	
Index ranges	-13<=h<=13, -17<=k<=17, -18<=l<=18	
Reflections collected	26448	
Independent reflections	7960 [R(int) = 0.0611]	
Completeness to theta = 25.03°	99.60%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6810	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7960 / 1 / 563	
Goodness-of-fit on F^2	1.11	
Final R indices [I>2sigma(I)]	R1 = 0.0646, wR2 = 0.1472	
R indices (all data)	R1 = 0.1432, wR2 = 0.1827	
Largest diff. peak and hole	0.690 and -0.308 e.$Å^{-3}$	

Table A.72: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_2^{Mipp}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
C(1)	-727(3)	6079(3)	5633(3)	30(1)	C(27)	-4135(7)	10242(6)	1334(5)	100(2)
N(1)	-1498(3)	8712(3)	2904(3)	42(1)	C(28)	-5041(6)	9972(6)	2004(7)	103(2)
O(1)	-75(2)	6249(2)	6258(2)	30(1)	C(29)	-4762(5)	9316(5)	2980(5)	80(2)
P(1)	-897(1)	8116(1)	3966(1)	32(1)	C(30)	-3602(5)	8903(4)	3283(4)	56(1)
C(2)	-1134(4)	6796(3)	4681(3)	32(1)	C(31)	-1967(6)	10207(5)	880(4)	74(2)
N(2)	2184(3)	6728(3)	7126(3)	44(1)	C(32)	-1820(7)	9604(5)	286(5)	118(3)
P(2)	1435(1)	6143(1)	8011(1)	35(1)	C(33)	-2155(7)	11352(5)	196(5)	104(2)
C(3)	-1759(4)	6437(3)	4193(3)	38(1)	C(34)	240(4)	7069(3)	8115(3)	32(1)

C(4)	-1972(4)	5434(3)	4644(3)	42(1)	C(35)	472(4)	8020(3)	7920(3)	43(1)
C(5)	-1567(4)	4750(3)	5596(3)	40(1)	C(36)	-363(5)	8715(4)	8101(4)	51(1)
C(6)	-932(4)	5071(3)	6105(3)	31(1)	C(37)	-1435(5)	8477(4)	8463(3)	54(1)
C(7)	-373(4)	4587(3)	7077(3)	33(1)	C(38)	-1684(4)	7538(4)	8644(3)	49(1)
C(8)	-246(4)	3609(3)	7894(3)	41(1)	C(39)	-846(4)	6838(3)	8475(3)	41(1)
C(9)	360(4)	3420(3)	8725(3)	47(1)	C(40)	2240(4)	5497(3)	9200(3)	40(1)
C(10)	842(4)	4181(3)	8768(3)	42(1)	C(41)	3230(4)	4723(4)	9365(4)	59(1)
C(11)	752(4)	5173(3)	7965(3)	32(1)	C(42)	3913(5)	4279(4)	10233(4)	69(2)
C(12)	137(4)	5329(3)	7141(3)	30(1)	C(43)	3612(5)	4602(5)	10949(4)	65(2)
C(13)	671(4)	8015(3)	3773(3)	30(1)	C(44)	2646(5)	5353(4)	10793(4)	58(1)
C(14)	1070(4)	8321(3)	2804(3)	39(1)	C(45)	1962(4)	5807(4)	9928(3)	44(1)
C(15)	2255(5)	8190(4)	2642(4)	49(1)	C(46)	3318(5)	6370(5)	6921(4)	62(2)
C(16)	3069(4)	7756(4)	3420(4)	50(1)	C(47)	4171(5)	7019(6)	6617(4)	73(2)
C(17)	2692(4)	7471(3)	4379(3)	43(1)	C(48)	5282(6)	6711(7)	6308(5)	87(2)
C(18)	1499(4)	7595(3)	4558(3)	35(1)	C(49)	5545(7)	5773(11)	6318(7)	143(4)
C(19)	-1315(4)	8737(3)	4748(3)	32(1)	C(50)	4732(8)	5109(8)	6590(6)	128(3)
C(20)	-1925(4)	8332(3)	5615(3)	40(1)	C(51)	3626(6)	5422(6)	6883(5)	88(2)
C(21)	-2306(4)	8917(4)	6111(3)	50(1)	C(52)	3879(5)	8016(5)	6657(4)	77(2)
C(22)	-2072(4)	9885(4)	5752(4)	51(1)	C(53)	4107(6)	7869(5)	7660(4)	79(2)
C(23)	-1474(4)	10289(4)	4889(4)	55(1)	C(54)	4517(6)	8841(6)	5885(5)	127(3)
C(24)	-1095(4)	9713(3)	4390(3)	43(1)	C(1S)	3350(40)	2580(30)	8412(14)	110(15)
C(25)	-2678(4)	9137(4)	2630(3)	47(1)	Cl(1)	4280(19)	3190(20)	7662(19)	290(13)
C(26)	-2954(5)	9861(5)	1625(4)	66(2)	Cl(2)	3809(17)	2077(12)	9524(14)	209(8)

Table A.73: Bond lengths [Å] for $\mathbf{L_2^{Mipp}}$.

C(1)-C(2)	1.378(5)	C(17)-H(17)	0.9500	C(37)-H(37)	0.9500
C(1)-O(1)	1.388(4)	C(18)-H(18)	0.9500	C(38)-C(39)	1.374(6)
C(1)-C(6)	1.396(5)	C(19)-C(24)	1.369(5)	C(38)-H(38)	0.9500
N(1)-C(25)	1.380(6)	C(19)-C(20)	1.378(5)	C(39)-H(39)	0.9500
N(1)-P(1)	1.560(4)	C(20)-C(21)	1.388(6)	C(40)-C(45)	1.380(6)
O(1)-C(12)	1.390(4)	C(20)-H(20)	0.9500	C(40)-C(41)	1.387(6)
P(1)-C(13)	1.801(4)	C(21)-C(22)	1.364(6)	C(41)-C(42)	1.381(7)
P(1)-C(19)	1.804(4)	C(21)-H(21)	0.9500	C(41)-H(41)	0.9500
P(1)-C(2)	1.821(4)	C(22)-C(23)	1.367(7)	C(42)-C(43)	1.378(7)
C(2)-C(3)	1.397(5)	C(22)-H(22)	0.9500	C(42)-H(42)	0.9500
N(2)-C(46)	1.380(6)	C(23)-C(24)	1.380(6)	C(43)-C(44)	1.352(7)
N(2)-P(2)	1.542(3)	C(23)-H(23)	0.9500	C(43)-H(43)	0.9500
P(2)-C(34)	1.794(4)	C(24)-H(24)	0.9500	C(44)-C(45)	1.378(6)
P(2)-C(11)	1.812(4)	C(25)-C(30)	1.389(7)	C(44)-H(44)	0.9500
P(2)-C(40)	1.813(5)	C(25)-C(26)	1.409(7)	C(45)-H(45)	0.9500
C(3)-C(4)	1.393(6)	C(26)-C(27)	1.380(8)	C(46)-C(51)	1.411(8)
C(3)-H(3)	0.9500	C(26)-C(31)	1.539(8)	C(46)-C(47)	1.426(8)
C(4)-C(5)	1.367(6)	C(27)-C(28)	1.391(9)	C(47)-C(48)	1.397(8)

C(4)-H(4)	0.9500	C(27)-H(27)	0.9500	C(47)-C(52)	1.482(8)
C(5)-C(6)	1.387(6)	C(28)-C(29)	1.356(9)	C(48)-C(49)	1.360(12)
C(5)-H(5)	0.9500	C(28)-H(28)	0.9500	C(48)-H(48)	0.9500
C(6)-C(7)	1.434(6)	C(29)-C(30)	1.366(7)	C(49)-C(50)	1.407(12)
C(7)-C(8)	1.392(6)	C(29)-H(29)	0.9500	C(49)-H(49)	0.9500
C(7)-C(12)	1.399(5)	C(30)-H(30)	0.9500	C(50)-C(51)	1.384(9)
C(8)-C(9)	1.366(6)	C(31)-C(33)	1.505(8)	C(50)-H(50)	0.9500
C(8)-H(8)	0.9500	C(31)-C(32)	1.523(8)	C(51)-H(51)	0.9500
C(9)-C(10)	1.389(6)	C(31)-H(31)	1.0000	C(52)-C(53)	1.467(8)
C(9)-H(9)	0.9500	C(32)-H(32A)	0.9800	C(52)-C(54)	1.531(8)
C(10)-C(11)	1.400(6)	C(32)-H(32B)	0.9800	C(52)-H(52)	1.0000
C(10)-H(10)	0.9500	C(32)-H(32C)	0.9800	C(53)-H(53A)	0.9800
C(11)-C(12)	1.378(6)	C(33)-H(33A)	0.9800	C(53)-H(53B)	0.9800
C(13)-C(18)	1.391(6)	C(33)-H(33B)	0.9800	C(53)-H(53C)	0.9800
C(13)-C(14)	1.398(5)	C(33)-H(33C)	0.9800	C(54)-H(54A)	0.9800
C(14)-C(15)	1.363(6)	C(34)-C(39)	1.378(6)	C(54)-H(54B)	0.9800
C(14)-H(14)	0.9500	C(34)-C(35)	1.386(6)	C(54)-H(54C)	0.9800
C(15)-C(16)	1.371(7)	C(35)-C(36)	1.376(6)	C(1S)-Cl(2)	1.57(2)
C(15)-H(15)	0.9500	C(35)-H(35)	0.9500	C(1S)-Cl(1)	1.59(2)
C(16)-C(17)	1.380(6)	C(36)-C(37)	1.366(7)	C(1S)-H(1S1)	0.9900
C(16)-H(16)	0.9500	C(36)-H(36)	0.9500	C(1S)-H(1S2)	0.9900
C(17)-C(18)	1.378(6)	C(37)-C(38)	1.383(7)		

Table A.74: Bond angles [°] for $\mathbf{L_2^{Mipp}}$

C(2)-C(1)-O(1)	125.6(3)	C(17)-C(18)-H(18)	119.9	C(38)-C(37)-H(37)	120.0
C(2)-C(1)-C(6)	123.8(4)	C(13)-C(18)-H(18)	119.9	C(39)-C(38)-C(37)	120.0(5)
O(1)-C(1)-C(6)	110.5(3)	C(24)-C(19)-C(20)	119.3(4)	C(39)-C(38)-H(38)	120.0
C(25)-N(1)-P(1)	129.1(3)	C(24)-C(19)-P(1)	116.1(3)	C(37)-C(38)-H(38)	120.0
C(1)-O(1)-C(12)	106.4(3)	C(20)-C(19)-P(1)	124.2(3)	C(38)-C(39)-C(34)	120.4(4)
N(1)-P(1)-C(13)	105.63(19)	C(19)-C(20)-C(21)	119.7(4)	C(38)-C(39)-H(39)	119.8
N(1)-P(1)-C(19)	114.85(19)	C(19)-C(20)-H(20)	120.2	C(34)-C(39)-H(39)	119.8
C(13)-P(1)-C(19)	108.89(18)	C(21)-C(20)-H(20)	120.2	C(45)-C(40)-C(41)	117.9(4)
N(1)-P(1)-C(2)	114.38(19)	C(22)-C(21)-C(20)	120.5(4)	C(45)-C(40)-P(2)	121.9(4)
C(13)-P(1)-C(2)	106.14(18)	C(22)-C(21)-H(21)	119.7	C(41)-C(40)-P(2)	119.9(3)
C(19)-P(1)-C(2)	106.53(18)	C(20)-C(21)-H(21)	119.7	C(42)-C(41)-C(40)	120.9(5)
C(1)-C(2)-C(3)	115.1(4)	C(21)-C(22)-C(23)	119.8(4)	C(42)-C(41)-H(41)	119.6
C(1)-C(2)-P(1)	128.3(3)	C(21)-C(22)-H(22)	120.1	C(40)-C(41)-H(41)	119.6
C(3)-C(2)-P(1)	116.5(3)	C(23)-C(22)-H(22)	120.1	C(43)-C(42)-C(41)	120.0(5)
C(46)-N(2)-P(2)	127.5(4)	C(22)-C(23)-C(24)	120.0(4)	C(43)-C(42)-H(42)	120.0
N(2)-P(2)-C(34)	108.30(19)	C(22)-C(23)-H(23)	120.0	C(41)-C(42)-H(42)	120.0
N(2)-P(2)-C(11)	117.81(19)	C(24)-C(23)-H(23)	120.0	C(44)-C(43)-C(42)	119.4(5)
C(34)-P(2)-C(11)	105.77(19)	C(19)-C(24)-C(23)	120.7(4)	C(44)-C(43)-H(43)	120.3
N(2)-P(2)-C(40)	113.3(2)	C(19)-C(24)-H(24)	119.7	C(42)-C(43)-H(43)	120.3

C(34)-P(2)-C(40)	105.37(19)	C(23)-C(24)-H(24)	119.7	C(43)-C(44)-C(45)	121.2(5)
C(11)-P(2)-C(40)	105.3(2)	N(1)-C(25)-C(30)	124.2(4)	C(43)-C(44)-H(44)	119.4
C(4)-C(3)-C(2)	122.4(4)	N(1)-C(25)-C(26)	117.5(4)	C(45)-C(44)-H(44)	119.4
C(4)-C(3)-H(3)	118.8	C(30)-C(25)-C(26)	118.3(5)	C(44)-C(45)-C(40)	120.6(5)
C(2)-C(3)-H(3)	118.8	C(27)-C(26)-C(25)	117.7(6)	C(44)-C(45)-H(45)	119.7
C(5)-C(4)-C(3)	120.8(4)	C(27)-C(26)-C(31)	121.4(5)	C(40)-C(45)-H(45)	119.7
C(5)-C(4)-H(4)	119.6	C(25)-C(26)-C(31)	120.8(5)	N(2)-C(46)-C(51)	121.6(5)
C(3)-C(4)-H(4)	119.6	C(26)-C(27)-C(28)	122.4(6)	N(2)-C(46)-C(47)	119.9(5)
C(4)-C(5)-C(6)	118.8(4)	C(26)-C(27)-H(27)	118.8	C(51)-C(46)-C(47)	118.0(6)
C(4)-C(5)-H(5)	120.6	C(28)-C(27)-H(27)	118.8	C(48)-C(47)-C(46)	120.6(7)
C(6)-C(5)-H(5)	120.6	C(29)-C(28)-C(27)	119.3(6)	C(48)-C(47)-C(52)	120.1(6)
C(5)-C(6)-C(1)	119.2(4)	C(29)-C(28)-H(28)	120.4	C(46)-C(47)-C(52)	119.3(5)
C(5)-C(6)-C(7)	134.5(4)	C(27)-C(28)-H(28)	120.4	C(49)-C(48)-C(47)	118.9(7)
C(1)-C(6)-C(7)	106.3(3)	C(28)-C(29)-C(30)	119.6(6)	C(49)-C(48)-H(48)	120.6
C(8)-C(7)-C(12)	118.4(4)	C(28)-C(29)-H(29)	120.2	C(47)-C(48)-H(48)	120.6
C(8)-C(7)-C(6)	135.0(4)	C(30)-C(29)-H(29)	120.2	C(48)-C(49)-C(50)	123.1(7)
C(12)-C(7)-C(6)	106.6(3)	C(29)-C(30)-C(25)	122.5(5)	C(48)-C(49)-H(49)	118.5
C(9)-C(8)-C(7)	118.6(4)	C(29)-C(30)-H(30)	118.7	C(50)-C(49)-H(49)	118.5
C(9)-C(8)-H(8)	120.7	C(25)-C(30)-H(30)	118.7	C(51)-C(50)-C(49)	117.9(8)
C(7)-C(8)-H(8)	120.7	C(33)-C(31)-C(32)	110.8(5)	C(51)-C(50)-H(50)	121.0
C(8)-C(9)-C(10)	121.4(4)	C(33)-C(31)-C(26)	114.9(5)	C(49)-C(50)-H(50)	121.0
C(8)-C(9)-H(9)	119.3	C(32)-C(31)-C(26)	108.1(5)	C(50)-C(51)-C(46)	121.5(7)
C(10)-C(9)-H(9)	119.3	C(33)-C(31)-H(31)	107.6	C(50)-C(51)-H(51)	119.3
C(9)-C(10)-C(11)	122.3(4)	C(32)-C(31)-H(31)	107.6	C(46)-C(51)-H(51)	119.3
C(9)-C(10)-H(10)	118.8	C(26)-C(31)-H(31)	107.6	C(53)-C(52)-C(47)	111.1(5)
C(11)-C(10)-H(10)	118.8	C(31)-C(32)-H(32A)	109.5	C(53)-C(52)-C(54)	110.3(6)
C(12)-C(11)-C(10)	114.4(4)	C(31)-C(32)-H(32B)	109.5	C(47)-C(52)-C(54)	113.5(6)
C(12)-C(11)-P(2)	123.7(3)	H(32A)-C(32)-H(32E	109.5	C(53)-C(52)-H(52)	107.2
C(10)-C(11)-P(2)	121.9(3)	C(31)-C(32)-H(32C)	109.5	C(47)-C(52)-H(52)	107.2
C(11)-C(12)-O(1)	125.0(3)	H(32A)-C(32)-H(32C	109.5	C(54)-C(52)-H(52)	107.2
C(11)-C(12)-C(7)	124.8(4)	H(32B)-C(32)-H(32C	109.5	C(52)-C(53)-H(53A)	109.5
O(1)-C(12)-C(7)	110.2(3)	C(31)-C(33)-H(33A)	109.5	C(52)-C(53)-H(53B)	109.5
C(18)-C(13)-C(14)	119.0(4)	C(31)-C(33)-H(33B)	109.5	H(53A)-C(53)-H(53B)	109.5
C(18)-C(13)-P(1)	122.4(3)	H(33A)-C(33)-H(33E	109.5	C(52)-C(53)-H(53C)	109.5
C(14)-C(13)-P(1)	118.6(3)	C(31)-C(33)-H(33C)	109.5	H(53A)-C(53)-H(53C)	109.5
C(15)-C(14)-C(13)	119.9(4)	H(33A)-C(33)-H(33C	109.5	H(53B)-C(53)-H(53C)	109.5
C(15)-C(14)-H(14)	120.1	H(33B)-C(33)-H(33C	109.5	C(52)-C(54)-H(54A)	109.5
C(13)-C(14)-H(14)	120.1	C(39)-C(34)-C(35)	119.1(4)	C(52)-C(54)-H(54B)	109.5
C(14)-C(15)-C(16)	121.0(4)	C(39)-C(34)-P(2)	122.9(3)	H(54A)-C(54)-H(54B)	109.5
C(14)-C(15)-H(15)	119.5	C(35)-C(34)-P(2)	117.7(3)	C(52)-C(54)-H(54C)	109.5
C(16)-C(15)-H(15)	119.5	C(36)-C(35)-C(34)	120.4(4)	H(54A)-C(54)-H(54C)	109.5
C(15)-C(16)-C(17)	120.0(4)	C(36)-C(35)-H(35)	119.8	H(54B)-C(54)-H(54C)	109.5
C(15)-C(16)-H(16)	120.0	C(34)-C(35)-H(35)	119.8	Cl(2)-C(1S)-Cl(1)	111(2)

C(17)-C(16)-H(16)	120.0	C(37)-C(36)-C(35)	120.1(5)	Cl(2)-C(1S)-H(1S1)	109.3
C(18)-C(17)-C(16)	119.9(4)	C(37)-C(36)-H(36)	119.9	Cl(1)-C(1S)-H(1S1)	109.3
C(18)-C(17)-H(17)	120.1	C(35)-C(36)-H(36)	119.9	Cl(2)-C(1S)-H(1S2)	109.3
C(16)-C(17)-H(17)	120.1	C(36)-C(37)-C(38)	120.0(5)	Cl(1)-C(1S)-H(1S2)	109.3
C(17)-C(18)-C(13)	120.3(4)	C(36)-C(37)-H(37)	120.0	H(1S1)-C(1S)-H(1S2)	108.0

Table A.75: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_2^{Mipp}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	35(2)	31(2)	28(2)	-17(2)	9(2)	-11(2)
N(1)	52(3)	41(2)	33(2)	-18(2)	0(2)	-6(2)
O(1)	43(2)	25(2)	27(2)	-13(1)	6(1)	-15(1)
P(1)	45(1)	29(1)	26(1)	-14(1)	5(1)	-11(1)
C(2)	38(3)	32(2)	32(2)	-20(2)	10(2)	-11(2)
N(2)	39(2)	53(2)	38(2)	-19(2)	12(2)	-14(2)
P(2)	42(1)	33(1)	32(1)	-16(1)	7(1)	-12(1)
C(3)	45(3)	40(3)	37(3)	-24(2)	4(2)	-10(2)
C(4)	49(3)	45(3)	51(3)	-36(3)	9(2)	-15(2)
C(5)	50(3)	35(3)	48(3)	-28(2)	13(2)	-16(2)
C(6)	38(2)	29(2)	35(2)	-22(2)	15(2)	-12(2)
C(7)	43(3)	25(2)	34(2)	-17(2)	12(2)	-10(2)
C(8)	62(3)	28(2)	40(3)	-20(2)	13(2)	-18(2)
C(9)	75(4)	24(2)	35(3)	-9(2)	11(2)	-15(2)
C(10)	55(3)	35(3)	32(2)	-13(2)	6(2)	-8(2)
C(11)	40(3)	28(2)	29(2)	-14(2)	7(2)	-7(2)
C(12)	39(3)	22(2)	29(2)	-12(2)	9(2)	-5(2)
C(13)	47(3)	19(2)	27(2)	-14(2)	7(2)	-11(2)
C(14)	57(3)	31(2)	32(2)	-16(2)	7(2)	-13(2)
C(15)	62(4)	53(3)	37(3)	-23(2)	21(3)	-23(3)
C(16)	45(3)	58(3)	60(3)	-38(3)	20(3)	-20(3)
C(17)	50(3)	44(3)	47(3)	-27(2)	5(2)	-17(2)
C(18)	50(3)	29(2)	30(2)	-16(2)	10(2)	-17(2)
C(19)	37(2)	30(2)	31(2)	-17(2)	1(2)	-5(2)
C(20)	48(3)	39(3)	35(3)	-19(2)	5(2)	-6(2)
C(21)	55(3)	59(3)	37(3)	-27(3)	8(2)	-5(3)
C(22)	56(3)	53(3)	58(3)	-41(3)	-1(3)	1(3)
C(23)	65(4)	47(3)	72(4)	-41(3)	6(3)	-14(3)
C(24)	49(3)	39(3)	50(3)	-27(2)	13(2)	-15(2)
C(25)	52(3)	54(3)	42(3)	-29(3)	-6(3)	-7(3)
C(26)	57(4)	85(4)	52(4)	-31(3)	-15(3)	1(3)
C(27)	78(5)	137(7)	68(4)	-40(5)	-23(4)	4(5)
C(28)	49(4)	143(7)	121(7)	-71(6)	-25(4)	4(4)
C(29)	56(4)	114(5)	87(5)	-60(4)	0(4)	-19(4)

C(30)	52(3)	67(4)	59(3)	-36(3)	3(3)	-14(3)
C(31)	82(4)	77(4)	36(3)	-11(3)	-8(3)	5(3)
C(32)	167(8)	75(5)	110(6)	-50(5)	54(5)	-17(5)
C(33)	156(7)	92(5)	65(4)	-34(4)	11(4)	-30(5)
C(34)	42(3)	30(2)	24(2)	-11(2)	1(2)	-11(2)
C(35)	52(3)	37(3)	41(3)	-18(2)	1(2)	-11(2)
C(36)	65(4)	40(3)	58(3)	-30(3)	-6(3)	-4(3)
C(37)	66(4)	53(3)	44(3)	-30(3)	-4(3)	8(3)
C(38)	45(3)	57(3)	37(3)	-19(2)	8(2)	-4(2)
C(39)	47(3)	41(3)	35(3)	-17(2)	7(2)	-12(2)
C(40)	39(3)	44(3)	40(3)	-21(2)	5(2)	-10(2)
C(41)	51(3)	73(4)	62(4)	-42(3)	-2(3)	-3(3)
C(42)	54(4)	68(4)	77(4)	-32(3)	-17(3)	5(3)
C(43)	66(4)	76(4)	52(3)	-27(3)	-16(3)	-12(3)
C(44)	62(4)	68(4)	45(3)	-29(3)	-5(3)	-11(3)
C(45)	51(3)	46(3)	36(3)	-19(2)	3(2)	-12(2)
C(46)	61(4)	86(4)	46(3)	-39(3)	7(3)	-11(3)
C(47)	50(4)	123(6)	45(3)	-37(4)	4(3)	-24(4)
C(48)	51(4)	157(7)	72(4)	-69(5)	16(3)	-21(4)
C(49)	51(5)	275(14)	137(8)	-134(9)	22(5)	-11(7)
C(50)	93(6)	194(10)	139(7)	-131(7)	9(6)	18(6)
C(51)	81(5)	119(6)	84(5)	-70(4)	8(4)	-1(4)
C(52)	63(4)	77(4)	73(4)	-13(4)	1(3)	-28(3)
C(53)	93(5)	65(4)	79(4)	-31(3)	-26(4)	-12(3)
C(54)	88(5)	166(8)	87(5)	-1(5)	-1(4)	-81(5)
C(1S)	190(40)	150(30)	34(16)	-29(18)	0(19)	-140(30)
Cl(1)	240(20)	470(40)	360(30)	-370(30)	100(20)	-90(20)
Cl(2)	260(20)	147(13)	226(18)	-108(13)	-48(15)	23(12)

Table A.76: Crystal data and structure refinement for $\mathbf{L_2^{Tol}}$.

Empirical formula	$C_{50}H_{40}N_2OP_2$	
Formula weight	746.78	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.0198(9) Å	α= 90°.
	b = 14.0045(7) Å	β= 109.6460(10)°.
	c = 16.7584(9) Å	γ = 90°.
Volume	3982.9(4) $Å^3$	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.150 mm^{-1}	
F(000)	1568	
Crystal size	0.46 x 0.25 x 0.21 mm^3	
Theta range for data collection	2.58 to 25.02°.	
Index ranges	-21<=h<=21, -16<=k<=16, -19<=l<=19	
Reflections collected	37535	
Independent reflections	7010 [R(int) = 0.0267]	
Completeness to theta = 25.02°	99.80%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6705	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7010 / 0 / 498	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1041	
R indices (all data)	R1 = 0.0465, wR2 = 0.1079	
Largest diff. peak and hole	0.533 and -0.585 $e.Å^{-3}$	

Table A.77: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_2^{Tol}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	1282(1)	5669(1)	4115(1)	27(1)	C(24)	1689(1)	6581(1)	2855(1)	36(1)
O(1)	2713(1)	4020(1)	4753(1)	30(1)	C(25)	578(1)	7158(1)	4584(1)	32(1)
N(1)	585(1)	6302(1)	4168(1)	33(1)	C(26)	1217(1)	7777(1)	4888(1)	44(1)
C(1)	2499(1)	4560(1)	5336(1)	28(1)	C(27)	1158(2)	8614(2)	5297(1)	57(1)
P(2)	3511(1)	2272(1)	3882(1)	36(1)	C(28)	460(2)	8860(2)	5412(1)	59(1)
C(2)	1886(1)	5217(1)	5149(1)	27(1)	C(29)	-177(1)	8260(2)	5104(1)	52(1)
N(2)	4203(1)	1644(1)	3788(1)	43(1)	C(30)	-137(1)	7414(1)	4693(1)	38(1)
C(3)	1750(1)	5610(1)	5854(1)	34(1)	C(31)	-833(1)	6765(2)	4363(2)	56(1)
C(4)	2211(1)	5394(1)	6683(1)	38(1)	C(32)	2719(1)	1459(1)	3818(1)	40(1)

C(5)	2846(1)	4794(1)	6845(1)	37(1)	C(33)	1943(1)	1763(2)	3573(1)	52(1)
C(6)	2990(1)	4368(1)	6161(1)	32(1)	C(34)	1346(2)	1124(2)	3525(2)	64(1)
C(7)	3567(1)	3700(1)	6088(1)	38(1)	C(35)	1528(2)	175(2)	3733(2)	66(1)
C(8)	4215(1)	3264(2)	6679(1)	51(1)	C(36)	2299(2)	-122(2)	3993(2)	65(1)
C(9)	4646(1)	2626(2)	6389(1)	60(1)	C(37)	2895(1)	508(2)	4032(1)	51(1)
C(10)	4427(1)	2404(2)	5536(1)	52(1)	C(38)	3122(1)	3169(1)	3074(1)	33(1)
C(11)	3773(1)	2823(1)	4921(1)	39(1)	C(39)	2723(1)	2847(1)	2257(1)	42(1)
C(12)	3367(1)	3490(1)	5230(1)	34(1)	C(40)	2513(1)	3477(2)	1586(1)	51(1)
C(13)	830(1)	4681(1)	3443(1)	30(1)	C(41)	2696(1)	4425(2)	1724(1)	52(1)
C(14)	1105(1)	4321(1)	2828(1)	39(1)	C(42)	3090(1)	4758(2)	2528(1)	48(1)
C(15)	704(1)	3586(2)	2307(1)	45(1)	C(43)	3304(1)	4129(1)	3208(1)	40(1)
C(16)	51(1)	3186(1)	2419(1)	45(1)	C(44)	4949(1)	1984(2)	3817(1)	43(1)
C(17)	-213(1)	3526(2)	3045(1)	56(1)	C(45)	5148(1)	2933(2)	3788(1)	51(1)
C(18)	163(1)	4282(2)	3545(1)	48(1)	C(46)	5883(1)	3214(2)	3771(1)	64(1)
C(19)	1970(1)	6231(1)	3680(1)	29(1)	C(47)	6440(1)	2544(3)	3802(2)	74(1)
C(20)	2741(1)	6441(1)	4180(1)	37(1)	C(48)	6259(1)	1595(2)	3845(2)	70(1)
C(21)	3213(1)	7000(2)	3865(1)	45(1)	C(49)	5524(1)	1288(2)	3846(1)	57(1)
C(22)	2924(1)	7349(1)	3048(1)	45(1)	C(50)	5324(2)	255(2)	3854(2)	81(1)
C(23)	2167(1)	7127(1)	2541(1)	42(1)					

Table A.78: Bond lengths [Å] for $\mathbf{L_2^{Tol}}$.

P(1)-N(1)	1.5638(14)	C(15)-C(16)	1.370(3)	C(33)-C(34)	1.381(3)
P(1)-C(13)	1.7965(16)	C(15)-H(15)	0.9500	C(33)-H(33)	0.9500
P(1)-C(19)	1.8143(17)	C(16)-C(17)	1.375(3)	C(34)-C(35)	1.385(4)
P(1)-C(2)	1.8223(16)	C(16)-H(16)	0.9500	C(34)-H(34)	0.9500
O(1)-C(1)	1.3886(19)	C(17)-C(18)	1.378(3)	C(35)-C(36)	1.374(4)
O(1)-C(12)	1.3951(19)	C(17)-H(17)	0.9500	C(35)-H(35)	0.9500
N(1)-C(25)	1.390(2)	C(18)-H(18)	0.9500	C(36)-C(37)	1.373(3)
C(1)-C(2)	1.390(2)	C(19)-C(24)	1.391(2)	C(36)-H(36)	0.9500
C(1)-C(6)	1.394(2)	C(19)-C(20)	1.392(2)	C(37)-H(37)	0.9500
P(2)-N(2)	1.5758(15)	C(20)-C(21)	1.385(3)	C(38)-C(43)	1.384(3)
P(2)-C(32)	1.801(2)	C(20)-H(20)	0.9500	C(38)-C(39)	1.391(3)
P(2)-C(38)	1.8063(17)	C(21)-C(22)	1.379(3)	C(39)-C(40)	1.378(3)
P(2)-C(11)	1.8169(19)	C(21)-H(21)	0.9500	C(39)-H(39)	0.9500
C(2)-C(3)	1.397(2)	C(22)-C(23)	1.377(3)	C(40)-C(41)	1.369(3)
N(2)-C(44)	1.411(3)	C(22)-H(22)	0.9500	C(40)-H(40)	0.9500
C(3)-C(4)	1.391(3)	C(23)-C(24)	1.382(3)	C(41)-C(42)	1.377(3)
C(3)-H(3)	0.9500	C(23)-H(23)	0.9500	C(41)-H(41)	0.9500
C(4)-C(5)	1.371(3)	C(24)-H(24)	0.9500	C(42)-C(43)	1.388(3)
C(4)-H(4)	0.9500	C(25)-C(26)	1.393(3)	C(42)-H(42)	0.9500
C(5)-C(6)	1.393(2)	C(25)-C(30)	1.408(2)	C(43)-H(43)	0.9500
C(5)-H(5)	0.9500	C(26)-C(27)	1.381(3)	C(44)-C(45)	1.382(3)
C(6)-C(7)	1.433(3)	C(26)-H(26)	0.9500	C(44)-C(49)	1.412(3)

C(7)-C(12)	1.391(2)	C(27)-C(28)	1.379(3)	C(45)-C(46)	1.391(3)
C(7)-C(8)	1.393(3)	C(27)-H(27)	0.9500	C(45)-H(45)	0.9500
C(8)-C(9)	1.374(3)	C(28)-C(29)	1.376(3)	C(46)-C(47)	1.362(4)
C(8)-H(8)	0.9500	C(28)-H(28)	0.9500	C(46)-H(46)	0.9500
C(9)-C(10)	1.385(3)	C(29)-C(30)	1.385(3)	C(47)-C(48)	1.375(4)
C(9)-H(9)	0.9500	C(29)-H(29)	0.9500	C(47)-H(47)	0.9500
C(10)-C(11)	1.406(3)	C(30)-C(31)	1.495(3)	C(48)-C(49)	1.393(4)
C(10)-H(10)	0.9500	C(31)-H(31A)	0.9800	C(48)-H(48)	0.9500
C(11)-C(12)	1.389(2)	C(31)-H(31B)	0.9800	C(49)-C(50)	1.492(4)
C(13)-C(14)	1.381(2)	C(31)-H(31C)	0.9800	C(50)-H(50A)	0.9800
C(13)-C(18)	1.386(3)	C(32)-C(33)	1.384(3)	C(50)-H(50B)	0.9800
C(14)-C(15)	1.386(3)	C(32)-C(37)	1.389(3)	C(50)-H(50C)	0.9800
C(14)-H(14)	0.9500				

Table A.79: Bond angles [°] for $\mathbf{L_2^{Tol}}$

N(1)-P(1)-C(13)	105.52(8)	C(16)-C(15)-C(14)	120.50(18)	C(34)-C(33)-C(32)	120.5(2)
N(1)-P(1)-C(19)	116.52(8)	C(16)-C(15)-H(15)	119.7	C(34)-C(33)-H(33)	119.8
C(13)-P(1)-C(19)	108.07(8)	C(14)-C(15)-H(15)	119.7	C(32)-C(33)-H(33)	119.8
N(1)-P(1)-C(2)	112.14(8)	C(15)-C(16)-C(17)	119.70(18)	C(33)-C(34)-C(35)	119.6(2)
C(13)-P(1)-C(2)	109.21(7)	C(15)-C(16)-H(16)	120.1	C(33)-C(34)-H(34)	120.2
C(19)-P(1)-C(2)	105.23(7)	C(17)-C(16)-H(16)	120.1	C(35)-C(34)-H(34)	120.2
C(1)-O(1)-C(12)	105.53(12)	C(16)-C(17)-C(18)	120.31(19)	C(36)-C(35)-C(34)	119.9(2)
C(25)-N(1)-P(1)	131.34(12)	C(16)-C(17)-H(17)	119.8	C(36)-C(35)-H(35)	120.1
O(1)-C(1)-C(2)	126.13(14)	C(18)-C(17)-H(17)	119.8	C(34)-C(35)-H(35)	120.1
O(1)-C(1)-C(6)	111.02(14)	C(17)-C(18)-C(13)	120.25(18)	C(37)-C(36)-C(35)	120.8(2)
C(2)-C(1)-C(6)	122.85(15)	C(17)-C(18)-H(18)	119.9	C(37)-C(36)-H(36)	119.6
N(2)-P(2)-C(32)	106.26(9)	C(13)-C(18)-H(18)	119.9	C(35)-C(36)-H(36)	119.6
N(2)-P(2)-C(38)	115.73(8)	C(24)-C(19)-C(20)	118.66(16)	C(36)-C(37)-C(32)	119.8(2)
C(32)-P(2)-C(38)	107.14(8)	C(24)-C(19)-P(1)	118.84(13)	C(36)-C(37)-H(37)	120.1
N(2)-P(2)-C(11)	111.94(8)	C(20)-C(19)-P(1)	121.90(13)	C(32)-C(37)-H(37)	120.1
C(32)-P(2)-C(11)	105.66(9)	C(21)-C(20)-C(19)	120.48(17)	C(43)-C(38)-C(39)	119.35(17)
C(38)-P(2)-C(11)	109.45(9)	C(21)-C(20)-H(20)	119.8	C(43)-C(38)-P(2)	122.88(14)
C(1)-C(2)-C(3)	114.97(15)	C(19)-C(20)-H(20)	119.8	C(39)-C(38)-P(2)	117.02(14)
C(1)-C(2)-P(1)	128.25(12)	C(22)-C(21)-C(20)	120.17(18)	C(40)-C(39)-C(38)	120.38(19)
C(3)-C(2)-P(1)	116.69(13)	C(22)-C(21)-H(21)	119.9	C(40)-C(39)-H(39)	119.8
C(44)-N(2)-P(2)	125.80(15)	C(20)-C(21)-H(21)	119.9	C(38)-C(39)-H(39)	119.8
C(4)-C(3)-C(2)	122.92(17)	C(23)-C(22)-C(21)	119.83(18)	C(41)-C(40)-C(39)	119.9(2)
C(4)-C(3)-H(3)	118.5	C(23)-C(22)-H(22)	120.1	C(41)-C(40)-H(40)	120.1
C(2)-C(3)-H(3)	118.5	C(21)-C(22)-H(22)	120.1	C(39)-C(40)-H(40)	120.1
C(5)-C(4)-C(3)	120.59(16)	C(22)-C(23)-C(24)	120.32(17)	C(40)-C(41)-C(42)	120.63(19)
C(5)-C(4)-H(4)	119.7	C(22)-C(23)-H(23)	119.8	C(40)-C(41)-H(41)	119.7
C(3)-C(4)-H(4)	119.7	C(24)-C(23)-H(23)	119.8	C(42)-C(41)-H(41)	119.7
C(4)-C(5)-C(6)	118.26(16)	C(23)-C(24)-C(19)	120.52(17)	C(41)-C(42)-C(43)	119.9(2)

C(4)-C(5)-H(5)	120.9	C(23)-C(24)-H(24)	119.7	C(41)-C(42)-H(42)	120.0
C(6)-C(5)-H(5)	120.9	C(19)-C(24)-H(24)	119.7	C(43)-C(42)-H(42)	120.0
C(5)-C(6)-C(1)	120.14(16)	N(1)-C(25)-C(26)	125.04(16)	C(38)-C(43)-C(42)	119.85(19)
C(5)-C(6)-C(7)	133.69(16)	N(1)-C(25)-C(30)	116.60(16)	C(38)-C(43)-H(43)	120.1
C(1)-C(6)-C(7)	106.15(14)	C(26)-C(25)-C(30)	118.36(16)	C(42)-C(43)-H(43)	120.1
C(12)-C(7)-C(8)	120.35(17)	C(27)-C(26)-C(25)	121.1(2)	C(45)-C(44)-N(2)	125.35(17)
C(12)-C(7)-C(6)	106.45(15)	C(27)-C(26)-H(26)	119.4	C(45)-C(44)-C(49)	118.0(2)
C(8)-C(7)-C(6)	133.19(17)	C(25)-C(26)-H(26)	119.4	N(2)-C(44)-C(49)	116.6(2)
C(9)-C(8)-C(7)	118.20(18)	C(28)-C(27)-C(26)	120.5(2)	C(44)-C(45)-C(46)	122.2(2)
C(9)-C(8)-H(8)	120.9	C(28)-C(27)-H(27)	119.7	C(44)-C(45)-H(45)	118.9
C(7)-C(8)-H(8)	120.9	C(26)-C(27)-H(27)	119.7	C(46)-C(45)-H(45)	118.9
C(8)-C(9)-C(10)	120.79(18)	C(29)-C(28)-C(27)	118.76(19)	C(47)-C(46)-C(45)	119.9(3)
C(8)-C(9)-H(9)	119.6	C(29)-C(28)-H(28)	120.6	C(47)-C(46)-H(46)	120.1
C(10)-C(9)-H(9)	119.6	C(27)-C(28)-H(28)	120.6	C(45)-C(46)-H(46)	120.1
C(9)-C(10)-C(11)	122.70(19)	C(28)-C(29)-C(30)	122.2(2)	C(46)-C(47)-C(48)	118.9(2)
C(9)-C(10)-H(10)	118.7	C(28)-C(29)-H(29)	118.9	C(46)-C(47)-H(47)	120.6
C(11)-C(10)-H(10)	118.7	C(30)-C(29)-H(29)	118.9	C(48)-C(47)-H(47)	120.6
C(12)-C(11)-C(10)	115.11(17)	C(29)-C(30)-C(25)	119.05(19)	C(47)-C(48)-C(49)	122.7(2)
C(12)-C(11)-P(2)	130.04(14)	C(29)-C(30)-C(31)	121.76(18)	C(47)-C(48)-H(48)	118.6
C(10)-C(11)-P(2)	114.11(14)	C(25)-C(30)-C(31)	119.19(16)	C(49)-C(48)-H(48)	118.6
C(11)-C(12)-C(7)	122.79(16)	C(30)-C(31)-H(31A)	109.5	C(48)-C(49)-C(44)	118.3(2)
C(11)-C(12)-O(1)	126.44(15)	C(30)-C(31)-H(31B)	109.5	C(48)-C(49)-C(50)	122.2(2)
C(7)-C(12)-O(1)	110.76(15)	H(31A)-C(31)-H(31B)	109.5	C(44)-C(49)-C(50)	119.6(2)
C(14)-C(13)-C(18)	119.20(16)	C(30)-C(31)-H(31C)	109.5	C(49)-C(50)-H(50A)	109.5
C(14)-C(13)-P(1)	123.18(13)	H(31A)-C(31)-H(31C)	109.5	C(49)-C(50)-H(50B)	109.5
C(18)-C(13)-P(1)	117.61(13)	H(31B)-C(31)-H(31C)	109.5	H(50A)-C(50)-H(50B)	109.5
C(13)-C(14)-C(15)	119.95(17)	C(33)-C(32)-C(37)	119.5(2)	C(49)-C(50)-H(50C)	109.5
C(13)-C(14)-H(14)	120.0	C(33)-C(32)-P(2)	121.62(15)	H(50A)-C(50)-H(50C)	109.5
C(15)-C(14)-H(14)	120.0	C(37)-C(32)-P(2)	118.91(16)	H(50B)-C(50)-H(50C)	109.5

Table A.80: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_2^{Tol}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	27(1)	27(1)	26(1)	-3(1)	8(1)	-1(1)
O(1)	30(1)	38(1)	22(1)	0(1)	8(1)	5(1)
N(1)	30(1)	31(1)	36(1)	-4(1)	10(1)	0(1)
C(1)	32(1)	31(1)	24(1)	-1(1)	12(1)	-5(1)
P(2)	39(1)	41(1)	30(1)	7(1)	15(1)	14(1)
C(2)	30(1)	27(1)	26(1)	-1(1)	11(1)	-5(1)
N(2)	48(1)	48(1)	35(1)	8(1)	18(1)	18(1)
C(3)	43(1)	29(1)	32(1)	-2(1)	17(1)	-1(1)
C(4)	58(1)	33(1)	28(1)	-4(1)	20(1)	-1(1)
C(5)	49(1)	39(1)	22(1)	-1(1)	11(1)	-6(1)

C(6)	35(1)	35(1)	26(1)	1(1)	10(1)	-2(1)
C(7)	37(1)	51(1)	26(1)	5(1)	10(1)	5(1)
C(8)	45(1)	80(2)	25(1)	8(1)	7(1)	15(1)
C(9)	47(1)	96(2)	34(1)	17(1)	9(1)	32(1)
C(10)	46(1)	76(2)	35(1)	13(1)	15(1)	28(1)
C(11)	38(1)	52(1)	28(1)	7(1)	13(1)	13(1)
C(12)	30(1)	44(1)	26(1)	7(1)	8(1)	8(1)
C(13)	29(1)	30(1)	26(1)	-2(1)	5(1)	0(1)
C(14)	36(1)	43(1)	40(1)	-10(1)	14(1)	-2(1)
C(15)	47(1)	49(1)	39(1)	-16(1)	13(1)	-2(1)
C(16)	46(1)	42(1)	40(1)	-14(1)	5(1)	-7(1)
C(17)	56(1)	56(1)	62(1)	-23(1)	29(1)	-26(1)
C(18)	55(1)	49(1)	49(1)	-20(1)	30(1)	-19(1)
C(19)	31(1)	27(1)	30(1)	0(1)	11(1)	0(1)
C(20)	38(1)	41(1)	30(1)	2(1)	9(1)	-6(1)
C(21)	40(1)	51(1)	44(1)	0(1)	13(1)	-12(1)
C(22)	51(1)	40(1)	48(1)	7(1)	25(1)	-5(1)
C(23)	50(1)	41(1)	37(1)	12(1)	17(1)	7(1)
C(24)	35(1)	39(1)	33(1)	4(1)	9(1)	4(1)
C(25)	40(1)	28(1)	26(1)	3(1)	9(1)	4(1)
C(26)	43(1)	36(1)	47(1)	-5(1)	8(1)	-2(1)
C(27)	69(2)	35(1)	51(1)	-7(1)	0(1)	-5(1)
C(28)	93(2)	35(1)	42(1)	-5(1)	11(1)	18(1)
C(29)	68(2)	44(1)	48(1)	3(1)	25(1)	19(1)
C(30)	46(1)	35(1)	36(1)	7(1)	18(1)	7(1)
C(31)	46(1)	50(1)	82(2)	4(1)	37(1)	5(1)
C(32)	51(1)	42(1)	33(1)	6(1)	21(1)	8(1)
C(33)	55(1)	49(1)	61(1)	10(1)	29(1)	3(1)
C(34)	60(1)	69(2)	69(2)	9(1)	31(1)	-2(1)
C(35)	84(2)	64(2)	59(1)	-2(1)	36(1)	-24(1)
C(36)	94(2)	47(1)	62(2)	6(1)	38(1)	2(1)
C(37)	68(1)	44(1)	49(1)	10(1)	28(1)	8(1)
C(38)	31(1)	40(1)	31(1)	7(1)	14(1)	10(1)
C(39)	43(1)	43(1)	37(1)	5(1)	12(1)	3(1)
C(40)	48(1)	64(1)	34(1)	11(1)	4(1)	0(1)
C(41)	47(1)	58(1)	50(1)	25(1)	15(1)	9(1)
C(42)	51(1)	41(1)	59(1)	11(1)	26(1)	6(1)
C(43)	41(1)	44(1)	39(1)	2(1)	19(1)	5(1)
C(44)	34(1)	74(2)	22(1)	1(1)	9(1)	18(1)
C(45)	39(1)	68(2)	43(1)	-2(1)	11(1)	3(1)
C(46)	43(1)	101(2)	45(1)	-14(1)	12(1)	-12(1)
C(47)	40(1)	134(3)	50(1)	-33(2)	17(1)	-7(2)
C(48)	37(1)	120(2)	52(1)	-23(2)	14(1)	25(1)

C(49)	52(1)	80(2)	38(1)	-5(1)	13(1)	26(1)
C(50)	78(2)	87(2)	83(2)	4(2)	34(2)	40(2)

Table A.81: Crystal data and structure refinement for $\mathbf{L_2^{Pipp}}$.

Empirical formula	$C_{54}H_{48}N_2OP_2 \cdot C_5H_{12}$	
Formula weight	875.03	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 26.938(3) Å	α= 90°.
	b = 18.8282(18) Å	β= 90°.
	c = 10.2745(10) Å	γ = 90°.
Volume	5211.1(9) $Å^3$	
Z	4	
Density (calculated)	1.115 Mg/m^3	
Absorption coefficient	0.123 mm^{-1}	
F(000)	1864	
Crystal size	0.49 x 0.15 x 0.14 mm^3	
Theta range for data collection	2.16 to 25.03°.	
Index ranges	-32<=h<=32, -22<=k<=22, -12<=l<=12	
Reflections collected	61302	
Independent reflections	9201 [R(int) = 0.0504]	
Completeness to theta = 25.03°	99.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6828	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9201 / 77 / 613	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1195	
R indices (all data)	R1 = 0.0602, wR2 = 0.1238	
Absolute structure parameter	-0.01(9)	
Largest diff. peak and hole	0.265 and -0.177 $e.Å^{-3}$	

Table A.82: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_2^{Pipp}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	3615(1)	2882(1)	4744(1)	38(1)	C(30)	3024(1)	3880(2)	2711(3)	50(1)
O(1)	3252(1)	1524(1)	3118(2)	36(1)	C(31)	2892(2)	5595(2)	712(5)	86(1)
N(1)	3774(1)	3236(1)	3436(3)	41(1)	C(32)	2908(3)	6223(2)	1543(7)	132(3)
C(1)	2913(1)	1879(2)	3915(3)	39(1)	C(33)	2403(3)	5483(3)	142(7)	154(3)
P(2)	3834(1)	440(1)	1070(1)	34(1)	C(34)	4125(1)	1283(2)	735(3)	36(1)
N(2)	3909(1)	-7(1)	-191(3)	40(1)	C(35)	4225(1)	1453(2)	-557(3)	40(1)
C(2)	3019(1)	2428(2)	4742(3)	42(1)	C(36)	4436(1)	2101(2)	-863(4)	54(1)

C(3)	2615(1)	2696(2)	5445(4)	50(1)	C(37)	4543(1)	2582(2)	117(4)	62(1)
C(4)	2135(1)	2428(2)	5310(4)	52(1)	C(38)	4454(1)	2407(2)	1395(4)	58(1)
C(5)	2046(1)	1897(2)	4439(4)	52(1)	C(39)	4243(1)	1758(2)	1708(3)	44(1)
C(6)	2435(1)	1605(2)	3715(3)	43(1)	C(40)	4095(1)	88(2)	2558(3)	34(1)
C(7)	2486(1)	1059(2)	2741(3)	42(1)	C(41)	3807(1)	-304(2)	3412(3)	42(1)
C(8)	2152(1)	604(2)	2116(4)	52(1)	C(42)	4029(1)	-671(2)	4436(3)	48(1)
C(9)	2330(1)	166(2)	1174(4)	52(1)	C(43)	4539(1)	-635(2)	4608(3)	48(1)
C(10)	2836(1)	144(2)	848(3)	46(1)	C(44)	4821(1)	-227(2)	3799(3)	45(1)
C(11)	3180(1)	580(2)	1483(3)	35(1)	C(45)	4607(1)	131(2)	2770(3)	40(1)
C(12)	2989(1)	1038(2)	2413(3)	36(1)	C(46)	3867(1)	-720(2)	-494(3)	41(1)
C(13)	4080(1)	2236(2)	5155(3)	39(1)	C(47)	3700(1)	-1261(2)	326(3)	48(1)
C(14)	3965(1)	1576(2)	5664(3)	44(1)	C(48)	3679(1)	-1952(2)	-77(4)	55(1)
C(15)	4335(1)	1106(2)	5973(4)	50(1)	C(49)	3822(1)	-2169(2)	-1303(4)	58(1)
C(16)	4820(1)	1279(2)	5792(3)	55(1)	C(50)	3984(2)	-1633(2)	-2127(4)	65(1)
C(17)	4942(1)	1947(2)	5308(4)	57(1)	C(51)	4009(1)	-936(2)	-1744(3)	53(1)
C(18)	4574(1)	2414(2)	4992(3)	47(1)	C(52)	3793(4)	-2984(8)	-1613(15)	61(3)
C(19)	3599(1)	3489(2)	6101(4)	46(1)	C(53)	3366(4)	-3142(6)	-2350(20)	148(9)
C(20)	3531(2)	3278(2)	7395(4)	64(1)	C(54)	4301(4)	-3206(8)	-2160(20)	123(6)
C(21)	3556(2)	3761(2)	8392(4)	71(1)	C(52B)	3805(12)	-2845(12)	-1940(20)	95(12)
C(22)	3654(2)	4455(3)	8131(4)	75(1)	C(53B)	3727(17)	-3018(10)	-3285(17)	175(16)
C(23)	3729(2)	4680(2)	6872(4)	76(1)	C(54B)	4153(9)	-3355(9)	-1220(30)	105(7)
C(24)	3700(1)	4195(2)	5866(4)	59(1)	C(1S)	5916(6)	2623(8)	8375(13)	284(8)
C(25)	3533(1)	3783(2)	2779(3)	41(1)	C(2S)	5600(4)	3238(7)	7801(10)	203(4)
C(26)	3824(1)	4277(2)	2106(3)	51(1)	C(3S)	5549(3)	3878(6)	8830(9)	173(3)
C(27)	3609(2)	4845(2)	1471(3)	59(1)	C(4S)	5167(4)	4386(6)	8322(11)	208(4)
C(28)	3110(2)	4940(2)	1422(4)	63(1)	C(5S)	5033(3)	4956(7)	9548(15)	252(6)
C(29)	2821(2)	4444(2)	2044(4)	61(1)					

Table A.83: Bond lengths [Å] for $\mathbf{L_2^{Pipp}}$.

P(1)-N(1)	1.560(3)	C(21)-H(21)	0.9500	C(45)-H(45)	0.9500
P(1)-C(13)	1.796(3)	C(22)-C(23)	1.377(6)	C(46)-C(47)	1.395(5)
P(1)-C(19)	1.804(4)	C(22)-H(22)	0.9500	C(46)-C(51)	1.401(5)
P(1)-C(2)	1.817(3)	C(23)-C(24)	1.381(5)	C(47)-C(48)	1.367(5)
O(1)-C(12)	1.363(4)	C(23)-H(23)	0.9500	C(47)-H(47)	0.9500
O(1)-C(1)	1.398(4)	C(24)-H(24)	0.9500	C(48)-C(49)	1.380(6)
N(1)-C(25)	1.392(4)	C(25)-C(30)	1.386(5)	C(48)-H(48)	0.9500
C(1)-C(2)	1.369(5)	C(25)-C(26)	1.399(5)	C(49)-C(50)	1.388(6)
C(1)-C(6)	1.401(4)	C(26)-C(27)	1.379(5)	C(49)-C(52B)	1.43(2)
P(2)-N(2)	1.558(3)	C(26)-H(26)	0.9500	C(49)-C(52)	1.569(12)
P(2)-C(34)	1.803(3)	C(27)-C(28)	1.359(6)	C(50)-C(51)	1.372(5)
P(2)-C(40)	1.809(3)	C(27)-H(27)	0.9500	C(50)-H(50)	0.9500
P(2)-C(11)	1.831(3)	C(28)-C(29)	1.373(5)	C(51)-H(51)	0.9500
N(2)-C(46)	1.383(4)	C(28)-C(31)	1.549(5)	C(52)-C(53)	1.409(13)

C(2)-C(3)	1.400(4)	C(29)-C(30)	1.376(5)	C(52)-C(54)	1.536(12)
C(3)-C(4)	1.395(5)	C(29)-H(29)	0.9500	C(52)-H(52)	1.0000
C(3)-H(3)	0.9500	C(30)-H(30)	0.9500	C(53)-H(53A)	0.9800
C(4)-C(5)	1.365(5)	C(31)-C(32)	1.459(7)	C(53)-H(53B)	0.9800
C(4)-H(4)	0.9500	C(31)-C(33)	1.458(8)	C(53)-H(53C)	0.9800
C(5)-C(6)	1.398(4)	C(31)-H(31)	1.0000	C(54)-H(54A)	0.9800
C(5)-H(5)	0.9500	C(32)-H(32A)	0.9800	C(54)-H(54B)	0.9800
C(6)-C(7)	1.440(5)	C(32)-H(32B)	0.9800	C(54)-H(54C)	0.9800
C(7)-C(12)	1.398(4)	C(32)-H(32C)	0.9800	C(52B)-C(53B)	1.433(18)
C(7)-C(8)	1.398(5)	C(33)-H(33A)	0.9800	C(52B)-C(54B)	1.533(17)
C(8)-C(9)	1.358(5)	C(33)-H(33B)	0.9800	C(52B)-H(52B)	1.0000
C(8)-H(8)	0.9500	C(33)-H(33C)	0.9800	C(53B)-H(53D)	0.9800
C(9)-C(10)	1.406(4)	C(34)-C(39)	1.380(4)	C(53B)-H(53E)	0.9800
C(9)-H(9)	0.9500	C(34)-C(35)	1.392(4)	C(53B)-H(53F)	0.9800
C(10)-C(11)	1.399(4)	C(35)-C(36)	1.383(5)	C(54B)-H(54D)	0.9800
C(10)-H(10)	0.9500	C(35)-H(35)	0.9500	C(54B)-H(54E)	0.9800
C(11)-C(12)	1.388(4)	C(36)-C(37)	1.385(5)	C(54B)-H(54F)	0.9800
C(13)-C(14)	1.384(4)	C(36)-H(36)	0.9500	C(1S)-C(2S)	1.554(15)
C(13)-C(18)	1.384(4)	C(37)-C(38)	1.374(5)	C(1S)-H(1S1)	0.9800
C(14)-C(15)	1.371(4)	C(37)-H(37)	0.9500	C(1S)-H(1S2)	0.9800
C(14)-H(14)	0.9500	C(38)-C(39)	1.384(5)	C(1S)-H(1S3)	0.9800
C(15)-C(16)	1.357(5)	C(38)-H(38)	0.9500	C(2S)-C(3S)	1.609(13)
C(15)-H(15)	0.9500	C(39)-H(39)	0.9500	C(2S)-H(2S1)	0.9900
C(16)-C(17)	1.392(5)	C(40)-C(41)	1.384(4)	C(2S)-H(2S2)	0.9900
C(16)-H(16)	0.9500	C(40)-C(45)	1.398(4)	C(3S)-C(4S)	1.500(13)
C(17)-C(18)	1.363(5)	C(41)-C(42)	1.394(4)	C(3S)-H(3S1)	0.9900
C(17)-H(17)	0.9500	C(41)-H(41)	0.9500	C(3S)-H(3S2)	0.9900
C(18)-H(18)	0.9500	C(42)-C(43)	1.385(5)	C(4S)-C(5S)	1.694(15)
C(19)-C(24)	1.376(5)	C(42)-H(42)	0.9500	C(4S)-H(4S1)	0.9900
C(19)-C(20)	1.400(5)	C(43)-C(44)	1.363(5)	C(4S)-H(4S2)	0.9900
C(20)-C(21)	1.371(6)	C(43)-H(43)	0.9500	C(5S)-H(5S1)	0.9800
C(20)-H(20)	0.9500	C(44)-C(45)	1.379(4)	C(5S)-H(5S2)	0.9800
C(21)-C(22)	1.359(6)	C(44)-H(44)	0.9500	C(5S)-H(5S3)	0.9800

Table A.84: Bond angles [°] for $\mathbf{L_2^{Pipp}}$

N(1)-P(1)-C(13)	107.48(14)	C(21)-C(22)-C(23)	120.6(4)	C(44)-C(45)-C(40)	120.1(3)
N(1)-P(1)-C(19)	113.70(15)	C(21)-C(22)-H(22)	119.7	C(44)-C(45)-H(45)	119.9
C(13)-P(1)-C(19)	105.25(15)	C(23)-C(22)-H(22)	119.7	C(40)-C(45)-H(45)	119.9
N(1)-P(1)-C(2)	116.24(15)	C(22)-C(23)-C(24)	119.4(4)	N(2)-C(46)-C(47)	126.8(3)
C(13)-P(1)-C(2)	107.29(14)	C(22)-C(23)-H(23)	120.3	N(2)-C(46)-C(51)	117.7(3)
C(19)-P(1)-C(2)	106.18(15)	C(24)-C(23)-H(23)	120.3	C(47)-C(46)-C(51)	115.5(3)
C(12)-O(1)-C(1)	107.0(2)	C(19)-C(24)-C(23)	121.2(4)	C(48)-C(47)-C(46)	121.7(3)
C(25)-N(1)-P(1)	127.3(2)	C(19)-C(24)-H(24)	119.4	C(48)-C(47)-H(47)	119.2

C(2)-C(1)-O(1)	126.0(3)	C(23)-C(24)-H(24)	119.4	C(46)-C(47)-H(47)	119.2
C(2)-C(1)-C(6)	124.3(3)	C(30)-C(25)-N(1)	125.7(3)	C(47)-C(48)-C(49)	123.2(4)
O(1)-C(1)-C(6)	109.7(3)	C(30)-C(25)-C(26)	116.2(3)	C(47)-C(48)-H(48)	118.4
N(2)-P(2)-C(34)	105.09(14)	N(1)-C(25)-C(26)	118.1(3)	C(49)-C(48)-H(48)	118.4
N(2)-P(2)-C(40)	117.06(13)	C(27)-C(26)-C(25)	121.0(4)	C(48)-C(49)-C(50)	115.4(3)
C(34)-P(2)-C(40)	108.36(14)	C(27)-C(26)-H(26)	119.5	C(48)-C(49)-C(52B)	132.3(12)
N(2)-P(2)-C(11)	113.25(14)	C(25)-C(26)-H(26)	119.5	C(50)-C(49)-C(52B)	112.1(11)
C(34)-P(2)-C(11)	109.61(13)	C(28)-C(27)-C(26)	122.4(4)	C(48)-C(49)-C(52)	117.5(7)
C(40)-P(2)-C(11)	103.35(13)	C(28)-C(27)-H(27)	118.8	C(50)-C(49)-C(52)	127.1(7)
C(46)-N(2)-P(2)	134.5(2)	C(26)-C(27)-H(27)	118.8	C(52B)-C(49)-C(52)	15.6(11)
C(1)-C(2)-C(3)	115.4(3)	C(27)-C(28)-C(29)	117.0(4)	C(51)-C(50)-C(49)	122.4(4)
C(1)-C(2)-P(1)	122.8(2)	C(27)-C(28)-C(31)	119.8(4)	C(51)-C(50)-H(50)	118.8
C(3)-C(2)-P(1)	121.0(3)	C(29)-C(28)-C(31)	123.2(4)	C(49)-C(50)-H(50)	118.8
C(4)-C(3)-C(2)	122.6(3)	C(28)-C(29)-C(30)	122.0(4)	C(50)-C(51)-C(46)	121.8(3)
C(4)-C(3)-H(3)	118.7	C(28)-C(29)-H(29)	119.0	C(50)-C(51)-H(51)	119.1
C(2)-C(3)-H(3)	118.7	C(30)-C(29)-H(29)	119.0	C(46)-C(51)-H(51)	119.1
C(5)-C(4)-C(3)	119.6(3)	C(29)-C(30)-C(25)	121.4(3)	C(53)-C(52)-C(54)	118.5(10)
C(5)-C(4)-H(4)	120.2	C(29)-C(30)-H(30)	119.3	C(53)-C(52)-C(49)	110.8(10)
C(3)-C(4)-H(4)	120.2	C(25)-C(30)-H(30)	119.3	C(54)-C(52)-C(49)	107.2(10)
C(4)-C(5)-C(6)	120.4(3)	C(32)-C(31)-C(33)	112.3(5)	C(53)-C(52)-H(52)	106.6
C(4)-C(5)-H(5)	119.8	C(32)-C(31)-C(28)	111.0(4)	C(54)-C(52)-H(52)	106.5
C(6)-C(5)-H(5)	119.8	C(33)-C(31)-C(28)	114.6(4)	C(49)-C(52)-H(52)	106.5
C(5)-C(6)-C(1)	117.7(3)	C(32)-C(31)-H(31)	106.1	C(49)-C(52B)-C(53B)	130.3(18)
C(5)-C(6)-C(7)	136.2(3)	C(33)-C(31)-H(31)	106.1	C(49)-C(52B)-C(54B)	108.3(14)
C(1)-C(6)-C(7)	106.2(3)	C(28)-C(31)-H(31)	106.1	C(53B)-C(52B)-C(54B)	114(2)
C(12)-C(7)-C(8)	119.7(3)	C(31)-C(32)-H(32A)	109.5	C(49)-C(52B)-H(52B)	98.7
C(12)-C(7)-C(6)	106.2(3)	C(31)-C(32)-H(32B)	109.5	C(53B)-C(52B)-H(52B)	98.7
C(8)-C(7)-C(6)	134.1(3)	H(32A)-C(32)-H(32E	109.5	C(54B)-C(52B)-H(52B)	98.7
C(9)-C(8)-C(7)	118.2(3)	C(31)-C(32)-H(32C)	109.5	C(52B)-C(53B)-H(53D	109.5
C(9)-C(8)-H(8)	120.9	H(32A)-C(32)-H(32C	109.5	C(52B)-C(53B)-H(53E)	109.5
C(7)-C(8)-H(8)	120.9	H(32B)-C(32)-H(32C	109.5	H(53D)-C(53B)-H(53E	109.5
C(8)-C(9)-C(10)	122.0(3)	C(31)-C(33)-H(33A)	109.5	C(52B)-C(53B)-H(53F)	109.5
C(8)-C(9)-H(9)	119.0	C(31)-C(33)-H(33B)	109.5	H(53D)-C(53B)-H(53F	109.5
C(10)-C(9)-H(9)	119.0	H(33A)-C(33)-H(33E	109.5	H(53E)-C(53B)-H(53F)	109.5
C(11)-C(10)-C(9)	120.9(3)	C(31)-C(33)-H(33C)	109.5	C(52B)-C(54B)-H(54D	109.5
C(11)-C(10)-H(10)	119.5	H(33A)-C(33)-H(33C	109.5	C(52B)-C(54B)-H(54E)	109.5
C(9)-C(10)-H(10)	119.5	H(33B)-C(33)-H(33C	109.5	H(54D)-C(54B)-H(54E	109.5
C(12)-C(11)-C(10)	116.2(3)	C(39)-C(34)-C(35)	119.8(3)	C(52B)-C(54B)-H(54F)	109.5
C(12)-C(11)-P(2)	127.3(2)	C(39)-C(34)-P(2)	122.3(2)	H(54D)-C(54B)-H(54F	109.5
C(10)-C(11)-P(2)	116.4(2)	C(35)-C(34)-P(2)	118.0(2)	H(54E)-C(54B)-H(54F)	109.5
O(1)-C(12)-C(11)	126.2(2)	C(36)-C(35)-C(34)	120.0(3)	C(2S)-C(1S)-H(1S1)	109.5
O(1)-C(12)-C(7)	110.9(3)	C(36)-C(35)-H(35)	120.0	C(2S)-C(1S)-H(1S2)	109.5
C(11)-C(12)-C(7)	122.9(3)	C(34)-C(35)-H(35)	120.0	H(1S1)-C(1S)-H(1S2)	109.5

C(14)-C(13)-C(18)	118.5(3)	C(35)-C(36)-C(37)	119.8(3)	C(2S)-C(1S)-H(1S3)	109.5
C(14)-C(13)-P(1)	122.8(2)	C(35)-C(36)-H(36)	120.1	H(1S1)-C(1S)-H(1S3)	109.5
C(18)-C(13)-P(1)	118.7(2)	C(37)-C(36)-H(36)	120.1	H(1S2)-C(1S)-H(1S3)	109.5
C(15)-C(14)-C(13)	120.4(3)	C(38)-C(37)-C(36)	120.1(3)	C(1S)-C(2S)-C(3S)	110.8(10)
C(15)-C(14)-H(14)	119.8	C(38)-C(37)-H(37)	119.9	C(1S)-C(2S)-H(2S1)	109.5
C(13)-C(14)-H(14)	119.8	C(36)-C(37)-H(37)	119.9	C(3S)-C(2S)-H(2S1)	109.5
C(16)-C(15)-C(14)	120.9(3)	C(37)-C(38)-C(39)	120.3(3)	C(1S)-C(2S)-H(2S2)	109.5
C(16)-C(15)-H(15)	119.6	C(37)-C(38)-H(38)	119.8	C(3S)-C(2S)-H(2S2)	109.5
C(14)-C(15)-H(15)	119.6	C(39)-C(38)-H(38)	119.8	H(2S1)-C(2S)-H(2S2)	108.1
C(15)-C(16)-C(17)	119.5(3)	C(34)-C(39)-C(38)	120.0(3)	C(4S)-C(3S)-C(2S)	107.9(9)
C(15)-C(16)-H(16)	120.3	C(34)-C(39)-H(39)	120.0	C(4S)-C(3S)-H(3S1)	110.1
C(17)-C(16)-H(16)	120.3	C(38)-C(39)-H(39)	120.0	C(2S)-C(3S)-H(3S1)	110.1
C(18)-C(17)-C(16)	119.8(3)	C(41)-C(40)-C(45)	119.1(3)	C(4S)-C(3S)-H(3S2)	110.1
C(18)-C(17)-H(17)	120.1	C(41)-C(40)-P(2)	120.9(2)	C(2S)-C(3S)-H(3S2)	110.1
C(16)-C(17)-H(17)	120.1	C(45)-C(40)-P(2)	119.6(2)	H(3S1)-C(3S)-H(3S2)	108.4
C(17)-C(18)-C(13)	121.0(3)	C(40)-C(41)-C(42)	120.1(3)	C(3S)-C(4S)-C(5S)	106.9(10)
C(17)-C(18)-H(18)	119.5	C(40)-C(41)-H(41)	119.9	C(3S)-C(4S)-H(4S1)	110.3
C(13)-C(18)-H(18)	119.5	C(42)-C(41)-H(41)	119.9	C(5S)-C(4S)-H(4S1)	110.3
C(24)-C(19)-C(20)	117.9(3)	C(43)-C(42)-C(41)	119.8(3)	C(3S)-C(4S)-H(4S2)	110.3
C(24)-C(19)-P(1)	118.1(3)	C(43)-C(42)-H(42)	120.1	C(5S)-C(4S)-H(4S2)	110.3
C(20)-C(19)-P(1)	123.8(3)	C(41)-C(42)-H(42)	120.1	H(4S1)-C(4S)-H(4S2)	108.6
C(21)-C(20)-C(19)	120.9(4)	C(44)-C(43)-C(42)	120.1(3)	C(4S)-C(5S)-H(5S1)	109.5
C(21)-C(20)-H(20)	119.5	C(44)-C(43)-H(43)	119.9	C(4S)-C(5S)-H(5S2)	109.5
C(19)-C(20)-H(20)	119.5	C(42)-C(43)-H(43)	119.9	H(5S1)-C(5S)-H(5S2)	109.5
C(22)-C(21)-C(20)	120.0(4)	C(43)-C(44)-C(45)	120.7(3)	C(4S)-C(5S)-H(5S3)	109.5
C(22)-C(21)-H(21)	120.0	C(43)-C(44)-H(44)	119.7	H(5S1)-C(5S)-H(5S3)	109.5
C(20)-C(21)-H(21)	120.0	C(45)-C(44)-H(44)	119.7	H(5S2)-C(5S)-H(5S3)	109.5

Table A.85: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_2^{Pipp}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	37(1)	35(1)	43(1)	2(1)	9(1)	3(1)
O(1)	26(1)	38(1)	45(1)	5(1)	4(1)	0(1)
N(1)	42(2)	36(1)	44(2)	3(1)	9(1)	0(1)
C(1)	26(2)	39(2)	52(2)	16(2)	8(1)	4(1)
P(2)	27(1)	37(1)	36(1)	2(1)	-2(1)	-1(1)
N(2)	42(1)	43(1)	37(1)	-1(1)	0(1)	-2(1)
C(2)	37(2)	40(2)	49(2)	6(2)	8(2)	6(1)
C(3)	45(2)	43(2)	62(2)	8(2)	19(2)	9(2)
C(4)	44(2)	42(2)	70(2)	11(2)	19(2)	14(2)
C(5)	22(2)	62(2)	73(3)	30(2)	12(2)	4(1)
C(6)	28(2)	42(2)	58(2)	18(2)	8(1)	4(1)
C(7)	26(1)	43(2)	58(2)	21(2)	1(1)	0(1)

C(8)	27(2)	53(2)	75(2)	21(2)	-5(2)	-3(2)
C(9)	36(2)	57(2)	65(2)	3(2)	-14(2)	-8(2)
C(10)	38(2)	45(2)	55(2)	6(2)	-15(2)	-5(1)
C(11)	26(1)	37(2)	43(2)	9(1)	-5(1)	2(1)
C(12)	27(1)	36(2)	45(2)	12(1)	0(1)	2(1)
C(13)	39(2)	35(2)	43(2)	2(1)	3(1)	6(1)
C(14)	48(2)	36(2)	48(2)	3(1)	6(1)	2(1)
C(15)	62(2)	41(2)	48(2)	4(2)	2(2)	8(2)
C(16)	56(2)	57(2)	52(2)	1(2)	1(2)	22(2)
C(17)	39(2)	64(2)	66(2)	5(2)	4(2)	7(2)
C(18)	41(2)	45(2)	55(2)	9(2)	6(2)	1(2)
C(19)	44(2)	48(2)	46(2)	-2(2)	7(2)	8(1)
C(20)	91(3)	48(2)	51(2)	4(2)	22(2)	13(2)
C(21)	86(3)	83(3)	45(2)	-8(2)	19(2)	8(2)
C(22)	85(3)	79(3)	60(3)	-22(2)	5(2)	-2(2)
C(23)	113(4)	57(2)	57(3)	-10(2)	6(2)	-14(2)
C(24)	81(3)	48(2)	47(2)	-2(2)	1(2)	-12(2)
C(25)	50(2)	32(2)	40(2)	-8(1)	1(1)	-2(1)
C(26)	60(2)	44(2)	50(2)	6(2)	1(2)	-2(2)
C(27)	87(3)	41(2)	49(2)	8(2)	2(2)	-8(2)
C(28)	90(3)	40(2)	58(2)	-1(2)	-8(2)	8(2)
C(29)	57(2)	66(2)	61(2)	9(2)	-10(2)	6(2)
C(30)	53(2)	43(2)	54(2)	-1(2)	-1(2)	-2(2)
C(31)	128(4)	60(3)	70(3)	14(2)	0(3)	29(3)
C(32)	183(6)	49(3)	164(6)	-5(3)	-43(5)	36(3)
C(33)	211(8)	96(4)	155(6)	18(4)	-111(6)	29(5)
C(34)	22(1)	40(2)	44(2)	3(1)	4(1)	4(1)
C(35)	29(2)	41(2)	48(2)	2(1)	5(1)	4(1)
C(36)	52(2)	48(2)	62(2)	9(2)	18(2)	4(2)
C(37)	66(2)	40(2)	79(3)	1(2)	31(2)	-8(2)
C(38)	55(2)	48(2)	70(3)	-16(2)	27(2)	-13(2)
C(39)	38(2)	40(2)	54(2)	-5(2)	16(2)	-9(1)
C(40)	29(2)	37(2)	35(2)	-2(1)	1(1)	4(1)
C(41)	33(2)	51(2)	43(2)	3(2)	-5(1)	-1(1)
C(42)	49(2)	54(2)	40(2)	10(2)	-3(2)	1(2)
C(43)	51(2)	49(2)	43(2)	-5(2)	-9(2)	5(2)
C(44)	32(2)	50(2)	53(2)	-5(2)	-7(2)	10(1)
C(45)	31(2)	47(2)	43(2)	-4(2)	1(1)	6(1)
C(46)	34(2)	45(2)	45(2)	-2(2)	-8(1)	-4(1)
C(47)	41(2)	53(2)	49(2)	-1(2)	-1(2)	-3(2)
C(48)	49(2)	44(2)	73(3)	2(2)	-3(2)	-8(2)
C(49)	50(2)	51(2)	74(3)	-16(2)	-6(2)	-7(2)
C(50)	77(3)	64(2)	53(2)	-21(2)	3(2)	-16(2)

C(51)	63(2)	57(2)	38(2)	-8(2)	1(2)	-7(2)
C(52)	76(6)	30(5)	76(6)	-15(6)	2(5)	-6(5)
C(53)	105(8)	80(7)	260(20)	-89(10)	-48(9)	-16(6)
C(54)	86(7)	67(7)	216(19)	-72(10)	-1(8)	9(6)
C(52B)	140(20)	52(12)	92(15)	33(10)	-17(12)	-46(11)
C(53B)	360(50)	90(12)	73(11)	-40(10)	-19(17)	-26(19)
C(54B)	97(14)	50(8)	170(20)	-26(11)	-3(14)	3(8)
C(1S)	351(19)	311(14)	190(12)	66(10)	132(12)	38(12)
C(2S)	196(9)	264(10)	148(8)	5(7)	18(7)	-98(7)
C(3S)	133(6)	245(9)	140(6)	38(6)	-5(5)	-81(5)
C(4S)	138(7)	274(10)	211(10)	88(7)	5(7)	-63(7)
C(5S)	110(6)	317(12)	329(15)	-33(11)	29(8)	-70(7)

Table A.86: Crystal data and structure refinement for $\mathbf{L_2^{Ph}}$.

Empirical formula	$C_{51}H_{39}N_2OP_2$	
Formula weight	757.78	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.373(11) Å	α= 104.285(15)°.
	b = 13.769(17) Å	β= 90.990(14)°.
	c = 17.95(2) Å	γ = 92.535(15)°.
Volume	2242(5) $Å^3$	
Z	2	
Density (calculated)	1.123 Mg/m^3	
Absorption coefficient	0.134 mm^{-1}	
F(000)	794	
Crystal size	0.27 x 0.12 x 0.08 mm^3	
Theta range for data collection	2.14 to 25.03°.	
Index ranges	-11<=h<=11, -16<=k<=16, -21<=l<=21	
Reflections collected	26495	
Independent reflections	7900 [R(int) = 0.1176]	
Completeness to theta = 25.03°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9898 and 0.9651	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7900 / 0 / 433	
Goodness-of-fit on F^2	0.915	
Final R indices [I>2sigma(I)]	R1 = 0.0794, wR2 = 0.1825	
R indices (all data)	R1 = 0.1780, wR2 = 0.2141	
Largest diff. peak and hole	0.236 and -0.238 $e.Å^{-3}$	

Table A.87: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for $\mathbf{L_2^{Ph}}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	7602(1)	321(1)	3062(1)	50(1)	C(24)	8792(3)	-914(2)	1773(2)	59(2)
O(1)	5947(3)	-1969(3)	2360(2)	51(1)	C(25)	7277(3)	2036(3)	4142(2)	54(1)
N(1)	7758(4)	1493(3)	3415(2)	54(1)	C(26)	7586(3)	3065(3)	4337(2)	55(1)
C(1)	5189(5)	-1094(4)	2525(3)	47(1)	C(27)	7189(4)	3646(2)	5045(2)	72(2)
P(2)	7116(1)	-4183(1)	1759(1)	76(1)	C(28)	6484(4)	3196(4)	5558(2)	83(2)
C(2)	5754(5)	-115(4)	2807(3)	48(1)	C(29)	6176(3)	2166(4)	5362(2)	80(2)
N(2)	8250(4)	-3630(4)	1356(3)	86(2)	C(30)	6572(4)	1586(2)	4655(2)	67(2)
C(3)	4765(5)	624(4)	2898(3)	59(2)	C(31)	7753(4)	-4055(3)	2749(2)	77(2)
C(4)	3309(5)	405(5)	2709(3)	67(2)	C(32)	9213(4)	-4007(3)	2913(3)	94(2)

C(5)	2780(5)	-554(5)	2457(3)	60(2)	C(33)	9709(3)	-4062(3)	3635(3)	95(2)
C(6)	3726(5)	-1327(5)	2365(3)	55(1)	C(34)	8744(5)	-4163(3)	4193(2)	88(2)
C(7)	3578(5)	-2394(5)	2082(3)	55(1)	C(35)	7284(5)	-4210(3)	4030(2)	76(2)
C(8)	2439(5)	-3087(5)	1827(3)	72(2)	C(36)	6789(3)	-4156(3)	3308(2)	70(2)
C(9)	2693(6)	-4082(5)	1577(3)	87(2)	C(37)	6904(3)	-5541(3)	1344(3)	77(2)
C(10)	4092(6)	-4434(5)	1564(3)	80(2)	C(38)	6818(3)	-5885(3)	548(2)	78(2)
C(11)	5294(5)	-3769(4)	1813(3)	61(2)	C(39)	6759(3)	-6910(4)	209(2)	94(2)
C(12)	4955(5)	-2765(4)	2081(3)	54(1)	C(40)	6787(3)	-7590(3)	666(3)	93(2)
C(13)	8335(3)	-463(2)	3638(2)	46(1)	C(41)	6873(4)	-7246(4)	1462(3)	94(2)
C(14)	7506(3)	-1054(3)	4007(2)	72(2)	C(42)	6931(4)	-6221(4)	1801(2)	89(2)
C(15)	8155(4)	-1586(3)	4473(2)	88(2)	C(43)	8169(4)	-3540(3)	592(2)	85(2)
C(16)	9633(5)	-1528(2)	4570(2)	76(2)	C(44)	6995(3)	-3170(3)	288(2)	83(2)
C(17)	10463(3)	-937(3)	4201(2)	65(2)	C(45)	7048(4)	-2994(3)	-441(3)	88(2)
C(18)	9814(3)	-405(2)	3735(2)	49(1)	C(46)	8275(5)	-3187(3)	-866(2)	96(2)
C(19)	8619(3)	67(3)	2187(2)	48(1)	C(47)	9448(4)	-3556(3)	-562(3)	106(3)
C(20)	9263(4)	862(2)	1947(2)	60(2)	C(48)	9395(3)	-3733(3)	167(3)	99(2)
C(21)	10081(3)	675(3)	1293(2)	78(2)	C(1S)	5836(9)	-10278(6)	-615(4)	99(2)
C(22)	10254(3)	-306(3)	879(2)	66(2)	C(2S)	6233(7)	-10453(5)	69(6)	100(2)
C(23)	9610(3)	-1101(2)	1119(2)	61(2)	C(3S)	5384(10)	-10195(6)	677(4)	96(2)

Table A.88: Bond lengths [Å] for $\mathbf{L_2^{Ph}}$.

P(1)-N(1)	1.582(4)	C(15)-C(16)	1.3900	C(34)-C(35)	1.3900
P(1)-C(13)	1.816(3)	C(15)-H(15)	0.9500	C(34)-H(34)	0.9500
P(1)-C(19)	1.817(3)	C(16)-C(17)	1.3900	C(35)-C(36)	1.3900
P(1)-C(2)	1.821(5)	C(16)-H(16)	0.9500	C(35)-H(35)	0.9500
O(1)-C(12)	1.393(5)	C(17)-C(18)	1.3900	C(36)-H(36)	0.9500
O(1)-C(1)	1.396(6)	C(17)-H(17)	0.9500	C(37)-C(38)	1.3900
N(1)-C(25)	1.425(5)	C(18)-H(18)	0.9500	C(37)-C(42)	1.3900
C(1)-C(2)	1.394(7)	C(19)-C(20)	1.3900	C(38)-C(39)	1.3900
C(1)-C(6)	1.403(6)	C(19)-C(24)	1.3900	C(38)-H(38)	0.9500
P(2)-N(2)	1.569(5)	C(20)-C(21)	1.3900	C(39)-C(40)	1.3900
P(2)-C(11)	1.820(6)	C(20)-H(20)	0.9500	C(39)-H(39)	0.9500
P(2)-C(31)	1.830(4)	C(21)-C(22)	1.3900	C(40)-C(41)	1.3900
P(2)-C(37)	1.835(4)	C(21)-H(21)	0.9500	C(40)-H(40)	0.9500
C(2)-C(3)	1.389(6)	C(22)-C(23)	1.3900	C(41)-C(42)	1.3900
N(2)-C(43)	1.407(6)	C(22)-H(22)	0.9500	C(41)-H(41)	0.9500
C(3)-C(4)	1.402(7)	C(23)-C(24)	1.3900	C(42)-H(42)	0.9500
C(3)-H(3)	0.9500	C(23)-H(23)	0.9500	C(43)-C(44)	1.3900
C(4)-C(5)	1.355(7)	C(24)-H(24)	0.9500	C(43)-C(48)	1.3900
C(4)-H(4)	0.9500	C(25)-C(26)	1.3900	C(44)-C(45)	1.3900
C(5)-C(6)	1.396(7)	C(25)-C(30)	1.3900	C(44)-H(44)	0.9500
C(5)-H(5)	0.9500	C(26)-C(27)	1.3900	C(45)-C(46)	1.3900
C(6)-C(7)	1.431(7)	C(26)-H(26)	0.9500	C(45)-H(45)	0.9500

C(7)-C(8)	1.392(7)	C(27)-C(28)	1.3900	C(46)-C(47)	1.3900
C(7)-C(12)	1.409(6)	C(27)-H(27)	0.9500	C(46)-H(46)	0.9500
C(8)-C(9)	1.366(7)	C(28)-C(29)	1.3900	C(47)-C(48)	1.3900
C(8)-H(8)	0.9500	C(28)-H(28)	0.9500	C(47)-H(47)	0.9500
C(9)-C(10)	1.417(7)	C(29)-C(30)	1.3900	C(48)-H(48)	0.9500
C(9)-H(9)	0.9500	C(29)-H(29)	0.9500	C(1S)-C(3S)#1	1.357(9)
C(10)-C(11)	1.413(7)	C(30)-H(30)	0.9500	C(1S)-C(2S)	1.358(9)
C(10)-H(10)	0.9500	C(31)-C(32)	1.3900	C(1S)-H(1S)	0.9500
C(11)-C(12)	1.400(7)	C(31)-C(36)	1.3900	C(2S)-C(3S)	1.346(9)
C(13)-C(14)	1.3900	C(32)-C(33)	1.3900	C(2S)-H(2S)	0.9500
C(13)-C(18)	1.3900	C(32)-H(32)	0.9500	C(3S)-C(1S)#1	1.357(9)
C(14)-C(15)	1.3900	C(33)-C(34)	1.3900	C(3S)-H(3S)	0.9500
C(14)-H(14)	0.9500	C(33)-H(33)	0.9500		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y-2,-z

Table A.89: Bond angles [°] for $\mathbf{L_2^{Ph}}$

N(1)-P(1)-C(13)	116.5(2)	C(13)-C(14)-H(14)	120.0	C(32)-C(33)-H(33)	120.0
N(1)-P(1)-C(19)	106.46(19)	C(14)-C(15)-C(16)	120.0	C(34)-C(33)-H(33)	120.0
C(13)-P(1)-C(19)	105.18(18)	C(14)-C(15)-H(15)	120.0	C(35)-C(34)-C(33)	120.0
N(1)-P(1)-C(2)	112.2(2)	C(16)-C(15)-H(15)	120.0	C(35)-C(34)-H(34)	120.0
C(13)-P(1)-C(2)	107.8(2)	C(15)-C(16)-C(17)	120.0	C(33)-C(34)-H(34)	120.0
C(19)-P(1)-C(2)	108.2(2)	C(15)-C(16)-H(16)	120.0	C(34)-C(35)-C(36)	120.0
C(12)-O(1)-C(1)	106.9(4)	C(17)-C(16)-H(16)	120.0	C(34)-C(35)-H(35)	120.0
C(25)-N(1)-P(1)	127.1(3)	C(18)-C(17)-C(16)	120.0	C(36)-C(35)-H(35)	120.0
C(2)-C(1)-O(1)	126.8(4)	C(18)-C(17)-H(17)	120.0	C(35)-C(36)-C(31)	120.0
C(2)-C(1)-C(6)	122.9(5)	C(16)-C(17)-H(17)	120.0	C(35)-C(36)-H(36)	120.0
O(1)-C(1)-C(6)	110.3(5)	C(17)-C(18)-C(13)	120.0	C(31)-C(36)-H(36)	120.0
N(2)-P(2)-C(11)	118.5(3)	C(17)-C(18)-H(18)	120.0	C(38)-C(37)-C(42)	120.0
N(2)-P(2)-C(31)	107.7(2)	C(13)-C(18)-H(18)	120.0	C(38)-C(37)-P(2)	118.2(3)
C(11)-P(2)-C(31)	106.6(2)	C(20)-C(19)-C(24)	120.0	C(42)-C(37)-P(2)	121.6(3)
N(2)-P(2)-C(37)	114.3(2)	C(20)-C(19)-P(1)	119.5(2)	C(39)-C(38)-C(37)	120.0
C(11)-P(2)-C(37)	104.0(2)	C(24)-C(19)-P(1)	120.5(2)	C(39)-C(38)-H(38)	120.0
C(31)-P(2)-C(37)	104.8(2)	C(21)-C(20)-C(19)	120.0	C(37)-C(38)-H(38)	120.0
C(3)-C(2)-C(1)	115.1(5)	C(21)-C(20)-H(20)	120.0	C(38)-C(39)-C(40)	120.0
C(3)-C(2)-P(1)	116.0(4)	C(19)-C(20)-H(20)	120.0	C(38)-C(39)-H(39)	120.0
C(1)-C(2)-P(1)	128.9(4)	C(20)-C(21)-C(22)	120.0	C(40)-C(39)-H(39)	120.0
C(43)-N(2)-P(2)	126.3(3)	C(20)-C(21)-H(21)	120.0	C(41)-C(40)-C(39)	120.0
C(2)-C(3)-C(4)	122.6(5)	C(22)-C(21)-H(21)	120.0	C(41)-C(40)-H(40)	120.0
C(2)-C(3)-H(3)	118.7	C(23)-C(22)-C(21)	120.0	C(39)-C(40)-H(40)	120.0
C(4)-C(3)-H(3)	118.7	C(23)-C(22)-H(22)	120.0	C(42)-C(41)-C(40)	120.0
C(5)-C(4)-C(3)	121.2(5)	C(21)-C(22)-H(22)	120.0	C(42)-C(41)-H(41)	120.0
C(5)-C(4)-H(4)	119.4	C(22)-C(23)-C(24)	120.0	C(40)-C(41)-H(41)	120.0

C(3)-C(4)-H(4)	119.4	C(22)-C(23)-H(23)	120.0	C(41)-C(42)-C(37)	120.0
C(4)-C(5)-C(6)	118.5(5)	C(24)-C(23)-H(23)	120.0	C(41)-C(42)-H(42)	120.0
C(4)-C(5)-H(5)	120.8	C(23)-C(24)-C(19)	120.0	C(37)-C(42)-H(42)	120.0
C(6)-C(5)-H(5)	120.8	C(23)-C(24)-H(24)	120.0	C(44)-C(43)-C(48)	120.0
C(5)-C(6)-C(1)	119.6(5)	C(19)-C(24)-H(24)	120.0	C(44)-C(43)-N(2)	122.9(3)
C(5)-C(6)-C(7)	134.1(5)	C(26)-C(25)-C(30)	120.0	C(48)-C(43)-N(2)	116.7(3)
C(1)-C(6)-C(7)	106.1(5)	C(26)-C(25)-N(1)	116.3(3)	C(43)-C(44)-C(45)	120.0
C(8)-C(7)-C(12)	117.6(5)	C(30)-C(25)-N(1)	123.6(3)	C(43)-C(44)-H(44)	120.0
C(8)-C(7)-C(6)	135.1(5)	C(25)-C(26)-C(27)	120.0	C(45)-C(44)-H(44)	120.0
C(12)-C(7)-C(6)	107.3(4)	C(25)-C(26)-H(26)	120.0	C(44)-C(45)-C(46)	120.0
C(9)-C(8)-C(7)	119.5(5)	C(27)-C(26)-H(26)	120.0	C(44)-C(45)-H(45)	120.0
C(9)-C(8)-H(8)	120.2	C(28)-C(27)-C(26)	120.0	C(46)-C(45)-H(45)	120.0
C(7)-C(8)-H(8)	120.2	C(28)-C(27)-H(27)	120.0	C(47)-C(46)-C(45)	120.0
C(8)-C(9)-C(10)	121.9(5)	C(26)-C(27)-H(27)	120.0	C(47)-C(46)-H(46)	120.0
C(8)-C(9)-H(9)	119.1	C(27)-C(28)-C(29)	120.0	C(45)-C(46)-H(46)	120.0
C(10)-C(9)-H(9)	119.1	C(27)-C(28)-H(28)	120.0	C(46)-C(47)-C(48)	120.0
C(11)-C(10)-C(9)	121.4(6)	C(29)-C(28)-H(28)	120.0	C(46)-C(47)-H(47)	120.0
C(11)-C(10)-H(10)	119.3	C(30)-C(29)-C(28)	120.0	C(48)-C(47)-H(47)	120.0
C(9)-C(10)-H(10)	119.3	C(30)-C(29)-H(29)	120.0	C(47)-C(48)-C(43)	120.0
C(12)-C(11)-C(10)	113.8(5)	C(28)-C(29)-H(29)	120.0	C(47)-C(48)-H(48)	120.0
C(12)-C(11)-P(2)	123.4(4)	C(29)-C(30)-C(25)	120.0	C(43)-C(48)-H(48)	120.0
C(10)-C(11)-P(2)	122.7(5)	C(29)-C(30)-H(30)	120.0	C(3S)#1-C(1S)-C(2S)	119.9(6)
O(1)-C(12)-C(11)	124.8(4)	C(25)-C(30)-H(30)	120.0	C(3S)#1-C(1S)-H(1S)	120.0
O(1)-C(12)-C(7)	109.3(5)	C(32)-C(31)-C(36)	120.0	C(2S)-C(1S)-H(1S)	120.0
C(11)-C(12)-C(7)	125.8(5)	C(32)-C(31)-P(2)	119.5(3)	C(3S)-C(2S)-C(1S)	119.9(6)
C(14)-C(13)-C(18)	120.0	C(36)-C(31)-P(2)	119.8(3)	C(3S)-C(2S)-H(2S)	120.1
C(14)-C(13)-P(1)	123.9(2)	C(31)-C(32)-C(33)	120.0	C(1S)-C(2S)-H(2S)	120.1
C(18)-C(13)-P(1)	116.0(2)	C(31)-C(32)-H(32)	120.0	C(2S)-C(3S)-C(1S)#1	120.1(6)
C(15)-C(14)-C(13)	120.0	C(33)-C(32)-H(32)	120.0	C(2S)-C(3S)-H(3S)	119.9
C(15)-C(14)-H(14)	120.0	C(32)-C(33)-C(34)	120.0	C(1S)#1-C(3S)-H(3S)	119.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y-2,-z

Table A.90: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_2^{Ph}}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	30(1)	73(1)	56(1)	34(1)	5(1)	4(1)
O(1)	28(2)	85(3)	38(2)	13(2)	1(2)	0(2)
N(1)	42(2)	52(3)	81(3)	39(2)	10(2)	5(2)
C(1)	26(3)	82(4)	38(3)	27(3)	3(2)	7(3)
P(2)	29(1)	102(1)	69(1)	-30(1)	4(1)	1(1)
C(2)	25(3)	73(4)	53(3)	29(3)	4(2)	1(3)
N(2)	29(3)	110(4)	94(4)	-20(3)	6(3)	-13(3)

C(3)	33(3)	97(4)	56(4)	35(3)	0(3)	9(3)
C(4)	29(3)	112(5)	69(4)	39(4)	3(3)	13(3)
C(5)	30(3)	104(5)	46(3)	20(3)	4(3)	0(3)
C(6)	27(3)	100(5)	34(3)	11(3)	1(2)	0(3)
C(7)	22(3)	100(5)	34(3)	2(3)	1(2)	-1(3)
C(8)	27(3)	112(5)	54(4)	-22(3)	2(3)	0(3)
C(9)	28(3)	123(6)	76(4)	-33(4)	-1(3)	-11(3)
C(10)	42(4)	100(5)	70(4)	-28(3)	-4(3)	-6(3)
C(11)	36(3)	91(4)	40(3)	-15(3)	2(2)	-8(3)
C(12)	27(3)	92(4)	31(3)	-5(3)	-1(2)	-16(3)
C(13)	38(3)	56(3)	44(3)	16(2)	-3(2)	-5(2)
C(14)	62(4)	95(4)	71(4)	48(4)	-27(3)	-30(3)
C(15)	104(5)	81(4)	93(5)	58(4)	-45(4)	-35(4)
C(16)	108(5)	47(4)	72(4)	17(3)	-47(4)	7(3)
C(17)	54(4)	73(4)	60(4)	2(3)	-17(3)	10(3)
C(18)	42(3)	63(3)	44(3)	16(3)	-10(2)	-1(3)
C(19)	30(3)	63(3)	59(3)	27(3)	7(2)	11(3)
C(20)	46(3)	75(4)	72(4)	41(3)	12(3)	9(3)
C(21)	54(4)	115(6)	83(5)	60(4)	7(3)	-15(4)
C(22)	36(3)	113(5)	58(4)	41(4)	7(3)	-5(3)
C(23)	34(3)	91(4)	56(4)	17(3)	8(3)	5(3)
C(24)	26(3)	92(4)	74(4)	46(3)	5(3)	6(3)
C(25)	30(3)	89(4)	56(4)	39(3)	6(3)	15(3)
C(26)	49(3)	55(4)	67(4)	28(3)	11(3)	9(3)
C(27)	50(4)	96(5)	72(4)	21(4)	4(3)	19(3)
C(28)	42(4)	151(7)	59(4)	30(5)	7(3)	17(4)
C(29)	40(3)	143(6)	67(5)	49(4)	6(3)	-3(4)
C(30)	39(3)	103(5)	68(4)	40(4)	4(3)	-11(3)
C(31)	38(3)	100(5)	68(4)	-27(3)	-2(3)	16(3)
C(32)	42(4)	114(5)	96(5)	-27(4)	0(4)	9(3)
C(33)	43(4)	103(5)	112(6)	-23(5)	-27(4)	13(3)
C(34)	85(5)	66(4)	95(5)	-17(4)	-36(4)	14(4)
C(35)	66(4)	72(4)	78(5)	-3(3)	-10(4)	10(3)
C(36)	45(3)	92(4)	58(4)	-11(3)	-9(3)	11(3)
C(37)	23(3)	115(5)	66(4)	-26(4)	3(3)	2(3)
C(38)	38(3)	97(5)	65(4)	-42(3)	10(3)	-12(3)
C(39)	32(3)	137(7)	76(5)	-42(5)	16(3)	-25(4)
C(40)	34(3)	101(5)	109(6)	-38(5)	4(4)	-7(3)
C(41)	47(4)	112(6)	100(6)	-19(4)	-3(4)	17(4)
C(42)	52(4)	114(6)	73(5)	-31(4)	-6(3)	20(4)
C(43)	52(4)	123(5)	47(4)	-38(4)	8(3)	-7(4)
C(44)	39(4)	115(5)	77(5)	-15(4)	21(3)	4(3)
C(45)	41(4)	126(6)	69(4)	-23(4)	15(3)	-19(3)

C(46)	57(4)	114(5)	78(5)	-43(4)	16(4)	-31(4)
C(47)	42(4)	146(6)	78(5)	-66(5)	15(4)	-20(4)
C(48)	32(3)	144(6)	77(5)	-54(4)	2(3)	-8(3)
C(1S)	60(5)	163(7)	66(5)	17(5)	12(4)	-27(5)
C(2S)	41(4)	125(6)	135(8)	36(6)	-19(5)	4(4)
C(3S)	86(6)	147(7)	75(6)	72(5)	-27(5)	-34(5)

Table A.91: Crystal data and structure refinement for **20b**.

Empirical formula	$C_{85}H_{77}BN_2OP_2Zn \cdot C_6H_6$	
Formula weight	1280.61	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.3702(7) Å	α= 81.4510(10)°.
	b = 15.2542(7) Å	β= 66.4690(10)°.
	c = 17.2588(8) Å	γ = 76.8670(10)°.
Volume	3370.8(3) $Å^3$	
Z	2	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	0.462 mm^{-1}	
F(000)	1348	
Crystal size	0.60 x 0.50 x 0.19 mm^3	
Theta range for data collection	2.27 to 25.03°.	
Index ranges	-17<=h<=17, -18<=k<=18, -20<=l<=20	
Reflections collected	32672	
Independent reflections	11879 [R(int) = 0.0203]	
Completeness to theta = 25.03°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9157 and 0.7684	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11879 / 0 / 834	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0302, wR2 = 0.0785	
R indices (all data)	R1 = 0.0370, wR2 = 0.0825	
Largest diff. peak and hole	0.337 and -0.287 $e.Å^{-3}$	

Table A.92: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **20b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	7939(1)	9209(1)	1771(1)	23(1)	C(34)	7682(1)	7332(1)	1360(1)	24(1)
P(1)	9045(1)	9010(1)	3094(1)	23(1)	C(35)	7871(1)	7559(1)	507(1)	30(1)
O(1)	7463(1)	7837(1)	3353(1)	25(1)	C(36)	8779(1)	7183(1)	-107(1)	36(1)
N(1)	8232(1)	9611(1)	2720(1)	23(1)	C(37)	9518(1)	6585(1)	126(1)	38(1)
C(1)	7810(1)	7756(1)	4002(1)	24(1)	C(38)	9340(2)	6356(1)	970(1)	40(1)
B(1)	2326(2)	4213(1)	1850(1)	28(1)	C(39)	8422(1)	6721(1)	1591(1)	32(1)
C(1S)	2035(3)	6962(3)	5249(2)	96(1)	C(40)	5495(1)	7685(1)	1747(1)	25(1)
P(2)	6459(1)	7840(1)	2111(1)	22(1)	C(41)	4666(1)	8361(1)	1731(1)	30(1)
N(2)	6507(1)	8868(1)	2176(1)	22(1)	C(42)	3968(1)	8186(1)	1428(1)	38(1)

C(2)	8535(1)	8229(1)	3986(1)	25(1)	C(43)	4090(2)	7353(1)	1142(1)	39(1)
C(2S)	2773(2)	7453(2)	4704(2)	80(1)	C(44)	4914(2)	6683(1)	1151(1)	37(1)
C(3)	8843(1)	8017(1)	4673(1)	30(1)	C(45)	5619(1)	6846(1)	1445(1)	31(1)
C(3S)	2863(2)	7636(2)	3899(2)	69(1)	C(46)	5576(1)	9484(1)	2616(1)	24(1)
C(4)	8424(2)	7388(1)	5328(1)	34(1)	C(47)	5371(1)	10349(1)	2238(1)	27(1)
C(4S)	2252(2)	7361(2)	3612(2)	66(1)	C(48)	4437(1)	10908(1)	2664(1)	37(1)
C(5)	7685(1)	6947(1)	5328(1)	32(1)	C(49)	3734(1)	10644(1)	3433(1)	41(1)
C(5S)	1524(2)	6892(2)	4118(2)	70(1)	C(50)	3949(1)	9805(1)	3808(1)	36(1)
C(6)	7366(1)	7132(1)	4648(1)	26(1)	C(51)	4869(1)	9232(1)	3403(1)	30(1)
C(6S)	1390(2)	6689(2)	4934(2)	85(1)	C(52)	6120(1)	10662(1)	1386(1)	31(1)
C(7)	6671(1)	6811(1)	4379(1)	26(1)	C(53)	6071(2)	10238(1)	656(1)	42(1)
C(8)	5999(1)	6196(1)	4697(1)	34(1)	C(54)	5981(2)	11688(1)	1224(1)	41(1)
C(9)	5462(2)	6077(1)	4224(1)	38(1)	C(55)	3127(1)	4292(1)	2291(1)	29(1)
C(10)	5580(1)	6540(1)	3441(1)	32(1)	C(56)	3183(2)	5117(1)	2523(1)	38(1)
C(11)	6254(1)	7151(1)	3099(1)	25(1)	C(57)	3872(2)	5197(2)	2875(1)	43(1)
C(12)	6770(1)	7260(1)	3595(1)	24(1)	C(58)	4563(2)	4454(2)	2996(1)	43(1)
C(13)	9711(1)	9638(1)	3448(1)	28(1)	C(59)	4535(2)	3633(2)	2778(1)	44(1)
C(14)	10785(1)	9415(1)	3179(1)	36(1)	C(60)	3827(2)	3557(1)	2439(1)	36(1)
C(15)	11312(2)	9882(2)	3445(1)	45(1)	C(61)	1116(1)	4559(1)	2482(1)	33(1)
C(16)	10782(2)	10576(2)	3964(1)	45(1)	C(62)	820(2)	4946(1)	3251(1)	43(1)
C(17)	9720(2)	10799(1)	4245(1)	45(1)	C(63)	-206(2)	5249(1)	3756(2)	56(1)
C(18)	9175(2)	10323(1)	4000(1)	37(1)	C(64)	-984(2)	5165(1)	3525(2)	58(1)
C(19)	10002(1)	8350(1)	2258(1)	25(1)	C(65)	-741(2)	4757(2)	2787(2)	54(1)
C(20)	10271(1)	7416(1)	2360(1)	30(1)	C(66)	288(2)	4464(1)	2284(1)	44(1)
C(21)	11041(2)	6944(1)	1700(1)	38(1)	C(67)	2482(1)	3156(1)	1647(1)	28(1)
C(22)	11540(1)	7394(1)	942(1)	38(1)	C(68)	1827(2)	2562(1)	2131(1)	37(1)
C(23)	11284(1)	8325(1)	844(1)	37(1)	C(69)	2007(2)	1671(1)	1929(1)	48(1)
C(24)	10520(1)	8802(1)	1496(1)	31(1)	C(70)	2864(2)	1334(1)	1252(1)	47(1)
C(25)	7479(1)	10363(1)	3151(1)	23(1)	C(71)	3538(2)	1898(1)	766(1)	39(1)
C(26)	7634(1)	11254(1)	2883(1)	27(1)	C(72)	3339(1)	2787(1)	960(1)	33(1)
C(27)	6836(2)	11947(1)	3288(1)	36(1)	C(73)	2625(1)	4802(1)	917(1)	28(1)
C(28)	5928(2)	11779(1)	3930(1)	38(1)	C(74)	3466(1)	5244(1)	563(1)	35(1)
C(29)	5790(1)	10902(1)	4193(1)	35(1)	C(75)	3764(2)	5669(1)	-247(1)	41(1)
C(30)	6564(1)	10202(1)	3804(1)	29(1)	C(76)	3221(2)	5667(1)	-748(1)	44(1)
C(31)	8616(1)	11474(1)	2182(1)	36(1)	C(77)	2376(2)	5236(1)	-423(1)	43(1)
C(32)	8462(2)	11752(2)	1353(1)	50(1)	C(78)	2100(2)	4816(1)	382(1)	37(1)
C(33)	9018(2)	12212(2)	2401(2)	58(1)	C(79)	8830(1)	9315(1)	568(1)	35(1)

Table A.93: Bond lengths [Å] for **20b**.

Zn(1)-C(79)	1.9609(17)	C(19)-C(24)	1.393(2)	C(49)-H(49)	0.95
Zn(1)-N(1)	2.0499(13)	C(19)-C(20)	1.394(2)	C(50)-C(51)	1.386(3)
Zn(1)-N(2)	2.0556(13)	C(20)-C(21)	1.384(3)	C(50)-H(50)	0.95
P(1)-N(1)	1.6009(14)	C(20)-H(20)	0.95	C(51)-H(51)	0.95

P(1)-C(19)	1.7905(17)	C(21)-C(22)	1.380(3)	C(52)-C(54)	1.529(2)
P(1)-C(13)	1.8067(17)	C(21)-H(21)	0.95	C(52)-C(53)	1.530(3)
P(1)-C(2)	1.8101(17)	C(22)-C(23)	1.386(3)	C(52)-H(52)	1
O(1)-C(1)	1.3766(19)	C(22)-H(22)	0.95	C(53)-H(53A)	0.98
O(1)-C(12)	1.3763(19)	C(23)-C(24)	1.377(3)	C(53)-H(53B)	0.98
N(1)-C(25)	1.445(2)	C(23)-H(23)	0.95	C(53)-H(53C)	0.98
C(1)-C(2)	1.385(2)	C(24)-H(24)	0.95	C(54)-H(54A)	0.98
C(1)-C(6)	1.395(2)	C(25)-C(30)	1.393(2)	C(54)-H(54B)	0.98
B(1)-C(55)	1.646(3)	C(25)-C(26)	1.406(2)	C(54)-H(54C)	0.98
B(1)-C(67)	1.648(3)	C(26)-C(27)	1.397(2)	C(55)-C(60)	1.394(3)
B(1)-C(61)	1.653(3)	C(26)-C(31)	1.516(2)	C(55)-C(56)	1.405(3)
B(1)-C(73)	1.666(3)	C(27)-C(28)	1.381(3)	C(56)-C(57)	1.386(3)
C(1S)-C(2S)	1.387(5)	C(27)-H(27)	0.95	C(56)-H(56)	0.95
C(1S)-C(6S)	1.405(5)	C(28)-C(29)	1.379(3)	C(57)-C(58)	1.377(3)
C(1S)-H(1S)	0.95	C(28)-H(28)	0.95	C(57)-H(57)	0.95
P(2)-N(2)	1.6074(13)	C(29)-C(30)	1.380(3)	C(58)-C(59)	1.373(3)
P(2)-C(34)	1.7974(17)	C(29)-H(29)	0.95	C(58)-H(58)	0.95
P(2)-C(40)	1.8054(16)	C(30)-H(30)	0.95	C(59)-C(60)	1.392(3)
P(2)-C(11)	1.8184(16)	C(31)-C(32)	1.519(3)	C(59)-H(59)	0.95
N(2)-C(46)	1.441(2)	C(31)-C(33)	1.528(3)	C(60)-H(60)	0.95
C(2)-C(3)	1.395(2)	C(31)-H(31)	1	C(61)-C(62)	1.399(3)
C(2S)-C(3S)	1.335(4)	C(32)-H(32A)	0.98	C(61)-C(66)	1.405(3)
C(2S)-H(2S)	0.95	C(32)-H(32B)	0.98	C(62)-C(63)	1.390(3)
C(3)-C(4)	1.400(3)	C(32)-H(32C)	0.98	C(62)-H(62)	0.95
C(3)-H(3)	0.95	C(33)-H(33A)	0.98	C(63)-C(64)	1.365(4)
C(3S)-C(4S)	1.330(4)	C(33)-H(33B)	0.98	C(63)-H(63)	0.95
C(3S)-H(3S)	0.95	C(33)-H(33C)	0.98	C(64)-C(65)	1.382(4)
C(4)-C(5)	1.381(3)	C(34)-C(35)	1.390(2)	C(64)-H(64)	0.95
C(4)-H(4)	0.95	C(34)-C(39)	1.391(2)	C(65)-C(66)	1.389(3)
C(4S)-C(5S)	1.338(4)	C(35)-C(36)	1.375(3)	C(65)-H(65)	0.95
C(4S)-H(4S)	0.95	C(35)-H(35)	0.95	C(66)-H(66)	0.95
C(5)-C(6)	1.393(2)	C(36)-C(37)	1.383(3)	C(67)-C(68)	1.393(3)
C(5)-H(5)	0.95	C(36)-H(36)	0.95	C(67)-C(72)	1.398(3)
C(5S)-C(6S)	1.340(4)	C(37)-C(38)	1.379(3)	C(68)-C(69)	1.395(3)
C(5S)-H(5S)	0.95	C(37)-H(37)	0.95	C(68)-H(68)	0.95
C(6)-C(7)	1.453(2)	C(38)-C(39)	1.383(3)	C(69)-C(70)	1.374(3)
C(6S)-H(6S)	0.95	C(38)-H(38)	0.95	C(69)-H(69)	0.95
C(7)-C(12)	1.391(2)	C(39)-H(39)	0.95	C(70)-C(71)	1.376(3)
C(7)-C(8)	1.396(2)	C(40)-C(41)	1.393(2)	C(70)-H(70)	0.95
C(8)-C(9)	1.381(3)	C(40)-C(45)	1.399(2)	C(71)-C(72)	1.383(3)
C(8)-H(8)	0.95	C(41)-C(42)	1.391(2)	C(71)-H(71)	0.95
C(9)-C(10)	1.392(3)	C(41)-H(41)	0.95	C(72)-H(72)	0.95
C(9)-H(9)	0.95	C(42)-C(43)	1.379(3)	C(73)-C(74)	1.395(3)

C(10)-C(11)	1.394(2)	C(42)-H(42)	0.95	C(73)-C(78)	1.403(3)
C(10)-H(10)	0.95	C(43)-C(44)	1.381(3)	C(74)-C(75)	1.393(3)
C(11)-C(12)	1.385(2)	C(43)-H(43)	0.95	C(74)-H(74)	0.95
C(13)-C(18)	1.391(3)	C(44)-C(45)	1.382(2)	C(75)-C(76)	1.377(3)
C(13)-C(14)	1.397(3)	C(44)-H(44)	0.95	C(75)-H(75)	0.95
C(14)-C(15)	1.381(3)	C(45)-H(45)	0.95	C(76)-C(77)	1.390(3)
C(14)-H(14)	0.95	C(46)-C(51)	1.395(2)	C(76)-H(76)	0.95
C(15)-C(16)	1.370(3)	C(46)-C(47)	1.405(2)	C(77)-C(78)	1.381(3)
C(15)-H(15)	0.95	C(47)-C(48)	1.395(2)	C(77)-H(77)	0.95
C(16)-C(17)	1.378(3)	C(47)-C(52)	1.520(2)	C(78)-H(78)	0.95
C(16)-H(16)	0.95	C(48)-C(49)	1.378(3)	C(79)-H(79A)	0.98
C(17)-C(18)	1.391(3)	C(48)-H(48)	0.95	C(79)-H(79B)	0.98
C(17)-H(17)	0.95	C(49)-C(50)	1.374(3)	C(79)-H(79C)	0.98
C(18)-H(18)	0.95				

Table A.94: Bond angles [°] for **20b**

C(79)-Zn(1)-N(1)	123.67(7)	C(20)-C(19)-P(1)	122.28(13)	C(49)-C(50)-H(50)	120.3
C(79)-Zn(1)-N(2)	122.37(7)	C(21)-C(20)-C(19)	119.68(17)	C(51)-C(50)-H(50)	120.3
N(1)-Zn(1)-N(2)	113.30(5)	C(21)-C(20)-H(20)	120.2	C(50)-C(51)-C(46)	121.40(17)
N(1)-P(1)-C(19)	106.73(7)	C(19)-C(20)-H(20)	120.2	C(50)-C(51)-H(51)	119.3
N(1)-P(1)-C(13)	115.21(7)	C(22)-C(21)-C(20)	120.35(17)	C(46)-C(51)-H(51)	119.3
C(19)-P(1)-C(13)	107.29(8)	C(22)-C(21)-H(21)	119.8	C(47)-C(52)-C(54)	113.83(15)
N(1)-P(1)-C(2)	115.98(7)	C(20)-C(21)-H(21)	119.8	C(47)-C(52)-C(53)	111.57(15)
C(19)-P(1)-C(2)	106.87(8)	C(21)-C(22)-C(23)	120.03(17)	C(54)-C(52)-C(53)	110.04(15)
C(13)-P(1)-C(2)	104.23(8)	C(21)-C(22)-H(22)	120.0	C(47)-C(52)-H(52)	107.0
C(1)-O(1)-C(12)	105.56(12)	C(23)-C(22)-H(22)	120.0	C(54)-C(52)-H(52)	107.0
C(25)-N(1)-P(1)	122.03(11)	C(24)-C(23)-C(22)	120.22(18)	C(53)-C(52)-H(52)	107.0
C(25)-N(1)-Zn(1)	113.73(10)	C(24)-C(23)-H(23)	119.9	C(52)-C(53)-H(53A)	109.5
P(1)-N(1)-Zn(1)	122.69(7)	C(22)-C(23)-H(23)	119.9	C(52)-C(53)-H(53B)	109.5
O(1)-C(1)-C(2)	122.78(14)	C(23)-C(24)-C(19)	120.03(17)	H(53A)-C(53)-H(53B)	109.5
O(1)-C(1)-C(6)	111.84(14)	C(23)-C(24)-H(24)	120.0	C(52)-C(53)-H(53C)	109.5
C(2)-C(1)-C(6)	125.36(15)	C(19)-C(24)-H(24)	120.0	H(53A)-C(53)-H(53C)	109.5
C(55)-B(1)-C(67)	109.36(14)	C(30)-C(25)-C(26)	119.97(15)	H(53B)-C(53)-H(53C)	109.5
C(55)-B(1)-C(61)	110.76(14)	C(30)-C(25)-N(1)	119.27(15)	C(52)-C(54)-H(54A)	109.5
C(67)-B(1)-C(61)	109.48(14)	C(26)-C(25)-N(1)	120.64(14)	C(52)-C(54)-H(54B)	109.5
C(55)-B(1)-C(73)	109.40(14)	C(27)-C(26)-C(25)	117.24(16)	H(54A)-C(54)-H(54B)	109.5
C(67)-B(1)-C(73)	106.22(14)	C(27)-C(26)-C(31)	120.20(16)	C(52)-C(54)-H(54C)	109.5
C(61)-B(1)-C(73)	111.51(14)	C(25)-C(26)-C(31)	122.56(15)	H(54A)-C(54)-H(54C)	109.5
C(2S)-C(1S)-C(6S)	118.4(3)	C(28)-C(27)-C(26)	122.28(17)	H(54B)-C(54)-H(54C)	109.5
C(2S)-C(1S)-H(1S)	120.8	C(28)-C(27)-H(27)	118.9	C(60)-C(55)-C(56)	114.45(17)
C(6S)-C(1S)-H(1S)	120.8	C(26)-C(27)-H(27)	118.9	C(60)-C(55)-B(1)	123.11(16)
N(2)-P(2)-C(34)	108.09(7)	C(27)-C(28)-C(29)	119.88(17)	C(56)-C(55)-B(1)	122.40(16)
N(2)-P(2)-C(40)	115.84(7)	C(27)-C(28)-H(28)	120.1	C(57)-C(56)-C(55)	122.99(18)

C(34)-P(2)-C(40)	106.00(8)	C(29)-C(28)-H(28)	120.1	C(57)-C(56)-H(56)	118.5
N(2)-P(2)-C(11)	113.91(7)	C(30)-C(29)-C(28)	119.25(17)	C(55)-C(56)-H(56)	118.5
C(34)-P(2)-C(11)	106.47(8)	C(30)-C(29)-H(29)	120.4	C(58)-C(57)-C(56)	120.51(19)
C(40)-P(2)-C(11)	105.88(7)	C(28)-C(29)-H(29)	120.4	C(58)-C(57)-H(57)	119.7
C(46)-N(2)-P(2)	119.97(11)	C(29)-C(30)-C(25)	121.38(17)	C(56)-C(57)-H(57)	119.7
C(46)-N(2)-Zn(1)	121.72(10)	C(29)-C(30)-H(30)	119.3	C(59)-C(58)-C(57)	118.44(19)
P(2)-N(2)-Zn(1)	117.73(7)	C(25)-C(30)-H(30)	119.3	C(59)-C(58)-H(58)	120.8
C(1)-C(2)-C(3)	114.71(15)	C(26)-C(31)-C(32)	111.16(16)	C(57)-C(58)-H(58)	120.8
C(1)-C(2)-P(1)	119.96(12)	C(26)-C(31)-C(33)	112.66(17)	C(58)-C(59)-C(60)	120.64(19)
C(3)-C(2)-P(1)	125.27(13)	C(32)-C(31)-C(33)	109.33(17)	C(58)-C(59)-H(59)	119.7
C(3S)-C(2S)-C(1S)	119.5(3)	C(26)-C(31)-H(31)	107.8	C(60)-C(59)-H(59)	119.7
C(3S)-C(2S)-H(2S)	120.3	C(32)-C(31)-H(31)	107.8	C(55)-C(60)-C(59)	122.94(18)
C(1S)-C(2S)-H(2S)	120.3	C(33)-C(31)-H(31)	107.8	C(55)-C(60)-H(60)	118.5
C(2)-C(3)-C(4)	121.59(16)	C(31)-C(32)-H(32A)	109.5	C(59)-C(60)-H(60)	118.5
C(2)-C(3)-H(3)	119.2	C(31)-C(32)-H(32B)	109.5	C(62)-C(61)-C(66)	114.34(18)
C(4)-C(3)-H(3)	119.2	H(32A)-C(32)-H(32B)	109.5	C(62)-C(61)-B(1)	124.47(17)
C(4S)-C(3S)-C(2S)	121.1(3)	C(31)-C(32)-H(32C)	109.5	C(66)-C(61)-B(1)	121.18(17)
C(4S)-C(3S)-H(3S)	119.5	H(32A)-C(32)-H(32C)	109.5	C(63)-C(62)-C(61)	122.8(2)
C(2S)-C(3S)-H(3S)	119.5	H(32B)-C(32)-H(32C)	109.5	C(63)-C(62)-H(62)	118.6
C(5)-C(4)-C(3)	121.73(16)	C(31)-C(33)-H(33A)	109.5	C(61)-C(62)-H(62)	118.6
C(5)-C(4)-H(4)	119.1	C(31)-C(33)-H(33B)	109.5	C(64)-C(63)-C(62)	120.7(2)
C(3)-C(4)-H(4)	119.1	H(33A)-C(33)-H(33B)	109.5	C(64)-C(63)-H(63)	119.7
C(3S)-C(4S)-C(5S)	121.4(3)	C(31)-C(33)-H(33C)	109.5	C(62)-C(63)-H(63)	119.7
C(3S)-C(4S)-H(4S)	119.3	H(33A)-C(33)-H(33C)	109.5	C(63)-C(64)-C(65)	119.1(2)
C(5S)-C(4S)-H(4S)	119.3	H(33B)-C(33)-H(33C)	109.5	C(63)-C(64)-H(64)	120.4
C(4)-C(5)-C(6)	118.36(16)	C(35)-C(34)-C(39)	119.49(16)	C(65)-C(64)-H(64)	120.4
C(4)-C(5)-H(5)	120.8	C(35)-C(34)-P(2)	117.03(12)	C(64)-C(65)-C(66)	119.7(2)
C(6)-C(5)-H(5)	120.8	C(39)-C(34)-P(2)	123.46(13)	C(64)-C(65)-H(65)	120.2
C(6S)-C(5S)-C(4S)	120.6(3)	C(36)-C(35)-C(34)	120.52(16)	C(66)-C(65)-H(65)	120.2
C(6S)-C(5S)-H(5S)	119.7	C(36)-C(35)-H(35)	119.7	C(65)-C(66)-C(61)	123.3(2)
C(4S)-C(5S)-H(5S)	119.7	C(34)-C(35)-H(35)	119.7	C(65)-C(66)-H(66)	118.3
C(5)-C(6)-C(1)	118.21(16)	C(35)-C(36)-C(37)	119.80(17)	C(61)-C(66)-H(66)	118.3
C(5)-C(6)-C(7)	136.52(16)	C(35)-C(36)-H(36)	120.1	C(68)-C(67)-C(72)	115.14(16)
C(1)-C(6)-C(7)	105.21(14)	C(37)-C(36)-H(36)	120.1	C(68)-C(67)-B(1)	124.76(16)
C(5S)-C(6S)-C(1S)	119.1(3)	C(38)-C(37)-C(36)	120.17(17)	C(72)-C(67)-B(1)	120.07(16)
C(5S)-C(6S)-H(6S)	120.5	C(38)-C(37)-H(37)	119.9	C(67)-C(68)-C(69)	121.95(19)
C(1S)-C(6S)-H(6S)	120.5	C(36)-C(37)-H(37)	119.9	C(67)-C(68)-H(68)	119.0
C(12)-C(7)-C(8)	117.84(16)	C(37)-C(38)-C(39)	120.36(17)	C(69)-C(68)-H(68)	119.0
C(12)-C(7)-C(6)	105.54(14)	C(37)-C(38)-H(38)	119.8	C(70)-C(69)-C(68)	120.9(2)
C(8)-C(7)-C(6)	136.62(16)	C(39)-C(38)-H(38)	119.8	C(70)-C(69)-H(69)	119.5
C(9)-C(8)-C(7)	118.39(16)	C(38)-C(39)-C(34)	119.63(17)	C(68)-C(69)-H(69)	119.5
C(9)-C(8)-H(8)	120.8	C(38)-C(39)-H(39)	120.2	C(69)-C(70)-C(71)	118.70(18)
C(7)-C(8)-H(8)	120.8	C(34)-C(39)-H(39)	120.2	C(69)-C(70)-H(70)	120.7

C(8)-C(9)-C(10)	122.17(17)	C(41)-C(40)-C(45)	119.43(15)	C(71)-C(70)-H(70)	120.7
C(8)-C(9)-H(9)	118.9	C(41)-C(40)-P(2)	123.26(13)	C(70)-C(71)-C(72)	119.95(19)
C(10)-C(9)-H(9)	118.9	C(45)-C(40)-P(2)	117.28(13)	C(70)-C(71)-H(71)	120.0
C(9)-C(10)-C(11)	121.06(17)	C(40)-C(41)-C(42)	119.39(17)	C(72)-C(71)-H(71)	120.0
C(9)-C(10)-H(10)	119.5	C(40)-C(41)-H(41)	120.3	C(71)-C(72)-C(67)	123.31(18)
C(11)-C(10)-H(10)	119.5	C(42)-C(41)-H(41)	120.3	C(71)-C(72)-H(72)	118.3
C(12)-C(11)-C(10)	115.17(15)	C(43)-C(42)-C(41)	120.70(18)	C(67)-C(72)-H(72)	118.3
C(12)-C(11)-P(2)	118.20(12)	C(43)-C(42)-H(42)	119.6	C(74)-C(73)-C(78)	114.11(17)
C(10)-C(11)-P(2)	126.55(13)	C(41)-C(42)-H(42)	119.6	C(74)-C(73)-B(1)	123.93(16)
O(1)-C(12)-C(11)	122.79(14)	C(42)-C(43)-C(44)	120.12(17)	C(78)-C(73)-B(1)	121.67(16)
O(1)-C(12)-C(7)	111.84(14)	C(42)-C(43)-H(43)	119.9	C(75)-C(74)-C(73)	123.60(18)
C(11)-C(12)-C(7)	125.36(15)	C(44)-C(43)-H(43)	119.9	C(75)-C(74)-H(74)	118.2
C(18)-C(13)-C(14)	119.36(16)	C(45)-C(44)-C(43)	119.99(18)	C(73)-C(74)-H(74)	118.2
C(18)-C(13)-P(1)	121.40(14)	C(45)-C(44)-H(44)	120.0	C(76)-C(75)-C(74)	120.08(19)
C(14)-C(13)-P(1)	119.21(13)	C(43)-C(44)-H(44)	120.0	C(76)-C(75)-H(75)	120.0
C(15)-C(14)-C(13)	120.30(18)	C(44)-C(45)-C(40)	120.36(17)	C(74)-C(75)-H(75)	120.0
C(15)-C(14)-H(14)	119.8	C(44)-C(45)-H(45)	119.8	C(75)-C(76)-C(77)	118.47(18)
C(13)-C(14)-H(14)	119.8	C(40)-C(45)-H(45)	119.8	C(75)-C(76)-H(76)	120.8
C(16)-C(15)-C(14)	120.0(2)	C(51)-C(46)-C(47)	119.46(15)	C(77)-C(76)-H(76)	120.8
C(16)-C(15)-H(15)	120.0	C(51)-C(46)-N(2)	121.23(15)	C(78)-C(77)-C(76)	120.24(19)
C(14)-C(15)-H(15)	120.0	C(47)-C(46)-N(2)	119.31(14)	C(78)-C(77)-H(77)	119.9
C(15)-C(16)-C(17)	120.52(18)	C(48)-C(47)-C(46)	117.55(16)	C(76)-C(77)-H(77)	119.9
C(15)-C(16)-H(16)	119.7	C(48)-C(47)-C(52)	120.76(15)	C(77)-C(78)-C(73)	123.50(18)
C(17)-C(16)-H(16)	119.7	C(46)-C(47)-C(52)	121.67(15)	C(77)-C(78)-H(78)	118.2
C(16)-C(17)-C(18)	120.30(19)	C(49)-C(48)-C(47)	122.43(18)	C(73)-C(78)-H(78)	118.2
C(16)-C(17)-H(17)	119.9	C(49)-C(48)-H(48)	118.8	Zn(1)-C(79)-H(79A)	109.5
C(18)-C(17)-H(17)	119.9	C(47)-C(48)-H(48)	118.8	Zn(1)-C(79)-H(79B)	109.5
C(13)-C(18)-C(17)	119.46(19)	C(50)-C(49)-C(48)	119.76(17)	H(79A)-C(79)-H(79B)	109.5
C(13)-C(18)-H(18)	120.3	C(50)-C(49)-H(49)	120.1	Zn(1)-C(79)-H(79C)	109.5
C(17)-C(18)-H(18)	120.3	C(48)-C(49)-H(49)	120.1	H(79A)-C(79)-H(79C)	109.5
C(24)-C(19)-C(20)	119.68(16)	C(49)-C(50)-C(51)	119.36(17)	H(79B)-C(79)-H(79C)	109.5
C(24)-C(19)-P(1)	117.98(13)				

Table A.95: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **20b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	22(1)	24(1)	22(1)	-2(1)	-7(1)	-4(1)
P(1)	23(1)	23(1)	22(1)	-4(1)	-9(1)	-4(1)
O(1)	29(1)	28(1)	22(1)	3(1)	-13(1)	-10(1)
N(1)	24(1)	23(1)	23(1)	-5(1)	-8(1)	-2(1)
C(1)	27(1)	26(1)	20(1)	-3(1)	-11(1)	-1(1)
B(1)	27(1)	25(1)	31(1)	-3(1)	-10(1)	-2(1)
C(1S)	108(3)	105(3)	47(2)	-4(2)	-26(2)	26(2)

P(2)	22(1)	22(1)	23(1)	1(1)	-10(1)	-5(1)
N(2)	21(1)	23(1)	24(1)	-1(1)	-9(1)	-4(1)
C(2)	28(1)	26(1)	22(1)	-5(1)	-10(1)	-3(1)
C(2S)	65(2)	88(2)	104(3)	-37(2)	-45(2)	-1(2)
C(3)	33(1)	33(1)	26(1)	-5(1)	-14(1)	-4(1)
C(3S)	51(2)	57(2)	85(2)	-3(1)	-9(1)	-14(1)
C(4)	42(1)	41(1)	24(1)	-3(1)	-18(1)	-4(1)
C(4S)	75(2)	54(2)	58(2)	-3(1)	-24(1)	5(1)
C(5)	37(1)	34(1)	20(1)	1(1)	-9(1)	-4(1)
C(5S)	66(2)	49(2)	109(2)	-13(2)	-49(2)	-4(1)
C(6)	27(1)	26(1)	21(1)	-2(1)	-7(1)	-2(1)
C(6S)	60(2)	52(2)	111(3)	21(2)	-7(2)	-15(1)
C(7)	27(1)	25(1)	22(1)	0(1)	-7(1)	-3(1)
C(8)	39(1)	33(1)	26(1)	7(1)	-10(1)	-12(1)
C(9)	42(1)	39(1)	37(1)	11(1)	-15(1)	-23(1)
C(10)	35(1)	33(1)	33(1)	3(1)	-16(1)	-13(1)
C(11)	25(1)	25(1)	24(1)	1(1)	-9(1)	-5(1)
C(12)	24(1)	23(1)	25(1)	0(1)	-7(1)	-6(1)
C(13)	34(1)	26(1)	28(1)	1(1)	-16(1)	-9(1)
C(14)	36(1)	38(1)	39(1)	-4(1)	-16(1)	-12(1)
C(15)	41(1)	58(1)	43(1)	-3(1)	-18(1)	-22(1)
C(16)	60(1)	54(1)	38(1)	1(1)	-25(1)	-31(1)
C(17)	71(2)	37(1)	37(1)	-8(1)	-29(1)	-10(1)
C(18)	45(1)	36(1)	35(1)	-7(1)	-22(1)	-4(1)
C(19)	23(1)	28(1)	26(1)	-6(1)	-12(1)	-3(1)
C(20)	30(1)	28(1)	33(1)	-4(1)	-13(1)	-3(1)
C(21)	36(1)	30(1)	47(1)	-11(1)	-17(1)	2(1)
C(22)	27(1)	46(1)	38(1)	-17(1)	-11(1)	5(1)
C(23)	29(1)	46(1)	29(1)	-4(1)	-7(1)	-1(1)
C(24)	28(1)	30(1)	32(1)	-2(1)	-10(1)	-1(1)
C(25)	24(1)	26(1)	22(1)	-5(1)	-12(1)	-2(1)
C(26)	28(1)	27(1)	29(1)	-1(1)	-13(1)	-4(1)
C(27)	41(1)	26(1)	41(1)	-3(1)	-17(1)	-1(1)
C(28)	35(1)	38(1)	36(1)	-13(1)	-13(1)	9(1)
C(29)	29(1)	43(1)	27(1)	-6(1)	-5(1)	-2(1)
C(30)	30(1)	30(1)	26(1)	0(1)	-9(1)	-7(1)
C(31)	32(1)	28(1)	42(1)	3(1)	-9(1)	-6(1)
C(32)	53(1)	65(1)	33(1)	-3(1)	-8(1)	-29(1)
C(33)	65(2)	75(2)	47(1)	7(1)	-22(1)	-42(1)
C(34)	23(1)	23(1)	27(1)	-2(1)	-10(1)	-5(1)
C(35)	29(1)	32(1)	30(1)	-1(1)	-14(1)	-4(1)
C(36)	35(1)	42(1)	27(1)	-2(1)	-8(1)	-8(1)
C(37)	28(1)	41(1)	39(1)	-12(1)	-5(1)	-2(1)

C(38)	33(1)	39(1)	45(1)	-5(1)	-19(1)	5(1)
C(39)	32(1)	33(1)	32(1)	-2(1)	-15(1)	0(1)
C(40)	23(1)	30(1)	24(1)	2(1)	-10(1)	-10(1)
C(41)	29(1)	34(1)	30(1)	-1(1)	-14(1)	-6(1)
C(42)	28(1)	50(1)	37(1)	1(1)	-17(1)	-5(1)
C(43)	36(1)	56(1)	37(1)	-1(1)	-19(1)	-20(1)
C(44)	41(1)	41(1)	36(1)	-4(1)	-15(1)	-19(1)
C(45)	31(1)	32(1)	32(1)	-1(1)	-13(1)	-9(1)
C(46)	21(1)	27(1)	25(1)	-6(1)	-10(1)	-4(1)
C(47)	25(1)	27(1)	31(1)	-4(1)	-12(1)	-3(1)
C(48)	30(1)	29(1)	47(1)	-5(1)	-11(1)	1(1)
C(49)	24(1)	41(1)	49(1)	-14(1)	-5(1)	2(1)
C(50)	28(1)	45(1)	30(1)	-8(1)	-3(1)	-9(1)
C(51)	29(1)	32(1)	29(1)	-3(1)	-10(1)	-7(1)
C(52)	26(1)	26(1)	36(1)	3(1)	-11(1)	-1(1)
C(53)	49(1)	37(1)	34(1)	1(1)	-15(1)	0(1)
C(54)	35(1)	29(1)	50(1)	5(1)	-13(1)	-2(1)
C(55)	28(1)	31(1)	25(1)	-1(1)	-6(1)	-5(1)
C(56)	38(1)	34(1)	43(1)	-4(1)	-18(1)	-5(1)
C(57)	44(1)	48(1)	40(1)	-6(1)	-16(1)	-16(1)
C(58)	38(1)	67(1)	28(1)	-3(1)	-14(1)	-14(1)
C(59)	41(1)	54(1)	33(1)	-3(1)	-19(1)	6(1)
C(60)	42(1)	36(1)	28(1)	-3(1)	-14(1)	-1(1)
C(61)	31(1)	24(1)	36(1)	2(1)	-8(1)	-2(1)
C(62)	43(1)	33(1)	43(1)	-8(1)	-3(1)	-9(1)
C(63)	53(1)	38(1)	53(1)	-14(1)	9(1)	-9(1)
C(64)	35(1)	36(1)	69(2)	2(1)	8(1)	3(1)
C(65)	31(1)	55(1)	63(2)	18(1)	-12(1)	-4(1)
C(66)	33(1)	48(1)	41(1)	5(1)	-11(1)	-4(1)
C(67)	32(1)	26(1)	30(1)	0(1)	-17(1)	-2(1)
C(68)	44(1)	32(1)	34(1)	3(1)	-15(1)	-7(1)
C(69)	68(2)	32(1)	51(1)	10(1)	-30(1)	-19(1)
C(70)	74(2)	25(1)	51(1)	-4(1)	-37(1)	0(1)
C(71)	46(1)	34(1)	39(1)	-9(1)	-26(1)	7(1)
C(72)	35(1)	32(1)	36(1)	-4(1)	-18(1)	-1(1)
C(73)	27(1)	21(1)	31(1)	-6(1)	-8(1)	2(1)
C(74)	33(1)	30(1)	38(1)	-3(1)	-11(1)	-4(1)
C(75)	36(1)	35(1)	41(1)	0(1)	-3(1)	-7(1)
C(76)	47(1)	37(1)	29(1)	1(1)	-4(1)	5(1)
C(77)	43(1)	50(1)	34(1)	-3(1)	-17(1)	2(1)
C(78)	34(1)	39(1)	35(1)	-2(1)	-12(1)	-7(1)
C(79)	31(1)	46(1)	26(1)	-3(1)	-5(1)	-14(1)

Table A.96: Crystal data and structure refinement for **21b**.

Empirical formula	$C_{76.18}H_{63.47}BN_2OP_2Zn$	
Formula weight	1160.98	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9214(8) Å	α= 86.7540(10)°.
	b = 17.1175(13) Å	β= 78.7250(10)°.
	c = 18.4747(14) Å	γ = 80.8590(10)°.
Volume	3036.9(4) $Å^3$	
Z	2	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.505 mm^{-1}	
F(000)	1215	
Crystal size	0.42 x 0.21 x 0.04 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-11<=h<=11, -20<=k<=20, -21<=l<=21	
Reflections collected	36687	
Independent reflections	10686 [R(int) = 0.0643]	
Completeness to theta = 25.03°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6780	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10686 / 84 / 784	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.0849	
R indices (all data)	R1 = 0.0878, wR2 = 0.0987	
Largest diff. peak and hole	0.338 and -0.327 $e.Å^{-3}$	

Table A.97: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **21b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	7322(1)	8038(1)	6364(1)	33(1)	C(38)	6355(3)	5411(2)	6479(2)	30(1)
P(1)	5835(1)	6422(1)	6754(1)	32(1)	C(39)	6160(3)	5159(2)	5808(2)	36(1)
O(1)	5112(2)	7704(1)	7911(1)	31(1)	C(40)	6688(3)	4392(2)	5590(2)	43(1)
N(1)	7117(2)	6905(1)	6654(1)	31(1)	C(41)	7395(3)	3876(2)	6035(2)	47(1)
C(1)	4559(3)	7020(2)	8121(2)	29(1)	C(42)	7574(3)	4122(2)	6700(2)	47(1)
B(1)	9162(3)	7074(2)	1507(2)	31(1)	C(43)	7064(3)	4883(2)	6922(2)	37(1)
P(2)	6271(1)	9249(1)	7748(1)	31(1)	C(44)	8374(3)	6489(2)	6883(2)	35(1)
N(2)	6234(2)	8980(1)	6936(1)	30(1)	C(45)	9421(3)	6071(2)	6374(2)	40(1)
C(2)	4822(3)	6366(2)	7677(2)	31(1)	C(46)	10589(3)	5678(2)	6635(2)	55(1)

C(3)	4167(3)	5726(2)	7988(2)	39(1)	C(47)	10718(4)	5707(2)	7354(3)	60(1)
C(4)	3309(3)	5764(2)	8685(2)	42(1)	C(48)	9697(4)	6142(2)	7851(2)	55(1)
C(5)	3061(3)	6431(2)	9105(2)	40(1)	C(49)	8516(3)	6534(2)	7616(2)	44(1)
C(6)	3688(3)	7084(2)	8816(2)	32(1)	C(50)	9339(3)	6025(2)	5578(2)	57(1)
C(7)	3676(3)	7886(2)	9044(2)	31(1)	C(51)	8313(3)	6724(2)	2276(2)	33(1)
C(8)	3046(3)	8349(2)	9648(2)	40(1)	C(52)	7045(3)	6437(2)	2350(2)	38(1)
C(9)	3346(3)	9108(2)	9658(2)	47(1)	C(53)	6332(3)	6176(2)	3021(2)	45(1)
C(10)	4265(3)	9419(2)	9088(2)	41(1)	C(54)	6861(4)	6179(2)	3647(2)	55(1)
C(11)	4914(3)	8973(2)	8470(2)	32(1)	C(55)	8115(4)	6442(2)	3604(2)	61(1)
C(12)	4567(3)	8219(2)	8478(2)	30(1)	C(56)	8815(3)	6706(2)	2933(2)	52(1)
C(13)	6192(3)	10296(2)	7804(2)	33(1)	C(57)	9105(3)	8034(2)	1534(2)	35(1)
C(14)	7387(3)	10627(2)	7796(2)	46(1)	C(58)	8765(3)	8483(2)	2167(2)	47(1)
C(15)	7356(4)	11434(2)	7725(2)	57(1)	C(59)	8804(4)	9292(2)	2145(3)	68(1)
C(16)	6123(4)	11922(2)	7655(2)	59(1)	C(60)	9166(4)	9690(2)	1492(3)	76(1)
C(17)	4926(3)	11604(2)	7677(2)	49(1)	C(61)	9498(4)	9269(2)	862(3)	76(1)
C(18)	4952(3)	10794(2)	7751(2)	39(1)	C(62)	9472(3)	8466(2)	883(2)	52(1)
C(19)	7864(3)	8751(2)	7973(2)	32(1)	C(63)	8449(3)	6881(2)	817(2)	32(1)
C(20)	9086(3)	8698(2)	7446(2)	38(1)	C(64)	8861(3)	6205(2)	395(2)	42(1)
C(21)	10325(3)	8310(2)	7619(2)	48(1)	C(65)	8144(4)	6015(2)	-128(2)	54(1)
C(22)	10350(3)	7971(2)	8311(2)	51(1)	C(66)	6970(4)	6505(2)	-256(2)	53(1)
C(23)	9162(4)	8021(2)	8834(2)	53(1)	C(67)	6542(3)	7185(2)	137(2)	46(1)
C(24)	7922(3)	8417(2)	8672(2)	42(1)	C(68)	7258(3)	7366(2)	661(2)	41(1)
C(25)	5152(3)	9389(2)	6564(2)	35(1)	C(69)	10801(3)	6650(2)	1391(2)	30(1)
C(26)	5352(4)	10057(2)	6120(2)	48(1)	C(70)	11919(3)	7066(2)	1233(2)	39(1)
C(27)	4239(4)	10419(2)	5787(2)	64(1)	C(71)	13295(3)	6701(2)	1096(2)	50(1)
C(28)	3025(4)	10114(2)	5875(2)	62(1)	C(72)	13609(3)	5892(2)	1111(2)	49(1)
C(29)	2859(4)	9439(2)	6286(2)	50(1)	C(73)	12539(3)	5451(2)	1292(2)	45(1)
C(30)	3909(3)	9078(2)	6636(2)	41(1)	C(74)	11168(3)	5826(2)	1436(2)	37(1)
C(31)	6679(4)	10399(2)	5990(2)	65(1)	C(75)	8652(5)	8234(3)	5459(3)	38(2)
C(32)	4674(3)	6917(2)	6181(2)	33(1)	C(75B)	8704(12)	8347(7)	5456(5)	56(7)
C(33)	3243(3)	6965(2)	6394(2)	38(1)	C(76B)	9387(11)	8997(6)	5449(5)	59(4)
C(34)	2376(3)	7316(2)	5926(2)	44(1)	C(77B)	10209(9)	9231(5)	4799(6)	65(4)
C(35)	2922(4)	7620(2)	5248(2)	45(1)	C(78B)	10349(9)	8815(6)	4158(5)	61(4)
C(36)	4344(4)	7564(2)	5021(2)	44(1)	C(79B)	9666(10)	8165(6)	4165(5)	56(4)
C(37)	5219(3)	7218(2)	5486(2)	41(1)	C(80B)	8844(10)	7931(5)	4815(6)	60(4)

Table A.98: Bond lengths [Å] for **21b**.

Zn(1)-C(75)	1.967(4)	C(22)-H(22)	0.9500	C(52)-C(53)	1.389(4)
Zn(1)-N(1)	2.013(2)	C(23)-C(24)	1.385(4)	C(52)-H(52)	0.9500
Zn(1)-N(2)	2.020(2)	C(23)-H(23)	0.9500	C(53)-C(54)	1.362(4)
Zn(1)-C(75B)	2.051(7)	C(24)-H(24)	0.9500	C(53)-H(53)	0.9500
P(1)-N(1)	1.599(2)	C(25)-C(26)	1.386(4)	C(54)-C(55)	1.376(5)
P(1)-C(32)	1.799(3)	C(25)-C(30)	1.399(4)	C(54)-H(54)	0.9500

P(1)-C(38)	1.799(3)	C(26)-C(27)	1.409(4)	C(55)-C(56)	1.387(4)
P(1)-C(2)	1.807(3)	C(26)-C(31)	1.496(5)	C(55)-H(55)	0.9500
O(1)-C(1)	1.375(3)	C(27)-C(28)	1.365(5)	C(56)-H(56)	0.9500
O(1)-C(12)	1.377(3)	C(27)-H(27)	0.9500	C(57)-C(58)	1.393(4)
N(1)-C(44)	1.460(3)	C(28)-C(29)	1.360(5)	C(57)-C(62)	1.393(4)
C(1)-C(2)	1.386(4)	C(28)-H(28)	0.9500	C(58)-C(59)	1.391(5)
C(1)-C(6)	1.400(4)	C(29)-C(30)	1.379(4)	C(58)-H(58)	0.9500
B(1)-C(51)	1.637(4)	C(29)-H(29)	0.9500	C(59)-C(60)	1.365(5)
B(1)-C(57)	1.638(4)	C(30)-H(30)	0.9500	C(59)-H(59)	0.9500
B(1)-C(63)	1.646(4)	C(31)-H(31A)	0.9800	C(60)-C(61)	1.362(6)
B(1)-C(69)	1.650(4)	C(31)-H(31B)	0.9800	C(60)-H(60)	0.9500
P(2)-N(2)	1.602(2)	C(31)-H(31C)	0.9800	C(61)-C(62)	1.376(5)
P(2)-C(19)	1.785(3)	C(32)-C(33)	1.388(4)	C(61)-H(61)	0.9500
P(2)-C(13)	1.789(3)	C(32)-C(37)	1.396(4)	C(62)-H(62)	0.9500
P(2)-C(11)	1.801(3)	C(33)-C(34)	1.384(4)	C(63)-C(64)	1.393(4)
N(2)-C(25)	1.453(3)	C(33)-H(33)	0.9500	C(63)-C(68)	1.402(4)
C(2)-C(3)	1.402(4)	C(34)-C(35)	1.373(4)	C(64)-C(65)	1.387(4)
C(3)-C(4)	1.395(4)	C(34)-H(34)	0.9500	C(64)-H(64)	0.9500
C(3)-H(3)	0.9500	C(35)-C(36)	1.381(4)	C(65)-C(66)	1.375(4)
C(4)-C(5)	1.380(4)	C(35)-H(35)	0.9500	C(65)-H(65)	0.9500
C(4)-H(4)	0.9500	C(36)-C(37)	1.383(4)	C(66)-C(67)	1.372(4)
C(5)-C(6)	1.394(4)	C(36)-H(36)	0.9500	C(66)-H(66)	0.9500
C(5)-H(5)	0.9500	C(37)-H(37)	0.9500	C(67)-C(68)	1.382(4)
C(6)-C(7)	1.458(4)	C(38)-C(43)	1.386(4)	C(67)-H(67)	0.9500
C(7)-C(12)	1.389(4)	C(38)-C(39)	1.393(4)	C(68)-H(68)	0.9500
C(7)-C(8)	1.390(4)	C(39)-C(40)	1.386(4)	C(69)-C(70)	1.386(4)
C(8)-C(9)	1.382(4)	C(39)-H(39)	0.9500	C(69)-C(74)	1.402(4)
C(8)-H(8)	0.9500	C(40)-C(41)	1.376(4)	C(70)-C(71)	1.389(4)
C(9)-C(10)	1.393(4)	C(40)-H(40)	0.9500	C(70)-H(70)	0.9500
C(9)-H(9)	0.9500	C(41)-C(42)	1.374(4)	C(71)-C(72)	1.370(4)
C(10)-C(11)	1.398(4)	C(41)-H(41)	0.9500	C(71)-H(71)	0.9500
C(10)-H(10)	0.9500	C(42)-C(43)	1.375(4)	C(72)-C(73)	1.377(4)
C(11)-C(12)	1.387(4)	C(42)-H(42)	0.9500	C(72)-H(72)	0.9500
C(13)-C(14)	1.390(4)	C(43)-H(43)	0.9500	C(73)-C(74)	1.390(4)
C(13)-C(18)	1.398(4)	C(44)-C(45)	1.391(4)	C(73)-H(73)	0.9500
C(14)-C(15)	1.376(4)	C(44)-C(49)	1.397(4)	C(74)-H(74)	0.9500
C(14)-H(14)	0.9500	C(45)-C(46)	1.400(4)	C(75)-H(75A)	0.9800
C(15)-C(16)	1.391(4)	C(45)-C(50)	1.496(4)	C(75)-H(75B)	0.9800
C(15)-H(15)	0.9500	C(46)-C(47)	1.363(5)	C(75)-H(75C)	0.9800
C(16)-C(17)	1.375(4)	C(46)-H(46)	0.9500	C(75B)-C(76B)	1.3900
C(16)-H(16)	0.9500	C(47)-C(48)	1.378(5)	C(75B)-C(80B)	1.3900
C(17)-C(18)	1.382(4)	C(47)-H(47)	0.9500	C(76B)-C(77B)	1.3900
C(17)-H(17)	0.9500	C(48)-C(49)	1.388(4)	C(76B)-H(76B)	0.9500

C(18)-H(18)	0.9500	C(48)-H(48)	0.9500	C(77B)-C(78B)	1.3900
C(19)-C(24)	1.392(4)	C(49)-H(49)	0.9500	C(77B)-H(77B)	0.9500
C(19)-C(20)	1.392(4)	C(50)-H(50A)	0.9800	C(78B)-C(79B)	1.3900
C(20)-C(21)	1.387(4)	C(50)-H(50B)	0.9800	C(78B)-H(78B)	0.9500
C(20)-H(20)	0.9500	C(50)-H(50C)	0.9800	C(79B)-C(80B)	1.3900
C(21)-C(22)	1.376(4)	C(51)-C(56)	1.398(4)	C(79B)-H(79B)	0.9500
C(21)-H(21)	0.9500	C(51)-C(52)	1.401(4)	C(80B)-H(80B)	0.9500
C(22)-C(23)	1.365(4)				

Table A.99: Bond angles [°] for **21b**

C(75)-Zn(1)-N(1)	117.57(18)	C(23)-C(22)-C(21)	120.4(3)	C(56)-C(51)-C(52)	114.0(3)
C(75)-Zn(1)-N(2)	118.22(18)	C(23)-C(22)-H(22)	119.8	C(56)-C(51)-B(1)	120.9(3)
N(1)-Zn(1)-N(2)	124.20(9)	C(21)-C(22)-H(22)	119.8	C(52)-C(51)-B(1)	125.1(3)
C(75)-Zn(1)-C(75B	5.4(4)	C(22)-C(23)-C(24)	120.0(3)	C(53)-C(52)-C(51)	123.1(3)
N(1)-Zn(1)-C(75B)	122.7(3)	C(22)-C(23)-H(23)	120.0	C(53)-C(52)-H(52)	118.5
N(2)-Zn(1)-C(75B)	113.1(3)	C(24)-C(23)-H(23)	120.0	C(51)-C(52)-H(52)	118.5
N(1)-P(1)-C(32)	106.73(13)	C(23)-C(24)-C(19)	120.6(3)	C(54)-C(53)-C(52)	120.5(3)
N(1)-P(1)-C(38)	112.77(12)	C(23)-C(24)-H(24)	119.7	C(54)-C(53)-H(53)	119.7
C(32)-P(1)-C(38)	108.91(13)	C(19)-C(24)-H(24)	119.7	C(52)-C(53)-H(53)	119.7
N(1)-P(1)-C(2)	116.38(13)	C(26)-C(25)-C(30)	119.9(3)	C(53)-C(54)-C(55)	118.9(3)
C(32)-P(1)-C(2)	106.71(13)	C(26)-C(25)-N(2)	121.3(3)	C(53)-C(54)-H(54)	120.6
C(38)-P(1)-C(2)	105.05(13)	C(30)-C(25)-N(2)	118.7(3)	C(55)-C(54)-H(54)	120.6
C(1)-O(1)-C(12)	105.6(2)	C(25)-C(26)-C(27)	117.3(3)	C(54)-C(55)-C(56)	120.2(3)
C(44)-N(1)-P(1)	116.08(18)	C(25)-C(26)-C(31)	122.8(3)	C(54)-C(55)-H(55)	119.9
C(44)-N(1)-Zn(1)	110.64(16)	C(27)-C(26)-C(31)	119.9(3)	C(56)-C(55)-H(55)	119.9
P(1)-N(1)-Zn(1)	132.94(13)	C(28)-C(27)-C(26)	121.8(3)	C(55)-C(56)-C(51)	123.3(3)
O(1)-C(1)-C(2)	122.9(2)	C(28)-C(27)-H(27)	119.1	C(55)-C(56)-H(56)	118.4
O(1)-C(1)-C(6)	111.6(2)	C(26)-C(27)-H(27)	119.1	C(51)-C(56)-H(56)	118.4
C(2)-C(1)-C(6)	125.5(3)	C(29)-C(28)-C(27)	120.5(3)	C(58)-C(57)-C(62)	114.2(3)
C(51)-B(1)-C(57)	111.3(2)	C(29)-C(28)-H(28)	119.8	C(58)-C(57)-B(1)	125.9(3)
C(51)-B(1)-C(63)	108.9(2)	C(27)-C(28)-H(28)	119.8	C(62)-C(57)-B(1)	119.8(3)
C(57)-B(1)-C(63)	108.6(2)	C(28)-C(29)-C(30)	119.5(3)	C(59)-C(58)-C(57)	122.3(4)
C(51)-B(1)-C(69)	108.7(2)	C(28)-C(29)-H(29)	120.3	C(59)-C(58)-H(58)	118.8
C(57)-B(1)-C(69)	108.7(2)	C(30)-C(29)-H(29)	120.3	C(57)-C(58)-H(58)	118.8
C(63)-B(1)-C(69)	110.6(2)	C(29)-C(30)-C(25)	120.9(3)	C(60)-C(59)-C(58)	121.2(4)
N(2)-P(2)-C(19)	106.32(13)	C(29)-C(30)-H(30)	119.6	C(60)-C(59)-H(59)	119.4
N(2)-P(2)-C(13)	112.92(13)	C(25)-C(30)-H(30)	119.6	C(58)-C(59)-H(59)	119.4
C(19)-P(2)-C(13)	109.88(13)	C(26)-C(31)-H(31A)	109.5	C(61)-C(60)-C(59)	117.9(4)
N(2)-P(2)-C(11)	115.44(13)	C(26)-C(31)-H(31B)	109.5	C(61)-C(60)-H(60)	121.1
C(19)-P(2)-C(11)	105.90(13)	H(31A)-C(31)-H(31B)	109.5	C(59)-C(60)-H(60)	121.1
C(13)-P(2)-C(11)	106.13(13)	C(26)-C(31)-H(31C)	109.5	C(60)-C(61)-C(62)	121.1(4)
C(25)-N(2)-P(2)	118.20(18)	H(31A)-C(31)-H(31C)	109.5	C(60)-C(61)-H(61)	119.5
C(25)-N(2)-Zn(1)	111.36(16)	H(31B)-C(31)-H(31C)	109.5	C(62)-C(61)-H(61)	119.5

P(2)-N(2)-Zn(1)	129.89(13)	C(33)-C(32)-C(37)	118.9(3)	C(61)-C(62)-C(57)	123.3(4)
C(1)-C(2)-C(3)	114.4(3)	C(33)-C(32)-P(1)	121.5(2)	C(61)-C(62)-H(62)	118.4
C(1)-C(2)-P(1)	119.5(2)	C(37)-C(32)-P(1)	119.5(2)	C(57)-C(62)-H(62)	118.4
C(3)-C(2)-P(1)	125.9(2)	C(34)-C(33)-C(32)	120.2(3)	C(64)-C(63)-C(68)	114.4(3)
C(4)-C(3)-C(2)	121.7(3)	C(34)-C(33)-H(33)	119.9	C(64)-C(63)-B(1)	124.6(2)
C(4)-C(3)-H(3)	119.2	C(32)-C(33)-H(33)	119.9	C(68)-C(63)-B(1)	120.7(3)
C(2)-C(3)-H(3)	119.2	C(35)-C(34)-C(33)	120.4(3)	C(65)-C(64)-C(63)	123.2(3)
C(5)-C(4)-C(3)	122.0(3)	C(35)-C(34)-H(34)	119.8	C(65)-C(64)-H(64)	118.4
C(5)-C(4)-H(4)	119.0	C(33)-C(34)-H(34)	119.8	C(63)-C(64)-H(64)	118.4
C(3)-C(4)-H(4)	119.0	C(34)-C(35)-C(36)	120.1(3)	C(66)-C(65)-C(64)	120.3(3)
C(4)-C(5)-C(6)	118.3(3)	C(34)-C(35)-H(35)	119.9	C(66)-C(65)-H(65)	119.9
C(4)-C(5)-H(5)	120.8	C(36)-C(35)-H(35)	119.9	C(64)-C(65)-H(65)	119.9
C(6)-C(5)-H(5)	120.8	C(35)-C(36)-C(37)	119.9(3)	C(67)-C(66)-C(65)	118.5(3)
C(5)-C(6)-C(1)	118.1(3)	C(35)-C(36)-H(36)	120.1	C(67)-C(66)-H(66)	120.7
C(5)-C(6)-C(7)	136.5(3)	C(37)-C(36)-H(36)	120.1	C(65)-C(66)-H(66)	120.7
C(1)-C(6)-C(7)	105.4(2)	C(36)-C(37)-C(32)	120.4(3)	C(66)-C(67)-C(68)	120.8(3)
C(12)-C(7)-C(8)	118.0(3)	C(36)-C(37)-H(37)	119.8	C(66)-C(67)-H(67)	119.6
C(12)-C(7)-C(6)	105.2(2)	C(32)-C(37)-H(37)	119.8	C(68)-C(67)-H(67)	119.6
C(8)-C(7)-C(6)	136.8(3)	C(43)-C(38)-C(39)	119.2(3)	C(67)-C(68)-C(63)	122.8(3)
C(9)-C(8)-C(7)	118.6(3)	C(43)-C(38)-P(1)	118.8(2)	C(67)-C(68)-H(68)	118.6
C(9)-C(8)-H(8)	120.7	C(39)-C(38)-P(1)	121.9(2)	C(63)-C(68)-H(68)	118.6
C(7)-C(8)-H(8)	120.7	C(40)-C(39)-C(38)	119.8(3)	C(70)-C(69)-C(74)	114.5(3)
C(8)-C(9)-C(10)	122.0(3)	C(40)-C(39)-H(39)	120.1	C(70)-C(69)-B(1)	123.8(3)
C(8)-C(9)-H(9)	119.0	C(38)-C(39)-H(39)	120.1	C(74)-C(69)-B(1)	121.7(3)
C(10)-C(9)-H(9)	119.0	C(41)-C(40)-C(39)	120.3(3)	C(69)-C(70)-C(71)	123.2(3)
C(9)-C(10)-C(11)	121.1(3)	C(41)-C(40)-H(40)	119.9	C(69)-C(70)-H(70)	118.4
C(9)-C(10)-H(10)	119.5	C(39)-C(40)-H(40)	119.9	C(71)-C(70)-H(70)	118.4
C(11)-C(10)-H(10)	119.5	C(42)-C(41)-C(40)	119.9(3)	C(72)-C(71)-C(70)	120.4(3)
C(12)-C(11)-C(10)	115.0(3)	C(42)-C(41)-H(41)	120.1	C(72)-C(71)-H(71)	119.8
C(12)-C(11)-P(2)	118.8(2)	C(40)-C(41)-H(41)	120.1	C(70)-C(71)-H(71)	119.8
C(10)-C(11)-P(2)	125.8(2)	C(41)-C(42)-C(43)	120.5(3)	C(71)-C(72)-C(73)	118.7(3)
O(1)-C(12)-C(11)	122.4(2)	C(41)-C(42)-H(42)	119.7	C(71)-C(72)-H(72)	120.6
O(1)-C(12)-C(7)	112.2(2)	C(43)-C(42)-H(42)	119.7	C(73)-C(72)-H(72)	120.6
C(11)-C(12)-C(7)	125.4(3)	C(42)-C(43)-C(38)	120.3(3)	C(72)-C(73)-C(74)	120.1(3)
C(14)-C(13)-C(18)	119.2(3)	C(42)-C(43)-H(43)	119.8	C(72)-C(73)-H(73)	120.0
C(14)-C(13)-P(2)	120.9(2)	C(38)-C(43)-H(43)	119.8	C(74)-C(73)-H(73)	120.0
C(18)-C(13)-P(2)	119.3(2)	C(45)-C(44)-C(49)	120.8(3)	C(73)-C(74)-C(69)	122.9(3)
C(15)-C(14)-C(13)	120.4(3)	C(45)-C(44)-N(1)	120.3(3)	C(73)-C(74)-H(74)	118.5
C(15)-C(14)-H(14)	119.8	C(49)-C(44)-N(1)	118.9(3)	C(69)-C(74)-H(74)	118.5
C(13)-C(14)-H(14)	119.8	C(44)-C(45)-C(46)	117.3(3)	Zn(1)-C(75)-H(75A)	109.5
C(14)-C(15)-C(16)	119.8(3)	C(44)-C(45)-C(50)	122.9(3)	Zn(1)-C(75)-H(75B)	109.5
C(14)-C(15)-H(15)	120.1	C(46)-C(45)-C(50)	119.8(3)	Zn(1)-C(75)-H(75C)	109.5
C(16)-C(15)-H(15)	120.1	C(47)-C(46)-C(45)	122.0(3)	C(76B)-C(75B)-C(80B)	120.0

C(17)-C(16)-C(15)	120.3(3)	C(47)-C(46)-H(46)	119.0	C(76B)-C(75B)-Zn(1)	122.0(6)
C(17)-C(16)-H(16)	119.8	C(45)-C(46)-H(46)	119.0	C(80B)-C(75B)-Zn(1)	117.7(6)
C(15)-C(16)-H(16)	119.8	C(46)-C(47)-C(48)	120.5(3)	C(75B)-C(76B)-C(77B)	120.0
C(16)-C(17)-C(18)	120.0(3)	C(46)-C(47)-H(47)	119.7	C(75B)-C(76B)-H(76B)	120.0
C(16)-C(17)-H(17)	120.0	C(48)-C(47)-H(47)	119.7	C(77B)-C(76B)-H(76B)	120.0
C(18)-C(17)-H(17)	120.0	C(47)-C(48)-C(49)	119.2(4)	C(78B)-C(77B)-C(76B)	120.0
C(17)-C(18)-C(13)	120.1(3)	C(47)-C(48)-H(48)	120.4	C(78B)-C(77B)-H(77B)	120.0
C(17)-C(18)-H(18)	119.9	C(49)-C(48)-H(48)	120.4	C(76B)-C(77B)-H(77B)	120.0
C(13)-C(18)-H(18)	119.9	C(48)-C(49)-C(44)	120.2(3)	C(77B)-C(78B)-C(79B)	120.0
C(24)-C(19)-C(20)	118.6(3)	C(48)-C(49)-H(49)	119.9	C(77B)-C(78B)-H(78B)	120.0
C(24)-C(19)-P(2)	121.3(2)	C(44)-C(49)-H(49)	119.9	C(79B)-C(78B)-H(78B)	120.0
C(20)-C(19)-P(2)	120.1(2)	C(45)-C(50)-H(50A)	109.5	C(80B)-C(79B)-C(78B)	120.0
C(21)-C(20)-C(19)	120.2(3)	C(45)-C(50)-H(50B)	109.5	C(80B)-C(79B)-H(79B)	120.0
C(21)-C(20)-H(20)	119.9	H(50A)-C(50)-H(50B)	109.5	C(78B)-C(79B)-H(79B)	120.0
C(19)-C(20)-H(20)	119.9	C(45)-C(50)-H(50C)	109.5	C(79B)-C(80B)-C(75B)	120.0
C(22)-C(21)-C(20)	120.1(3)	H(50A)-C(50)-H(50C)	109.5	C(79B)-C(80B)-H(80B)	120.0
C(22)-C(21)-H(21)	119.9	H(50B)-C(50)-H(50C)	109.5	C(75B)-C(80B)-H(80B)	120.0
C(20)-C(21)-H(21)	119.9				

Table A.100: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **21b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	34(1)	30(1)	33(1)	0(1)	-5(1)	0(1)
P(1)	32(1)	30(1)	32(1)	-2(1)	-5(1)	-2(1)
O(1)	32(1)	30(1)	29(1)	-4(1)	-1(1)	-5(1)
N(1)	31(1)	29(1)	33(2)	-2(1)	-6(1)	-3(1)
C(1)	25(2)	30(2)	33(2)	3(1)	-9(1)	-4(1)
B(1)	30(2)	33(2)	28(2)	-2(2)	-7(2)	-1(2)
P(2)	29(1)	29(1)	33(1)	-3(1)	-7(1)	1(1)
N(2)	34(1)	28(1)	29(1)	-1(1)	-10(1)	-1(1)
C(2)	29(2)	33(2)	32(2)	2(1)	-6(1)	-4(1)
C(3)	38(2)	35(2)	43(2)	1(2)	-8(2)	-6(1)
C(4)	33(2)	45(2)	46(2)	12(2)	-4(2)	-10(2)
C(5)	31(2)	49(2)	34(2)	8(2)	-1(1)	-1(2)
C(6)	24(2)	42(2)	28(2)	7(1)	-7(1)	1(1)
C(7)	25(2)	37(2)	28(2)	2(1)	-8(1)	3(1)
C(8)	35(2)	52(2)	29(2)	-1(2)	0(1)	3(2)
C(9)	48(2)	52(2)	35(2)	-11(2)	2(2)	6(2)
C(10)	41(2)	38(2)	44(2)	-9(2)	-9(2)	2(2)
C(11)	29(2)	36(2)	31(2)	-4(1)	-9(1)	2(1)
C(12)	25(2)	37(2)	27(2)	-4(1)	-7(1)	3(1)
C(13)	31(2)	30(2)	38(2)	-7(1)	-9(1)	0(1)
C(14)	40(2)	41(2)	60(2)	-14(2)	-15(2)	-2(2)

C(15)	45(2)	41(2)	92(3)	-18(2)	-15(2)	-13(2)
C(16)	53(2)	33(2)	92(3)	-13(2)	-12(2)	-4(2)
C(17)	43(2)	30(2)	71(3)	-8(2)	-10(2)	4(2)
C(18)	34(2)	36(2)	49(2)	-8(2)	-8(2)	-1(1)
C(19)	30(2)	34(2)	33(2)	-5(1)	-9(1)	-2(1)
C(20)	35(2)	38(2)	39(2)	-1(2)	-7(2)	1(1)
C(21)	30(2)	44(2)	66(3)	-6(2)	-5(2)	0(2)
C(22)	36(2)	43(2)	76(3)	0(2)	-22(2)	2(2)
C(23)	50(2)	61(2)	50(2)	6(2)	-27(2)	0(2)
C(24)	33(2)	57(2)	36(2)	-2(2)	-8(2)	-3(2)
C(25)	45(2)	30(2)	29(2)	-5(1)	-13(2)	3(1)
C(26)	67(2)	36(2)	45(2)	3(2)	-19(2)	-8(2)
C(27)	92(3)	44(2)	61(3)	13(2)	-39(2)	0(2)
C(28)	77(3)	50(2)	63(3)	0(2)	-41(2)	7(2)
C(29)	51(2)	47(2)	56(2)	-6(2)	-24(2)	1(2)
C(30)	43(2)	34(2)	45(2)	-5(2)	-14(2)	3(2)
C(31)	87(3)	58(2)	56(3)	17(2)	-22(2)	-29(2)
C(32)	36(2)	27(2)	34(2)	-2(1)	-7(1)	-1(1)
C(33)	38(2)	35(2)	40(2)	-2(2)	-7(2)	0(1)
C(34)	37(2)	38(2)	62(3)	-6(2)	-21(2)	-2(2)
C(35)	54(2)	34(2)	52(2)	0(2)	-28(2)	2(2)
C(36)	62(2)	37(2)	35(2)	6(2)	-16(2)	-4(2)
C(37)	41(2)	37(2)	45(2)	-1(2)	-9(2)	-5(2)
C(38)	29(2)	27(2)	32(2)	0(1)	-5(1)	-2(1)
C(39)	35(2)	37(2)	36(2)	0(2)	-8(2)	-4(1)
C(40)	43(2)	45(2)	41(2)	-15(2)	-5(2)	-7(2)
C(41)	41(2)	32(2)	67(3)	-14(2)	-9(2)	0(2)
C(42)	41(2)	34(2)	64(3)	4(2)	-18(2)	3(2)
C(43)	38(2)	34(2)	41(2)	-1(2)	-12(2)	0(1)
C(44)	32(2)	26(2)	49(2)	-3(1)	-10(2)	-4(1)
C(45)	33(2)	28(2)	58(2)	-5(2)	-5(2)	-5(1)
C(46)	33(2)	37(2)	92(3)	6(2)	-6(2)	-6(2)
C(47)	37(2)	50(2)	96(3)	21(2)	-27(2)	-10(2)
C(48)	59(2)	49(2)	68(3)	20(2)	-34(2)	-21(2)
C(49)	47(2)	36(2)	51(2)	2(2)	-18(2)	-9(2)
C(50)	50(2)	57(2)	56(3)	-14(2)	7(2)	-2(2)
C(51)	36(2)	28(2)	34(2)	-1(1)	-6(1)	3(1)
C(52)	45(2)	30(2)	36(2)	-3(1)	-5(2)	-3(1)
C(53)	47(2)	36(2)	47(2)	-1(2)	7(2)	-8(2)
C(54)	59(2)	54(2)	40(2)	8(2)	11(2)	1(2)
C(55)	61(3)	87(3)	28(2)	11(2)	-8(2)	1(2)
C(56)	43(2)	76(3)	36(2)	9(2)	-10(2)	-6(2)
C(57)	29(2)	39(2)	37(2)	-2(2)	-11(1)	0(1)

C(58)	32(2)	52(2)	56(2)	-13(2)	-8(2)	-3(2)
C(59)	47(2)	52(3)	106(4)	-36(2)	-20(2)	5(2)
C(60)	59(3)	33(2)	145(5)	-4(3)	-44(3)	-1(2)
C(61)	81(3)	45(2)	105(4)	32(2)	-32(3)	-18(2)
C(62)	67(2)	42(2)	49(2)	9(2)	-12(2)	-13(2)
C(63)	29(2)	40(2)	27(2)	3(1)	-4(1)	-4(1)
C(64)	42(2)	48(2)	39(2)	-3(2)	-18(2)	0(2)
C(65)	61(2)	53(2)	53(2)	-15(2)	-27(2)	0(2)
C(66)	49(2)	72(3)	44(2)	-2(2)	-20(2)	-16(2)
C(67)	32(2)	65(2)	40(2)	11(2)	-11(2)	-4(2)
C(68)	34(2)	50(2)	35(2)	0(2)	-4(2)	0(2)
C(69)	32(2)	35(2)	25(2)	0(1)	-9(1)	-3(1)
C(70)	40(2)	43(2)	35(2)	2(2)	-6(2)	-9(2)
C(71)	33(2)	66(2)	49(2)	6(2)	-5(2)	-11(2)
C(72)	37(2)	66(2)	39(2)	-3(2)	-12(2)	9(2)
C(73)	52(2)	45(2)	39(2)	-7(2)	-22(2)	9(2)
C(74)	41(2)	37(2)	35(2)	-1(1)	-18(2)	-3(1)
C(75)	43(4)	35(3)	34(4)	-2(3)	-3(3)	-5(3)
C(75B)	76(17)	16(10)	56(11)	11(9)	28(13)	-3(9)
C(76B)	40(8)	74(9)	61(8)	-1(7)	0(7)	-17(7)
C(77B)	53(9)	82(10)	67(9)	15(7)	-9(8)	-38(8)
C(78B)	40(8)	95(11)	47(7)	23(7)	-14(7)	-11(7)
C(79B)	54(9)	72(9)	41(8)	-6(7)	-17(6)	10(6)
C(80B)	36(8)	51(8)	81(11)	-13(7)	11(7)	5(6)

Table A.101: Crystal data and structure refinement for **22b**.

Empirical formula	$C_{79}H_{71}BN_2OP_2Zn$	
Formula weight	1202.5	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.878(7) Å	α= 80.235(8)°.
	b = 17.426(11) Å	β= 82.751(8)°.
	c = 21.932(14) Å	γ = 80.160(8)°.
Volume	3647(4) $Å^3$	
Z	2	
Density (calculated)	1.095 Mg/m^3	
Absorption coefficient	0.423 mm^{-1}	
F(000)	1264	
Crystal size	0.58 x 0.40 x 0.14 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-11<=h<=11, -20<=k<=20, -26<=l<=26	
Reflections collected	44021	
Independent reflections	12848 [R(int) = 0.0270]	
Completeness to theta = 25.03°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6589	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12848 / 252 / 927	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0507, wR2 = 0.1231	
R indices (all data)	R1 = 0.0621, wR2 = 0.1284	
Largest diff. peak and hole	0.536 and -0.525 $e.Å^{-3}$	

Table A.102: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **22b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	3430(1)	2982(1)	2079(1)	36(1)	C(42)	5081(4)	6110(2)	2917(2)	58(1)
P(1)	4752(1)	1185(1)	1913(1)	41(1)	C(43)	3727(5)	6419(2)	2827(2)	64(1)
O(1)	4031(2)	2154(1)	2960(1)	33(1)	C(44)	2773(4)	5934(2)	2805(2)	70(1)
N(1)	4173(3)	2059(1)	1605(1)	36(1)	C(45)	3175(4)	5134(2)	2866(2)	56(1)
C(1)	3482(3)	1460(2)	3070(1)	34(1)	C(46)	5841(3)	3787(2)	1762(1)	39(1)
B(1)	9143(3)	7617(2)	3325(2)	39(1)	C(47)	7173(4)	3942(2)	1774(2)	54(1)
P(2)	4986(1)	3761(1)	2966(1)	36(1)	C(48)	7996(4)	4130(2)	1223(2)	63(1)
N(2)	4974(3)	3510(1)	2295(1)	37(1)	C(49)	7543(4)	4174(2)	645(2)	56(1)

C(2)	3725(3)	941(2)	2641(1)	39(1)
C(3)	3091(4)	264(2)	2824(1)	48(1)
C(4)	2290(4)	155(2)	3388(1)	50(1)
C(5)	2051(3)	698(2)	3795(1)	43(1)
C(6)	2661(3)	1377(2)	3633(1)	35(1)
C(7)	2683(3)	2094(2)	3895(1)	34(1)
C(8)	2098(3)	2399(2)	4439(1)	40(1)
C(9)	2322(3)	3143(2)	4496(1)	46(1)
C(10)	3109(3)	3580(2)	4045(1)	45(1)
C(11)	3740(3)	3287(2)	3502(1)	36(1)
C(12)	3495(3)	2541(2)	3465(1)	32(1)
C(13)	4522(7)	483(3)	1413(2)	37(1)
C(14)	3234(7)	542(4)	1182(3)	51(2)
C(15)	3053(8)	41(4)	776(3)	73(2)
C(16)	4138(10)	-507(5)	619(4)	84(3)
C(17)	5418(10)	-589(6)	837(5)	80(2)
C(18)	5603(7)	-75(3)	1243(2)	58(2)
C(13B)	5102(6)	424(4)	1479(3)	43(4)
C(14B)	3870(8)	403(6)	1243(4)	49(4)
C(15B)	3814(12)	-136(7)	850(5)	67(4)
C(16B)	4992(14)	-654(6)	692(5)	80(6)
C(17B)	6225(12)	-633(5)	928(4)	76(5)
C(18B)	6280(8)	-94(3)	1321(3)	64(5)
C(19)	6494(3)	1070(2)	2096(1)	52(1)
C(20)	7070(4)	383(2)	2469(1)	83(1)
C(21)	8419(6)	291(4)	2572(2)	124(2)
C(22)	9245(5)	866(4)	2319(2)	117(2)
C(23)	8680(4)	1553(3)	1954(2)	83(1)
C(24)	7309(4)	1649(2)	1850(2)	55(1)
C(25)	4176(3)	2265(2)	940(1)	37(1)
C(26)	2993(4)	2649(2)	695(1)	52(1)
C(27)	2996(4)	2909(2)	53(2)	61(1)
C(28)	4177(4)	2789(2)	-349(1)	51(1)
C(29)	5354(4)	2397(2)	-100(1)	48(1)
C(30)	5372(4)	2130(2)	534(1)	45(1)
C(31)	4235(4)	3108(2)	-1045(2)	63(1)
C(32)	4806(6)	3879(3)	-1172(2)	89(2)
C(33)	2921(6)	3153(4)	-1309(2)	128(2)
C(34)	6533(3)	3376(2)	3343(1)	44(1)
C(35)	6781(4)	3637(2)	3878(2)	60(1)
C(36)	7882(5)	3239(3)	4200(2)	81(1)
C(37)	8715(4)	2591(3)	3995(2)	83(1)
C(38)	8477(4)	2332(3)	3468(2)	76(1)
C(50)	6207(4)	4058(2)	635(1)	51(1)
C(51)	5364(3)	3877(2)	1180(1)	44(1)
C(52)	8516(5)	4312(3)	49(2)	80(1)
C(53)	7894(6)	4965(3)	-435(2)	108(2)
C(54)	8966(6)	3541(4)	-209(3)	119(2)
C(55)	1413(5)	3397(3)	2207(2)	55(1)
C(62)	9378(5)	6645(3)	3530(3)	45(1)
C(63)	10031(5)	6239(3)	4044(2)	63(1)
C(64)	10236(6)	5407(4)	4177(3)	90(2)
C(65)	9834(6)	4963(3)	3792(4)	92(2)
C(66)	9170(5)	5335(3)	3286(4)	90(2)
C(67)	8921(5)	6158(3)	3167(3)	72(1)
C(56)	1873(10)	3729(5)	2110(6)	27(3)
C(57)	1806(10)	4488(6)	1781(5)	39(4)
C(58)	669(12)	5054(5)	1897(5)	45(4)
C(59)	-399(10)	4861(6)	2343(6)	46(4)
C(60)	-331(11)	4103(7)	2673(5)	45(4)
C(61)	805(12)	3537(5)	2556(6)	43(4)
C(62B)	9570(30)	6678(10)	3626(18)	84(10)
C(63B)	10880(20)	6296(14)	3747(17)	129(10)
C(64B)	11110(20)	5483(14)	3922(18)	140(11)
C(65B)	10030(30)	5053(10)	3977(18)	136(13)
C(66B)	8720(20)	5435(10)	3856(14)	92(8)
C(67B)	8480(20)	6248(10)	3681(14)	88(7)
C(68)	9569(3)	8103(2)	3833(1)	40(1)
C(69)	8736(3)	8754(2)	4037(1)	42(1)
C(70)	9128(3)	9197(2)	4435(1)	47(1)
C(71)	10410(3)	9000(2)	4652(1)	49(1)
C(72)	11292(3)	8364(2)	4458(2)	55(1)
C(73)	10886(3)	7933(2)	4052(2)	51(1)
C(74)	10093(3)	7844(2)	2663(1)	38(1)
C(75)	10189(5)	7444(2)	2165(2)	75(1)
C(76)	11022(6)	7620(3)	1619(2)	100(2)
C(77)	11772(5)	8216(3)	1537(2)	78(1)
C(78)	11737(4)	8618(3)	2010(2)	66(1)
C(79)	10911(4)	8437(2)	2564(2)	54(1)
C(80)	7483(3)	7858(2)	3244(1)	38(1)
C(81)	6513(3)	7686(2)	3748(2)	51(1)
C(82)	5097(3)	7851(2)	3719(2)	57(1)
C(83)	4591(3)	8201(2)	3162(2)	57(1)
C(84)	5501(4)	8367(2)	2654(2)	58(1)
C(85)	6920(3)	8207(2)	2696(2)	46(1)
C(3S)	5410(8)	5586(3)	4559(2)	97(2)

C(39)	7377(4)	2721(2)	3146(2)	58(1)	C(1S)	3651(6)	4875(4)	5082(3)	105(2)
C(40)	4547(3)	4804(2)	2961(1)	41(1)	C(2S)	4070(8)	5465(4)	4632(3)	108(2)
C(41)	5505(4)	5290(2)	2989(1)	47(1)					

Table A.103: Bond lengths [Å] for **22b**.

Zn(1)-C(56)	1.840(7)	C(22)-H(22)	0.9500	C(63)-C(64)	1.415(7)
Zn(1)-C(55)	2.001(5)	C(23)-C(24)	1.380(5)	C(63)-H(63)	0.9500
Zn(1)-N(1)	2.044(2)	C(23)-H(23)	0.9500	C(64)-C(65)	1.370(10)
Zn(1)-N(2)	2.050(2)	C(24)-H(24)	0.9500	C(64)-H(64)	0.9500
Zn(1)-O(1)	2.284(2)	C(25)-C(26)	1.367(4)	C(65)-C(66)	1.369(10)
P(1)-N(1)	1.599(2)	C(25)-C(30)	1.398(4)	C(65)-H(65)	0.9500
P(1)-C(13B)	1.724(6)	C(26)-C(27)	1.404(5)	C(66)-C(67)	1.399(6)
P(1)-C(19)	1.786(3)	C(26)-H(26)	0.9500	C(66)-H(66)	0.9500
P(1)-C(2)	1.809(3)	C(27)-C(28)	1.380(5)	C(67)-H(67)	0.9500
P(1)-C(13)	1.833(6)	C(27)-H(27)	0.9500	C(56)-C(57)	1.3900
O(1)-C(1)	1.381(3)	C(28)-C(29)	1.372(5)	C(56)-C(61)	1.3900
O(1)-C(12)	1.395(3)	C(28)-C(31)	1.529(4)	C(57)-C(58)	1.3900
N(1)-C(25)	1.442(3)	C(29)-C(30)	1.390(4)	C(57)-H(57)	0.9500
C(1)-C(2)	1.384(4)	C(29)-H(29)	0.9500	C(58)-C(59)	1.3900
C(1)-C(6)	1.389(4)	C(30)-H(30)	0.9500	C(58)-H(58)	0.9500
B(1)-C(68)	1.642(5)	C(31)-C(33)	1.473(6)	C(59)-C(60)	1.3900
B(1)-C(80)	1.646(4)	C(31)-C(32)	1.513(5)	C(59)-H(59)	0.9500
B(1)-C(74)	1.653(4)	C(31)-H(31)	1.0000	C(60)-C(61)	1.3900
B(1)-C(62B)	1.661(18)	C(32)-H(32A)	0.9800	C(60)-H(60)	0.9500
B(1)-C(62)	1.662(5)	C(32)-H(32B)	0.9800	C(61)-H(61)	0.9500
P(2)-N(2)	1.608(2)	C(32)-H(32C)	0.9800	C(62B)-C(63B)	1.3900
P(2)-C(40)	1.793(3)	C(33)-H(33A)	0.9800	C(62B)-C(67B)	1.3900
P(2)-C(11)	1.797(3)	C(33)-H(33B)	0.9800	C(63B)-C(64B)	1.3900
P(2)-C(34)	1.802(3)	C(33)-H(33C)	0.9800	C(63B)-H(63B)	0.9500
N(2)-C(46)	1.424(4)	C(34)-C(35)	1.392(4)	C(64B)-C(65B)	1.3900
C(2)-C(3)	1.404(4)	C(34)-C(39)	1.392(5)	C(64B)-H(64B)	0.9500
C(3)-C(4)	1.385(4)	C(35)-C(36)	1.389(5)	C(65B)-C(66B)	1.3900
C(3)-H(3)	0.9500	C(35)-H(35)	0.9500	C(65B)-H(65B)	0.9500
C(4)-C(5)	1.381(4)	C(36)-C(37)	1.383(7)	C(66B)-C(67B)	1.3900
C(4)-H(4)	0.9500	C(36)-H(36)	0.9500	C(66B)-H(66B)	0.9500
C(5)-C(6)	1.392(4)	C(37)-C(38)	1.370(6)	C(67B)-H(67B)	0.9500
C(5)-H(5)	0.9500	C(37)-H(37)	0.9500	C(68)-C(69)	1.388(4)
C(6)-C(7)	1.465(4)	C(38)-C(39)	1.385(5)	C(68)-C(73)	1.410(4)
C(7)-C(12)	1.383(4)	C(38)-H(38)	0.9500	C(69)-C(70)	1.385(4)
C(7)-C(8)	1.405(4)	C(39)-H(39)	0.9500	C(69)-H(69)	0.9500
C(8)-C(9)	1.382(4)	C(40)-C(41)	1.387(4)	C(70)-C(71)	1.378(5)
C(8)-H(8)	0.9500	C(40)-C(45)	1.406(5)	C(70)-H(70)	0.9500
C(9)-C(10)	1.384(4)	C(41)-C(42)	1.405(5)	C(71)-C(72)	1.380(5)

C(9)-H(9)	0.9500	C(41)-H(41)	0.9500	C(71)-H(71)	0.9500
C(10)-C(11)	1.406(4)	C(42)-C(43)	1.380(5)	C(72)-C(73)	1.392(5)
C(10)-H(10)	0.9500	C(42)-H(42)	0.9500	C(72)-H(72)	0.9500
C(11)-C(12)	1.380(4)	C(43)-C(44)	1.378(5)	C(73)-H(73)	0.9500
C(13)-C(18)	1.376(7)	C(43)-H(43)	0.9500	C(74)-C(75)	1.376(5)
C(13)-C(14)	1.409(8)	C(44)-C(45)	1.372(5)	C(74)-C(79)	1.391(4)
C(14)-C(15)	1.393(8)	C(44)-H(44)	0.9500	C(75)-C(76)	1.385(6)
C(14)-H(14)	0.9500	C(45)-H(45)	0.9500	C(75)-H(75)	0.9500
C(15)-C(16)	1.361(10)	C(46)-C(51)	1.391(4)	C(76)-C(77)	1.351(6)
C(15)-H(15)	0.9500	C(46)-C(47)	1.392(4)	C(76)-H(76)	0.9500
C(16)-C(17)	1.384(11)	C(47)-C(48)	1.392(5)	C(77)-C(78)	1.339(5)
C(16)-H(16)	0.9500	C(47)-H(47)	0.9500	C(77)-H(77)	0.9500
C(17)-C(18)	1.412(10)	C(48)-C(49)	1.382(5)	C(78)-C(79)	1.396(5)
C(17)-H(17)	0.9500	C(48)-H(48)	0.9500	C(78)-H(78)	0.9500
C(18)-H(18)	0.9500	C(49)-C(50)	1.372(5)	C(79)-H(79)	0.9500
C(13B)-C(14B)	1.3900	C(49)-C(52)	1.532(5)	C(80)-C(85)	1.388(4)
C(13B)-C(18B)	1.3900	C(50)-C(51)	1.390(4)	C(80)-C(81)	1.397(4)
C(14B)-C(15B)	1.3900	C(50)-H(50)	0.9500	C(81)-C(82)	1.387(5)
C(14B)-H(14B)	0.9500	C(51)-H(51)	0.9500	C(81)-H(81)	0.9500
C(15B)-C(16B)	1.3900	C(52)-C(54)	1.521(7)	C(82)-C(83)	1.382(5)
C(15B)-H(15B)	0.9500	C(52)-C(53)	1.521(6)	C(82)-H(82)	0.9500
C(16B)-C(17B)	1.3900	C(52)-H(52)	1.0000	C(83)-C(84)	1.364(5)
C(16B)-H(16B)	0.9500	C(53)-H(53A)	0.9800	C(83)-H(83)	0.9500
C(17B)-C(18B)	1.3900	C(53)-H(53B)	0.9800	C(84)-C(85)	1.393(5)
C(17B)-H(17B)	0.9500	C(53)-H(53C)	0.9800	C(84)-H(84)	0.9500
C(18B)-H(18B)	0.9500	C(54)-H(54A)	0.9800	C(85)-H(85)	0.9500
C(19)-C(24)	1.393(5)	C(54)-H(54B)	0.9800	C(3S)-C(1S)#1	1.357(8)
C(19)-C(20)	1.4070	C(54)-H(54C)	0.9800	C(3S)-C(2S)	1.361(8)
C(20)-C(21)	1.357(6)	C(55)-H(55A)	0.9800	C(3S)-H(3S)	0.9500
C(20)-H(20)	0.9500	C(55)-H(55B)	0.9800	C(1S)-C(3S)#1	1.357(8)
C(21)-C(22)	1.399(8)	C(55)-H(55C)	0.9800	C(1S)-C(2S)	1.379(8)
C(21)-H(21)	0.9500	C(62)-C(63)	1.393(7)	C(1S)-H(1S)	0.9500
C(22)-C(23)	1.394(7)	C(62)-C(67)	1.417(8)	C(2S)-H(2S)	0.9500

Table A.104: Bond angles [°] for **22b**

C(56)-Zn(1)-C(55)	23.0(3)	C(21)-C(20)-H(20)	120.4	H(54B)-C(54)-H(54C)	109.5
C(56)-Zn(1)-N(1)	136.9(4)	C(19)-C(20)-H(20)	120.4	Zn(1)-C(55)-H(55A)	109.5
C(55)-Zn(1)-N(1)	122.43(15)	C(20)-C(21)-C(22)	121.4(4)	Zn(1)-C(55)-H(55B)	109.5
C(56)-Zn(1)-N(2)	105.1(4)	C(20)-C(21)-H(21)	119.3	Zn(1)-C(55)-H(55C)	109.5
C(55)-Zn(1)-N(2)	124.56(16)	C(22)-C(21)-H(21)	119.3	C(63)-C(62)-C(67)	114.7(4)
N(1)-Zn(1)-N(2)	112.51(10)	C(23)-C(22)-C(21)	119.8(5)	C(63)-C(62)-B(1)	125.1(5)
C(56)-Zn(1)-O(1)	120.1(4)	C(23)-C(22)-H(22)	120.1	C(67)-C(62)-B(1)	120.2(4)
C(55)-Zn(1)-O(1)	108.02(15)	C(21)-C(22)-H(22)	120.1	C(62)-C(63)-C(64)	121.8(6)

N(1)-Zn(1)-O(1)	87.17(9)	C(24)-C(23)-C(22)	118.9(5)	C(62)-C(63)-H(63)	119.1
N(2)-Zn(1)-O(1)	80.16(8)	C(24)-C(23)-H(23)	120.6	C(64)-C(63)-H(63)	119.1
N(1)-P(1)-C(13B)	120.8(2)	C(22)-C(23)-H(23)	120.6	C(65)-C(64)-C(63)	121.0(6)
N(1)-P(1)-C(19)	113.57(13)	C(23)-C(24)-C(19)	121.2(4)	C(65)-C(64)-H(64)	119.5
C(13B)-P(1)-C(19)	93.18(19)	C(23)-C(24)-H(24)	119.4	C(63)-C(64)-H(64)	119.5
N(1)-P(1)-C(2)	108.88(13)	C(19)-C(24)-H(24)	119.4	C(66)-C(65)-C(64)	119.3(5)
C(13B)-P(1)-C(2)	112.7(2)	C(26)-C(25)-C(30)	118.4(3)	C(66)-C(65)-H(65)	120.4
C(19)-P(1)-C(2)	106.11(14)	C(26)-C(25)-N(1)	119.2(3)	C(64)-C(65)-H(65)	120.4
N(1)-P(1)-C(13)	109.46(19)	C(30)-C(25)-N(1)	122.3(3)	C(65)-C(66)-C(67)	119.7(6)
C(13B)-P(1)-C(13)	19.0(2)	C(25)-C(26)-C(27)	120.4(3)	C(65)-C(66)-H(66)	120.1
C(19)-P(1)-C(13)	112.1(2)	C(25)-C(26)-H(26)	119.8	C(67)-C(66)-H(66)	120.1
C(2)-P(1)-C(13)	106.3(2)	C(27)-C(26)-H(26)	119.8	C(66)-C(67)-C(62)	123.3(5)
C(1)-O(1)-C(12)	105.3(2)	C(28)-C(27)-C(26)	121.7(3)	C(66)-C(67)-H(67)	118.3
C(1)-O(1)-Zn(1)	114.96(15)	C(28)-C(27)-H(27)	119.2	C(62)-C(67)-H(67)	118.3
C(12)-O(1)-Zn(1)	107.41(15)	C(26)-C(27)-H(27)	119.2	C(57)-C(56)-C(61)	120.0
C(25)-N(1)-P(1)	120.87(18)	C(29)-C(28)-C(27)	117.4(3)	C(57)-C(56)-Zn(1)	123.4(6)
C(25)-N(1)-Zn(1)	113.74(17)	C(29)-C(28)-C(31)	119.6(3)	C(61)-C(56)-Zn(1)	115.9(6)
P(1)-N(1)-Zn(1)	125.36(13)	C(27)-C(28)-C(31)	122.9(3)	C(56)-C(57)-C(58)	120.0
O(1)-C(1)-C(2)	121.5(2)	C(28)-C(29)-C(30)	121.9(3)	C(56)-C(57)-H(57)	120.0
O(1)-C(1)-C(6)	112.2(2)	C(28)-C(29)-H(29)	119.1	C(58)-C(57)-H(57)	120.0
C(2)-C(1)-C(6)	126.3(3)	C(30)-C(29)-H(29)	119.1	C(57)-C(58)-C(59)	120.0
C(68)-B(1)-C(80)	110.0(2)	C(29)-C(30)-C(25)	120.3(3)	C(57)-C(58)-H(58)	120.0
C(68)-B(1)-C(74)	107.2(2)	C(29)-C(30)-H(30)	119.9	C(59)-C(58)-H(58)	120.0
C(80)-B(1)-C(74)	111.4(2)	C(25)-C(30)-H(30)	119.9	C(60)-C(59)-C(58)	120.0
C(68)-B(1)-C(62B)	103.8(12)	C(33)-C(31)-C(32)	113.5(4)	C(60)-C(59)-H(59)	120.0
C(80)-B(1)-C(62B)	112.7(8)	C(33)-C(31)-C(28)	113.6(3)	C(58)-C(59)-H(59)	120.0
C(74)-B(1)-C(62B)	111.3(13)	C(32)-C(31)-C(28)	109.9(3)	C(61)-C(60)-C(59)	120.0
C(68)-B(1)-C(62)	114.3(3)	C(33)-C(31)-H(31)	106.5	C(61)-C(60)-H(60)	120.0
C(80)-B(1)-C(62)	104.7(3)	C(32)-C(31)-H(31)	106.5	C(59)-C(60)-H(60)	120.0
C(74)-B(1)-C(62)	109.2(3)	C(28)-C(31)-H(31)	106.5	C(60)-C(61)-C(56)	120.0
C(62B)-B(1)-C(62)	11.0(11)	C(31)-C(32)-H(32A)	109.5	C(60)-C(61)-H(61)	120.0
N(2)-P(2)-C(40)	112.82(13)	C(31)-C(32)-H(32B)	109.5	C(56)-C(61)-H(61)	120.0
N(2)-P(2)-C(11)	108.41(13)	H(32A)-C(32)-H(32E	109.5	C(63B)-C(62B)-C(67B)	120.0
C(40)-P(2)-C(11)	108.08(14)	C(31)-C(32)-H(32C)	109.5	C(63B)-C(62B)-B(1)	126.5(14)
N(2)-P(2)-C(34)	115.21(14)	H(32A)-C(32)-H(32C	109.5	C(67B)-C(62B)-B(1)	113.0(13)
C(40)-P(2)-C(34)	111.01(14)	H(32B)-C(32)-H(32C	109.5	C(62B)-C(63B)-C(64B)	120.0
C(11)-P(2)-C(34)	100.33(14)	C(31)-C(33)-H(33A)	109.5	C(62B)-C(63B)-H(63B)	120.0
C(46)-N(2)-P(2)	122.85(19)	C(31)-C(33)-H(33B)	109.5	C(64B)-C(63B)-H(63B)	120.0
C(46)-N(2)-Zn(1)	112.98(17)	H(33A)-C(33)-H(33E	109.5	C(65B)-C(64B)-C(63B)	120.0
P(2)-N(2)-Zn(1)	122.74(14)	C(31)-C(33)-H(33C)	109.5	C(65B)-C(64B)-H(64B)	120.0
C(1)-C(2)-C(3)	114.4(3)	H(33A)-C(33)-H(33C	109.5	C(63B)-C(64B)-H(64B)	120.0
C(1)-C(2)-P(1)	119.4(2)	H(33B)-C(33)-H(33C	109.5	C(64B)-C(65B)-C(66B)	120.0
C(3)-C(2)-P(1)	126.2(2)	C(35)-C(34)-C(39)	119.6(3)	C(64B)-C(65B)-H(65B)	120.0

C(4)-C(3)-C(2)	120.8(3)	C(35)-C(34)-P(2)	121.5(3)	C(66B)-C(65B)-H(65B)	120.0
C(4)-C(3)-H(3)	119.6	C(39)-C(34)-P(2)	118.1(2)	C(65B)-C(66B)-C(67B)	120.0
C(2)-C(3)-H(3)	119.6	C(36)-C(35)-C(34)	118.8(4)	C(65B)-C(66B)-H(66B)	120.0
C(5)-C(4)-C(3)	122.8(3)	C(36)-C(35)-H(35)	120.6	C(67B)-C(66B)-H(66B)	120.0
C(5)-C(4)-H(4)	118.6	C(34)-C(35)-H(35)	120.6	C(66B)-C(67B)-C(62B)	120.0
C(3)-C(4)-H(4)	118.6	C(37)-C(36)-C(35)	120.8(4)	C(66B)-C(67B)-H(67B)	120.0
C(4)-C(5)-C(6)	118.3(3)	C(37)-C(36)-H(36)	119.6	C(62B)-C(67B)-H(67B)	120.0
C(4)-C(5)-H(5)	120.9	C(35)-C(36)-H(36)	119.6	C(69)-C(68)-C(73)	114.2(3)
C(6)-C(5)-H(5)	120.9	C(38)-C(37)-C(36)	120.6(4)	C(69)-C(68)-B(1)	123.7(3)
C(1)-C(6)-C(5)	117.4(3)	C(38)-C(37)-H(37)	119.7	C(73)-C(68)-B(1)	121.8(3)
C(1)-C(6)-C(7)	105.2(2)	C(36)-C(37)-H(37)	119.7	C(70)-C(69)-C(68)	123.9(3)
C(5)-C(6)-C(7)	137.4(3)	C(37)-C(38)-C(39)	119.1(4)	C(70)-C(69)-H(69)	118.0
C(12)-C(7)-C(8)	118.1(3)	C(37)-C(38)-H(38)	120.4	C(68)-C(69)-H(69)	118.0
C(12)-C(7)-C(6)	105.9(2)	C(39)-C(38)-H(38)	120.4	C(71)-C(70)-C(69)	120.1(3)
C(8)-C(7)-C(6)	136.0(3)	C(38)-C(39)-C(34)	121.0(4)	C(71)-C(70)-H(70)	120.0
C(9)-C(8)-C(7)	117.6(3)	C(38)-C(39)-H(39)	119.5	C(69)-C(70)-H(70)	120.0
C(9)-C(8)-H(8)	121.2	C(34)-C(39)-H(39)	119.5	C(70)-C(71)-C(72)	118.7(3)
C(7)-C(8)-H(8)	121.2	C(41)-C(40)-C(45)	119.9(3)	C(70)-C(71)-H(71)	120.7
C(8)-C(9)-C(10)	122.2(3)	C(41)-C(40)-P(2)	123.5(3)	C(72)-C(71)-H(71)	120.7
C(8)-C(9)-H(9)	118.9	C(45)-C(40)-P(2)	116.3(2)	C(71)-C(72)-C(73)	120.3(3)
C(10)-C(9)-H(9)	118.9	C(40)-C(41)-C(42)	119.0(3)	C(71)-C(72)-H(72)	119.8
C(9)-C(10)-C(11)	121.8(3)	C(40)-C(41)-H(41)	120.5	C(73)-C(72)-H(72)	119.8
C(9)-C(10)-H(10)	119.1	C(42)-C(41)-H(41)	120.5	C(72)-C(73)-C(68)	122.7(3)
C(11)-C(10)-H(10)	119.1	C(43)-C(42)-C(41)	120.0(3)	C(72)-C(73)-H(73)	118.6
C(12)-C(11)-C(10)	114.0(3)	C(43)-C(42)-H(42)	120.0	C(68)-C(73)-H(73)	118.6
C(12)-C(11)-P(2)	122.0(2)	C(41)-C(42)-H(42)	120.0	C(75)-C(74)-C(79)	113.5(3)
C(10)-C(11)-P(2)	123.2(2)	C(44)-C(43)-C(42)	120.9(3)	C(75)-C(74)-B(1)	123.2(3)
C(11)-C(12)-C(7)	126.1(2)	C(44)-C(43)-H(43)	119.5	C(79)-C(74)-B(1)	123.2(3)
C(11)-C(12)-O(1)	122.4(2)	C(42)-C(43)-H(43)	119.5	C(74)-C(75)-C(76)	123.0(4)
C(7)-C(12)-O(1)	111.5(2)	C(45)-C(44)-C(43)	119.8(4)	C(74)-C(75)-H(75)	118.5
C(18)-C(13)-C(14)	120.0(5)	C(45)-C(44)-H(44)	120.1	C(76)-C(75)-H(75)	118.5
C(18)-C(13)-P(1)	120.8(5)	C(43)-C(44)-H(44)	120.1	C(77)-C(76)-C(75)	121.4(4)
C(14)-C(13)-P(1)	119.1(4)	C(44)-C(45)-C(40)	120.4(3)	C(77)-C(76)-H(76)	119.3
C(15)-C(14)-C(13)	120.3(6)	C(44)-C(45)-H(45)	119.8	C(75)-C(76)-H(76)	119.3
C(15)-C(14)-H(14)	119.9	C(40)-C(45)-H(45)	119.8	C(78)-C(77)-C(76)	118.3(4)
C(13)-C(14)-H(14)	119.9	C(51)-C(46)-C(47)	116.6(3)	C(78)-C(77)-H(77)	120.8
C(16)-C(15)-C(14)	118.4(7)	C(51)-C(46)-N(2)	118.5(3)	C(76)-C(77)-H(77)	120.8
C(16)-C(15)-H(15)	120.8	C(47)-C(46)-N(2)	124.9(3)	C(77)-C(78)-C(79)	120.4(4)
C(14)-C(15)-H(15)	120.8	C(46)-C(47)-C(48)	120.6(3)	C(77)-C(78)-H(78)	119.8
C(15)-C(16)-C(17)	123.3(7)	C(46)-C(47)-H(47)	119.7	C(79)-C(78)-H(78)	119.8
C(15)-C(16)-H(16)	118.4	C(48)-C(47)-H(47)	119.7	C(74)-C(79)-C(78)	123.3(3)
C(17)-C(16)-H(16)	118.4	C(49)-C(48)-C(47)	122.4(3)	C(74)-C(79)-H(79)	118.3
C(16)-C(17)-C(18)	118.2(7)	C(49)-C(48)-H(48)	118.8	C(78)-C(79)-H(79)	118.3

C(16)-C(17)-H(17)	120.9	C(47)-C(48)-H(48)	118.8	C(85)-C(80)-C(81)	114.6(3)
C(18)-C(17)-H(17)	120.9	C(50)-C(49)-C(48)	116.9(3)	C(85)-C(80)-B(1)	125.5(3)
C(13)-C(18)-C(17)	119.8(7)	C(50)-C(49)-C(52)	122.1(3)	C(81)-C(80)-B(1)	119.8(3)
C(13)-C(18)-H(18)	120.1	C(48)-C(49)-C(52)	121.0(3)	C(82)-C(81)-C(80)	123.8(3)
C(17)-C(18)-H(18)	120.1	C(49)-C(50)-C(51)	121.6(3)	C(82)-C(81)-H(81)	118.1
C(14B)-C(13B)-C(1	120.0	C(49)-C(50)-H(50)	119.2	C(80)-C(81)-H(81)	118.1
C(14B)-C(13B)-P(1	105.46(10)	C(51)-C(50)-H(50)	119.2	C(83)-C(82)-C(81)	119.2(3)
C(18B)-C(13B)-P(1	134.49(11)	C(50)-C(51)-C(46)	121.8(3)	C(83)-C(82)-H(82)	120.4
C(13B)-C(14B)-C(1	120.0	C(50)-C(51)-H(51)	119.1	C(81)-C(82)-H(82)	120.4
C(13B)-C(14B)-H(1	120.0	C(46)-C(51)-H(51)	119.1	C(84)-C(83)-C(82)	119.0(3)
C(15B)-C(14B)-H(1	120.0	C(54)-C(52)-C(53)	111.8(4)	C(84)-C(83)-H(83)	120.5
C(16B)-C(15B)-C(1	120.0	C(54)-C(52)-C(49)	109.4(4)	C(82)-C(83)-H(83)	120.5
C(16B)-C(15B)-H(1	120.0	C(53)-C(52)-C(49)	113.0(4)	C(83)-C(84)-C(85)	120.8(3)
C(14B)-C(15B)-H(1	120.0	C(54)-C(52)-H(52)	107.5	C(83)-C(84)-H(84)	119.6
C(15B)-C(16B)-C(1	120.0	C(53)-C(52)-H(52)	107.5	C(85)-C(84)-H(84)	119.6
C(15B)-C(16B)-H(1	120.0	C(49)-C(52)-H(52)	107.5	C(80)-C(85)-C(84)	122.5(3)
C(17B)-C(16B)-H(1	120.0	C(52)-C(53)-H(53A)	109.5	C(80)-C(85)-H(85)	118.7
C(18B)-C(17B)-C(1	120.0	C(52)-C(53)-H(53B)	109.5	C(84)-C(85)-H(85)	118.7
C(18B)-C(17B)-H(1	120.0	H(53A)-C(53)-H(53E	109.5	C(1S)#1-C(3S)-C(2S)	120.9(5)
C(16B)-C(17B)-H(1	120.0	C(52)-C(53)-H(53C)	109.5	C(1S)#1-C(3S)-H(3S)	119.6
C(17B)-C(18B)-C(1	120.0	H(53A)-C(53)-H(53C	109.5	C(2S)-C(3S)-H(3S)	119.6
C(17B)-C(18B)-H(1	120.0	H(53B)-C(53)-H(53C	109.5	C(3S)#1-C(1S)-C(2S)	119.3(5)
C(13B)-C(18B)-H(1	120.0	C(52)-C(54)-H(54A)	109.5	C(3S)#1-C(1S)-H(1S)	120.4
C(24)-C(19)-C(20)	119.5(3)	C(52)-C(54)-H(54B)	109.5	C(2S)-C(1S)-H(1S)	120.4
C(24)-C(19)-P(1)	120.0(2)	H(54A)-C(54)-H(54E	109.5	C(3S)-C(2S)-C(1S)	119.8(6)
C(20)-C(19)-P(1)	120.5(2)	C(52)-C(54)-H(54C)	109.5	C(3S)-C(2S)-H(2S)	120.1
C(21)-C(20)-C(19)	119.3(4)	H(54A)-C(54)-H(54C	109.5	C(1S)-C(2S)-H(2S)	120.1

Table A.105: Anisotropic displacement parameters ($Å^2$x 10^3)for **22b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	48(1)	29(1)	32(1)	-4(1)	-11(1)	-6(1)
P(1)	64(1)	25(1)	29(1)	-3(1)	6(1)	-5(1)
O(1)	44(1)	27(1)	28(1)	-4(1)	1(1)	-7(1)
N(1)	53(2)	27(1)	27(1)	-4(1)	-2(1)	-8(1)
C(1)	42(2)	26(1)	33(1)	-1(1)	-1(1)	-7(1)
B(1)	34(2)	39(2)	40(2)	0(1)	1(1)	-4(1)
P(2)	48(1)	32(1)	30(1)	-4(1)	-10(1)	-11(1)
N(2)	50(2)	31(1)	31(1)	-2(1)	-9(1)	-13(1)
C(2)	55(2)	27(1)	33(2)	0(1)	1(1)	-8(1)
C(3)	79(2)	29(2)	38(2)	-4(1)	-2(2)	-15(2)
C(4)	72(2)	37(2)	41(2)	3(1)	-1(2)	-24(2)
C(5)	51(2)	42(2)	33(2)	2(1)	2(1)	-14(1)

C(6)	39(2)	32(1)	31(1)	-1(1)	-4(1)	-4(1)
C(7)	36(2)	34(1)	28(1)	-1(1)	-8(1)	-1(1)
C(8)	43(2)	45(2)	29(1)	-2(1)	-3(1)	-1(1)
C(9)	62(2)	49(2)	27(1)	-11(1)	-3(1)	-5(2)
C(10)	65(2)	39(2)	34(2)	-12(1)	-7(1)	-6(2)
C(11)	46(2)	34(2)	29(1)	-4(1)	-9(1)	-5(1)
C(12)	39(2)	33(1)	25(1)	-5(1)	-7(1)	-1(1)
C(13)	59(4)	27(2)	25(3)	-2(2)	-2(2)	-11(2)
C(14)	73(4)	49(3)	38(3)	-6(2)	-6(3)	-29(3)
C(15)	116(6)	71(4)	46(3)	-7(3)	-13(4)	-53(4)
C(16)	160(8)	50(4)	49(4)	-17(3)	14(5)	-49(5)
C(17)	132(7)	46(4)	58(5)	-18(3)	14(5)	-12(4)
C(18)	89(5)	36(3)	40(3)	-7(2)	13(3)	3(3)
C(13B)	65(10)	33(7)	33(7)	2(5)	-12(6)	-12(6)
C(14B)	73(11)	43(8)	39(9)	-3(6)	-9(9)	-27(9)
C(15B)	112(12)	53(9)	53(9)	-18(7)	-2(9)	-55(9)
C(16B)	135(16)	54(11)	55(14)	-12(10)	21(13)	-45(13)
C(17B)	112(11)	40(8)	73(11)	-19(7)	26(9)	-21(8)
C(18B)	87(10)	39(7)	62(9)	-20(6)	16(8)	0(7)
C(19)	61(2)	46(2)	36(2)	2(1)	11(2)	9(2)
C(20)	76(3)	77(3)	62(2)	21(2)	17(2)	31(2)
C(21)	82(4)	155(5)	78(3)	50(3)	14(3)	56(4)
C(22)	53(3)	181(6)	82(3)	22(4)	-1(2)	34(3)
C(23)	52(2)	118(4)	67(3)	-6(2)	4(2)	3(2)
C(24)	52(2)	62(2)	45(2)	-5(2)	2(2)	5(2)
C(25)	58(2)	26(1)	28(1)	-5(1)	-3(1)	-12(1)
C(26)	55(2)	66(2)	36(2)	-5(2)	-6(2)	-14(2)
C(27)	68(2)	75(2)	39(2)	-2(2)	-14(2)	-9(2)
C(28)	79(2)	46(2)	32(2)	-8(1)	-4(2)	-21(2)
C(29)	72(2)	38(2)	33(2)	-7(1)	5(2)	-10(2)
C(30)	68(2)	33(2)	34(2)	-8(1)	-2(2)	-6(1)
C(31)	97(3)	60(2)	32(2)	-4(2)	-9(2)	-16(2)
C(32)	158(5)	71(3)	42(2)	6(2)	-13(2)	-39(3)
C(33)	124(5)	230(7)	39(2)	7(3)	-22(3)	-70(5)
C(34)	53(2)	45(2)	37(2)	6(1)	-14(1)	-17(2)
C(35)	80(3)	59(2)	47(2)	5(2)	-28(2)	-30(2)
C(36)	102(3)	95(3)	57(2)	22(2)	-48(2)	-51(3)
C(37)	57(3)	98(3)	86(3)	40(3)	-36(2)	-22(2)
C(38)	58(2)	89(3)	71(3)	16(2)	-21(2)	-3(2)
C(39)	54(2)	64(2)	51(2)	4(2)	-11(2)	-7(2)
C(40)	61(2)	32(2)	33(2)	-7(1)	-7(1)	-12(1)
C(41)	65(2)	45(2)	34(2)	-4(1)	-8(1)	-18(2)
C(42)	95(3)	44(2)	41(2)	-8(1)	-1(2)	-33(2)

C(43)	92(3)	38(2)	61(2)	-10(2)	0(2)	-6(2)
C(44)	67(3)	51(2)	91(3)	-24(2)	-6(2)	4(2)
C(45)	57(2)	43(2)	70(2)	-11(2)	-10(2)	-8(2)
C(46)	53(2)	28(1)	37(2)	-3(1)	-8(1)	-11(1)
C(47)	59(2)	64(2)	41(2)	3(2)	-14(2)	-21(2)
C(48)	55(2)	78(3)	58(2)	4(2)	-10(2)	-26(2)
C(49)	66(2)	58(2)	44(2)	0(2)	-2(2)	-21(2)
C(50)	77(2)	45(2)	35(2)	-1(1)	-10(2)	-24(2)
C(51)	60(2)	39(2)	36(2)	-2(1)	-10(1)	-20(1)
C(52)	79(3)	103(3)	58(2)	0(2)	1(2)	-34(3)
C(53)	113(4)	122(4)	73(3)	32(3)	8(3)	-34(3)
C(54)	91(4)	153(6)	104(4)	-36(4)	40(3)	-16(4)
C(55)	47(3)	62(3)	54(3)	-11(2)	-13(2)	-2(2)
C(62)	25(2)	39(2)	63(3)	9(2)	5(2)	-4(2)
C(63)	49(3)	55(3)	66(3)	18(2)	17(2)	8(2)
C(64)	57(3)	74(4)	103(5)	44(4)	16(3)	13(3)
C(65)	47(3)	44(3)	173(7)	16(4)	6(4)	-16(2)
C(66)	58(3)	43(3)	169(6)	-3(3)	-18(4)	-13(2)
C(67)	58(3)	44(2)	115(4)	-2(3)	-21(3)	-16(2)
C(56)	35(8)	16(6)	34(9)	3(6)	-21(6)	-7(6)
C(57)	46(9)	18(7)	44(9)	0(6)	3(7)	8(6)
C(58)	55(10)	25(7)	43(9)	10(7)	4(7)	9(6)
C(59)	30(8)	35(7)	65(11)	-1(7)	0(7)	9(7)
C(60)	44(9)	36(8)	50(10)	0(7)	9(8)	-7(7)
C(61)	38(9)	42(9)	42(10)	12(8)	-19(7)	6(6)
C(62B)	56(16)	81(15)	130(30)	-32(18)	-18(18)	-23(11)
C(63B)	95(15)	76(14)	220(30)	-20(20)	-60(20)	5(14)
C(64B)	132(19)	73(14)	230(30)	-40(20)	-60(20)	-6(15)
C(65B)	110(20)	80(18)	200(30)	20(20)	-30(30)	-4(13)
C(66B)	108(16)	44(10)	130(20)	-27(13)	-14(17)	3(11)
C(67B)	94(15)	48(10)	140(20)	-18(14)	-48(17)	-21(11)
C(68)	34(2)	49(2)	32(2)	6(1)	2(1)	-8(1)
C(69)	38(2)	49(2)	37(2)	5(1)	-8(1)	-8(1)
C(70)	50(2)	48(2)	40(2)	2(1)	-3(1)	-11(2)
C(71)	54(2)	61(2)	35(2)	5(1)	-5(1)	-28(2)
C(72)	39(2)	84(3)	41(2)	5(2)	-7(1)	-17(2)
C(73)	37(2)	67(2)	44(2)	1(2)	-1(1)	-2(2)
C(74)	35(2)	34(2)	45(2)	-9(1)	1(1)	-2(1)
C(75)	105(3)	60(2)	69(3)	-28(2)	13(2)	-35(2)
C(76)	143(5)	99(4)	65(3)	-51(3)	32(3)	-31(3)
C(77)	85(3)	95(3)	51(2)	-18(2)	26(2)	-23(3)
C(78)	70(2)	88(3)	43(2)	-3(2)	3(2)	-35(2)
C(79)	63(2)	64(2)	41(2)	-9(2)	3(2)	-28(2)

C(80)	36(2)	31(1)	47(2)	-7(1)	-2(1)	-3(1)
C(81)	38(2)	68(2)	46(2)	-9(2)	-1(1)	-7(2)
C(82)	40(2)	56(2)	74(2)	-19(2)	9(2)	-10(2)
C(83)	36(2)	34(2)	101(3)	-13(2)	-13(2)	2(1)
C(84)	53(2)	41(2)	79(3)	8(2)	-28(2)	-5(2)
C(85)	45(2)	37(2)	53(2)	1(1)	-6(2)	-8(1)
C(3S)	176(6)	92(3)	44(2)	-19(2)	-10(3)	-71(4)
C(1S)	128(5)	148(5)	64(3)	-51(3)	-2(3)	-60(4)
C(2S)	157(6)	111(4)	71(3)	-41(3)	-39(4)	-15(4)

Table A.106: Crystal data and structure refinement for **23c**.

Empirical formula	$C_{80.65}H_{63.86}BN_2OP_2Zn \cdot C_6H_6$	
Formula weight	1215.12	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9023(5) Å	α= 101.9740(10)°.
	b = 16.8670(9) Å	β= 91.1140(10)°.
	c = 20.7112(11) Å	γ = 95.2960(10)°.
Volume	3366.9(3) $Å^3$	
Z	2	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.459 mm^{-1}	
F(000)	1270	
Crystal size	0.45 x 0.38 x 0.21 mm^3	
Theta range for data collection	2.58 to 25.03°.	
Index ranges	-11<=h<=11, -20<=k<=20, -24<=l<=24	
Reflections collected	40833	
Independent reflections	11870 [R(int) = 0.0212]	
Completeness to theta = 25.03°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11870 / 0 / 829	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1026	
R indices (all data)	R1 = 0.0465, wR2 = 0.1073	
Largest diff. peak and hole	0.684 and -0.421 $e.Å^{-3}$	

Table A.107: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **23c**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	8734(1)	6639(1)	6623(1)	32(1)	C(34)	9082(3)	2336(2)	5973(2)	63(1)
P(1)	9996(1)	5039(1)	6894(1)	27(1)	C(35)	9975(3)	2825(2)	5690(1)	57(1)
N(1)	8715(2)	5546(1)	6862(1)	29(1)	C(36)	10252(2)	3641(1)	5979(1)	43(1)
P(1B)	9434(4)	4954(2)	7059(2)	30(1)	C(37)	11254(2)	5516(2)	6420(1)	48(1)
N(1B)	9843(8)	5628(5)	6626(4)	28(2)	C(38)	12578(2)	5624(2)	6644(1)	49(1)
P(2)	9617(1)	8171(1)	7827(1)	27(1)	C(39)	13577(3)	5943(2)	6297(2)	64(1)
N(2)	9820(2)	7660(1)	7100(1)	30(1)	C(40)	13250(4)	6181(2)	5725(2)	77(1)
P(2B)	10220(4)	8232(2)	7638(2)	24(1)	C(41)	11899(4)	6078(2)	5492(2)	75(1)

N(2B)	8833(9)	7626(6)	7434(5)	19(2)	C(42)	10907(3)	5728(2)	5838(1)	59(1)
O(1)	10517(2)	6559(1)	7953(1)	39(1)	C(43)	7484(2)	5241(2)	7131(1)	46(1)
C(1)	10951(2)	5873(1)	8123(1)	33(1)	C(44)	7206(3)	5519(2)	7796(1)	48(1)
B(1)	4682(2)	2311(2)	8600(1)	34(1)	C(45)	5986(3)	5297(2)	8031(1)	49(1)
C(1S)	-984(3)	9415(2)	104(1)	59(1)	C(46)	5046(3)	4763(2)	7617(1)	60(1)
C(2)	10710(2)	5109(1)	7721(1)	35(1)	C(47)	5313(2)	4486(2)	6970(1)	55(1)
C(2S)	193(3)	9574(2)	486(1)	58(1)	C(48)	6542(2)	4717(1)	6727(1)	45(1)
C(3)	11238(2)	4484(1)	7965(1)	35(1)	C(49)	7561(2)	6694(1)	5854(1)	33(1)
C(3S)	1186(3)	10159(2)	386(1)	58(1)	C(50)	7119(2)	7440(2)	5763(1)	39(1)
C(4)	11965(2)	4645(1)	8571(1)	35(1)	C(51)	6312(3)	7480(2)	5218(1)	48(1)
C(5)	12210(2)	5422(1)	8949(1)	34(1)	C(52)	5909(3)	6783(2)	4756(1)	51(1)
C(6)	11704(2)	6061(1)	8719(1)	31(1)	C(53)	6310(3)	6052(2)	4834(1)	50(1)
C(7)	11764(2)	6943(1)	8928(1)	31(1)	C(54)	7116(2)	6014(2)	5382(1)	41(1)
C(8)	12372(2)	7533(1)	9451(1)	36(1)	C(49B)	7561(2)	6694(1)	5854(1)	33(1)
C(9)	12212(2)	8335(1)	9457(1)	40(1)	C(55)	4064(2)	2405(1)	7878(1)	34(1)
C(10)	11447(2)	8573(1)	8973(1)	40(1)	C(56)	2712(2)	2504(1)	7749(1)	34(1)
C(11)	10813(2)	8000(1)	8445(1)	37(1)	C(57)	2188(2)	2484(1)	7120(1)	42(1)
C(12)	11033(2)	7201(1)	8446(1)	33(1)	C(58)	3002(3)	2364(2)	6588(1)	51(1)
C(13)	9745(2)	9253(1)	7846(1)	32(1)	C(59)	4352(3)	2272(2)	6694(1)	60(1)
C(14)	10976(2)	9708(1)	7823(1)	41(1)	C(60)	4867(3)	2299(2)	7324(1)	52(1)
C(15)	11008(3)	10512(2)	7776(1)	48(1)	C(61)	4547(2)	1332(1)	8610(1)	38(1)
C(16)	9810(3)	10865(1)	7758(1)	50(1)	C(62)	4702(2)	736(2)	8043(1)	50(1)
C(17)	8580(2)	10420(1)	7789(1)	47(1)	C(63)	4737(3)	-82(2)	8056(2)	65(1)
C(18)	8546(2)	9615(1)	7830(1)	39(1)	C(64)	4581(3)	-344(2)	8635(2)	76(1)
C(19)	7920(2)	7811(1)	8042(1)	40(1)	C(65)	4387(3)	217(2)	9202(2)	72(1)
C(20)	7706(2)	7759(1)	8679(1)	40(1)	C(66)	4397(3)	1038(2)	9188(1)	52(1)
C(21)	6433(2)	7539(2)	8876(1)	46(1)	C(67)	6301(2)	2640(1)	8668(1)	32(1)
C(22)	5358(2)	7349(2)	8418(2)	52(1)	C(68)	7314(2)	2196(1)	8842(1)	34(1)
C(23)	5572(3)	7393(2)	7772(1)	55(1)	C(69)	8673(2)	2503(1)	8921(1)	43(1)
C(24)	6845(3)	7638(2)	7584(1)	49(1)	C(70)	9067(2)	3277(2)	8833(1)	46(1)
C(25)	10966(2)	7966(1)	6762(1)	43(1)	C(71)	8097(2)	3729(2)	8649(1)	47(1)
C(26)	10692(3)	8294(2)	6237(1)	56(1)	C(72)	6752(2)	3414(1)	8561(1)	42(1)
C(27)	11722(3)	8542(2)	5866(1)	71(1)	C(73)	3859(2)	2830(1)	9203(1)	34(1)
C(28)	13048(3)	8479(2)	6032(2)	67(1)	C(74)	4368(2)	3587(1)	9588(1)	41(1)
C(29)	13348(3)	8151(2)	6561(2)	60(1)	C(75)	3626(3)	4049(2)	10062(1)	51(1)
C(30)	12313(3)	7897(2)	6932(1)	57(1)	C(76)	2331(3)	3767(2)	10180(1)	54(1)
C(31)	9632(2)	3957(1)	6560(1)	33(1)	C(77)	1792(2)	3015(2)	9828(1)	50(1)
C(32)	8764(2)	3451(1)	6848(1)	42(1)	C(78)	2539(2)	2564(2)	9352(1)	41(1)
C(33)	8488(3)	2648(2)	6550(1)	55(1)					

Table A.108: Bond lengths [Å] for **23c**.

Zn(1)-C(49)	1.977(2)	C(14)-H(14)	0.9500	C(46)-H(46)	0.9500
Zn(1)-N(2)	2.0015(19)	C(15)-C(16)	1.379(4)	C(47)-C(48)	1.380(3)

Zn(1)-N(1)	2.004(2)	C(15)-H(15)	0.9500	C(47)-H(47)	0.9500
Zn(1)-N(2B)	2.099(9)	C(16)-C(17)	1.381(3)	C(48)-H(48)	0.9500
Zn(1)-N(1B)	2.112(8)	C(16)-H(16)	0.9500	C(49)-C(54)	1.375(3)
P(1)-N(1)	1.601(2)	C(17)-C(18)	1.375(3)	C(49)-C(50)	1.417(3)
P(1)-C(31)	1.811(2)	C(17)-H(17)	0.9500	C(50)-C(51)	1.387(3)
P(1)-C(2)	1.817(2)	C(18)-H(18)	0.9500	C(50)-H(50)	0.9500
P(1)-C(37)	1.830(3)	C(19)-C(20)	1.358(3)	C(51)-C(52)	1.373(4)
N(1)-C(43)	1.446(3)	C(19)-C(24)	1.382(3)	C(51)-H(51)	0.9500
P(1B)-N(1B)	1.618(9)	C(20)-C(21)	1.375(3)	C(52)-C(53)	1.369(4)
P(1B)-C(2)	1.807(4)	C(20)-H(20)	0.9500	C(52)-H(52)	0.9500
P(1B)-C(31)	1.811(4)	C(21)-C(22)	1.382(4)	C(53)-C(54)	1.392(3)
P(1B)-C(43)	2.035(5)	C(21)-H(21)	0.9500	C(53)-H(53)	0.9500
N(1B)-C(37)	1.485(8)	C(22)-C(23)	1.375(4)	C(54)-H(54)	0.9500
P(2)-N(2)	1.600(2)	C(22)-H(22)	0.9500	C(55)-C(56)	1.392(3)
P(2)-C(13)	1.810(2)	C(23)-C(24)	1.379(4)	C(55)-C(60)	1.398(3)
P(2)-C(11)	1.810(2)	C(23)-H(23)	0.9500	C(56)-C(57)	1.387(3)
P(2)-C(19)	1.829(2)	C(24)-H(24)	0.9500	C(56)-H(56)	0.9500
N(2)-C(25)	1.455(3)	C(25)-C(26)	1.351(3)	C(57)-C(58)	1.369(3)
P(2B)-N(2B)	1.628(10)	C(25)-C(30)	1.395(4)	C(57)-H(57)	0.9500
P(2B)-C(13)	1.794(4)	C(26)-C(27)	1.376(4)	C(58)-C(59)	1.378(4)
P(2B)-C(11)	1.888(4)	C(26)-H(26)	0.9500	C(58)-H(58)	0.9500
P(2B)-C(25)	1.953(5)	C(27)-C(28)	1.371(4)	C(59)-C(60)	1.384(3)
N(2B)-C(19)	1.560(10)	C(27)-H(27)	0.9500	C(59)-H(59)	0.9500
O(1)-C(12)	1.376(2)	C(28)-C(29)	1.365(4)	C(60)-H(60)	0.9500
O(1)-C(1)	1.378(2)	C(28)-H(28)	0.9500	C(61)-C(66)	1.393(3)
C(1)-C(2)	1.378(3)	C(29)-C(30)	1.382(4)	C(61)-C(62)	1.398(3)
C(1)-C(6)	1.392(3)	C(29)-H(29)	0.9500	C(62)-C(63)	1.390(4)
B(1)-C(67)	1.641(3)	C(30)-H(30)	0.9500	C(62)-H(62)	0.9500
B(1)-C(73)	1.647(3)	C(31)-C(32)	1.386(3)	C(63)-C(64)	1.368(5)
B(1)-C(55)	1.648(3)	C(31)-C(36)	1.389(3)	C(63)-H(63)	0.9500
B(1)-C(61)	1.649(3)	C(32)-C(33)	1.367(3)	C(64)-C(65)	1.377(5)
C(1S)-C(2S)	1.370(4)	C(32)-H(32)	0.9500	C(64)-H(64)	0.9500
C(1S)-C(3S)#1	1.380(4)	C(33)-C(34)	1.369(4)	C(65)-C(66)	1.389(4)
C(1S)-H(1S)	0.9500	C(33)-H(33)	0.9500	C(65)-H(65)	0.9500
C(2)-C(3)	1.398(3)	C(34)-C(35)	1.376(4)	C(66)-H(66)	0.9500
C(2S)-C(3S)	1.378(4)	C(34)-H(34)	0.9500	C(67)-C(68)	1.390(3)
C(2S)-H(2S)	0.9500	C(35)-C(36)	1.382(3)	C(67)-C(72)	1.404(3)
C(3)-C(4)	1.397(3)	C(35)-H(35)	0.9500	C(68)-C(69)	1.391(3)
C(3)-H(3)	0.9500	C(36)-H(36)	0.9500	C(68)-H(68)	0.9500
C(3S)-C(1S)#1	1.380(4)	C(37)-C(38)	1.366(3)	C(69)-C(70)	1.376(3)
C(3S)-H(3S)	0.9500	C(37)-C(42)	1.373(4)	C(69)-H(69)	0.9500
C(4)-C(5)	1.378(3)	C(38)-C(39)	1.369(4)	C(70)-C(71)	1.376(3)
C(4)-H(4)	0.9500	C(38)-H(38)	0.9500	C(70)-H(70)	0.9500

C(5)-C(6)	1.395(3)	C(39)-C(40)	1.371(5)	C(71)-C(72)	1.381(3)
C(5)-H(5)	0.9500	C(39)-H(39)	0.9500	C(71)-H(71)	0.9500
C(6)-C(7)	1.456(3)	C(40)-C(41)	1.395(5)	C(72)-H(72)	0.9500
C(7)-C(12)	1.386(3)	C(40)-H(40)	0.9500	C(73)-C(74)	1.400(3)
C(7)-C(8)	1.394(3)	C(41)-C(42)	1.387(4)	C(73)-C(78)	1.404(3)
C(8)-C(9)	1.375(3)	C(41)-H(41)	0.9500	C(74)-C(75)	1.389(3)
C(8)-H(8)	0.9500	C(42)-H(42)	0.9500	C(74)-H(74)	0.9500
C(9)-C(10)	1.392(3)	C(43)-C(48)	1.366(3)	C(75)-C(76)	1.371(4)
C(9)-H(9)	0.9500	C(43)-C(44)	1.401(3)	C(75)-H(75)	0.9500
C(10)-C(11)	1.395(3)	C(44)-C(45)	1.360(3)	C(76)-C(77)	1.379(4)
C(10)-H(10)	0.9500	C(44)-H(44)	0.9500	C(76)-H(76)	0.9500
C(11)-C(12)	1.386(3)	C(45)-C(46)	1.380(4)	C(77)-C(78)	1.384(3)
C(13)-C(14)	1.386(3)	C(45)-H(45)	0.9500	C(77)-H(77)	0.9500
C(13)-C(18)	1.387(3)	C(46)-C(47)	1.366(4)	C(78)-H(78)	0.9500
C(14)-C(15)	1.378(3)				

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z

Table A.109: Bond angles [°] for **23c**

C(49)-Zn(1)-N(2)	118.36(8)	C(14)-C(13)-P(2)	122.55(16)	N(1)-C(43)-P(1B)	43.45(15)
C(49)-Zn(1)-N(1)	116.12(8)	C(18)-C(13)-P(2)	117.62(16)	C(45)-C(44)-C(43)	120.4(2)
N(2)-Zn(1)-N(1)	125.52(8)	P(2B)-C(13)-P(2)	23.41(13)	C(45)-C(44)-H(44)	119.8
C(49)-Zn(1)-N(2B)	117.2(3)	C(15)-C(14)-C(13)	120.2(2)	C(43)-C(44)-H(44)	119.8
N(2)-Zn(1)-N(2B)	34.3(3)	C(15)-C(14)-H(14)	119.9	C(44)-C(45)-C(46)	119.5(2)
N(1)-Zn(1)-N(2B)	114.6(3)	C(13)-C(14)-H(14)	119.9	C(44)-C(45)-H(45)	120.2
C(49)-Zn(1)-N(1B)	121.2(2)	C(14)-C(15)-C(16)	119.7(2)	C(46)-C(45)-H(45)	120.2
N(2)-Zn(1)-N(1B)	109.8(2)	C(14)-C(15)-H(15)	120.2	C(47)-C(46)-C(45)	120.3(2)
N(1)-Zn(1)-N(1B)	34.8(2)	C(16)-C(15)-H(15)	120.2	C(47)-C(46)-H(46)	119.8
N(2B)-Zn(1)-N(1B)	121.6(3)	C(15)-C(16)-C(17)	120.5(2)	C(45)-C(46)-H(46)	119.8
N(1)-P(1)-C(31)	113.63(11)	C(15)-C(16)-H(16)	119.8	C(46)-C(47)-C(48)	120.4(2)
N(1)-P(1)-C(2)	114.52(11)	C(17)-C(16)-H(16)	119.8	C(46)-C(47)-H(47)	119.8
C(31)-P(1)-C(2)	104.89(10)	C(18)-C(17)-C(16)	119.9(2)	C(48)-C(47)-H(47)	119.8
N(1)-P(1)-C(37)	103.21(12)	C(18)-C(17)-H(17)	120.1	C(43)-C(48)-C(47)	119.9(2)
C(31)-P(1)-C(37)	112.13(11)	C(16)-C(17)-H(17)	120.1	C(43)-C(48)-H(48)	120.1
C(2)-P(1)-C(37)	108.58(11)	C(17)-C(18)-C(13)	120.1(2)	C(47)-C(48)-H(48)	120.1
C(43)-N(1)-P(1)	115.95(17)	C(17)-C(18)-H(18)	120.0	C(54)-C(49)-C(50)	116.3(2)
C(43)-N(1)-Zn(1)	116.99(15)	C(13)-C(18)-H(18)	120.0	C(54)-C(49)-Zn(1)	122.15(17)
P(1)-N(1)-Zn(1)	126.30(12)	C(20)-C(19)-C(24)	119.7(2)	C(50)-C(49)-Zn(1)	121.58(16)
N(1B)-P(1B)-C(2)	106.4(4)	C(20)-C(19)-N(2B)	147.6(4)	C(51)-C(50)-C(49)	121.5(2)
N(1B)-P(1B)-C(31)	108.2(4)	C(24)-C(19)-N(2B)	85.4(4)	C(51)-C(50)-H(50)	119.3
C(2)-P(1B)-C(31)	105.3(2)	C(20)-C(19)-P(2)	118.63(18)	C(49)-C(50)-H(50)	119.3
N(1B)-P(1B)-C(43)	92.8(3)	C(24)-C(19)-P(2)	121.61(18)	C(52)-C(51)-C(50)	119.9(2)
C(2)-P(1B)-C(43)	127.1(2)	N(2B)-C(19)-P(2)	43.6(3)	C(52)-C(51)-H(51)	120.0

C(31)-P(1B)-C(43)	114.7(2)	C(19)-C(20)-C(21)	121.1(2)	C(50)-C(51)-H(51)	120.0
C(37)-N(1B)-P(1B)	106.6(5)	C(19)-C(20)-H(20)	119.4	C(53)-C(52)-C(51)	119.9(2)
C(37)-N(1B)-Zn(1)	128.5(5)	C(21)-C(20)-H(20)	119.4	C(53)-C(52)-H(52)	120.0
P(1B)-N(1B)-Zn(1)	122.7(5)	C(20)-C(21)-C(22)	119.6(2)	C(51)-C(52)-H(52)	120.0
N(2)-P(2)-C(13)	111.26(10)	C(20)-C(21)-H(21)	120.2	C(52)-C(53)-C(54)	120.0(3)
N(2)-P(2)-C(11)	113.92(11)	C(22)-C(21)-H(21)	120.2	C(52)-C(53)-H(53)	120.0
C(13)-P(2)-C(11)	107.94(10)	C(23)-C(22)-C(21)	119.5(2)	C(54)-C(53)-H(53)	120.0
N(2)-P(2)-C(19)	105.21(11)	C(23)-C(22)-H(22)	120.2	C(49)-C(54)-C(53)	122.3(2)
C(13)-P(2)-C(19)	110.82(10)	C(21)-C(22)-H(22)	120.2	C(49)-C(54)-H(54)	118.8
C(11)-P(2)-C(19)	107.64(11)	C(22)-C(23)-C(24)	120.3(2)	C(53)-C(54)-H(54)	118.8
C(25)-N(2)-P(2)	115.13(16)	C(22)-C(23)-H(23)	119.8	C(56)-C(55)-C(60)	114.9(2)
C(25)-N(2)-Zn(1)	117.07(15)	C(24)-C(23)-H(23)	119.8	C(56)-C(55)-B(1)	124.28(19)
P(2)-N(2)-Zn(1)	127.75(12)	C(23)-C(24)-C(19)	119.8(2)	C(60)-C(55)-B(1)	120.50(19)
N(2B)-P(2B)-C(13)	107.4(4)	C(23)-C(24)-H(24)	120.1	C(57)-C(56)-C(55)	122.9(2)
N(2B)-P(2B)-C(11)	103.8(4)	C(19)-C(24)-H(24)	120.1	C(57)-C(56)-H(56)	118.6
C(13)-P(2B)-C(11)	105.3(2)	C(26)-C(25)-C(30)	119.1(2)	C(55)-C(56)-H(56)	118.6
N(2B)-P(2B)-C(25)	94.4(4)	C(26)-C(25)-N(2)	117.6(2)	C(58)-C(57)-C(56)	120.5(2)
C(13)-P(2B)-C(25)	113.1(2)	C(30)-C(25)-N(2)	123.2(2)	C(58)-C(57)-H(57)	119.7
C(11)-P(2B)-C(25)	129.9(2)	C(26)-C(25)-P(2B)	127.0(2)	C(56)-C(57)-H(57)	119.7
C(19)-N(2B)-P(2B)	105.2(6)	C(30)-C(25)-P(2B)	100.4(2)	C(57)-C(58)-C(59)	118.6(2)
C(19)-N(2B)-Zn(1)	131.4(5)	N(2)-C(25)-P(2B)	43.35(15)	C(57)-C(58)-H(58)	120.7
P(2B)-N(2B)-Zn(1)	121.4(5)	C(25)-C(26)-C(27)	120.8(3)	C(59)-C(58)-H(58)	120.7
C(12)-O(1)-C(1)	105.55(15)	C(25)-C(26)-H(26)	119.6	C(58)-C(59)-C(60)	120.4(2)
O(1)-C(1)-C(2)	122.56(18)	C(27)-C(26)-H(26)	119.6	C(58)-C(59)-H(59)	119.8
O(1)-C(1)-C(6)	111.81(17)	C(28)-C(27)-C(26)	120.4(3)	C(60)-C(59)-H(59)	119.8
C(2)-C(1)-C(6)	125.54(19)	C(28)-C(27)-H(27)	119.8	C(59)-C(60)-C(55)	122.7(2)
C(67)-B(1)-C(73)	110.31(17)	C(26)-C(27)-H(27)	119.8	C(59)-C(60)-H(60)	118.6
C(67)-B(1)-C(55)	108.99(17)	C(29)-C(28)-C(27)	119.8(3)	C(55)-C(60)-H(60)	118.6
C(73)-B(1)-C(55)	110.44(17)	C(29)-C(28)-H(28)	120.1	C(66)-C(61)-C(62)	114.7(2)
C(67)-B(1)-C(61)	107.87(17)	C(27)-C(28)-H(28)	120.1	C(66)-C(61)-B(1)	123.0(2)
C(73)-B(1)-C(61)	111.59(17)	C(28)-C(29)-C(30)	119.8(3)	C(62)-C(61)-B(1)	122.1(2)
C(55)-B(1)-C(61)	107.54(17)	C(28)-C(29)-H(29)	120.1	C(63)-C(62)-C(61)	122.9(3)
C(2S)-C(1S)-C(3S)i	120.2(2)	C(30)-C(29)-H(29)	120.1	C(63)-C(62)-H(62)	118.6
C(2S)-C(1S)-H(1S)	119.9	C(29)-C(30)-C(25)	120.1(2)	C(61)-C(62)-H(62)	118.6
C(3S)#1-C(1S)-H(1	119.9	C(29)-C(30)-H(30)	119.9	C(64)-C(63)-C(62)	120.4(3)
C(1)-C(2)-C(3)	115.02(19)	C(25)-C(30)-H(30)	119.9	C(64)-C(63)-H(63)	119.8
C(1)-C(2)-P(1B)	118.45(19)	C(32)-C(31)-C(36)	119.8(2)	C(62)-C(63)-H(63)	119.8
C(3)-C(2)-P(1B)	124.6(2)	C(32)-C(31)-P(1)	123.31(17)	C(63)-C(64)-C(65)	118.7(3)
C(1)-C(2)-P(1)	117.70(15)	C(36)-C(31)-P(1)	116.87(17)	C(63)-C(64)-H(64)	120.6
C(3)-C(2)-P(1)	126.52(17)	C(32)-C(31)-P(1B)	102.3(2)	C(65)-C(64)-H(64)	120.6
P(1B)-C(2)-P(1)	21.60(11)	C(36)-C(31)-P(1B)	137.3(2)	C(64)-C(65)-C(66)	120.3(3)
C(1S)-C(2S)-C(3S)	120.3(3)	P(1)-C(31)-P(1B)	21.62(11)	C(64)-C(65)-H(65)	119.9
C(1S)-C(2S)-H(2S)	119.8	C(33)-C(32)-C(31)	120.0(2)	C(66)-C(65)-H(65)	119.9

C(3S)-C(2S)-H(2S)	119.8	C(33)-C(32)-H(32)	120.0	C(65)-C(66)-C(61)	122.9(3)
C(4)-C(3)-C(2)	121.1(2)	C(31)-C(32)-H(32)	120.0	C(65)-C(66)-H(66)	118.5
C(4)-C(3)-H(3)	119.5	C(32)-C(33)-C(34)	120.4(2)	C(61)-C(66)-H(66)	118.5
C(2)-C(3)-H(3)	119.5	C(32)-C(33)-H(33)	119.8	C(68)-C(67)-C(72)	115.16(19)
C(2S)-C(3S)-C(1S)i	119.4(3)	C(34)-C(33)-H(33)	119.8	C(68)-C(67)-B(1)	123.81(18)
C(2S)-C(3S)-H(3S)	120.3	C(33)-C(34)-C(35)	120.4(2)	C(72)-C(67)-B(1)	121.03(18)
C(1S)#1-C(3S)-H(3	120.3	C(33)-C(34)-H(34)	119.8	C(67)-C(68)-C(69)	122.5(2)
C(5)-C(4)-C(3)	121.90(19)	C(35)-C(34)-H(34)	119.8	C(67)-C(68)-H(68)	118.7
C(5)-C(4)-H(4)	119.0	C(34)-C(35)-C(36)	120.0(2)	C(69)-C(68)-H(68)	118.7
C(3)-C(4)-H(4)	119.0	C(34)-C(35)-H(35)	120.0	C(70)-C(69)-C(68)	120.4(2)
C(4)-C(5)-C(6)	118.54(19)	C(36)-C(35)-H(35)	120.0	C(70)-C(69)-H(69)	119.8
C(4)-C(5)-H(5)	120.7	C(35)-C(36)-C(31)	119.4(2)	C(68)-C(69)-H(69)	119.8
C(6)-C(5)-H(5)	120.7	C(35)-C(36)-H(36)	120.3	C(71)-C(70)-C(69)	118.7(2)
C(1)-C(6)-C(5)	117.84(19)	C(31)-C(36)-H(36)	120.3	C(71)-C(70)-H(70)	120.6
C(1)-C(6)-C(7)	105.14(17)	C(38)-C(37)-C(42)	119.9(2)	C(69)-C(70)-H(70)	120.6
C(5)-C(6)-C(7)	136.99(19)	C(38)-C(37)-N(1B)	143.6(4)	C(70)-C(71)-C(72)	120.4(2)
C(12)-C(7)-C(8)	118.00(19)	C(42)-C(37)-N(1B)	87.9(3)	C(70)-C(71)-H(71)	119.8
C(12)-C(7)-C(6)	105.65(17)	C(38)-C(37)-P(1)	118.2(2)	C(72)-C(71)-H(71)	119.8
C(8)-C(7)-C(6)	136.32(19)	C(42)-C(37)-P(1)	121.8(2)	C(71)-C(72)-C(67)	122.6(2)
C(9)-C(8)-C(7)	118.02(19)	N(1B)-C(37)-P(1)	42.9(3)	C(71)-C(72)-H(72)	118.7
C(9)-C(8)-H(8)	121.0	C(37)-C(38)-C(39)	121.1(3)	C(67)-C(72)-H(72)	118.7
C(7)-C(8)-H(8)	121.0	C(37)-C(38)-H(38)	119.4	C(74)-C(73)-C(78)	114.0(2)
C(8)-C(9)-C(10)	122.6(2)	C(39)-C(38)-H(38)	119.4	C(74)-C(73)-B(1)	123.84(19)
C(8)-C(9)-H(9)	118.7	C(38)-C(39)-C(40)	119.9(3)	C(78)-C(73)-B(1)	122.05(19)
C(10)-C(9)-H(9)	118.7	C(38)-C(39)-H(39)	120.0	C(75)-C(74)-C(73)	123.4(2)
C(9)-C(10)-C(11)	121.1(2)	C(40)-C(39)-H(39)	120.0	C(75)-C(74)-H(74)	118.3
C(9)-C(10)-H(10)	119.5	C(39)-C(40)-C(41)	119.5(3)	C(73)-C(74)-H(74)	118.3
C(11)-C(10)-H(10)	119.5	C(39)-C(40)-H(40)	120.2	C(76)-C(75)-C(74)	120.1(2)
C(12)-C(11)-C(10)	114.60(19)	C(41)-C(40)-H(40)	120.2	C(76)-C(75)-H(75)	119.9
C(12)-C(11)-P(2)	117.43(15)	C(42)-C(41)-C(40)	119.7(3)	C(74)-C(75)-H(75)	119.9
C(10)-C(11)-P(2)	127.60(17)	C(42)-C(41)-H(41)	120.1	C(75)-C(76)-C(77)	118.9(2)
C(12)-C(11)-P(2B)	117.35(19)	C(40)-C(41)-H(41)	120.1	C(75)-C(76)-H(76)	120.6
C(10)-C(11)-P(2B)	124.9(2)	C(37)-C(42)-C(41)	119.7(3)	C(77)-C(76)-H(76)	120.6
P(2)-C(11)-P(2B)	22.68(12)	C(37)-C(42)-H(42)	120.2	C(76)-C(77)-C(78)	120.3(2)
O(1)-C(12)-C(11)	122.45(18)	C(41)-C(42)-H(42)	120.2	C(76)-C(77)-H(77)	119.9
O(1)-C(12)-C(7)	111.82(17)	C(48)-C(43)-C(44)	119.4(2)	C(78)-C(77)-H(77)	119.9
C(11)-C(12)-C(7)	125.72(19)	C(48)-C(43)-N(1)	119.9(2)	C(77)-C(78)-C(73)	123.2(2)
C(14)-C(13)-C(18)	119.63(19)	C(44)-C(43)-N(1)	120.6(2)	C(77)-C(78)-H(78)	118.4
C(14)-C(13)-P(2B)	101.7(2)	C(48)-C(43)-P(1B)	115.9(2)	C(73)-C(78)-H(78)	118.4
C(18)-C(13)-P(2B)	135.5(2)	C(44)-C(43)-P(1B)	109.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z

Table A.110: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **23c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	36(1)	28(1)	32(1)	8(1)	-5(1)	0(1)
P(1)	27(1)	24(1)	30(1)	5(1)	-1(1)	3(1)
N(1)	28(1)	28(1)	32(1)	7(1)	0(1)	2(1)
P(1B)	28(2)	30(2)	31(2)	4(1)	-1(1)	2(2)
N(1B)	30(4)	33(5)	22(4)	5(3)	0(3)	8(3)
P(2)	29(1)	24(1)	29(1)	5(1)	-1(1)	3(1)
N(2)	32(1)	27(1)	30(1)	6(1)	1(1)	2(1)
P(2B)	19(2)	27(2)	28(2)	8(2)	6(2)	0(2)
N(2B)	17(5)	19(5)	22(5)	3(4)	-1(4)	3(4)
O(1)	52(1)	25(1)	38(1)	2(1)	-17(1)	7(1)
C(1)	34(1)	28(1)	37(1)	9(1)	-7(1)	5(1)
B(1)	30(1)	35(1)	37(1)	11(1)	-2(1)	1(1)
C(1S)	80(2)	36(1)	53(2)	-2(1)	28(2)	-11(1)
C(2)	36(1)	30(1)	39(1)	7(1)	-8(1)	5(1)
C(2S)	94(2)	39(1)	40(1)	4(1)	20(1)	8(1)
C(3)	35(1)	28(1)	44(1)	10(1)	-3(1)	4(1)
C(3S)	68(2)	51(2)	46(2)	-9(1)	11(1)	3(1)
C(4)	34(1)	34(1)	43(1)	18(1)	-3(1)	5(1)
C(5)	32(1)	40(1)	33(1)	15(1)	-3(1)	2(1)
C(6)	28(1)	34(1)	32(1)	9(1)	-1(1)	2(1)
C(7)	29(1)	34(1)	29(1)	7(1)	0(1)	4(1)
C(8)	34(1)	44(1)	29(1)	5(1)	-3(1)	4(1)
C(9)	44(1)	38(1)	34(1)	-3(1)	-9(1)	1(1)
C(10)	47(1)	30(1)	39(1)	0(1)	-7(1)	3(1)
C(11)	43(1)	30(1)	35(1)	4(1)	-7(1)	5(1)
C(12)	37(1)	28(1)	32(1)	2(1)	-7(1)	1(1)
C(13)	37(1)	26(1)	32(1)	2(1)	-2(1)	5(1)
C(14)	35(1)	42(1)	44(1)	6(1)	3(1)	5(1)
C(15)	46(1)	44(1)	54(2)	14(1)	0(1)	-9(1)
C(16)	63(2)	27(1)	60(2)	12(1)	-3(1)	0(1)
C(17)	45(1)	39(1)	60(2)	10(1)	0(1)	16(1)
C(18)	34(1)	35(1)	46(1)	7(1)	1(1)	1(1)
C(19)	35(1)	38(1)	53(1)	20(1)	12(1)	12(1)
C(20)	36(1)	32(1)	50(1)	4(1)	-4(1)	1(1)
C(21)	50(1)	51(1)	40(1)	13(1)	14(1)	12(1)
C(22)	32(1)	48(1)	81(2)	22(1)	14(1)	4(1)
C(23)	49(2)	51(2)	61(2)	3(1)	-20(1)	7(1)
C(24)	52(2)	59(2)	39(1)	12(1)	8(1)	23(1)
C(25)	48(1)	33(1)	54(1)	15(1)	21(1)	10(1)
C(26)	46(1)	64(2)	60(2)	22(1)	-2(1)	-8(1)

C(27)	67(2)	103(3)	48(2)	34(2)	2(1)	-8(2)
C(28)	59(2)	84(2)	62(2)	27(2)	23(1)	-4(2)
C(29)	42(1)	68(2)	74(2)	24(2)	15(1)	5(1)
C(30)	59(2)	64(2)	62(2)	34(1)	23(1)	26(1)
C(31)	32(1)	29(1)	38(1)	3(1)	-6(1)	5(1)
C(32)	33(1)	49(1)	44(1)	9(1)	4(1)	6(1)
C(33)	52(2)	46(2)	66(2)	16(1)	-6(1)	-14(1)
C(34)	84(2)	29(1)	67(2)	-5(1)	-15(2)	-1(1)
C(35)	74(2)	50(2)	45(1)	-4(1)	7(1)	19(1)
C(36)	43(1)	42(1)	44(1)	11(1)	5(1)	4(1)
C(37)	38(1)	54(2)	44(1)	-3(1)	11(1)	-5(1)
C(38)	45(1)	44(1)	58(2)	9(1)	7(1)	-3(1)
C(39)	38(1)	54(2)	95(2)	10(2)	15(1)	-3(1)
C(40)	88(2)	53(2)	93(2)	24(2)	49(2)	-4(2)
C(41)	112(3)	59(2)	62(2)	24(2)	16(2)	32(2)
C(42)	52(2)	69(2)	57(2)	7(1)	12(1)	23(1)
C(43)	37(1)	44(1)	50(1)	-1(1)	11(1)	-4(1)
C(44)	50(1)	42(1)	47(1)	-1(1)	13(1)	-2(1)
C(45)	49(1)	59(2)	47(1)	23(1)	17(1)	17(1)
C(46)	31(1)	94(2)	62(2)	35(2)	9(1)	8(1)
C(47)	31(1)	71(2)	65(2)	21(1)	-8(1)	-1(1)
C(48)	41(1)	44(1)	47(1)	4(1)	4(1)	0(1)
C(49)	32(1)	38(1)	32(1)	11(1)	-1(1)	3(1)
C(50)	39(1)	42(1)	38(1)	12(1)	4(1)	4(1)
C(51)	43(1)	62(2)	48(2)	31(1)	5(1)	11(1)
C(52)	42(1)	82(2)	33(1)	22(1)	-2(1)	3(1)
C(53)	48(2)	65(2)	31(1)	-1(1)	-1(1)	1(1)
C(54)	40(1)	47(1)	36(1)	7(1)	2(1)	7(1)
C(49B)	32(1)	38(1)	32(1)	11(1)	-1(1)	3(1)
C(55)	34(1)	32(1)	37(1)	8(1)	-1(1)	2(1)
C(56)	37(1)	29(1)	38(1)	7(1)	-1(1)	5(1)
C(57)	42(1)	38(1)	46(1)	8(1)	-7(1)	9(1)
C(58)	58(2)	59(2)	37(1)	12(1)	-7(1)	5(1)
C(59)	53(2)	90(2)	41(1)	20(1)	8(1)	11(1)
C(60)	39(1)	76(2)	44(1)	18(1)	1(1)	7(1)
C(61)	23(1)	37(1)	55(1)	13(1)	-3(1)	-3(1)
C(62)	36(1)	42(1)	67(2)	4(1)	1(1)	2(1)
C(63)	41(1)	41(2)	106(2)	-1(2)	2(2)	2(1)
C(64)	51(2)	40(2)	140(3)	27(2)	0(2)	2(1)
C(65)	66(2)	60(2)	101(3)	48(2)	-2(2)	-4(2)
C(66)	51(2)	45(1)	63(2)	23(1)	-2(1)	-2(1)
C(67)	31(1)	35(1)	32(1)	10(1)	1(1)	0(1)
C(68)	33(1)	32(1)	38(1)	9(1)	-1(1)	-1(1)

C(69)	33(1)	45(1)	53(1)	14(1)	-5(1)	4(1)
C(70)	32(1)	53(1)	55(1)	20(1)	-2(1)	-8(1)
C(71)	44(1)	43(1)	57(2)	25(1)	1(1)	-8(1)
C(72)	34(1)	44(1)	54(1)	24(1)	-2(1)	2(1)
C(73)	33(1)	37(1)	35(1)	13(1)	-4(1)	4(1)
C(74)	45(1)	41(1)	39(1)	11(1)	-2(1)	0(1)
C(75)	71(2)	42(1)	40(1)	7(1)	-4(1)	8(1)
C(76)	61(2)	69(2)	34(1)	8(1)	0(1)	26(1)
C(77)	36(1)	76(2)	38(1)	15(1)	0(1)	10(1)
C(78)	35(1)	51(1)	35(1)	10(1)	-5(1)	2(1)

Table A.116: Crystal data and structure refinement for **24**.

Empirical formula	$C_{86}H_{59}BF_{24}N_2O_4P_2Zn \cdot 0.83\ CH_2Cl_2$	
Formula weight	1848.96	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4655(17) Å	α= 99.640(2)°.
	b = 19.564(3) Å	β= 103.416(2)°.
	c = 19.662(3) Å	γ = 92.916(2)°.
Volume	4210.9(11) $Å^3$	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.487 mm^{-1}	
F(000)	1874	
Crystal size	0.35 x 0.07 x 0.05 mm^3	
Theta range for data collection	1.65 to 25.12°.	
Index ranges	-13<=h<=13, -23<=k<=23, -23<=l<=23	
Reflections collected	41317	
Independent reflections	14955 [R(int) = 0.1034]	
Completeness to theta = 25.12°	99.30%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9770 and 0.8476	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14955 / 225 / 1170	
Goodness-of-fit on F^2	1.02	
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.1742	
R indices (all data)	R1 = 0.1704, wR2 = 0.2148	
Largest diff. peak and hole	0.724 and -0.665 e.$Å^{-3}$	

Table A.117: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **24**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	14623(1)	3039(1)	13389(1)	36(1)	C(55)	15382(5)	-2020(3)	12626(3)	36(2)
P(1)	12493(1)	2224(1)	12020(1)	33(1)	C(56)	15822(6)	-1393(3)	13096(3)	43(2)
N(1)	16313(4)	3208(2)	13281(2)	34(1)	C(57)	16852(6)	-1322(3)	13644(3)	45(2)
O(1)	14974(3)	2591(2)	11787(2)	34(1)	C(58)	17492(6)	-1878(4)	13760(3)	48(2)
B(1)	14121(6)	-2093(4)	12019(4)	35(2)	C(59)	17058(6)	-2521(3)	13313(4)	47(2)
C(1)	14203(5)	2133(3)	11229(3)	36(2)	C(60)	16027(5)	-2587(3)	12767(3)	38(2)
P(2)	16868(1)	3646(1)	12798(1)	33(1)	C(61)	17262(8)	-627(4)	14100(4)	71(2)
O(2)	15058(4)	2628(2)	14330(2)	41(1)	F(1)	16449(5)	-370(3)	14416(3)	110(2)
N(2)	13404(4)	2284(2)	12783(2)	32(1)	F(2)	18225(4)	-627(2)	14617(2)	94(2)

C(2)	13065(5)	1896(3)	11256(3)	34(1)	F(3)	17528(6)	-165(2)	13734(3)	127(2)
C(3)	12397(6)	1456(3)	10645(3)	39(2)	C(62)	17728(8)	-3127(5)	13431(5)	71(2)
O(3)	14002(4)	3749(2)	13970(2)	49(1)	F(4)	18277(7)	-3320(4)	12899(4)	163(3)
C(4)	12863(6)	1289(3)	10050(3)	44(2)	F(5)	18588(6)	-3059(3)	13973(4)	157(3)
O(4)	14839(5)	2873(3)	15434(2)	73(2)	F(6)	17077(5)	-3692(3)	13386(4)	148(3)
C(5)	14018(6)	1540(3)	10046(3)	46(2)	C(63)	13927(5)	-1427(3)	11622(3)	30(1)
C(6)	14710(5)	1970(3)	10656(3)	32(1)	C(64)	12810(5)	-1338(3)	11204(3)	37(2)
C(7)	15910(5)	2337(3)	10869(3)	34(1)	C(65)	12617(5)	-814(3)	10810(3)	38(2)
C(8)	16877(6)	2414(3)	10564(3)	40(2)	C(66)	13559(6)	-330(3)	10834(3)	45(2)
C(9)	17872(6)	2843(3)	10952(3)	42(2)	C(67)	14692(6)	-404(3)	11247(3)	39(2)
C(10)	17937(5)	3210(3)	11632(3)	38(2)	C(68)	14876(5)	-940(3)	11625(3)	36(2)
C(11)	16995(5)	3150(3)	11955(3)	34(1)	C(69)	11395(6)	-770(4)	10353(4)	54(2)
C(12)	16003(5)	2699(3)	11550(3)	34(1)	F(7)	11321(4)	-253(3)	10025(3)	126(2)
C(13)	11157(5)	1666(3)	11941(3)	39(2)	F(8)	11019(4)	-1336(3)	9882(3)	108(2)
C(14)	10080(6)	1945(3)	11964(3)	47(2)	F(9)	10560(4)	-717(3)	10711(3)	101(2)
C(15)	9098(6)	1524(4)	11983(4)	62(2)	C(70)	15728(7)	107(4)	11293(5)	57(2)
C(16)	9207(7)	828(5)	11994(4)	67(2)	F(10)	15929(11)	621(5)	11737(8)	91(4)
C(17)	10244(7)	544(4)	11959(4)	55(2)	F(11)	16753(10)	-224(5)	11304(6)	57(3)
C(18)	11247(6)	960(3)	11917(3)	47(2)	F(12)	15633(8)	326(6)	10623(5)	94(3)
C(19)	12087(5)	3071(3)	11897(3)	35(1)	F(10B)	16351(14)	321(8)	12044(7)	65(4)
C(20)	11979(5)	3564(3)	12466(3)	43(2)	F(11B)	15365(13)	759(7)	11248(11)	85(6)
C(21)	11568(6)	4196(3)	12351(4)	53(2)	F(12B)	16470(20)	-21(9)	10987(10)	82(7)
C(22)	11284(6)	4345(3)	11679(4)	57(2)	C(71)	13083(5)	-2176(3)	12460(3)	33(1)
C(23)	11407(6)	3858(4)	11107(4)	57(2)	C(72)	12754(6)	-2821(3)	12614(3)	43(2)
C(24)	11816(6)	3228(3)	11213(3)	48(2)	C(73)	11918(6)	-2907(3)	13016(3)	44(2)
C(25)	13525(6)	1649(3)	13075(3)	38(2)	C(74)	11421(6)	-2346(3)	13296(3)	47(2)
C(26)	14308(6)	1188(3)	12869(4)	49(2)	C(75)	11754(6)	-1694(3)	13187(3)	48(2)
C(27)	14481(7)	601(4)	13140(4)	67(2)	C(76)	12554(6)	-1622(3)	12768(3)	42(2)
C(28)	13886(8)	451(4)	13632(5)	76(2)	C(77)	11592(9)	-3619(4)	13107(5)	75(3)
C(29)	13082(7)	905(4)	13839(4)	59(2)	F(13)	11168(9)	-4052(3)	12512(3)	195(4)
C(30)	12897(6)	1504(3)	13569(3)	46(2)	F(14)	12520(5)	-3909(3)	13445(4)	130(3)
C(31)	12034(6)	1990(4)	13793(3)	54(2)	F(15)	10813(4)	-3652(2)	13498(2)	74(1)
C(32)	15913(5)	4307(3)	12568(3)	37(2)	C(78)	11281(8)	-1072(4)	13535(5)	68(2)
C(33)	15225(6)	4597(3)	13014(4)	50(2)	F(16)	12055(5)	-741(2)	14130(3)	102(2)
C(34)	14497(7)	5106(4)	12823(5)	73(2)	F(17)	11050(5)	-600(2)	13135(3)	90(2)
C(35)	14465(7)	5339(4)	12202(5)	72(2)	F(18)	10270(5)	-1224(2)	13723(3)	106(2)
C(36)	15162(9)	5070(4)	11770(5)	88(3)	C(79)	14046(5)	-2763(3)	11381(3)	35(1)
C(37)	15874(7)	4555(3)	11938(4)	59(2)	C(80)	15037(6)	-2905(3)	11089(3)	38(2)
C(38)	18367(5)	4037(3)	13245(3)	37(2)	C(81)	14998(6)	-3461(3)	10542(3)	44(2)
C(39)	19306(5)	3625(3)	13394(3)	41(2)	C(82)	13954(7)	-3892(3)	10239(3)	49(2)
C(40)	20400(6)	3925(4)	13821(4)	55(2)	C(83)	12953(6)	-3757(3)	10500(3)	42(2)
C(41)	20542(7)	4634(4)	14103(4)	58(2)	C(84)	12996(6)	-3203(3)	11047(3)	39(2)
C(42)	19635(6)	5043(4)	13960(4)	57(2)	C(85)	16078(8)	-3608(5)	10263(5)	69(2)

C(43)	18529(6)	4750(3)	13532(3)	46(2)	F(19)	16519(13)	-4145(7)	10364(9)	110(5)
C(44)	17102(5)	2753(3)	13638(3)	37(2)	F(20)	15796(8)	-3644(7)	9526(4)	90(3)
C(45)	17182(6)	2089(3)	13278(4)	47(2)	F(21)	16912(16)	-3073(8)	10446(8)	106(7)
C(46)	17891(8)	1641(4)	13609(5)	70(2)	F(19B)	16986(16)	-3776(15)	10864(8)	107(8)
C(47)	18547(8)	1851(5)	14292(6)	82(3)	F(20B)	16005(18)	-4189(13)	9833(15)	125(9)
C(48)	18484(7)	2507(5)	14653(4)	72(2)	F(21B)	16640(30)	-3129(11)	10137(17)	101(11)
C(49)	17757(6)	2976(4)	14334(4)	50(2)	C(86)	11838(7)	-4224(4)	10195(4)	64(2)
C(50)	17699(7)	3685(4)	14751(4)	65(2)	F(22)	11803(6)	-4765(3)	10467(4)	173(4)
C(51A)	14178(9)	3679(4)	14661(4)	87(3)	F(23)	11634(6)	-4477(3)	9520(3)	141(3)
C(52A)	14551(15)	4258(8)	15216(8)	67(4)	F(24)	10866(5)	-3942(3)	10240(4)	169(3)
C(51B)	14178(9)	3679(4)	14661(4)	87(3)	C(87)	19258(3)	-2495(2)	11655(2)	214(6)
C(52B)	13448(16)	3956(10)	15080(9)	85(6)	Cl(1)	18395(3)	-1708(2)	11841(2)	201(2)
C(53)	14730(6)	3020(4)	14789(4)	51(2)	Cl(2)	19664(3)	-2449(2)	10889(2)	204(2)
C(54)	15358(7)	2230(4)	15553(4)	69(2)					

Table A.118: Bond lengths [Å] for **24**.

Zn(1)-O(3)	1.921(4)	C(27)-C(28)	1.367(10)	C(60)-H(60)	0.9500
Zn(1)-N(2)	1.996(4)	C(27)-H(27)	0.9500	C(61)-F(1)	1.312(9)
Zn(1)-N(1)	2.014(5)	C(28)-C(29)	1.391(10)	C(61)-F(3)	1.313(8)
Zn(1)-O(2)	2.105(4)	C(28)-H(28)	0.9500	C(61)-F(2)	1.316(8)
P(1)-N(2)	1.599(5)	C(29)-C(30)	1.372(9)	C(62)-F(5)	1.256(9)
P(1)-C(19)	1.783(6)	C(29)-H(29)	0.9500	C(62)-F(6)	1.280(9)
P(1)-C(13)	1.796(6)	C(30)-C(31)	1.495(9)	C(62)-F(4)	1.353(10)
P(1)-C(2)	1.811(6)	C(31)-H(31A)	0.9800	C(63)-C(64)	1.389(8)
N(1)-C(44)	1.449(7)	C(31)-H(31B)	0.9800	C(63)-C(68)	1.407(8)
N(1)-P(2)	1.593(5)	C(31)-H(31C)	0.9800	C(64)-C(65)	1.381(8)
O(1)-C(12)	1.384(6)	C(32)-C(33)	1.383(8)	C(64)-H(64)	0.9500
O(1)-C(1)	1.389(6)	C(32)-C(37)	1.396(8)	C(65)-C(66)	1.386(8)
B(1)-C(63)	1.627(8)	C(33)-C(34)	1.376(9)	C(65)-C(69)	1.494(9)
B(1)-C(55)	1.630(9)	C(33)-H(33)	0.9500	C(66)-C(67)	1.392(8)
B(1)-C(79)	1.639(9)	C(34)-C(35)	1.366(11)	C(66)-H(66)	0.9500
B(1)-C(71)	1.642(9)	C(34)-H(34)	0.9500	C(67)-C(68)	1.380(8)
C(1)-C(2)	1.377(8)	C(35)-C(36)	1.358(11)	C(67)-C(70)	1.490(9)
C(1)-C(6)	1.382(7)	C(35)-H(35)	0.9500	C(68)-H(68)	0.9500
P(2)-C(32)	1.784(6)	C(36)-C(37)	1.365(9)	C(69)-F(7)	1.285(8)
P(2)-C(38)	1.803(6)	C(36)-H(36)	0.9500	C(69)-F(8)	1.302(8)
P(2)-C(11)	1.816(6)	C(37)-H(37)	0.9500	C(69)-F(9)	1.311(8)
O(2)-C(53)	1.224(7)	C(38)-C(39)	1.384(8)	C(70)-F(12B)	1.162(17)
N(2)-C(25)	1.453(7)	C(38)-C(43)	1.401(8)	C(70)-F(10)	1.189(11)
C(2)-C(3)	1.389(8)	C(39)-C(40)	1.376(8)	C(70)-F(11)	1.367(14)
C(3)-C(4)	1.393(8)	C(39)-H(39)	0.9500	C(70)-F(11B)	1.371(15)
C(3)-H(3)	0.9500	C(40)-C(41)	1.392(9)	C(70)-F(12)	1.435(11)
O(3)-C(51A)	1.357(8)	C(40)-H(40)	0.9500	C(70)-F(10B)	1.462(16)

C(4)-C(5)	1.391(9)	C(41)-C(42)	1.350(9)	C(71)-C(76)	1.388(8)
C(4)-H(4)	0.9500	C(41)-H(41)	0.9500	C(71)-C(72)	1.400(8)
O(4)-C(53)	1.326(8)	C(42)-C(43)	1.384(9)	C(72)-C(73)	1.396(8)
O(4)-C(54)	1.449(8)	C(42)-H(42)	0.9500	C(72)-H(72)	0.9500
C(5)-C(6)	1.390(8)	C(43)-H(43)	0.9500	C(73)-C(74)	1.357(8)
C(5)-H(5)	0.9500	C(44)-C(49)	1.386(8)	C(73)-C(77)	1.474(9)
C(6)-C(7)	1.454(8)	C(44)-C(45)	1.389(8)	C(74)-C(75)	1.380(8)
C(7)-C(12)	1.384(7)	C(45)-C(46)	1.368(9)	C(74)-H(74)	0.9500
C(7)-C(8)	1.390(8)	C(45)-H(45)	0.9500	C(75)-C(76)	1.385(8)
C(8)-C(9)	1.368(8)	C(46)-C(47)	1.361(11)	C(75)-C(78)	1.484(9)
C(8)-H(8)	0.9500	C(46)-H(46)	0.9500	C(76)-H(76)	0.9500
C(9)-C(10)	1.391(8)	C(47)-C(48)	1.372(11)	C(77)-F(13)	1.298(9)
C(9)-H(9)	0.9500	C(47)-H(47)	0.9500	C(77)-F(15)	1.312(8)
C(10)-C(11)	1.385(8)	C(48)-C(49)	1.400(9)	C(77)-F(14)	1.325(10)
C(10)-H(10)	0.9500	C(48)-H(48)	0.9500	C(78)-F(17)	1.309(8)
C(11)-C(12)	1.396(8)	C(49)-C(50)	1.501(9)	C(78)-F(18)	1.331(8)
C(13)-C(14)	1.383(8)	C(50)-H(50A)	0.9800	C(78)-F(16)	1.336(9)
C(13)-C(18)	1.384(8)	C(50)-H(50B)	0.9800	C(79)-C(84)	1.399(8)
C(14)-C(15)	1.373(9)	C(50)-H(50C)	0.9800	C(79)-C(80)	1.408(8)
C(14)-H(14)	0.9500	C(51A)-C(52A)	1.406(16)	C(80)-C(81)	1.386(8)
C(15)-C(16)	1.375(10)	C(51A)-C(53)	1.499(10)	C(80)-H(80)	0.9500
C(15)-H(15)	0.9500	C(51A)-H(51A)	1.0000	C(81)-C(82)	1.377(9)
C(16)-C(17)	1.350(10)	C(52A)-H(52A)	0.9800	C(81)-C(85)	1.488(10)
C(16)-H(16)	0.9500	C(52A)-H(52B)	0.9800	C(82)-C(83)	1.382(9)
C(17)-C(18)	1.400(9)	C(52A)-H(52C)	0.9800	C(82)-H(82)	0.9500
C(17)-H(17)	0.9500	C(52B)-H(52D)	0.9800	C(83)-C(84)	1.384(8)
C(18)-H(18)	0.9500	C(52B)-H(52E)	0.9800	C(83)-C(86)	1.473(9)
C(19)-C(20)	1.383(8)	C(52B)-H(52F)	0.9800	C(84)-H(84)	0.9500
C(19)-C(24)	1.398(8)	C(54)-H(54A)	0.9800	C(85)-F(21B)	1.20(2)
C(20)-C(21)	1.380(8)	C(54)-H(54B)	0.9800	C(85)-F(19)	1.216(12)
C(20)-H(20)	0.9500	C(54)-H(54C)	0.9800	C(85)-F(20B)	1.285(17)
C(21)-C(22)	1.370(9)	C(55)-C(60)	1.395(8)	C(85)-F(21)	1.324(16)
C(21)-H(21)	0.9500	C(55)-C(56)	1.398(8)	C(85)-F(20)	1.398(12)
C(22)-C(23)	1.385(9)	C(56)-C(57)	1.385(8)	C(85)-F(19B)	1.478(19)
C(22)-H(22)	0.9500	C(56)-H(56)	0.9500	C(86)-F(22)	1.266(8)
C(23)-C(24)	1.372(8)	C(57)-C(58)	1.364(8)	C(86)-F(24)	1.284(8)
C(23)-H(23)	0.9500	C(57)-C(61)	1.484(10)	C(86)-F(23)	1.298(8)
C(24)-H(24)	0.9500	C(58)-C(59)	1.401(9)	C(87)-Cl(2)	1.6911
C(25)-C(26)	1.382(8)	C(58)-H(58)	0.9500	C(87)-Cl(1)	1.9015
C(25)-C(30)	1.392(8)	C(59)-C(60)	1.383(8)	C(87)-H(87A)	0.9900
C(26)-C(27)	1.350(9)	C(59)-C(62)	1.466(10)	C(87)-H(87B)	0.9900
C(26)-H(26)	0.9500				

Table A.119: Bond angles [°] for **24**

O(3)-Zn(1)-N(2)	115.28(19)	C(29)-C(30)-C(31)	121.1(6)	C(63)-C(64)-H(64)	118.3
O(3)-Zn(1)-N(1)	118.59(19)	C(25)-C(30)-C(31)	120.4(6)	C(64)-C(65)-C(66)	120.1(6)
N(2)-Zn(1)-N(1)	124.84(18)	C(30)-C(31)-H(31A)	109.5	C(64)-C(65)-C(69)	120.1(6)
O(3)-Zn(1)-O(2)	83.22(17)	C(30)-C(31)-H(31B)	109.5	C(66)-C(65)-C(69)	119.8(6)
N(2)-Zn(1)-O(2)	99.56(16)	H(31A)-C(31)-H(31E	109.5	C(65)-C(66)-C(67)	118.0(6)
N(1)-Zn(1)-O(2)	97.59(17)	C(30)-C(31)-H(31C)	109.5	C(65)-C(66)-H(66)	121.0
N(2)-P(1)-C(19)	109.1(3)	H(31A)-C(31)-H(31C	109.5	C(67)-C(66)-H(66)	121.0
N(2)-P(1)-C(13)	111.3(3)	H(31B)-C(31)-H(31C	109.5	C(68)-C(67)-C(66)	121.3(6)
C(19)-P(1)-C(13)	109.3(3)	C(33)-C(32)-C(37)	118.7(6)	C(68)-C(67)-C(70)	119.0(6)
N(2)-P(1)-C(2)	116.4(3)	C(33)-C(32)-P(2)	121.2(5)	C(66)-C(67)-C(70)	119.8(6)
C(19)-P(1)-C(2)	104.5(3)	C(37)-C(32)-P(2)	120.1(5)	C(67)-C(68)-C(63)	121.7(6)
C(13)-P(1)-C(2)	105.8(3)	C(34)-C(33)-C(32)	119.9(7)	C(67)-C(68)-H(68)	119.1
C(44)-N(1)-P(2)	116.0(4)	C(34)-C(33)-H(33)	120.1	C(63)-C(68)-H(68)	119.1
C(44)-N(1)-Zn(1)	110.9(3)	C(32)-C(33)-H(33)	120.1	F(7)-C(69)-F(8)	107.9(7)
P(2)-N(1)-Zn(1)	132.4(3)	C(35)-C(34)-C(33)	120.6(8)	F(7)-C(69)-F(9)	105.7(6)
C(12)-O(1)-C(1)	104.6(4)	C(35)-C(34)-H(34)	119.7	F(8)-C(69)-F(9)	103.3(6)
C(63)-B(1)-C(55)	114.0(5)	C(33)-C(34)-H(34)	119.7	F(7)-C(69)-C(65)	114.4(6)
C(63)-B(1)-C(79)	105.2(5)	C(36)-C(35)-C(34)	119.9(8)	F(8)-C(69)-C(65)	111.7(6)
C(55)-B(1)-C(79)	111.4(5)	C(36)-C(35)-H(35)	120.0	F(9)-C(69)-C(65)	113.0(6)
C(63)-B(1)-C(71)	110.3(5)	C(34)-C(35)-H(35)	120.0	F(12B)-C(70)-F(10)	116.8(12)
C(55)-B(1)-C(71)	103.8(5)	C(35)-C(36)-C(37)	120.8(8)	F(12B)-C(70)-F(11)	36.2(10)
C(79)-B(1)-C(71)	112.4(5)	C(35)-C(36)-H(36)	119.6	F(10)-C(70)-F(11)	110.2(10)
C(2)-C(1)-C(6)	125.7(5)	C(37)-C(36)-H(36)	119.6	F(12B)-C(70)-F(11B)	111.9(12)
C(2)-C(1)-O(1)	122.6(5)	C(36)-C(37)-C(32)	120.1(7)	F(10)-C(70)-F(11B)	50.8(9)
C(6)-C(1)-O(1)	111.7(5)	C(36)-C(37)-H(37)	120.0	F(11)-C(70)-F(11B)	138.0(10)
N(1)-P(2)-C(32)	109.4(3)	C(32)-C(37)-H(37)	120.0	F(12B)-C(70)-F(12)	61.1(11)
N(1)-P(2)-C(38)	111.6(3)	C(39)-C(38)-C(43)	120.2(6)	F(10)-C(70)-F(12)	106.8(9)
C(32)-P(2)-C(38)	109.8(3)	C(39)-C(38)-P(2)	120.5(5)	F(11)-C(70)-F(12)	97.2(9)
N(1)-P(2)-C(11)	114.9(3)	C(43)-C(38)-P(2)	118.7(5)	F(11B)-C(70)-F(12)	63.4(8)
C(32)-P(2)-C(11)	105.2(3)	C(40)-C(39)-C(38)	119.3(6)	F(12B)-C(70)-F(10B)	106.5(13)
C(38)-P(2)-C(11)	105.6(3)	C(40)-C(39)-H(39)	120.4	F(10)-C(70)-F(10B)	41.7(8)
C(53)-O(2)-Zn(1)	107.5(4)	C(38)-C(39)-H(39)	120.4	F(11)-C(70)-F(10B)	79.9(9)
C(25)-N(2)-P(1)	116.6(4)	C(39)-C(40)-C(41)	119.7(7)	F(11B)-C(70)-F(10B)	92.4(12)
C(25)-N(2)-Zn(1)	110.1(3)	C(39)-C(40)-H(40)	120.1	F(12)-C(70)-F(10B)	140.3(9)
P(1)-N(2)-Zn(1)	132.7(3)	C(41)-C(40)-H(40)	120.1	F(12B)-C(70)-C(67)	122.4(12)
C(1)-C(2)-C(3)	115.4(5)	C(42)-C(41)-C(40)	121.6(7)	F(10)-C(70)-C(67)	119.8(9)
C(1)-C(2)-P(1)	119.8(4)	C(42)-C(41)-H(41)	119.2	F(11)-C(70)-C(67)	110.2(7)
C(3)-C(2)-P(1)	124.6(5)	C(40)-C(41)-H(41)	119.2	F(11B)-C(70)-C(67)	111.4(9)
C(2)-C(3)-C(4)	120.8(6)	C(41)-C(42)-C(43)	119.5(7)	F(12)-C(70)-C(67)	110.2(7)
C(2)-C(3)-H(3)	119.6	C(41)-C(42)-H(42)	120.3	F(10B)-C(70)-C(67)	107.7(8)
C(4)-C(3)-H(3)	119.6	C(43)-C(42)-H(42)	120.3	C(76)-C(71)-C(72)	114.5(5)
C(51A)-O(3)-Zn(1)	114.5(4)	C(42)-C(43)-C(38)	119.7(6)	C(76)-C(71)-B(1)	124.1(5)

C(5)-C(4)-C(3)	121.9(6)	C(42)-C(43)-H(43)	120.1	C(72)-C(71)-B(1)	121.1(5)
C(5)-C(4)-H(4)	119.1	C(38)-C(43)-H(43)	120.1	C(73)-C(72)-C(71)	122.9(6)
C(3)-C(4)-H(4)	119.1	C(49)-C(44)-C(45)	120.5(6)	C(73)-C(72)-H(72)	118.5
C(53)-O(4)-C(54)	116.1(6)	C(49)-C(44)-N(1)	120.1(6)	C(71)-C(72)-H(72)	118.5
C(6)-C(5)-C(4)	118.1(6)	C(45)-C(44)-N(1)	119.4(5)	C(74)-C(73)-C(72)	119.8(6)
C(6)-C(5)-H(5)	120.9	C(46)-C(45)-C(44)	120.6(7)	C(74)-C(73)-C(77)	122.3(6)
C(4)-C(5)-H(5)	120.9	C(46)-C(45)-H(45)	119.7	C(72)-C(73)-C(77)	117.9(6)
C(1)-C(6)-C(5)	118.0(6)	C(44)-C(45)-H(45)	119.7	C(73)-C(74)-C(75)	119.6(6)
C(1)-C(6)-C(7)	106.2(5)	C(47)-C(46)-C(45)	119.9(8)	C(73)-C(74)-H(74)	120.2
C(5)-C(6)-C(7)	135.7(6)	C(47)-C(46)-H(46)	120.0	C(75)-C(74)-H(74)	120.2
C(12)-C(7)-C(8)	118.3(6)	C(45)-C(46)-H(46)	120.0	C(74)-C(75)-C(76)	119.7(6)
C(12)-C(7)-C(6)	104.8(5)	C(46)-C(47)-C(48)	120.2(8)	C(74)-C(75)-C(78)	119.9(6)
C(8)-C(7)-C(6)	136.9(5)	C(46)-C(47)-H(47)	119.9	C(76)-C(75)-C(78)	120.4(6)
C(9)-C(8)-C(7)	118.5(5)	C(48)-C(47)-H(47)	119.9	C(75)-C(76)-C(71)	123.4(6)
C(9)-C(8)-H(8)	120.8	C(47)-C(48)-C(49)	121.5(8)	C(75)-C(76)-H(76)	118.3
C(7)-C(8)-H(8)	120.8	C(47)-C(48)-H(48)	119.2	C(71)-C(76)-H(76)	118.3
C(8)-C(9)-C(10)	122.2(6)	C(49)-C(48)-H(48)	119.2	F(13)-C(77)-F(15)	107.5(8)
C(8)-C(9)-H(9)	118.9	C(44)-C(49)-C(48)	117.3(7)	F(13)-C(77)-F(14)	104.7(8)
C(10)-C(9)-H(9)	118.9	C(44)-C(49)-C(50)	122.8(6)	F(15)-C(77)-F(14)	103.2(7)
C(11)-C(10)-C(9)	121.3(6)	C(48)-C(49)-C(50)	119.9(7)	F(13)-C(77)-C(73)	113.7(7)
C(11)-C(10)-H(10)	119.4	C(49)-C(50)-H(50A)	109.5	F(15)-C(77)-C(73)	113.9(7)
C(9)-C(10)-H(10)	119.4	C(49)-C(50)-H(50B)	109.5	F(14)-C(77)-C(73)	112.9(8)
C(10)-C(11)-C(12)	115.0(5)	H(50A)-C(50)-H(50E	109.5	F(17)-C(78)-F(18)	106.5(7)
C(10)-C(11)-P(2)	127.1(5)	C(49)-C(50)-H(50C)	109.5	F(17)-C(78)-F(16)	105.0(7)
C(12)-C(11)-P(2)	117.6(4)	H(50A)-C(50)-H(50C	109.5	F(18)-C(78)-F(16)	105.6(7)
O(1)-C(12)-C(7)	112.7(5)	H(50B)-C(50)-H(50C	109.5	F(17)-C(78)-C(75)	113.3(6)
O(1)-C(12)-C(11)	122.5(5)	O(3)-C(51A)-C(52A)	121.2(10)	F(18)-C(78)-C(75)	113.1(6)
C(7)-C(12)-C(11)	124.7(5)	O(3)-C(51A)-C(53)	111.7(6)	F(16)-C(78)-C(75)	112.7(7)
C(14)-C(13)-C(18)	120.6(6)	C(52A)-C(51A)-C(53	115.9(9)	C(84)-C(79)-C(80)	114.5(5)
C(14)-C(13)-P(1)	120.4(5)	O(3)-C(51A)-H(51A)	101.3	C(84)-C(79)-B(1)	124.0(5)
C(18)-C(13)-P(1)	118.8(5)	C(52A)-C(51A)-H(51	101.3	C(80)-C(79)-B(1)	121.2(5)
C(15)-C(14)-C(13)	119.9(6)	C(53)-C(51A)-H(51A	101.3	C(81)-C(80)-C(79)	122.7(6)
C(15)-C(14)-H(14)	120.0	H(52D)-C(52B)-H(52	109.5	C(81)-C(80)-H(80)	118.6
C(13)-C(14)-H(14)	120.0	H(52D)-C(52B)-H(52	109.5	C(79)-C(80)-H(80)	118.6
C(14)-C(15)-C(16)	119.3(7)	H(52E)-C(52B)-H(52	109.5	C(82)-C(81)-C(80)	120.8(6)
C(14)-C(15)-H(15)	120.3	O(2)-C(53)-O(4)	120.9(7)	C(82)-C(81)-C(85)	118.0(6)
C(16)-C(15)-H(15)	120.3	O(2)-C(53)-C(51A)	122.9(6)	C(80)-C(81)-C(85)	121.1(7)
C(17)-C(16)-C(15)	121.6(7)	O(4)-C(53)-C(51A)	116.3(7)	C(81)-C(82)-C(83)	118.1(6)
C(17)-C(16)-H(16)	119.2	O(4)-C(54)-H(54A)	109.5	C(81)-C(82)-H(82)	121.0
C(15)-C(16)-H(16)	119.2	O(4)-C(54)-H(54B)	109.5	C(83)-C(82)-H(82)	121.0
C(16)-C(17)-C(18)	120.0(7)	H(54A)-C(54)-H(54E	109.5	C(82)-C(83)-C(84)	120.9(6)
C(16)-C(17)-H(17)	120.0	O(4)-C(54)-H(54C)	109.5	C(82)-C(83)-C(86)	118.8(6)
C(18)-C(17)-H(17)	120.0	H(54A)-C(54)-H(54C	109.5	C(84)-C(83)-C(86)	120.3(6)

C(13)-C(18)-C(17)	118.5(6)	H(54B)-C(54)-H(54C	109.5	C(83)-C(84)-C(79)	122.8(6)
C(13)-C(18)-H(18)	120.8	C(60)-C(55)-C(56)	115.1(6)	C(83)-C(84)-H(84)	118.6
C(17)-C(18)-H(18)	120.8	C(60)-C(55)-B(1)	122.9(5)	C(79)-C(84)-H(84)	118.6
C(20)-C(19)-C(24)	119.4(6)	C(56)-C(55)-B(1)	121.7(5)	F(21B)-C(85)-F(19)	122.1(15)
C(20)-C(19)-P(1)	120.8(5)	C(57)-C(56)-C(55)	123.2(6)	F(21B)-C(85)-F(20B)	115.5(18)
C(24)-C(19)-P(1)	119.7(5)	C(57)-C(56)-H(56)	118.4	F(19)-C(85)-F(20B)	50.1(12)
C(21)-C(20)-C(19)	120.0(6)	C(55)-C(56)-H(56)	118.4	F(21B)-C(85)-F(21)	27.1(16)
C(21)-C(20)-H(20)	120.0	C(58)-C(57)-C(56)	120.8(6)	F(19)-C(85)-F(21)	111.1(13)
C(19)-C(20)-H(20)	120.0	C(58)-C(57)-C(61)	120.2(6)	F(20B)-C(85)-F(21)	130.5(14)
C(22)-C(21)-C(20)	120.5(6)	C(56)-C(57)-C(61)	118.9(6)	F(21B)-C(85)-F(20)	71.8(17)
C(22)-C(21)-H(21)	119.8	C(57)-C(58)-C(59)	117.6(6)	F(19)-C(85)-F(20)	105.7(10)
C(20)-C(21)-H(21)	119.8	C(57)-C(58)-H(58)	121.2	F(20B)-C(85)-F(20)	58.6(14)
C(21)-C(22)-C(23)	120.0(6)	C(59)-C(58)-H(58)	121.2	F(21)-C(85)-F(20)	98.6(10)
C(21)-C(22)-H(22)	120.0	C(60)-C(59)-C(58)	121.2(6)	F(21B)-C(85)-F(19B)	99.3(16)
C(23)-C(22)-H(22)	120.0	C(60)-C(59)-C(62)	120.3(7)	F(19)-C(85)-F(19B)	47.9(10)
C(24)-C(23)-C(22)	120.2(6)	C(58)-C(59)-C(62)	118.5(6)	F(20B)-C(85)-F(19B)	97.5(16)
C(24)-C(23)-H(23)	119.9	C(59)-C(60)-C(55)	122.1(6)	F(21)-C(85)-F(19B)	75.2(13)
C(22)-C(23)-H(23)	119.9	C(59)-C(60)-H(60)	119.0	F(20)-C(85)-F(19B)	143.2(10)
C(23)-C(24)-C(19)	119.9(6)	C(55)-C(60)-H(60)	119.0	F(21B)-C(85)-C(81)	117.9(14)
C(23)-C(24)-H(24)	120.0	F(1)-C(61)-F(3)	105.9(7)	F(19)-C(85)-C(81)	116.8(9)
C(19)-C(24)-H(24)	120.0	F(1)-C(61)-F(2)	105.2(7)	F(20B)-C(85)-C(81)	116.2(12)
C(26)-C(25)-C(30)	119.4(6)	F(3)-C(61)-F(2)	106.3(7)	F(21)-C(85)-C(81)	112.9(10)
C(26)-C(25)-N(2)	118.9(5)	F(1)-C(61)-C(57)	113.2(7)	F(20)-C(85)-C(81)	110.0(8)
C(30)-C(25)-N(2)	121.6(6)	F(3)-C(61)-C(57)	111.9(7)	F(19B)-C(85)-C(81)	105.6(9)
C(27)-C(26)-C(25)	121.4(7)	F(2)-C(61)-C(57)	113.7(7)	F(22)-C(86)-F(24)	105.9(8)
C(27)-C(26)-H(26)	119.3	F(5)-C(62)-F(6)	108.5(8)	F(22)-C(86)-F(23)	102.9(7)
C(25)-C(26)-H(26)	119.3	F(5)-C(62)-F(4)	102.1(8)	F(24)-C(86)-F(23)	102.5(7)
C(26)-C(27)-C(28)	120.3(8)	F(6)-C(62)-F(4)	100.2(8)	F(22)-C(86)-C(83)	113.8(7)
C(26)-C(27)-H(27)	119.8	F(5)-C(62)-C(59)	118.0(8)	F(24)-C(86)-C(83)	114.7(7)
C(28)-C(27)-H(27)	119.8	F(6)-C(62)-C(59)	115.1(7)	F(23)-C(86)-C(83)	115.6(7)
C(27)-C(28)-C(29)	119.1(7)	F(4)-C(62)-C(59)	110.7(7)	Cl(2)-C(87)-Cl(1)	106.4
C(27)-C(28)-H(28)	120.4	C(64)-C(63)-C(68)	115.4(5)	Cl(2)-C(87)-H(87A)	110.4
C(29)-C(28)-H(28)	120.4	C(64)-C(63)-B(1)	121.1(5)	Cl(1)-C(87)-H(87A)	110.4
C(30)-C(29)-C(28)	121.2(7)	C(68)-C(63)-B(1)	123.2(5)	Cl(2)-C(87)-H(87B)	110.4
C(30)-C(29)-H(29)	119.4	C(65)-C(64)-C(63)	123.5(6)	Cl(1)-C(87)-H(87B)	110.4
C(28)-C(29)-H(29)	119.4	C(65)-C(64)-H(64)	118.3	H(87A)-C(87)-H(87B)	108.6
C(29)-C(30)-C(25)	118.6(7)				

Table A.120: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **24**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	38(1)	36(1)	33(1)	6(1)	11(1)	-2(1)
P(1)	33(1)	32(1)	35(1)	6(1)	9(1)	-1(1)

N(1)	36(3)	35(3)	28(3)	8(2)	6(2)	-1(2)
O(1)	32(2)	37(2)	31(2)	2(2)	9(2)	-2(2)
B(1)	38(4)	37(4)	30(4)	8(3)	4(3)	2(3)
C(1)	45(4)	29(3)	26(3)	-3(3)	1(3)	-1(3)
P(2)	33(1)	29(1)	36(1)	6(1)	10(1)	-1(1)
O(2)	39(3)	46(3)	39(3)	10(2)	12(2)	-9(2)
N(2)	38(3)	30(3)	29(3)	8(2)	6(2)	-1(2)
C(2)	34(4)	35(3)	33(3)	6(3)	11(3)	3(3)
C(3)	44(4)	32(3)	37(4)	3(3)	8(3)	-3(3)
O(3)	65(3)	42(3)	46(3)	11(2)	21(2)	10(2)
C(4)	54(5)	39(4)	31(4)	-2(3)	1(3)	-4(3)
O(4)	98(4)	96(4)	33(3)	21(3)	23(3)	13(3)
C(5)	52(4)	45(4)	39(4)	4(3)	11(3)	9(3)
C(6)	39(4)	31(3)	25(3)	3(3)	10(3)	5(3)
C(7)	41(4)	32(3)	29(3)	5(3)	10(3)	3(3)
C(8)	49(4)	48(4)	27(3)	5(3)	17(3)	9(3)
C(9)	41(4)	50(4)	41(4)	14(3)	19(3)	1(3)
C(10)	31(4)	41(4)	44(4)	17(3)	7(3)	2(3)
C(11)	37(4)	30(3)	36(4)	4(3)	12(3)	0(3)
C(12)	38(4)	33(3)	37(4)	10(3)	17(3)	3(3)
C(13)	37(4)	39(4)	36(4)	9(3)	-1(3)	-2(3)
C(14)	38(4)	48(4)	53(4)	12(3)	10(3)	-1(3)
C(15)	37(4)	77(6)	73(5)	18(4)	17(4)	-3(4)
C(16)	41(5)	81(6)	71(6)	13(5)	2(4)	-21(4)
C(17)	60(5)	43(4)	56(5)	13(3)	4(4)	-14(4)
C(18)	46(4)	41(4)	50(4)	6(3)	7(3)	-6(3)
C(19)	25(3)	35(3)	44(4)	10(3)	6(3)	3(3)
C(20)	44(4)	37(4)	48(4)	8(3)	12(3)	10(3)
C(21)	60(5)	37(4)	61(5)	5(4)	16(4)	11(3)
C(22)	61(5)	35(4)	77(6)	20(4)	16(4)	16(4)
C(23)	70(5)	56(5)	51(5)	23(4)	17(4)	17(4)
C(24)	54(4)	44(4)	48(4)	13(3)	11(4)	6(3)
C(25)	43(4)	32(3)	37(4)	14(3)	1(3)	-7(3)
C(26)	51(4)	37(4)	61(5)	9(3)	18(4)	3(3)
C(27)	69(6)	50(5)	82(6)	16(4)	13(5)	10(4)
C(28)	84(6)	56(5)	87(6)	35(5)	7(5)	-2(5)
C(29)	60(5)	60(5)	54(5)	22(4)	5(4)	-11(4)
C(30)	51(4)	44(4)	38(4)	10(3)	5(3)	-16(3)
C(31)	52(4)	69(5)	41(4)	5(4)	15(4)	0(4)
C(32)	36(4)	25(3)	44(4)	4(3)	4(3)	-5(3)
C(33)	48(4)	29(4)	81(5)	8(4)	31(4)	1(3)
C(34)	61(5)	37(4)	123(8)	8(5)	29(5)	10(4)
C(35)	69(6)	39(5)	97(7)	8(5)	-1(5)	19(4)

C(36)	128(8)	55(5)	68(6)	17(4)	-10(6)	37(6)
C(37)	88(6)	46(4)	45(4)	12(4)	17(4)	18(4)
C(38)	40(4)	37(4)	33(3)	7(3)	10(3)	-10(3)
C(39)	33(4)	42(4)	45(4)	4(3)	7(3)	-4(3)
C(40)	41(4)	70(5)	51(4)	11(4)	8(4)	6(4)
C(41)	42(4)	63(5)	56(5)	-4(4)	2(4)	-25(4)
C(42)	50(5)	48(4)	70(5)	8(4)	13(4)	-20(4)
C(43)	47(4)	39(4)	50(4)	12(3)	10(3)	-10(3)
C(44)	30(4)	44(4)	37(4)	14(3)	6(3)	1(3)
C(45)	54(4)	35(4)	56(4)	13(3)	18(4)	10(3)
C(46)	82(6)	54(5)	83(6)	28(5)	27(5)	17(5)
C(47)	78(6)	89(7)	100(8)	59(6)	30(6)	32(6)
C(48)	54(5)	98(7)	72(6)	46(5)	7(4)	10(5)
C(49)	41(4)	65(5)	49(4)	21(4)	14(4)	0(4)
C(50)	66(5)	73(5)	51(5)	0(4)	15(4)	-18(4)
C(51A)	142(9)	78(6)	46(5)	7(5)	31(6)	44(6)
C(52A)	64(11)	70(11)	61(10)	2(9)	12(9)	2(9)
C(51B)	142(9)	78(6)	46(5)	7(5)	31(6)	44(6)
C(52B)	68(12)	125(16)	62(11)	1(11)	20(10)	28(12)
C(53)	47(4)	66(5)	36(4)	4(4)	9(3)	-5(4)
C(54)	70(5)	94(6)	47(5)	31(4)	11(4)	1(5)
C(55)	37(4)	34(4)	38(4)	5(3)	15(3)	-1(3)
C(56)	53(4)	39(4)	40(4)	8(3)	16(3)	3(3)
C(57)	52(4)	42(4)	39(4)	7(3)	7(3)	-1(3)
C(58)	35(4)	60(5)	46(4)	12(4)	7(3)	-3(4)
C(59)	39(4)	50(4)	54(4)	18(4)	11(4)	9(3)
C(60)	32(4)	42(4)	39(4)	11(3)	6(3)	-5(3)
C(61)	76(6)	63(6)	56(5)	0(5)	-8(5)	-5(5)
F(1)	100(4)	96(4)	101(4)	-44(3)	2(3)	20(3)
F(2)	88(4)	81(3)	82(3)	-10(3)	-22(3)	-1(3)
F(3)	210(7)	59(3)	81(4)	10(3)	-13(4)	-60(4)
C(62)	59(6)	70(6)	78(6)	15(5)	5(5)	8(5)
F(4)	174(7)	183(7)	169(7)	62(5)	70(6)	125(6)
F(5)	151(5)	85(4)	165(6)	3(4)	-97(5)	48(4)
F(6)	76(4)	60(3)	309(9)	84(4)	7(5)	17(3)
C(63)	35(4)	29(3)	26(3)	0(3)	8(3)	1(3)
C(64)	39(4)	38(4)	34(4)	6(3)	9(3)	-1(3)
C(65)	39(4)	39(4)	33(3)	4(3)	5(3)	7(3)
C(66)	45(4)	44(4)	51(4)	20(3)	11(3)	10(3)
C(67)	41(4)	35(4)	43(4)	10(3)	14(3)	-1(3)
C(68)	37(4)	35(3)	35(4)	13(3)	4(3)	6(3)
C(69)	43(5)	53(5)	63(5)	17(4)	0(4)	6(4)
F(7)	68(3)	125(4)	174(5)	111(4)	-43(3)	-18(3)

F(8)	77(3)	108(4)	96(4)	-27(3)	-35(3)	24(3)
F(9)	53(3)	162(5)	91(4)	22(3)	18(3)	40(3)
C(70)	47(5)	47(5)	81(6)	36(5)	7(5)	-1(4)
F(10)	100(12)	40(7)	137(13)	-29(7)	77(10)	-33(6)
F(11)	35(4)	44(5)	92(8)	11(5)	23(5)	-11(4)
F(12)	70(6)	126(8)	107(8)	78(7)	31(5)	-12(6)
F(10B)	62(9)	70(11)	58(8)	23(7)	6(6)	-35(7)
F(11B)	65(10)	48(8)	133(15)	39(9)	-5(10)	-15(6)
F(12B)	102(18)	60(13)	92(16)	-17(10)	73(15)	-33(11)
C(71)	36(4)	36(3)	30(3)	12(3)	9(3)	1(3)
C(72)	51(4)	38(4)	44(4)	11(3)	16(3)	7(3)
C(73)	61(5)	33(4)	46(4)	15(3)	22(4)	-2(3)
C(74)	57(4)	42(4)	50(4)	9(3)	27(4)	0(3)
C(75)	57(5)	36(4)	51(4)	6(3)	19(4)	0(3)
C(76)	47(4)	35(4)	44(4)	5(3)	16(3)	-2(3)
C(77)	117(8)	45(5)	83(6)	24(5)	59(6)	6(5)
F(13)	441(13)	55(3)	84(4)	-18(3)	106(6)	-104(5)
F(14)	126(5)	86(4)	257(8)	110(5)	136(5)	62(4)
F(15)	76(3)	55(3)	112(4)	44(2)	44(3)	-1(2)
C(78)	80(6)	54(5)	84(6)	8(5)	52(5)	3(5)
F(16)	124(4)	79(3)	91(4)	-30(3)	35(3)	0(3)
F(17)	125(4)	59(3)	116(4)	34(3)	67(3)	40(3)
F(18)	115(4)	58(3)	181(5)	12(3)	114(4)	11(3)
C(79)	36(4)	33(3)	38(4)	14(3)	8(3)	8(3)
C(80)	44(4)	33(3)	36(4)	4(3)	9(3)	0(3)
C(81)	47(4)	45(4)	41(4)	7(3)	11(3)	11(3)
C(82)	69(5)	43(4)	32(4)	7(3)	5(4)	6(4)
C(83)	50(4)	29(3)	44(4)	10(3)	4(3)	2(3)
C(84)	40(4)	37(4)	41(4)	12(3)	10(3)	5(3)
C(85)	73(6)	54(6)	81(7)	0(6)	31(6)	7(5)
F(19)	128(13)	122(11)	140(12)	85(10)	90(11)	89(10)
F(20)	99(7)	117(8)	59(5)	-1(6)	40(5)	17(7)
F(21)	74(7)	124(12)	103(11)	-38(9)	40(7)	-25(7)
F(19B)	58(10)	210(20)	62(10)	28(13)	20(9)	57(12)
F(20B)	106(16)	102(15)	140(20)	-72(16)	53(16)	9(13)
F(21B)	130(20)	81(17)	170(30)	86(17)	120(20)	67(16)
C(86)	67(6)	60(5)	57(5)	6(4)	6(4)	-17(5)
F(22)	137(5)	142(5)	215(7)	127(5)	-53(5)	-93(5)
F(23)	146(5)	169(6)	67(4)	-25(4)	2(3)	-96(5)
F(24)	51(3)	134(5)	259(8)	-93(5)	10(4)	-21(4)
C(87)	216(17)	222(16)	122(10)	63(11)	-133(7)	-41(10)
Cl(1)	163(4)	292(7)	120(3)	36(4)	-5(3)	-31(4)
Cl(2)	83(3)	204(5)	309(7)	41(5)	29(4)	-16(3)

Table A.111: Crystal data and structure refinement for **25**.

Empirical formula	$C_{90}H_{67}BF_{24}N_2O_4P_2Zn \cdot C_6H_6$	
Formula weight	1912.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.0867(15) Å	α= 90°.
	b = 26.603(2) Å	β= 116.1330(10)°.
	c = 19.5381(15) Å	γ = 90°.
Volume	8906.6(12) $Å^3$	
Z	4	
Density (calculated)	1.426 Mg/m^3	
Absorption coefficient	0.415 mm^{-1}	
F(000)	3904	
Crystal size	0.27 x 0.15 x 0.09 mm^3	
Theta range for data collection	1.92 to 20.81°.	
Index ranges	-19<=h<=19, -26<=k<=26, -19<=l<=19	
Reflections collected	72717	
Independent reflections	9322 [R(int) = 0.0803]	
Completeness to theta = 20.81°	99.90%	
Max. and min. transmission	0.9628 and 0.8965	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9322 / 699 / 1298	
Goodness-of-fit on F^2	1.275	
Final R indices [I>2sigma(I)]	R1 = 0.0761, wR2 = 0.1605	
R indices (all data)	R1 = 0.0932, wR2 = 0.1665	
Largest diff. peak and hole	0.486 and -0.424 $e.Å^{-3}$	

Table A.112: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **25**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	15209(1)	-457(1)	7393(1)	26(1)	C(63)	9906(4)	1155(3)	5133(4)	33(2)
P(1)	13494(1)	-112(1)	6709(1)	26(1)	C(64)	9961(4)	1670(3)	5253(4)	34(2)
P(2)	16853(1)	139(1)	7743(1)	28(1)	C(65)	9159(6)	715(3)	6511(6)	43(2)
N(1)	14301(3)	-113(2)	7459(3)	24(2)	F(1)	9170(20)	909(8)	7142(16)	91(9)
N(2)	16276(3)	-168(2)	7982(3)	26(2)	F(2)	8487(13)	530(15)	6140(9)	94(9)
O(1)	15003(3)	197(2)	6526(3)	27(1)	F(3)	9634(15)	314(8)	6790(18)	79(7)
C(1)	15563(4)	371(2)	6313(4)	22(2)	F(1B)	8442(14)	849(11)	6364(19)	84(8)
C(2)	16362(4)	383(3)	6783(4)	28(2)	F(2B)	9090(30)	245(6)	6290(20)	95(9)
C(3)	16803(5)	591(3)	6458(4)	35(2)	F(3B)	9558(17)	751(15)	7194(14)	100(12)
C(4)	16482(5)	768(3)	5709(5)	35(2)	C(66)	10160(8)	931(4)	4564(6)	60(3)

C(5)	15692(5)	739(3)	5251(4)	32(2)	F(4)	9830(20)	527(10)	4230(20)	108(11)
C(6)	15217(4)	543(3)	5561(4)	24(2)	F(5)	10010(20)	1253(9)	3959(15)	91(8)
C(7)	14384(4)	465(3)	5296(4)	28(2)	F(6)	10923(11)	890(20)	4826(12)	118(12)
C(8)	13727(5)	567(3)	4624(4)	35(2)	F(4B)	9572(16)	656(16)	4086(16)	95(11)
C(9)	12999(5)	459(3)	4581(4)	38(2)	F(5B)	10430(30)	1203(9)	4290(30)	96(10)
C(10)	12927(4)	256(3)	5200(4)	36(2)	F(6B)	10710(19)	546(12)	4931(11)	90(9)
C(11)	13574(4)	140(3)	5885(4)	28(2)	C(67)	9765(4)	2851(3)	5248(4)	26(2)
C(12)	14282(4)	256(3)	5894(4)	26(2)	C(68)	9310(4)	2725(3)	4489(4)	34(2)
C(13)	17290(3)	660(2)	8373(3)	31(2)	C(69)	9203(5)	3047(3)	3898(5)	40(2)
C(14)	17888(3)	577(2)	9098(3)	41(2)	C(70)	9541(5)	3519(3)	4034(5)	41(2)
C(15)	18138(3)	966(3)	9628(2)	55(3)	C(71)	9978(5)	3662(3)	4784(5)	32(2)
C(16)	17790(4)	1436(2)	9433(3)	63(3)	C(72)	10105(4)	3333(3)	5365(4)	29(2)
C(17)	17191(4)	1519(2)	8709(4)	63(3)	C(73)	8727(8)	2875(5)	3080(6)	60(3)
C(18)	16942(3)	1131(2)	8179(3)	46(2)	F(7)	8190(30)	2587(15)	3044(19)	112(15)
C(19)	17630(3)	-235(2)	7723(3)	29(2)	F(8)	9113(12)	2740(20)	2751(14)	105(12)
C(20)	17443(3)	-722(2)	7442(3)	38(2)	F(9)	8310(20)	3293(9)	2655(15)	92(9)
C(21)	17998(4)	-1018(2)	7353(3)	49(2)	F(7B)	9059(16)	2411(13)	2972(13)	106(9)
C(22)	18739(3)	-827(2)	7546(3)	58(3)	F(8B)	8730(30)	3157(14)	2568(11)	109(12)
C(23)	18926(2)	-341(2)	7827(3)	53(3)	F(9B)	8011(17)	2722(15)	2886(17)	82(10)
C(24)	18371(3)	-45(2)	7915(3)	44(2)	C(74)	10303(5)	4182(3)	4968(5)	49(2)
C(25)	16624(4)	-332(3)	8779(4)	30(2)	F(10)	10166(4)	4452(2)	4342(3)	81(2)
C(26)	16563(4)	-39(3)	9326(4)	34(2)	F(11)	11062(3)	4192(2)	5399(4)	78(2)
C(27)	16913(5)	-200(3)	10082(5)	42(2)	F(12)	9984(3)	4438(2)	5345(3)	61(2)
C(28)	17316(5)	-644(4)	10307(5)	42(2)	C(75)	10665(5)	2566(3)	6707(5)	35(2)
C(29)	17342(5)	-936(3)	9737(5)	48(2)	C(76)	11353(5)	2563(3)	6630(5)	45(2)
C(30)	17015(4)	-786(3)	8974(5)	38(2)	C(77)	12073(5)	2571(3)	7249(8)	66(3)
C(31)	17705(5)	-820(4)	11116(5)	57(3)	C(78)	12149(7)	2582(4)	7977(8)	79(4)
C(32)	17342(6)	-1298(4)	11239(5)	73(3)	C(79)	11481(7)	2589(3)	8071(5)	66(3)
C(33)	18579(6)	-875(6)	11400(6)	125(6)	C(80)	10748(5)	2579(3)	7456(5)	45(2)
C(34)	12734(3)	257(2)	6767(3)	31(2)	C(81)	12786(7)	2601(5)	7114(10)	102(5)
C(35)	12747(3)	775(2)	6681(3)	45(2)	F(13)	12717(5)	2352(4)	6505(8)	164(5)
C(36)	12155(3)	1071(1)	6700(3)	54(3)	F(14)	12973(4)	3053(3)	7001(4)	112(3)
C(37)	11551(3)	848(2)	6805(3)	52(3)	F(15)	13408(4)	2396(4)	7660(6)	201(6)
C(38)	11538(3)	330(2)	6890(3)	54(3)	C(82)	11532(10)	2611(8)	8858(8)	124(7)
C(39)	12130(3)	34(2)	6871(3)	39(2)	F(16)	12196(7)	2488(4)	9401(4)	222(6)
C(40)	13147(3)	-749(1)	6512(3)	30(2)	F(17)	11451(9)	3061(5)	9049(5)	222(7)
C(41)	12645(3)	-912(2)	5783(2)	44(2)	F(18)	11061(10)	2367(8)	8972(5)	278(11)
C(42)	12345(3)	-1397(2)	5672(3)	60(3)	C(83)	9105(4)	2725(3)	6133(4)	25(2)
C(43)	12548(3)	-1720(2)	6291(4)	57(3)	C(84)	9169(4)	3197(3)	6474(4)	33(2)
C(44)	13050(3)	-1557(2)	7019(3)	47(2)	C(85)	8560(5)	3410(3)	6585(5)	41(2)
C(45)	13349(3)	-1071(2)	7130(2)	36(2)	C(86)	7861(5)	3162(3)	6349(5)	48(2)
C(46)	14485(4)	268(3)	8033(4)	26(2)	C(87)	7781(5)	2697(3)	6005(5)	39(2)
C(47)	14346(5)	184(3)	8658(5)	47(2)	C(88)	8379(4)	2492(3)	5887(4)	32(2)

C(48)	14566(6)	529(4)	9241(5)	57(3)	C(89)	8642(8)	3925(4)	6933(7)	64(3)
C(49)	14909(6)	977(4)	9217(5)	54(3)	F(19)	9359(8)	4098(5)	7242(12)	97(6)
C(50)	15058(5)	1053(3)	8596(5)	50(2)	F(20)	8162(13)	4250(5)	6467(8)	129(8)
C(51)	14850(5)	709(3)	8018(4)	37(2)	F(21)	8448(10)	3918(4)	7507(8)	98(5)
C(52)	15076(17)	1320(9)	9895(11)	50(6)	F(19B)	8980(30)	4230(11)	6590(30)	84(12)
C(53)	14828(7)	1846(4)	9634(6)	79(3)	F(20B)	8010(20)	4110(20)	6830(40)	107(16)
C(54)	15921(18)	1236(11)	10466(17)	67(8)	F(21B)	9090(40)	3919(16)	7610(20)	140(20)
C(52B)	15330(30)	1431(14)	9800(20)	38(11)	C(90)	7040(6)	2417(4)	5737(8)	71(3)
C(53B)	14828(7)	1846(4)	9634(6)	79(3)	F(22)	6574(4)	2581(2)	6047(5)	113(3)
C(54B)	15630(30)	1246(19)	10610(30)	53(11)	F(23)	6597(4)	2469(3)	4990(5)	113(3)
C(55)	15066(8)	-1404(4)	6760(6)	78(4)	F(24)	7123(4)	1932(2)	5854(5)	117(3)
C(56)	15362(12)	-1734(7)	6367(10)	56(5)	C(1S)	5091(8)	3195(6)	1987(8)	120(6)
C(55B)	15066(8)	-1404(4)	6760(6)	78(4)	C(2S)	5470(6)	3129(5)	1528(9)	112(6)
C(56B)	14606(11)	-1756(7)	6337(10)	49(5)	C(3S)	5050(8)	3149(5)	739(9)	101(5)
O(2)	15027(3)	-904(2)	6567(3)	44(2)	C(4S)	4250(8)	3236(6)	409(8)	107(5)
O(3)	15293(3)	-1131(2)	8003(3)	36(1)	C(5S)	3871(6)	3302(6)	868(10)	104(6)
C(57)	15246(6)	-1474(3)	7592(5)	50(3)	C(6S)	4291(8)	3282(6)	1657(9)	103(6)
O(4)	15358(6)	-1939(2)	7839(5)	117(4)	C(1SB)	4990(20)	3347(15)	1420(20)	107(9)
C(58)	15562(10)	-2005(4)	8642(7)	129(6)	C(2SB)	5086(18)	3213(15)	780(30)	106(9)
B(1)	9827(5)	2504(3)	5970(5)	28(2)	C(3SB)	4440(20)	3132(15)	90(20)	105(9)
C(59)	9747(4)	1896(3)	5791(4)	27(2)	C(4SB)	3690(20)	3185(15)	40(20)	105(9)
C(60)	9506(4)	1565(3)	6203(4)	31(2)	C(5SB)	3593(18)	3319(19)	680(30)	105(9)
C(61)	9448(4)	1050(3)	6068(4)	28(2)	C(6SB)	4240(20)	3400(18)	1370(20)	102(9)
C(62)	9636(4)	845(3)	5531(5)	40(2)					

Table A.113: Bond lengths [Å] for **25**.

Zn(1)-O(2)	1.909(5)	C(37)-C(38)	1.3900	C(66)-F(5)	1.38(3)
Zn(1)-N(2)	2.000(5)	C(37)-H(37)	0.9500	C(66)-F(6B)	1.41(2)
Zn(1)-N(1)	2.014(6)	C(38)-C(39)	1.3900	C(67)-C(68)	1.390(10)
Zn(1)-O(3)	2.120(5)	C(38)-H(38)	0.9500	C(67)-C(72)	1.410(10)
Zn(1)-O(1)	2.337(5)	C(39)-H(39)	0.9500	C(68)-C(69)	1.380(11)
P(1)-N(1)	1.591(6)	C(40)-C(41)	1.3900	C(68)-H(68)	0.9500
P(1)-C(34)	1.795(4)	C(40)-C(45)	1.3900	C(69)-C(70)	1.384(11)
P(1)-C(40)	1.798(4)	C(41)-C(42)	1.3900	C(69)-C(73)	1.520(12)
P(1)-C(11)	1.813(8)	C(41)-H(41)	0.9500	C(70)-C(71)	1.382(11)
P(2)-N(2)	1.598(6)	C(42)-C(43)	1.3900	C(70)-H(70)	0.9500
P(2)-C(13)	1.796(4)	C(42)-H(42)	0.9500	C(71)-C(72)	1.368(10)
P(2)-C(19)	1.801(4)	C(43)-C(44)	1.3900	C(71)-C(74)	1.493(11)
P(2)-C(2)	1.807(7)	C(43)-H(43)	0.9500	C(72)-H(72)	0.9500
N(1)-C(46)	1.435(9)	C(44)-C(45)	1.3900	C(73)-F(8)	1.22(2)
N(2)-C(25)	1.465(9)	C(44)-H(44)	0.9500	C(73)-F(8B)	1.25(2)
O(1)-C(1)	1.386(8)	C(45)-H(45)	0.9500	C(73)-F(7)	1.25(3)
O(1)-C(12)	1.395(8)	C(46)-C(51)	1.372(10)	C(73)-F(9B)	1.31(3)

C(1)-C(2)	1.392(10)	C(46)-C(47)	1.378(10)	C(73)-F(9)	1.41(2)
C(1)-C(6)	1.395(10)	C(47)-C(48)	1.377(11)	C(73)-F(7B)	1.44(2)
C(2)-C(3)	1.376(10)	C(47)-H(47)	0.9500	C(74)-F(11)	1.317(10)
C(3)-C(4)	1.394(10)	C(48)-C(49)	1.370(13)	C(74)-F(12)	1.332(10)
C(3)-H(3)	0.9500	C(48)-H(48)	0.9500	C(74)-F(10)	1.341(10)
C(4)-C(5)	1.376(10)	C(49)-C(50)	1.377(12)	C(75)-C(76)	1.385(11)
C(4)-H(4)	0.9500	C(49)-C(52)	1.521(17)	C(75)-C(80)	1.402(11)
C(5)-C(6)	1.394(10)	C(49)-C(52B)	1.61(4)	C(76)-C(77)	1.374(13)
C(5)-H(5)	0.9500	C(50)-C(51)	1.371(11)	C(76)-H(76)	0.9500
C(6)-C(7)	1.454(10)	C(50)-H(50)	0.9500	C(77)-C(78)	1.365(15)
C(7)-C(12)	1.383(10)	C(51)-H(51)	0.9500	C(77)-C(81)	1.498(17)
C(7)-C(8)	1.386(10)	C(52)-C(53)	1.49(2)	C(78)-C(79)	1.366(15)
C(8)-C(9)	1.385(11)	C(52)-C(54)	1.52(4)	C(78)-H(78)	0.9500
C(8)-H(8)	0.9500	C(52)-H(52)	1.0000	C(79)-C(80)	1.386(13)
C(9)-C(10)	1.385(11)	C(53)-H(53A)	0.9800	C(79)-C(82)	1.500(18)
C(9)-H(9)	0.9500	C(53)-H(53B)	0.9800	C(80)-H(80)	0.9500
C(10)-C(11)	1.399(10)	C(53)-H(53C)	0.9800	C(81)-F(14)	1.300(13)
C(10)-H(10)	0.9500	C(54)-H(54A)	0.9800	C(81)-F(15)	1.315(14)
C(11)-C(12)	1.378(10)	C(54)-H(54B)	0.9800	C(81)-F(13)	1.317(17)
C(13)-C(14)	1.3900	C(54)-H(54C)	0.9800	C(82)-F(18)	1.21(2)
C(13)-C(18)	1.3900	C(52B)-C(54B)	1.52(7)	C(82)-F(17)	1.284(18)
C(14)-C(15)	1.3900	C(52B)-H(52B)	1.0000	C(82)-F(16)	1.286(15)
C(14)-H(14)	0.9500	C(54B)-H(54D)	0.9800	C(83)-C(88)	1.396(10)
C(15)-C(16)	1.3900	C(54B)-H(54E)	0.9800	C(83)-C(84)	1.402(10)
C(15)-H(15)	0.9500	C(54B)-H(54F)	0.9800	C(84)-C(85)	1.393(11)
C(16)-C(17)	1.3900	C(55)-O(2)	1.375(10)	C(84)-H(84)	0.9500
C(16)-H(16)	0.9500	C(55)-C(56)	1.436(18)	C(85)-C(86)	1.375(11)
C(17)-C(18)	1.3900	C(55)-C(57)	1.517(13)	C(85)-C(89)	1.506(13)
C(17)-H(17)	0.9500	C(55)-H(55)	1.0000	C(86)-C(87)	1.384(11)
C(18)-H(18)	0.9500	C(56)-H(56A)	0.9800	C(86)-H(86)	0.9500
C(19)-C(20)	1.3900	C(56)-H(56B)	0.9800	C(87)-C(88)	1.373(10)
C(19)-C(24)	1.3900	C(56)-H(56C)	0.9800	C(87)-C(90)	1.475(12)
C(20)-C(21)	1.3900	C(56B)-H(56D)	0.9800	C(88)-H(88)	0.9500
C(20)-H(20)	0.9500	C(56B)-H(56E)	0.9800	C(89)-F(21B)	1.22(4)
C(21)-C(22)	1.3900	C(56B)-H(56F)	0.9800	C(89)-F(20B)	1.24(4)
C(21)-H(21)	0.9500	O(3)-C(57)	1.193(9)	C(89)-F(20)	1.296(17)
C(22)-C(23)	1.3900	C(57)-O(4)	1.311(10)	C(89)-F(19)	1.312(16)
C(22)-H(22)	0.9500	O(4)-C(58)	1.452(13)	C(89)-F(21)	1.328(15)
C(23)-C(24)	1.3900	C(58)-H(58D)	0.9800	C(89)-F(19B)	1.37(3)
C(23)-H(23)	0.9500	C(58)-H(58E)	0.9800	C(90)-F(24)	1.308(11)
C(24)-H(24)	0.9500	C(58)-H(58F)	0.9800	C(90)-F(23)	1.333(13)
C(25)-C(26)	1.368(10)	B(1)-C(75)	1.621(12)	C(90)-F(22)	1.351(12)
C(25)-C(30)	1.381(10)	B(1)-C(67)	1.644(11)	C(1S)-C(2S)	1.3900

C(26)-C(27)	1.392(11)	B(1)-C(59)	1.648(11)	C(1S)-C(6S)	1.3900
C(26)-H(26)	0.9500	B(1)-C(83)	1.653(11)	C(1S)-H(1S)	0.9500
C(27)-C(28)	1.373(12)	C(59)-C(60)	1.401(10)	C(2S)-C(3S)	1.3900
C(27)-H(27)	0.9500	C(59)-C(64)	1.417(10)	C(2S)-H(2S)	0.9500
C(28)-C(29)	1.376(12)	C(60)-C(61)	1.390(10)	C(3S)-C(4S)	1.3900
C(28)-C(31)	1.494(12)	C(60)-H(60)	0.9500	C(3S)-H(3S)	0.9500
C(29)-C(30)	1.398(11)	C(61)-C(62)	1.363(11)	C(4S)-C(5S)	1.3900
C(29)-H(29)	0.9500	C(61)-C(65)	1.506(11)	C(4S)-H(4S)	0.9500
C(30)-H(30)	0.9500	C(62)-C(63)	1.381(11)	C(5S)-C(6S)	1.3900
C(31)-C(33)	1.515(13)	C(62)-H(62)	0.9500	C(5S)-H(5S)	0.9500
C(31)-C(32)	1.517(13)	C(63)-C(64)	1.388(10)	C(6S)-H(6S)	0.9500
C(31)-H(31)	1.0000	C(63)-C(66)	1.515(12)	C(1SB)-C(2SB)	1.3900
C(32)-H(32A)	0.9800	C(64)-H(64)	0.9500	C(1SB)-C(6SB)	1.3900
C(32)-H(32B)	0.9800	C(65)-F(3B)	1.21(2)	C(1SB)-H(1SB)	0.9500
C(32)-H(32C)	0.9800	C(65)-F(2)	1.264(17)	C(2SB)-C(3SB)	1.3900
C(33)-H(33A)	0.9800	C(65)-F(2B)	1.311(17)	C(2SB)-H(2SB)	0.9500
C(33)-H(33B)	0.9800	C(65)-F(1B)	1.32(2)	C(3SB)-C(4SB)	1.3900
C(33)-H(33C)	0.9800	C(65)-F(1)	1.33(2)	C(3SB)-H(3SB)	0.9500
C(34)-C(35)	1.3900	C(65)-F(3)	1.350(16)	C(4SB)-C(5SB)	1.3900
C(34)-C(39)	1.3900	C(66)-F(5B)	1.15(2)	C(4SB)-H(4SB)	0.9500
C(35)-C(36)	1.3900	C(66)-F(4)	1.27(3)	C(5SB)-C(6SB)	1.3900
C(35)-H(35)	0.9500	C(66)-F(6)	1.32(2)	C(5SB)-H(5SB)	0.9500
C(36)-C(37)	1.3900	C(66)-F(4B)	1.32(3)	C(6SB)-H(6SB)	0.9500
C(36)-H(36)	0.9500				

Table A.114: Bond angles [°] for **25**

O(2)-Zn(1)-N(2)	119.1(2)	C(39)-C(38)-H(38)	120.0	C(67)-C(68)-H(68)	118.8
O(2)-Zn(1)-N(1)	119.8(2)	C(37)-C(38)-H(38)	120.0	C(68)-C(69)-C(70)	121.3(8)
N(2)-Zn(1)-N(1)	118.3(2)	C(38)-C(39)-C(34)	120.0	C(68)-C(69)-C(73)	119.5(8)
O(2)-Zn(1)-O(3)	83.6(2)	C(38)-C(39)-H(39)	120.0	C(70)-C(69)-C(73)	119.2(8)
N(2)-Zn(1)-O(3)	101.3(2)	C(34)-C(39)-H(39)	120.0	C(71)-C(70)-C(69)	117.7(7)
N(1)-Zn(1)-O(3)	101.7(2)	C(41)-C(40)-C(45)	120.0	C(71)-C(70)-H(70)	121.1
O(2)-Zn(1)-O(1)	86.64(19)	C(41)-C(40)-P(1)	122.4(3)	C(69)-C(70)-H(70)	121.1
N(2)-Zn(1)-O(1)	86.3(2)	C(45)-C(40)-P(1)	117.4(3)	C(72)-C(71)-C(70)	120.5(7)
N(1)-Zn(1)-O(1)	80.4(2)	C(42)-C(41)-C(40)	120.0	C(72)-C(71)-C(74)	119.4(7)
O(3)-Zn(1)-O(1)	169.77(19)	C(42)-C(41)-H(41)	120.0	C(70)-C(71)-C(74)	120.1(8)
N(1)-P(1)-C(34)	115.1(3)	C(40)-C(41)-H(41)	120.0	C(71)-C(72)-C(67)	123.2(7)
N(1)-P(1)-C(40)	108.2(3)	C(41)-C(42)-C(43)	120.0	C(71)-C(72)-H(72)	118.4
C(34)-P(1)-C(40)	107.3(2)	C(41)-C(42)-H(42)	120.0	C(67)-C(72)-H(72)	118.4
N(1)-P(1)-C(11)	113.0(3)	C(43)-C(42)-H(42)	120.0	F(8)-C(73)-F(8B)	62.4(15)
C(34)-P(1)-C(11)	103.9(3)	C(42)-C(43)-C(44)	120.0	F(8)-C(73)-F(7)	117(2)
C(40)-P(1)-C(11)	109.0(3)	C(42)-C(43)-H(43)	120.0	F(8B)-C(73)-F(7)	128(2)
N(2)-P(2)-C(13)	111.5(3)	C(44)-C(43)-H(43)	120.0	F(8)-C(73)-F(9B)	123(2)

N(2)-P(2)-C(19)	113.7(3)	C(45)-C(44)-C(43)	120.0	F(8B)-C(73)-F(9B)	109(2)
C(13)-P(2)-C(19)	107.7(3)	C(45)-C(44)-H(44)	120.0	F(7)-C(73)-F(9B)	22(3)
N(2)-P(2)-C(2)	112.2(3)	C(43)-C(44)-H(44)	120.0	F(8)-C(73)-F(9)	103.5(18)
C(13)-P(2)-C(2)	107.9(3)	C(44)-C(45)-C(40)	120.0	F(8B)-C(73)-F(9)	41.9(15)
C(19)-P(2)-C(2)	103.4(3)	C(44)-C(45)-H(45)	120.0	F(7)-C(73)-F(9)	102(2)
C(46)-N(1)-P(1)	121.5(5)	C(40)-C(45)-H(45)	120.0	F(9B)-C(73)-F(9)	80(2)
C(46)-N(1)-Zn(1)	116.7(4)	C(51)-C(46)-C(47)	117.2(7)	F(8)-C(73)-F(7B)	43.4(17)
P(1)-N(1)-Zn(1)	116.9(3)	C(51)-C(46)-N(1)	122.6(6)	F(8B)-C(73)-F(7B)	103.8(19)
C(25)-N(2)-P(2)	114.6(4)	C(47)-C(46)-N(1)	120.1(7)	F(7)-C(73)-F(7B)	83(2)
C(25)-N(2)-Zn(1)	111.5(4)	C(48)-C(47)-C(46)	121.1(8)	F(9B)-C(73)-F(7B)	99.2(19)
P(2)-N(2)-Zn(1)	133.3(3)	C(48)-C(47)-H(47)	119.5	F(9)-C(73)-F(7B)	139.5(13)
C(1)-O(1)-C(12)	106.6(5)	C(46)-C(47)-H(47)	119.5	F(8)-C(73)-C(69)	114.8(14)
C(1)-O(1)-Zn(1)	124.1(4)	C(49)-C(48)-C(47)	121.9(9)	F(8B)-C(73)-C(69)	116.7(12)
C(12)-O(1)-Zn(1)	120.8(4)	C(49)-C(48)-H(48)	119.0	F(7)-C(73)-C(69)	109.7(17)
O(1)-C(1)-C(2)	125.1(6)	C(47)-C(48)-H(48)	119.0	F(9B)-C(73)-C(69)	117.5(13)
O(1)-C(1)-C(6)	110.8(6)	C(48)-C(49)-C(50)	116.5(8)	F(9)-C(73)-C(69)	107.6(14)
C(2)-C(1)-C(6)	124.0(7)	C(48)-C(49)-C(52)	114.3(16)	F(7B)-C(73)-C(69)	108.3(12)
C(3)-C(2)-C(1)	114.9(7)	C(50)-C(49)-C(52)	129.3(17)	F(11)-C(74)-F(12)	106.1(8)
C(3)-C(2)-P(2)	118.7(6)	C(48)-C(49)-C(52B)	136(2)	F(11)-C(74)-F(10)	106.9(7)
C(1)-C(2)-P(2)	126.4(6)	C(50)-C(49)-C(52B)	106(2)	F(12)-C(74)-F(10)	106.1(7)
C(2)-C(3)-C(4)	123.0(7)	C(52)-C(49)-C(52B)	24.0(13)	F(11)-C(74)-C(71)	113.4(8)
C(2)-C(3)-H(3)	118.5	C(51)-C(50)-C(49)	122.0(8)	F(12)-C(74)-C(71)	111.2(7)
C(4)-C(3)-H(3)	118.5	C(51)-C(50)-H(50)	119.0	F(10)-C(74)-C(71)	112.6(8)
C(5)-C(4)-C(3)	120.8(7)	C(49)-C(50)-H(50)	119.0	C(76)-C(75)-C(80)	115.8(8)
C(5)-C(4)-H(4)	119.6	C(50)-C(51)-C(46)	121.3(7)	C(76)-C(75)-B(1)	121.0(8)
C(3)-C(4)-H(4)	119.6	C(50)-C(51)-H(51)	119.4	C(80)-C(75)-B(1)	123.0(7)
C(4)-C(5)-C(6)	118.4(7)	C(46)-C(51)-H(51)	119.4	C(77)-C(76)-C(75)	122.2(10)
C(4)-C(5)-H(5)	120.8	C(53)-C(52)-C(54)	118(3)	C(77)-C(76)-H(76)	118.9
C(6)-C(5)-H(5)	120.8	C(53)-C(52)-C(49)	110.6(15)	C(75)-C(76)-H(76)	118.9
C(5)-C(6)-C(1)	118.9(7)	C(54)-C(52)-C(49)	107(2)	C(78)-C(77)-C(76)	121.6(11)
C(5)-C(6)-C(7)	135.7(7)	C(53)-C(52)-H(52)	106.9	C(78)-C(77)-C(81)	119.7(12)
C(1)-C(6)-C(7)	105.4(6)	C(54)-C(52)-H(52)	106.9	C(76)-C(77)-C(81)	118.7(13)
C(12)-C(7)-C(8)	118.3(7)	C(49)-C(52)-H(52)	106.9	C(77)-C(78)-C(79)	117.6(10)
C(12)-C(7)-C(6)	107.1(6)	C(54B)-C(52B)-C(49)	110(4)	C(77)-C(78)-H(78)	121.2
C(8)-C(7)-C(6)	134.6(7)	C(54B)-C(52B)-H(52B)	107.4	C(79)-C(78)-H(78)	121.2
C(9)-C(8)-C(7)	118.8(7)	C(49)-C(52B)-H(52B)	107.4	C(78)-C(79)-C(80)	121.9(10)
C(9)-C(8)-H(8)	120.6	C(52B)-C(54B)-H(54D)	109.5	C(78)-C(79)-C(82)	119.7(12)
C(7)-C(8)-H(8)	120.6	C(52B)-C(54B)-H(54E)	109.5	C(80)-C(79)-C(82)	118.3(12)
C(8)-C(9)-C(10)	120.8(7)	H(54D)-C(54B)-H(54E)	109.5	C(79)-C(80)-C(75)	120.8(9)
C(8)-C(9)-H(9)	119.6	C(52B)-C(54B)-H(54F)	109.5	C(79)-C(80)-H(80)	119.6
C(10)-C(9)-H(9)	119.6	H(54D)-C(54B)-H(54F)	109.5	C(75)-C(80)-H(80)	119.6
C(9)-C(10)-C(11)	122.3(7)	H(54E)-C(54B)-H(54F)	109.5	F(14)-C(81)-F(15)	107.7(10)
C(9)-C(10)-H(10)	118.8	O(2)-C(55)-C(56)	115.5(10)	F(14)-C(81)-F(13)	103.7(15)

C(11)-C(10)-H(10)	118.8	O(2)-C(55)-C(57)	111.9(8)	F(15)-C(81)-F(13)	102.6(12)
C(12)-C(11)-C(10)	114.3(7)	C(56)-C(55)-C(57)	122.7(11)	F(14)-C(81)-C(77)	114.6(11)
C(12)-C(11)-P(1)	122.5(6)	O(2)-C(55)-H(55)	100.6	F(15)-C(81)-C(77)	113.7(14)
C(10)-C(11)-P(1)	123.1(6)	C(56)-C(55)-H(55)	100.6	F(13)-C(81)-C(77)	113.4(11)
C(11)-C(12)-C(7)	125.5(7)	C(57)-C(55)-H(55)	100.6	F(18)-C(82)-F(17)	104.7(17)
C(11)-C(12)-O(1)	124.4(7)	H(56D)-C(56B)-H(56E)	109.5	F(18)-C(82)-F(16)	104.7(19)
C(7)-C(12)-O(1)	110.1(6)	H(56D)-C(56B)-H(56F)	109.5	F(17)-C(82)-F(16)	101.5(15)
C(14)-C(13)-C(18)	120.0	H(56E)-C(56B)-H(56F)	109.5	F(18)-C(82)-C(79)	116.8(16)
C(14)-C(13)-P(2)	120.1(3)	C(55)-O(2)-Zn(1)	113.7(5)	F(17)-C(82)-C(79)	111.9(16)
C(18)-C(13)-P(2)	119.0(3)	C(57)-O(3)-Zn(1)	107.7(5)	F(16)-C(82)-C(79)	115.6(14)
C(13)-C(14)-C(15)	120.0	O(3)-C(57)-O(4)	121.6(8)	C(88)-C(83)-C(84)	115.2(7)
C(13)-C(14)-H(14)	120.0	O(3)-C(57)-C(55)	122.7(8)	C(88)-C(83)-B(1)	124.2(7)
C(15)-C(14)-H(14)	120.0	O(4)-C(57)-C(55)	115.7(8)	C(84)-C(83)-B(1)	120.3(7)
C(16)-C(15)-C(14)	120.0	C(57)-O(4)-C(58)	115.8(8)	C(85)-C(84)-C(83)	122.3(7)
C(16)-C(15)-H(15)	120.0	O(4)-C(58)-H(58D)	109.5	C(85)-C(84)-H(84)	118.8
C(14)-C(15)-H(15)	120.0	O(4)-C(58)-H(58E)	109.5	C(83)-C(84)-H(84)	118.8
C(15)-C(16)-C(17)	120.0	H(58D)-C(58)-H(58E)	109.5	C(86)-C(85)-C(84)	120.3(8)
C(15)-C(16)-H(16)	120.0	O(4)-C(58)-H(58F)	109.5	C(86)-C(85)-C(89)	118.7(9)
C(17)-C(16)-H(16)	120.0	H(58D)-C(58)-H(58F)	109.5	C(84)-C(85)-C(89)	120.9(9)
C(18)-C(17)-C(16)	120.0	H(58E)-C(58)-H(58F)	109.5	C(85)-C(86)-C(87)	118.4(8)
C(18)-C(17)-H(17)	120.0	C(75)-B(1)-C(67)	112.1(6)	C(85)-C(86)-H(86)	120.8
C(16)-C(17)-H(17)	120.0	C(75)-B(1)-C(59)	104.5(6)	C(87)-C(86)-H(86)	120.8
C(17)-C(18)-C(13)	120.0	C(67)-B(1)-C(59)	113.8(6)	C(88)-C(87)-C(86)	120.9(8)
C(17)-C(18)-H(18)	120.0	C(75)-B(1)-C(83)	111.9(6)	C(88)-C(87)-C(90)	118.6(8)
C(13)-C(18)-H(18)	120.0	C(67)-B(1)-C(83)	102.3(6)	C(86)-C(87)-C(90)	120.5(8)
C(20)-C(19)-C(24)	120.0	C(59)-B(1)-C(83)	112.4(6)	C(87)-C(88)-C(83)	122.7(7)
C(20)-C(19)-P(2)	117.0(3)	C(60)-C(59)-C(64)	115.8(7)	C(87)-C(88)-H(88)	118.7
C(24)-C(19)-P(2)	122.8(3)	C(60)-C(59)-B(1)	121.3(7)	C(83)-C(88)-H(88)	118.7
C(21)-C(20)-C(19)	120.0	C(64)-C(59)-B(1)	122.9(7)	F(21B)-C(89)-F(20B)	110(3)
C(21)-C(20)-H(20)	120.0	C(61)-C(60)-C(59)	122.0(7)	F(21B)-C(89)-F(20)	135(2)
C(19)-C(20)-H(20)	120.0	C(61)-C(60)-H(60)	119.0	F(20B)-C(89)-F(20)	44(3)
C(20)-C(21)-C(22)	120.0	C(59)-C(60)-H(60)	119.0	F(21B)-C(89)-F(19)	55(3)
C(20)-C(21)-H(21)	120.0	C(62)-C(61)-C(60)	121.0(7)	F(20B)-C(89)-F(19)	133(2)
C(22)-C(21)-H(21)	120.0	C(62)-C(61)-C(65)	119.6(7)	F(20)-C(89)-F(19)	111.1(13)
C(23)-C(22)-C(21)	120.0	C(60)-C(61)-C(65)	119.4(7)	F(21B)-C(89)-F(21)	53(4)
C(23)-C(22)-H(22)	120.0	C(61)-C(62)-C(63)	119.0(7)	F(20B)-C(89)-F(21)	62(3)
C(21)-C(22)-H(22)	120.0	C(61)-C(62)-H(62)	120.5	F(20)-C(89)-F(21)	103.3(14)
C(24)-C(23)-C(22)	120.0	C(63)-C(62)-H(62)	120.5	F(19)-C(89)-F(21)	103.8(13)
C(24)-C(23)-H(23)	120.0	C(62)-C(63)-C(64)	120.9(7)	F(21B)-C(89)-F(19B)	107(3)
C(22)-C(23)-H(23)	120.0	C(62)-C(63)-C(66)	119.8(8)	F(20B)-C(89)-F(19B)	108(3)
C(23)-C(24)-C(19)	120.0	C(64)-C(63)-C(66)	119.3(8)	F(20)-C(89)-F(19B)	66(2)
C(23)-C(24)-H(24)	120.0	C(63)-C(64)-C(59)	121.3(7)	F(19)-C(89)-F(19B)	53(2)
C(19)-C(24)-H(24)	120.0	C(63)-C(64)-H(64)	119.3	F(21)-C(89)-F(19B)	141.3(16)

C(26)-C(25)-C(30)	120.2(7)	C(59)-C(64)-H(64)	119.3	F(21B)-C(89)-C(85)	111(2)
C(26)-C(25)-N(2)	120.4(7)	F(3B)-C(65)-F(2)	130.4(15)	F(20B)-C(89)-C(85)	113(2)
C(30)-C(25)-N(2)	119.3(7)	F(3B)-C(65)-F(2B)	111.1(18)	F(20)-C(89)-C(85)	112.9(11)
C(25)-C(26)-C(27)	119.2(8)	F(2)-C(65)-F(2B)	60.3(13)	F(19)-C(89)-C(85)	113.9(10)
C(25)-C(26)-H(26)	120.4	F(3B)-C(65)-F(1B)	108.0(17)	F(21)-C(89)-C(85)	110.9(10)
C(27)-C(26)-H(26)	120.4	F(2)-C(65)-F(1B)	44.4(12)	F(19B)-C(89)-C(85)	107.3(15)
C(28)-C(27)-C(26)	122.9(8)	F(2B)-C(65)-F(1B)	103.6(16)	F(24)-C(90)-F(23)	105.4(10)
C(28)-C(27)-H(27)	118.5	F(3B)-C(65)-F(1)	37.5(15)	F(24)-C(90)-F(22)	107.1(9)
C(26)-C(27)-H(27)	118.5	F(2)-C(65)-F(1)	106.1(14)	F(23)-C(90)-F(22)	103.4(9)
C(27)-C(28)-C(29)	116.1(8)	F(2B)-C(65)-F(1)	129.1(14)	F(24)-C(90)-C(87)	114.4(9)
C(27)-C(28)-C(31)	123.7(8)	F(1B)-C(65)-F(1)	71.6(14)	F(23)-C(90)-C(87)	112.5(9)
C(29)-C(28)-C(31)	120.2(9)	F(3B)-C(65)-F(3)	68.5(16)	F(22)-C(90)-C(87)	113.2(10)
C(28)-C(29)-C(30)	123.0(8)	F(2)-C(65)-F(3)	104.7(14)	C(2S)-C(1S)-C(6S)	120.0
C(28)-C(29)-H(29)	118.5	F(2B)-C(65)-F(3)	48.2(12)	C(2S)-C(1S)-H(1S)	120.0
C(30)-C(29)-H(29)	118.5	F(1B)-C(65)-F(3)	138.6(12)	C(6S)-C(1S)-H(1S)	120.0
C(25)-C(30)-C(29)	118.4(8)	F(1)-C(65)-F(3)	101.6(15)	C(3S)-C(2S)-C(1S)	120.0
C(25)-C(30)-H(30)	120.8	F(3B)-C(65)-C(61)	112.0(14)	C(3S)-C(2S)-H(2S)	120.0
C(29)-C(30)-H(30)	120.8	F(2)-C(65)-C(61)	115.9(11)	C(1S)-C(2S)-H(2S)	120.0
C(28)-C(31)-C(33)	111.8(8)	F(2B)-C(65)-C(61)	112.8(11)	C(4S)-C(3S)-C(2S)	120.0
C(28)-C(31)-C(32)	112.4(8)	F(1B)-C(65)-C(61)	108.9(12)	C(4S)-C(3S)-H(3S)	120.0
C(33)-C(31)-C(32)	111.5(10)	F(1)-C(65)-C(61)	116.6(11)	C(2S)-C(3S)-H(3S)	120.0
C(28)-C(31)-H(31)	106.9	F(3)-C(65)-C(61)	110.4(9)	C(3S)-C(4S)-C(5S)	120.0
C(33)-C(31)-H(31)	106.9	F(5B)-C(66)-F(4)	121(3)	C(3S)-C(4S)-H(4S)	120.0
C(32)-C(31)-H(31)	106.9	F(5B)-C(66)-F(6)	65.2(19)	C(5S)-C(4S)-H(4S)	120.0
C(31)-C(32)-H(32A)	109.5	F(4)-C(66)-F(6)	110.0(19)	C(4S)-C(5S)-C(6S)	120.0
C(31)-C(32)-H(32B)	109.5	F(5B)-C(66)-F(4B)	116(2)	C(4S)-C(5S)-H(5S)	120.0
H(32A)-C(32)-H(32)	109.5	F(4)-C(66)-F(4B)	25(2)	C(6S)-C(5S)-H(5S)	120.0
C(31)-C(32)-H(32C)	109.5	F(6)-C(66)-F(4B)	133(2)	C(5S)-C(6S)-C(1S)	120.0
H(32A)-C(32)-H(32(	109.5	F(5B)-C(66)-F(5)	35(2)	C(5S)-C(6S)-H(6S)	120.0
H(32B)-C(32)-H(32(	109.5	F(4)-C(66)-F(5)	102.3(18)	C(1S)-C(6S)-H(6S)	120.0
C(31)-C(33)-H(33A)	109.5	F(6)-C(66)-F(5)	99.1(19)	C(2SB)-C(1SB)-C(6SI	120.0
C(31)-C(33)-H(33B)	109.5	F(4B)-C(66)-F(5)	87(2)	C(2SB)-C(1SB)-H(1SI	120.0
H(33A)-C(33)-H(33)	109.5	F(5B)-C(66)-F(6B)	108(2)	C(6SB)-C(1SB)-H(1SI	120.0
C(31)-C(33)-H(33C)	109.5	F(4)-C(66)-F(6B)	74.6(18)	C(3SB)-C(2SB)-C(1SI	120.0
H(33A)-C(33)-H(33(	109.5	F(6)-C(66)-F(6B)	45.7(15)	C(3SB)-C(2SB)-H(2SI	120.0
H(33B)-C(33)-H(33(	109.5	F(4B)-C(66)-F(6B)	99.6(17)	C(1SB)-C(2SB)-H(2SI	120.0
C(35)-C(34)-C(39)	120.0	F(5)-C(66)-F(6B)	135.3(17)	C(4SB)-C(3SB)-C(2SI	120.0
C(35)-C(34)-P(1)	118.5(3)	F(5B)-C(66)-C(63)	116.4(15)	C(4SB)-C(3SB)-H(3SI	120.0
C(39)-C(34)-P(1)	121.4(3)	F(4)-C(66)-C(63)	118.0(18)	C(2SB)-C(3SB)-H(3SI	120.0
C(36)-C(35)-C(34)	120.0	F(6)-C(66)-C(63)	113.6(12)	C(3SB)-C(4SB)-C(5SI	120.0
C(36)-C(35)-H(35)	120.0	F(4B)-C(66)-C(63)	106.9(17)	C(3SB)-C(4SB)-H(4SI	120.0
C(34)-C(35)-H(35)	120.0	F(5)-C(66)-C(63)	111.6(15)	C(5SB)-C(4SB)-H(4SI	120.0
C(35)-C(36)-C(37)	120.0	F(6B)-C(66)-C(63)	108.6(12)	C(6SB)-C(5SB)-C(4SI	120.0

C(35)-C(36)-H(36)	120.0	C(68)-C(67)-C(72)	114.8(7)	C(6SB)-C(5SB)-H(5SI	120.0
C(37)-C(36)-H(36)	120.0	C(68)-C(67)-B(1)	123.7(7)	C(4SB)-C(5SB)-H(5SI	120.0
C(38)-C(37)-C(36)	120.0	C(72)-C(67)-B(1)	121.1(7)	C(5SB)-C(6SB)-C(1SI	120.0
C(38)-C(37)-H(37)	120.0	C(69)-C(68)-C(67)	122.4(7)	C(5SB)-C(6SB)-H(6SI	120.0
C(36)-C(37)-H(37)	120.0	C(69)-C(68)-H(68)	118.8	C(1SB)-C(6SB)-H(6SI	120.0
C(39)-C(38)-C(37)	120.0				

Table A.115: Anisotropic displacement parameters ($Å^2$x 10^3)for **25**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	25(1)	26(1)	25(1)	1(1)	10(1)	-1(1)
P(1)	24(1)	29(1)	23(1)	-2(1)	9(1)	-1(1)
P(2)	26(1)	30(1)	24(1)	0(1)	9(1)	-3(1)
N(1)	24(4)	26(4)	25(4)	0(3)	14(3)	-1(3)
N(2)	22(3)	31(4)	19(4)	1(3)	3(3)	-6(3)
O(1)	24(3)	26(3)	27(3)	4(2)	8(3)	-2(2)
C(1)	27(5)	16(4)	27(5)	-1(3)	16(4)	-2(3)
C(2)	30(5)	23(4)	33(5)	2(4)	14(4)	-4(4)
C(3)	29(5)	29(5)	39(5)	6(4)	9(4)	-2(4)
C(4)	36(6)	31(5)	49(6)	6(4)	29(5)	-1(4)
C(5)	46(6)	22(4)	32(5)	8(4)	19(5)	5(4)
C(6)	31(5)	20(4)	22(5)	3(3)	13(4)	3(4)
C(7)	41(6)	21(4)	19(5)	1(4)	12(4)	3(4)
C(8)	47(6)	28(5)	28(5)	4(4)	14(5)	2(4)
C(9)	33(5)	39(5)	30(5)	8(4)	3(4)	2(4)
C(10)	23(5)	34(5)	40(5)	4(4)	4(4)	-3(4)
C(11)	27(5)	24(4)	30(5)	-1(4)	10(4)	0(4)
C(12)	26(5)	21(4)	23(5)	0(4)	3(4)	5(4)
C(13)	32(5)	31(5)	33(5)	-1(4)	18(4)	-5(4)
C(14)	37(5)	52(6)	33(5)	-6(5)	15(5)	-12(4)
C(15)	41(6)	79(8)	46(6)	-18(6)	20(5)	-24(6)
C(16)	52(7)	72(8)	59(7)	-34(6)	20(6)	-36(6)
C(17)	70(7)	39(6)	89(9)	-22(6)	42(7)	-15(5)
C(18)	44(6)	42(6)	49(6)	-13(5)	18(5)	-15(5)
C(19)	28(5)	30(5)	27(5)	5(4)	10(4)	2(4)
C(20)	39(5)	43(6)	34(5)	5(4)	18(4)	7(5)
C(21)	72(7)	41(6)	41(6)	12(4)	33(5)	11(5)
C(22)	64(8)	68(8)	58(7)	23(6)	40(6)	35(6)
C(23)	38(6)	77(8)	49(6)	26(5)	23(5)	19(6)
C(24)	33(5)	43(5)	49(6)	15(4)	13(5)	8(5)
C(25)	19(4)	35(5)	29(5)	6(4)	5(4)	1(4)
C(26)	28(5)	39(5)	33(5)	1(4)	12(4)	-5(4)
C(27)	42(5)	52(6)	27(5)	-3(5)	11(4)	-6(5)

C(28)	30(5)	68(7)	29(5)	-2(5)	13(4)	-8(5)
C(29)	48(6)	51(6)	45(6)	22(5)	20(5)	11(5)
C(30)	36(5)	40(6)	36(5)	7(4)	14(4)	-2(4)
C(31)	47(6)	87(8)	34(6)	16(5)	17(5)	5(5)
C(32)	92(8)	82(8)	45(6)	23(6)	31(6)	18(7)
C(33)	46(7)	290(20)	37(7)	44(9)	16(6)	27(9)
C(34)	27(5)	32(5)	30(5)	0(4)	9(4)	1(4)
C(35)	43(6)	36(6)	68(7)	4(5)	36(5)	9(5)
C(36)	53(6)	43(6)	57(6)	0(5)	17(5)	6(5)
C(37)	32(6)	68(7)	47(6)	-8(5)	9(5)	17(5)
C(38)	33(6)	59(7)	74(7)	-6(5)	29(5)	1(5)
C(39)	30(5)	45(5)	42(5)	-4(4)	15(4)	-5(4)
C(40)	25(5)	34(5)	37(5)	1(4)	18(4)	1(4)
C(41)	39(5)	43(6)	39(6)	-11(4)	5(5)	-8(4)
C(42)	61(7)	38(6)	55(7)	-21(5)	3(5)	-11(5)
C(43)	47(6)	36(6)	77(8)	-1(6)	18(6)	-12(5)
C(44)	50(6)	41(6)	54(6)	-3(5)	25(5)	-5(5)
C(45)	37(5)	31(5)	42(6)	-7(4)	18(4)	-9(4)
C(46)	25(4)	30(5)	23(5)	-5(4)	11(4)	3(4)
C(47)	56(6)	47(6)	43(6)	-6(5)	26(5)	-11(5)
C(48)	86(8)	56(7)	40(6)	-14(5)	39(6)	0(6)
C(49)	73(7)	48(7)	35(6)	-13(5)	19(5)	7(5)
C(50)	65(7)	28(5)	59(7)	-3(5)	29(5)	-10(5)
C(51)	65(6)	32(5)	27(5)	-7(4)	31(5)	-11(5)
C(52)	62(13)	53(11)	51(12)	-18(8)	39(11)	-21(10)
C(53)	110(10)	47(7)	70(8)	-17(6)	30(7)	11(7)
C(54)	68(18)	73(13)	55(16)	-42(11)	22(12)	-15(13)
C(53B)	110(10)	47(7)	70(8)	-17(6)	30(7)	11(7)
C(54B)	90(30)	60(20)	30(20)	-9(13)	38(19)	-10(20)
C(55)	162(12)	31(6)	76(8)	-9(6)	84(8)	-3(7)
C(56)	82(15)	57(12)	40(11)	11(9)	36(10)	23(11)
C(55B)	162(12)	31(6)	76(8)	-9(6)	84(8)	-3(7)
C(56B)	73(14)	43(12)	41(11)	-5(9)	33(10)	-3(10)
O(2)	75(4)	25(3)	34(3)	0(3)	27(3)	-1(3)
O(3)	44(4)	25(3)	38(3)	4(3)	16(3)	-2(3)
C(57)	92(8)	25(6)	60(7)	6(5)	58(6)	-3(5)
O(4)	270(12)	29(4)	121(7)	19(4)	150(8)	20(5)
C(58)	282(19)	51(7)	124(10)	47(8)	154(13)	44(10)
B(1)	27(5)	26(5)	35(6)	-4(4)	19(5)	-5(4)
C(59)	23(4)	30(5)	28(5)	3(4)	11(4)	-1(4)
C(60)	21(4)	35(5)	38(5)	0(4)	13(4)	3(4)
C(61)	22(4)	30(5)	35(5)	1(4)	16(4)	3(4)
C(62)	33(5)	24(5)	54(6)	-7(5)	10(5)	-6(4)

C(63)	33(5)	34(5)	33(5)	-10(4)	14(4)	-3(4)
C(64)	28(5)	34(5)	42(5)	-5(4)	18(4)	0(4)
C(65)	38(7)	39(6)	55(7)	-5(6)	24(6)	-3(6)
F(1)	180(20)	56(9)	102(17)	-20(9)	125(19)	-41(13)
F(2)	52(11)	160(20)	57(9)	19(13)	7(8)	-68(15)
F(3)	81(14)	54(11)	134(17)	50(11)	77(13)	24(10)
F(1B)	66(13)	91(16)	120(20)	37(13)	67(14)	11(12)
F(2B)	140(30)	32(9)	150(20)	-27(11)	110(20)	-36(13)
F(3B)	85(17)	150(30)	52(13)	17(15)	21(12)	-65(17)
C(66)	99(11)	41(8)	57(8)	-13(6)	50(9)	-8(8)
F(4)	160(30)	52(10)	160(20)	-36(12)	110(20)	-16(15)
F(5)	150(20)	80(12)	57(13)	1(9)	62(13)	34(13)
F(6)	77(12)	210(30)	81(13)	-6(17)	46(9)	57(16)
F(4B)	103(15)	130(30)	67(13)	-73(15)	48(11)	-29(16)
F(5B)	180(30)	53(13)	130(30)	-12(13)	140(20)	-23(17)
F(6B)	126(18)	94(17)	75(11)	7(11)	67(12)	70(14)
C(67)	20(4)	33(5)	33(5)	-4(4)	18(4)	-2(4)
C(68)	38(5)	32(5)	34(5)	-6(4)	18(4)	-4(4)
C(69)	49(6)	47(6)	31(5)	-9(5)	25(5)	-6(5)
C(70)	58(6)	36(6)	46(6)	10(5)	37(5)	1(5)
C(71)	46(5)	22(5)	40(6)	-3(4)	28(5)	-4(4)
C(72)	29(5)	30(5)	30(5)	-6(4)	15(4)	2(4)
C(73)	87(10)	68(9)	42(7)	-7(7)	44(8)	-24(8)
F(7)	130(20)	126(19)	25(13)	16(12)	-20(13)	-90(20)
F(8)	112(14)	150(30)	68(14)	-28(19)	53(11)	11(18)
F(9)	120(18)	97(14)	32(11)	16(9)	9(10)	3(13)
F(7B)	156(18)	85(18)	53(12)	-36(11)	24(10)	21(13)
F(8B)	200(30)	107(19)	34(9)	-14(11)	61(15)	-78(19)
F(9B)	81(14)	150(20)	15(12)	-17(13)	17(12)	-25(13)
C(74)	48(7)	43(6)	57(6)	7(5)	25(6)	-9(5)
F(10)	139(6)	39(3)	80(4)	9(3)	62(4)	-17(3)
F(11)	44(4)	52(4)	125(5)	-1(3)	25(4)	-16(3)
F(12)	79(4)	38(3)	80(4)	-20(3)	48(3)	-9(3)
C(75)	33(5)	19(4)	39(6)	-3(4)	4(4)	-3(4)
C(76)	42(6)	28(5)	60(7)	3(4)	16(5)	-1(4)
C(77)	25(7)	40(6)	102(10)	7(6)	-1(7)	0(5)
C(78)	47(8)	35(6)	90(10)	0(6)	-29(7)	0(5)
C(79)	77(9)	39(6)	38(7)	1(5)	-14(7)	8(6)
C(80)	50(6)	40(5)	34(6)	3(4)	10(5)	1(4)
C(81)	37(8)	51(8)	188(17)	7(9)	21(9)	5(6)
F(13)	73(6)	130(8)	328(15)	-46(9)	125(8)	-12(5)
F(14)	90(5)	82(5)	153(7)	25(5)	44(5)	-21(4)
F(15)	37(4)	262(12)	266(12)	174(10)	30(6)	40(6)

C(82)	108(13)	159(16)	44(10)	-20(10)	-22(9)	69(12)
F(16)	246(12)	255(12)	44(5)	-19(6)	-48(6)	125(10)
F(17)	380(20)	182(10)	103(7)	1(7)	104(10)	140(12)
F(18)	289(17)	490(30)	36(5)	-33(9)	57(8)	-193(18)
C(83)	31(5)	25(5)	19(4)	7(4)	10(4)	4(4)
C(84)	30(5)	33(5)	36(5)	2(4)	16(4)	-5(4)
C(85)	52(6)	34(5)	45(6)	-8(4)	28(5)	0(5)
C(86)	55(7)	37(6)	69(7)	4(5)	43(6)	10(5)
C(87)	29(5)	39(6)	54(6)	3(5)	22(5)	0(4)
C(88)	30(5)	32(5)	34(5)	-1(4)	14(4)	-2(4)
C(89)	71(10)	57(8)	73(9)	-12(7)	40(8)	3(7)
F(19)	92(9)	81(8)	152(14)	-81(10)	84(9)	-40(7)
F(20)	188(17)	44(7)	115(10)	-11(6)	30(10)	44(9)
F(21)	127(12)	102(8)	107(10)	-61(8)	89(10)	-28(8)
F(19B)	130(30)	29(15)	110(30)	-35(17)	70(20)	-40(18)
F(20B)	90(20)	110(30)	150(40)	-50(30)	70(30)	0(20)
F(21B)	170(40)	110(30)	100(30)	-40(20)	20(30)	20(30)
C(90)	42(7)	47(7)	129(11)	2(7)	41(8)	-1(6)
F(22)	83(5)	72(4)	238(9)	-21(5)	120(6)	-18(4)
F(23)	49(4)	116(6)	143(7)	-24(5)	14(5)	-26(4)
F(24)	72(4)	40(4)	257(10)	-3(5)	88(5)	-12(3)
C(1S)	88(8)	116(14)	178(13)	-111(12)	80(10)	-41(10)
C(2S)	91(10)	91(12)	182(13)	-93(12)	86(9)	-19(9)
C(3S)	101(10)	55(10)	190(12)	12(11)	102(10)	-6(10)
C(4S)	111(10)	54(10)	191(14)	26(11)	99(10)	12(10)
C(5S)	102(11)	48(9)	198(14)	15(12)	100(10)	8(10)
C(6S)	91(9)	57(12)	197(13)	-49(13)	96(10)	-28(9)
C(1SB)	106(12)	57(16)	186(16)	-12(16)	89(15)	-26(14)
C(2SB)	106(14)	54(17)	195(17)	10(17)	100(13)	-4(16)
C(3SB)	121(16)	58(18)	176(17)	15(18)	101(13)	11(18)
C(4SB)	113(13)	67(18)	171(17)	6(18)	93(15)	-9(19)
C(5SB)	108(14)	67(18)	175(18)	-1(18)	94(13)	-13(18)
C(6SB)	109(14)	44(17)	184(17)	-25(17)	92(14)	-16(16)

Table A.121: Crystal data and structure refinement for **26**.

Empirical formula	$C_{84}H_{55}BF_{24}N_2O_4P_2Zn \cdot C_6H_5Br_{0.38}$	
Formula weight	1857.89	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.7810(11) Å	α= 90°.
	b = 27.1179(16) Å	β= 116.7850(10)°.
	c = 18.6506(11) Å	γ = 90°.
Volume	8479.6(9) $Å^3$	
Z	4	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	0.612 mm^{-1}	
F(000)	3761	
Crystal size	0.47 x 0.35 x 0.28 mm^3	
Theta range for data collection	2.56 to 25.03°.	
Index ranges	-22<=h<=22, -32<=k<=32, -22<=l<=22	
Reflections collected	101702	
Independent reflections	14960 [R(int) = 0.0443]	
Completeness to theta = 25.03°	99.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8489 and 0.7608	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14960 / 815 / 1339	
Goodness-of-fit on F^2	1.117	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1516	
R indices (all data)	R1 = 0.0797, wR2 = 0.1617	
Largest diff. peak and hole	0.852 and -0.636 e.$Å^{-3}$	

Table A.122: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **26**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	10136(1)	4628(1)	2609(1)	37(1)	C(68)	3267(5)	2454(5)	1027(4)	128(4)
P(1)	8407(1)	4981(1)	1930(1)	34(1)	C(69)	5751(2)	2713(1)	3958(2)	32(1)
P(2)	11793(1)	5111(1)	2763(1)	36(1)	C(70)	6542(2)	2564(1)	4364(2)	37(1)
O(1)	9885(1)	5229(1)	1603(1)	32(1)	C(71)	7161(2)	2826(2)	4328(3)	48(1)
N(1)	9254(2)	4999(1)	2708(2)	35(1)	C(72)	7001(3)	3255(2)	3880(3)	59(1)
O(3)	9930(2)	4162(1)	1775(2)	56(1)	C(73)	6229(3)	3414(2)	3480(3)	56(1)
N(2)	11211(2)	4937(1)	3126(2)	45(1)	C(74)	5613(2)	3152(1)	3518(2)	43(1)
C(1)	9130(2)	5313(1)	988(2)	35(1)	C(75)	7998(3)	2646(2)	4783(4)	75(2)

C(2)	8425(2)	5232(1)	1042(2)	37(1)
C(3)	7727(2)	5359(2)	350(2)	51(1)
C(4)	7752(3)	5546(2)	-332(2)	57(1)
C(5)	8464(3)	5618(2)	-361(2)	50(1)
C(6)	9171(2)	5502(1)	311(2)	39(1)
C(7)	10008(2)	5535(1)	523(2)	37(1)
C(8)	10455(3)	5692(1)	134(2)	45(1)
C(9)	11268(3)	5681(2)	553(3)	51(1)
C(10)	11657(3)	5510(2)	1339(2)	46(1)
C(11)	11237(2)	5343(1)	1749(2)	36(1)
C(12)	10418(2)	5367(1)	1315(2)	33(1)
C(13)	7622(2)	5304(1)	2038(2)	40(1)
C(14)	7011(2)	5055(2)	2105(2)	45(1)
C(15)	6439(3)	5307(2)	2224(3)	55(1)
C(16)	6462(3)	5805(2)	2284(3)	62(1)
C(17)	7046(3)	6057(2)	2198(4)	86(2)
C(18)	7625(3)	5815(2)	2070(4)	76(2)
C(19)	8101(2)	4349(1)	1737(2)	37(1)
C(20)	8266(3)	4044(1)	2399(3)	48(1)
C(21)	7981(3)	3562(2)	2269(3)	60(1)
C(22)	7545(3)	3388(2)	1498(3)	64(1)
C(23)	7382(3)	3688(2)	853(3)	65(1)
C(24)	7659(2)	4167(2)	966(3)	47(1)
C(25)	9471(2)	5412(1)	3246(2)	41(1)
C(26)	9720(3)	5859(2)	3063(3)	63(1)
C(27)	9932(4)	6245(2)	3598(4)	88(2)
C(28)	9896(4)	6194(2)	4318(4)	92(2)
C(29)	9650(3)	5762(2)	4500(3)	78(2)
C(30)	9437(3)	5371(2)	3966(3)	57(1)
C(31)	12438(2)	5584(2)	3370(2)	44(1)
C(32)	12193(3)	6066(2)	3228(3)	57(1)
C(33)	12629(4)	6428(2)	3784(4)	83(2)
C(34)	13288(4)	6298(3)	4458(4)	90(2)
C(35)	13547(4)	5819(2)	4613(3)	81(2)
C(36)	13120(3)	5455(2)	4070(3)	58(1)
C(37)	12431(2)	4637(2)	2682(2)	43(1)
C(38)	13166(3)	4742(2)	2703(3)	60(1)
C(39)	13608(4)	4357(3)	2598(3)	83(2)
C(40)	13302(5)	3883(3)	2459(3)	98(2)
C(41)	12590(5)	3794(2)	2447(4)	93(2)
C(42)	12147(3)	4159(2)	2544(3)	64(1)
C(43)	11570(2)	4911(2)	4008(3)	71(2)
C(44)	11937(3)	4490(3)	4395(3)	109(3)
C(76)	6039(5)	3883(3)	2989(4)	102(2)
C(77)	5059(2)	2753(1)	4853(2)	39(1)
C(78)	5596(2)	2639(1)	5642(2)	41(1)
C(79)	5714(3)	2944(2)	6282(2)	50(1)
C(80)	5282(3)	3377(2)	6162(3)	68(1)
C(81)	4743(3)	3496(2)	5392(3)	69(1)
C(82)	4631(3)	3193(2)	4750(3)	52(1)
C(83)	6294(3)	2803(2)	7112(3)	72(2)
C(84)	4256(6)	3953(3)	5236(5)	111(3)
O(2)	10273(2)	3984(1)	3314(2)	49(1)
O(4)	10276(4)	3179(1)	3154(3)	120(2)
B(1)	5036(2)	2444(1)	4090(2)	33(1)
F(1)	4295(2)	1092(1)	5617(2)	97(1)
F(2)	5250(2)	586(1)	5963(2)	72(1)
F(3)	4185(2)	447(1)	4923(2)	81(1)
F(4)	6719(3)	931(2)	3754(4)	92(2)
F(5)	5601(4)	802(2)	2789(3)	82(2)
F(6)	6058(5)	293(2)	3741(5)	102(3)
F(4B)	6329(19)	1008(5)	3167(17)	89(6)
F(5B)	5451(11)	497(10)	2904(16)	107(9)
F(6B)	6496(16)	445(10)	3951(13)	96(10)
F(7)	2099(5)	2073(5)	3450(7)	151(6)
F(8)	1912(12)	2825(6)	3194(13)	152(7)
F(9)	1345(6)	2312(5)	2283(7)	148(6)
F(7B)	1996(14)	2664(9)	3426(15)	117(8)
F(8B)	1797(11)	1948(4)	2919(18)	165(10)
F(9B)	1369(10)	2580(9)	2196(13)	161(10)
F(10)	3445(14)	1948(6)	910(10)	184(6)
F(11)	2549(9)	2485(12)	464(10)	175(10)
F(12)	3724(17)	2708(9)	935(12)	181(11)
F(10B)	2727(15)	2188(8)	545(10)	207(10)
F(11B)	2962(13)	2960(5)	671(9)	171(5)
F(12B)	3901(8)	2466(11)	957(10)	175(11)
F(13)	8244(4)	2632(4)	5582(4)	121(2)
F(14)	8533(4)	2878(3)	4665(6)	118(3)
F(15)	8069(7)	2165(3)	4633(6)	105(3)
F(13B)	8386(12)	2983(11)	5340(20)	138(11)
F(14B)	8340(18)	2733(15)	4272(18)	133(13)
F(15B)	8084(18)	2243(10)	4990(20)	122(15)
F(16)	5297(9)	3888(6)	2373(7)	126(7)
F(17)	5867(7)	4283(2)	3438(6)	110(3)
F(18)	6510(7)	4036(5)	2793(9)	110(5)
F(16B)	5430(9)	4027(5)	2724(11)	113(6)

C(45)	12263(4)	4462(5)	5224(5)	162(6)	F(17B)	6108(10)	3700(6)	2233(8)	178(6)
C(46)	12215(5)	4856(7)	5637(5)	196(8)	F(18B)	6664(11)	4161(7)	3235(13)	206(11)
C(47)	11860(4)	5295(5)	5267(4)	155(5)	F(19)	6037(7)	2342(4)	7312(5)	148(4)
C(48)	11523(3)	5325(3)	4431(3)	92(2)	F(20)	6431(8)	3076(5)	7677(6)	131(6)
C(49A)	9943(6)	3688(2)	1986(4)	110(3)	F(21)	6987(13)	2632(8)	7169(16)	78(4)
C(50A)	9524(7)	3332(4)	1528(6)	62(2)	F(19B)	5958(6)	2696(5)	7535(6)	80(3)
C(49B)	9943(6)	3688(2)	1986(4)	110(3)	F(20B)	6709(10)	3249(5)	7520(7)	97(4)
C(50B)	10110(7)	3324(4)	1578(6)	65(3)	F(21B)	6834(17)	2531(9)	7160(20)	110(10)
C(51)	10183(3)	3633(2)	2881(3)	65(1)	F(22)	4516(6)	4297(2)	4916(7)	260(5)
C(52)	10520(7)	3126(2)	4007(4)	150(4)	F(23)	3543(4)	3922(3)	4685(3)	229(5)
C(53)	5194(2)	1852(1)	4266(2)	33(1)	F(24)	4214(3)	4137(2)	5837(2)	177(3)
C(54)	4920(2)	1593(1)	4745(2)	36(1)	Br(1)	917(2)	3171(1)	10616(2)	78(1)
C(55)	4994(2)	1084(1)	4842(2)	38(1)	C(1S)	403(5)	3170(3)	9600(5)	145(6)
C(56)	5346(2)	813(1)	4466(2)	39(1)	C(2S)	-413(5)	3086(3)	9277(6)	137(6)
C(57)	5616(2)	1054(1)	3988(2)	37(1)	C(3S)	-868(4)	3048(3)	8450(6)	191(10)
C(58)	5535(2)	1560(1)	3889(2)	34(1)	C(4S)	-508(6)	3094(4)	7946(5)	146(5)
C(59)	4684(3)	815(2)	5341(3)	50(1)	C(5S)	309(6)	3179(4)	8270(6)	162(7)
C(60)	5986(3)	764(2)	3562(3)	50(1)	C(6S)	764(4)	3217(4)	9097(6)	142(6)
C(61)	4167(2)	2473(1)	3301(2)	39(1)	Br(1B)	-975(5)	2837(3)	7662(9)	298(8)
C(62)	3469(2)	2452(1)	3384(3)	50(1)	C(1SB)	-205(10)	2979(5)	8564(12)	212(10)
C(63)	2724(3)	2428(2)	2735(3)	60(1)	C(2SB)	-258(12)	2881(8)	9270(14)	243(12)
C(64)	2647(3)	2428(2)	1966(3)	71(2)	C(3SB)	379(16)	2992(9)	10008(12)	216(10)
C(65)	3324(3)	2450(2)	1857(3)	73(2)	C(4SB)	1069(13)	3199(8)	10041(14)	159(9)
C(66)	4074(2)	2470(2)	2520(3)	53(1)	C(5SB)	1123(12)	3297(9)	9335(16)	157(10)
C(67)	2000(4)	2390(3)	2867(5)	93(2)	C(6SB)	486(12)	3186(8)	8597(14)	169(11)

Table A.123: Bond lengths [Å] for **26**.

Zn(1)-O(3)	1.904(3)	C(35)-C(36)	1.384(7)	C(67)-F(8)	1.370(19)
Zn(1)-N(2)	1.988(3)	C(35)-H(35)	0.9500	C(67)-F(9B)	1.378(19)
Zn(1)-N(1)	2.016(3)	C(36)-H(36)	0.9500	C(68)-F(12)	1.17(2)
Zn(1)-O(2)	2.131(3)	C(37)-C(42)	1.381(6)	C(68)-F(10B)	1.240(18)
Zn(1)-O(1)	2.367(2)	C(37)-C(38)	1.392(6)	C(68)-F(12B)	1.26(2)
P(1)-N(1)	1.600(3)	C(38)-C(39)	1.401(7)	C(68)-F(11)	1.285(16)
P(1)-C(19)	1.792(4)	C(38)-H(38)	0.9500	C(68)-F(10)	1.453(19)
P(1)-C(13)	1.802(4)	C(39)-C(40)	1.385(10)	C(68)-F(11B)	1.518(18)
P(1)-C(2)	1.803(4)	C(39)-H(39)	0.9500	C(69)-C(70)	1.389(5)
P(2)-N(2)	1.596(3)	C(40)-C(41)	1.348(10)	C(69)-C(74)	1.402(5)
P(2)-C(31)	1.777(4)	C(40)-H(40)	0.9500	C(69)-B(1)	1.642(5)
P(2)-C(11)	1.810(4)	C(41)-C(42)	1.357(8)	C(70)-C(71)	1.389(5)
P(2)-C(37)	1.811(4)	C(41)-H(41)	0.9500	C(70)-H(70)	0.9500
O(1)-C(1)	1.383(4)	C(42)-H(42)	0.9500	C(71)-C(72)	1.385(6)
O(1)-C(12)	1.383(4)	C(43)-C(44)	1.360(9)	C(71)-C(75)	1.493(7)
N(1)-C(25)	1.435(5)	C(43)-C(48)	1.398(9)	C(72)-C(73)	1.367(7)

O(3)-C(49A)	1.341(6)	C(44)-C(45)	1.384(9)	C(72)-H(72)	0.9500
N(2)-C(43)	1.471(5)	C(44)-H(44)	0.9500	C(73)-C(74)	1.386(6)
C(1)-C(2)	1.390(5)	C(45)-C(46)	1.345(19)	C(73)-C(76)	1.514(7)
C(1)-C(6)	1.397(5)	C(45)-H(45)	0.9500	C(74)-H(74)	0.9500
C(2)-C(3)	1.407(5)	C(46)-C(47)	1.386(17)	C(75)-F(15B)	1.14(2)
C(3)-C(4)	1.390(6)	C(46)-H(46)	0.9500	C(75)-F(14)	1.285(8)
C(3)-H(3)	0.9500	C(47)-C(48)	1.397(8)	C(75)-F(13B)	1.32(2)
C(4)-C(5)	1.377(6)	C(47)-H(47)	0.9500	C(75)-F(13)	1.346(8)
C(4)-H(4)	0.9500	C(48)-H(48)	0.9500	C(75)-F(15)	1.354(10)
C(5)-C(6)	1.389(5)	C(49A)-C(50A)	1.293(11)	C(75)-F(14B)	1.39(3)
C(5)-H(5)	0.9500	C(49A)-C(51)	1.528(7)	C(76)-F(16B)	1.093(13)
C(6)-C(7)	1.441(5)	C(49A)-H(49A)	1.0000	C(76)-F(18)	1.175(12)
C(7)-C(12)	1.398(5)	C(50A)-H(50A)	0.9800	C(76)-F(18B)	1.292(16)
C(7)-C(8)	1.400(5)	C(50A)-H(50B)	0.9800	C(76)-F(16)	1.349(16)
C(8)-C(9)	1.367(6)	C(50A)-H(50C)	0.9800	C(76)-F(17)	1.490(13)
C(8)-H(8)	0.9500	C(50B)-H(50D)	0.9800	C(76)-F(17B)	1.556(15)
C(9)-C(10)	1.390(6)	C(50B)-H(50E)	0.9800	C(77)-C(78)	1.393(5)
C(9)-H(9)	0.9500	C(50B)-H(50F)	0.9800	C(77)-C(82)	1.403(5)
C(10)-C(11)	1.399(5)	C(51)-O(2)	1.210(5)	C(77)-B(1)	1.635(5)
C(10)-H(10)	0.9500	C(51)-O(4)	1.313(5)	C(78)-C(79)	1.384(6)
C(11)-C(12)	1.381(5)	C(52)-O(4)	1.451(7)	C(78)-H(78)	0.9500
C(13)-C(14)	1.384(5)	C(52)-H(52A)	0.9800	C(79)-C(80)	1.388(6)
C(13)-C(18)	1.388(6)	C(52)-H(52B)	0.9800	C(79)-C(83)	1.486(6)
C(14)-C(15)	1.373(6)	C(52)-H(52C)	0.9800	C(80)-C(81)	1.372(7)
C(14)-H(14)	0.9500	C(53)-C(58)	1.391(5)	C(80)-H(80)	0.9500
C(15)-C(16)	1.353(6)	C(53)-C(54)	1.405(5)	C(81)-C(82)	1.389(6)
C(15)-H(15)	0.9500	C(53)-B(1)	1.638(5)	C(81)-C(84)	1.489(7)
C(16)-C(17)	1.364(7)	C(54)-C(55)	1.390(5)	C(82)-H(82)	0.9500
C(16)-H(16)	0.9500	C(54)-H(54)	0.9500	C(83)-F(20)	1.216(11)
C(17)-C(18)	1.379(7)	C(55)-C(56)	1.375(5)	C(83)-F(21B)	1.22(2)
C(17)-H(17)	0.9500	C(55)-C(59)	1.493(5)	C(83)-F(19B)	1.247(9)
C(18)-H(18)	0.9500	C(56)-C(57)	1.373(5)	C(83)-F(21)	1.339(18)
C(19)-C(24)	1.388(5)	C(56)-H(56)	0.9500	C(83)-F(19)	1.448(10)
C(19)-C(20)	1.401(5)	C(57)-C(58)	1.386(5)	C(83)-F(20B)	1.454(15)
C(20)-C(21)	1.390(6)	C(57)-C(60)	1.492(5)	C(84)-F(24)	1.262(8)
C(20)-H(20)	0.9500	C(58)-H(58)	0.9500	C(84)-F(23)	1.271(10)
C(21)-C(22)	1.378(7)	C(59)-F(1)	1.306(5)	C(84)-F(22)	1.315(11)
C(21)-H(21)	0.9500	C(59)-F(2)	1.322(5)	Br(1)-C(1S)	1.694(9)
C(22)-C(23)	1.368(7)	C(59)-F(3)	1.350(5)	C(1S)-C(2S)	1.3900
C(22)-H(22)	0.9500	C(60)-F(6B)	1.253(16)	C(1S)-C(6S)	1.3900
C(23)-C(24)	1.378(6)	C(60)-F(5)	1.294(6)	C(2S)-C(3S)	1.3900
C(23)-H(23)	0.9500	C(60)-F(6)	1.312(7)	C(2S)-H(2S)	0.9500
C(24)-H(24)	0.9500	C(60)-F(4)	1.336(6)	C(3S)-C(4S)	1.3900

C(25)-C(30)	1.378(6)	C(60)-F(4B)	1.352(16)	C(3S)-H(3S)	0.9500
C(25)-C(26)	1.394(6)	C(60)-F(5B)	1.389(17)	C(4S)-C(5S)	1.3900
C(26)-C(27)	1.377(6)	C(61)-C(66)	1.387(6)	C(4S)-H(4S)	0.9500
C(26)-H(26)	0.9500	C(61)-C(62)	1.388(6)	C(5S)-C(6S)	1.3900
C(27)-C(28)	1.382(8)	C(61)-B(1)	1.635(5)	C(5S)-H(5S)	0.9500
C(27)-H(27)	0.9500	C(62)-C(63)	1.379(6)	C(6S)-H(6S)	0.9500
C(28)-C(29)	1.358(8)	C(62)-H(62)	0.9500	Br(1B)-C(1SB)	1.697(18)
C(28)-H(28)	0.9500	C(63)-C(64)	1.375(7)	C(1SB)-C(2SB)	1.3900
C(29)-C(30)	1.384(7)	C(63)-C(67)	1.492(8)	C(1SB)-C(6SB)	1.3900
C(29)-H(29)	0.9500	C(64)-C(65)	1.376(8)	C(2SB)-C(3SB)	1.3900
C(30)-H(30)	0.9500	C(64)-H(64)	0.9500	C(2SB)-H(2SB)	0.9500
C(31)-C(32)	1.371(6)	C(65)-C(66)	1.395(6)	C(3SB)-C(4SB)	1.3900
C(31)-C(36)	1.401(6)	C(65)-C(68)	1.502(10)	C(3SB)-H(3SB)	0.9500
C(32)-C(33)	1.395(7)	C(66)-H(66)	0.9500	C(4SB)-C(5SB)	1.3900
C(32)-H(32)	0.9500	C(67)-F(9)	1.239(11)	C(4SB)-H(4SB)	0.9500
C(33)-C(34)	1.354(9)	C(67)-F(8B)	1.275(14)	C(5SB)-C(6SB)	1.3900
C(33)-H(33)	0.9500	C(67)-F(7B)	1.28(3)	C(5SB)-H(5SB)	0.9500
C(34)-C(35)	1.372(9)	C(67)-F(7)	1.330(11)	C(6SB)-H(6SB)	0.9500
C(34)-H(34)	0.9500				

Table A.124: Bond angles [°] for **26**

O(3)-Zn(1)-N(2)	117.66(14)	C(41)-C(40)-H(40)	120.2	C(70)-C(69)-C(74)	115.8(3)
O(3)-Zn(1)-N(1)	122.25(13)	C(39)-C(40)-H(40)	120.2	C(70)-C(69)-B(1)	122.3(3)
N(2)-Zn(1)-N(1)	116.18(13)	C(40)-C(41)-C(42)	122.0(6)	C(74)-C(69)-B(1)	121.2(3)
O(3)-Zn(1)-O(2)	83.29(11)	C(40)-C(41)-H(41)	119.0	C(71)-C(70)-C(69)	122.5(3)
N(2)-Zn(1)-O(2)	103.42(12)	C(42)-C(41)-H(41)	119.0	C(71)-C(70)-H(70)	118.8
N(1)-Zn(1)-O(2)	103.23(11)	C(41)-C(42)-C(37)	120.1(6)	C(69)-C(70)-H(70)	118.8
O(3)-Zn(1)-O(1)	85.14(10)	C(41)-C(42)-H(42)	120.0	C(72)-C(71)-C(70)	120.1(4)
N(2)-Zn(1)-O(1)	83.69(10)	C(37)-C(42)-H(42)	120.0	C(72)-C(71)-C(75)	120.3(4)
N(1)-Zn(1)-O(1)	81.39(10)	C(44)-C(43)-C(48)	121.3(5)	C(70)-C(71)-C(75)	119.6(4)
O(2)-Zn(1)-O(1)	168.28(10)	C(44)-C(43)-N(2)	120.1(6)	C(73)-C(72)-C(71)	118.8(4)
N(1)-P(1)-C(19)	108.02(16)	C(48)-C(43)-N(2)	118.6(5)	C(73)-C(72)-H(72)	120.6
N(1)-P(1)-C(13)	114.40(17)	C(43)-C(44)-C(45)	120.2(9)	C(71)-C(72)-H(72)	120.6
C(19)-P(1)-C(13)	106.37(17)	C(43)-C(44)-H(44)	119.9	C(72)-C(73)-C(74)	121.0(4)
N(1)-P(1)-C(2)	113.49(16)	C(45)-C(44)-H(44)	119.9	C(72)-C(73)-C(76)	119.8(5)
C(19)-P(1)-C(2)	108.22(17)	C(46)-C(45)-C(44)	119.0(11)	C(74)-C(73)-C(76)	119.2(5)
C(13)-P(1)-C(2)	105.98(17)	C(46)-C(45)-H(45)	120.5	C(73)-C(74)-C(69)	121.8(4)
N(2)-P(2)-C(31)	110.09(18)	C(44)-C(45)-H(45)	120.5	C(73)-C(74)-H(74)	119.1
N(2)-P(2)-C(11)	111.31(16)	C(45)-C(46)-C(47)	122.6(8)	C(69)-C(74)-H(74)	119.1
C(31)-P(2)-C(11)	108.76(18)	C(45)-C(46)-H(46)	118.7	F(15B)-C(75)-F(14)	121.2(17)
N(2)-P(2)-C(37)	115.52(19)	C(47)-C(46)-H(46)	118.7	F(15B)-C(75)-F(13B)	117(2)
C(31)-P(2)-C(37)	106.21(19)	C(46)-C(47)-C(48)	118.7(10)	F(14)-C(75)-F(13B)	66.3(16)
C(11)-P(2)-C(37)	104.58(16)	C(46)-C(47)-H(47)	120.6	F(15B)-C(75)-F(13)	71(2)

C(1)-O(1)-C(12)	106.5(3)	C(48)-C(47)-H(47)	120.6	F(14)-C(75)-F(13)	107.4(6)
C(1)-O(1)-Zn(1)	122.29(19)	C(47)-C(48)-C(43)	118.1(8)	F(13B)-C(75)-F(13)	50.5(17)
C(12)-O(1)-Zn(1)	125.0(2)	C(47)-C(48)-H(48)	120.9	F(15B)-C(75)-F(15)	30(2)
C(25)-N(1)-P(1)	120.7(2)	C(43)-C(48)-H(48)	121.0	F(14)-C(75)-F(15)	106.1(7)
C(25)-N(1)-Zn(1)	117.9(2)	C(50A)-C(49A)-O(3)	126.5(7)	F(13B)-C(75)-F(15)	139.1(14)
P(1)-N(1)-Zn(1)	115.08(16)	C(50A)-C(49A)-C(51)	116.1(6)	F(13)-C(75)-F(15)	100.7(7)
C(49A)-O(3)-Zn(1)	115.3(3)	O(3)-C(49A)-C(51)	111.8(4)	F(15B)-C(75)-F(14B)	110(2)
C(43)-N(2)-P(2)	115.6(3)	C(50A)-C(49A)-H(49A)	97.8	F(14)-C(75)-F(14B)	32.9(14)
C(43)-N(2)-Zn(1)	112.1(2)	O(3)-C(49A)-H(49A)	97.8	F(13B)-C(75)-F(14B)	98.9(16)
P(2)-N(2)-Zn(1)	131.21(19)	C(51)-C(49A)-H(49A)	97.8	F(13)-C(75)-F(14B)	136.9(14)
O(1)-C(1)-C(2)	124.6(3)	H(50D)-C(50B)-H(50E)	109.5	F(15)-C(75)-F(14B)	84.4(18)
O(1)-C(1)-C(6)	110.9(3)	H(50D)-C(50B)-H(50F)	109.5	F(15B)-C(75)-C(71)	117.2(16)
C(2)-C(1)-C(6)	124.5(3)	H(50E)-C(50B)-H(50F)	109.5	F(14)-C(75)-C(71)	116.5(7)
C(1)-C(2)-C(3)	114.8(3)	O(2)-C(51)-O(4)	121.7(4)	F(13B)-C(75)-C(71)	106.6(11)
C(1)-C(2)-P(1)	122.6(3)	O(2)-C(51)-C(49A)	122.4(4)	F(13)-C(75)-C(71)	112.7(5)
C(3)-C(2)-P(1)	122.6(3)	O(4)-C(51)-C(49A)	115.9(4)	F(15)-C(75)-C(71)	112.0(6)
C(4)-C(3)-C(2)	121.8(4)	O(4)-C(52)-H(52A)	109.5	F(14B)-C(75)-C(71)	104.4(14)
C(4)-C(3)-H(3)	119.1	O(4)-C(52)-H(52B)	109.5	F(16B)-C(76)-F(18)	121.0(10)
C(2)-C(3)-H(3)	119.1	H(52A)-C(52)-H(52B)	109.5	F(16B)-C(76)-F(18B)	123.5(14)
C(5)-C(4)-C(3)	121.4(4)	O(4)-C(52)-H(52C)	109.5	F(18)-C(76)-F(18B)	38.2(11)
C(5)-C(4)-H(4)	119.3	H(52A)-C(52)-H(52C)	109.5	F(16B)-C(76)-F(16)	30.9(11)
C(3)-C(4)-H(4)	119.3	H(52B)-C(52)-H(52C)	109.5	F(18)-C(76)-F(16)	111.4(10)
C(4)-C(5)-C(6)	118.9(4)	C(58)-C(53)-C(54)	115.0(3)	F(18B)-C(76)-F(16)	136.2(12)
C(4)-C(5)-H(5)	120.6	C(58)-C(53)-B(1)	122.6(3)	F(16B)-C(76)-F(17)	63.1(14)
C(6)-C(5)-H(5)	120.6	C(54)-C(53)-B(1)	122.1(3)	F(18)-C(76)-F(17)	107.7(9)
C(5)-C(6)-C(1)	118.6(4)	C(55)-C(54)-C(53)	122.3(3)	F(18B)-C(76)-F(17)	76.7(12)
C(5)-C(6)-C(7)	135.6(4)	C(55)-C(54)-H(54)	118.8	F(16)-C(76)-F(17)	93.9(10)
C(1)-C(6)-C(7)	105.7(3)	C(53)-C(54)-H(54)	118.8	F(16B)-C(76)-C(73)	119.1(9)
C(12)-C(7)-C(8)	118.3(4)	C(56)-C(55)-C(54)	120.5(3)	F(18)-C(76)-C(73)	118.6(10)
C(12)-C(7)-C(6)	106.5(3)	C(56)-C(55)-C(59)	117.9(3)	F(18B)-C(76)-C(73)	110.3(10)
C(8)-C(7)-C(6)	135.3(3)	C(54)-C(55)-C(59)	121.5(4)	F(16)-C(76)-C(73)	113.2(9)
C(9)-C(8)-C(7)	118.2(4)	C(57)-C(56)-C(55)	118.6(3)	F(17)-C(76)-C(73)	108.9(6)
C(9)-C(8)-H(8)	120.9	C(57)-C(56)-H(56)	120.7	F(16B)-C(76)-F(17B)	101.6(11)
C(7)-C(8)-H(8)	120.9	C(55)-C(56)-H(56)	120.7	F(18)-C(76)-F(17B)	56.5(9)
C(8)-C(9)-C(10)	122.1(4)	C(56)-C(57)-C(58)	120.6(3)	F(18B)-C(76)-F(17B)	94.3(12)
C(8)-C(9)-H(9)	118.9	C(56)-C(57)-C(60)	119.5(3)	F(16)-C(76)-F(17B)	73.0(9)
C(10)-C(9)-H(9)	118.9	C(58)-C(57)-C(60)	119.9(3)	F(17)-C(76)-F(17B)	150.4(7)
C(9)-C(10)-C(11)	121.8(4)	C(57)-C(58)-C(53)	122.9(3)	C(73)-C(76)-F(17B)	100.7(8)
C(9)-C(10)-H(10)	119.1	C(57)-C(58)-H(58)	118.5	C(78)-C(77)-C(82)	115.5(3)
C(11)-C(10)-H(10)	119.1	C(53)-C(58)-H(58)	118.5	C(78)-C(77)-B(1)	122.0(3)
C(12)-C(11)-C(10)	114.7(3)	F(1)-C(59)-F(2)	107.2(4)	C(82)-C(77)-B(1)	121.8(3)
C(12)-C(11)-P(2)	126.5(3)	F(1)-C(59)-F(3)	106.7(4)	C(79)-C(78)-C(77)	122.5(4)
C(10)-C(11)-P(2)	118.8(3)	F(2)-C(59)-F(3)	103.5(3)	C(79)-C(78)-H(78)	118.7

C(11)-C(12)-O(1)	124.7(3)	F(1)-C(59)-C(55)	114.1(3)	C(77)-C(78)-H(78)	118.7
C(11)-C(12)-C(7)	124.9(3)	F(2)-C(59)-C(55)	113.0(3)	C(78)-C(79)-C(80)	120.8(4)
O(1)-C(12)-C(7)	110.4(3)	F(3)-C(59)-C(55)	111.5(4)	C(78)-C(79)-C(83)	120.1(4)
C(14)-C(13)-C(18)	118.1(4)	F(6B)-C(60)-F(5)	126.8(12)	C(80)-C(79)-C(83)	119.1(4)
C(14)-C(13)-P(1)	121.8(3)	F(6B)-C(60)-F(6)	38.2(14)	C(81)-C(80)-C(79)	118.0(4)
C(18)-C(13)-P(1)	120.1(3)	F(5)-C(60)-F(6)	107.6(5)	C(81)-C(80)-H(80)	121.0
C(15)-C(14)-C(13)	120.8(4)	F(6B)-C(60)-F(4)	69.6(14)	C(79)-C(80)-H(80)	121.0
C(15)-C(14)-H(14)	119.6	F(5)-C(60)-F(4)	105.2(5)	C(80)-C(81)-C(82)	121.2(4)
C(13)-C(14)-H(14)	119.6	F(6)-C(60)-F(4)	106.6(5)	C(80)-C(81)-C(84)	119.9(5)
C(16)-C(15)-C(14)	120.9(4)	F(6B)-C(60)-F(4B)	103.1(14)	C(82)-C(81)-C(84)	118.9(5)
C(16)-C(15)-H(15)	119.6	F(5)-C(60)-F(4B)	61.1(13)	C(81)-C(82)-C(77)	122.1(4)
C(14)-C(15)-H(15)	119.6	F(6)-C(60)-F(4B)	126.5(8)	C(81)-C(82)-H(82)	119.0
C(15)-C(16)-C(17)	119.2(4)	F(4)-C(60)-F(4B)	45.0(12)	C(77)-C(82)-H(82)	119.0
C(15)-C(16)-H(16)	120.4	F(6B)-C(60)-F(5B)	102.2(14)	F(20)-C(83)-F(21B)	117.1(16)
C(17)-C(16)-H(16)	120.4	F(5)-C(60)-F(5B)	40.4(13)	F(20)-C(83)-F(19B)	64.1(7)
C(16)-C(17)-C(18)	121.3(5)	F(6)-C(60)-F(5B)	70.6(13)	F(21B)-C(83)-F(19B)	116.7(16)
C(16)-C(17)-H(17)	119.3	F(4)-C(60)-F(5B)	131.4(11)	F(20)-C(83)-F(21)	108.8(12)
C(18)-C(17)-H(17)	119.3	F(4B)-C(60)-F(5B)	96.1(13)	F(21B)-C(83)-F(21)	16.9(19)
C(17)-C(18)-C(13)	119.7(5)	F(6B)-C(60)-C(57)	118.2(11)	F(19B)-C(83)-F(21)	128.3(12)
C(17)-C(18)-H(18)	120.1	F(5)-C(60)-C(57)	113.0(4)	F(20)-C(83)-F(19)	105.5(8)
C(13)-C(18)-H(18)	120.1	F(6)-C(60)-C(57)	113.3(5)	F(21B)-C(83)-F(19)	79.6(15)
C(24)-C(19)-C(20)	119.6(4)	F(4)-C(60)-C(57)	110.5(4)	F(19B)-C(83)-F(19)	46.6(6)
C(24)-C(19)-P(1)	122.5(3)	F(4B)-C(60)-C(57)	119.0(7)	F(21)-C(83)-F(19)	96.0(10)
C(20)-C(19)-P(1)	117.7(3)	F(5B)-C(60)-C(57)	114.8(9)	F(20)-C(83)-F(20B)	35.5(7)
C(21)-C(20)-C(19)	119.2(4)	C(66)-C(61)-C(62)	116.0(4)	F(21B)-C(83)-F(20B)	103.5(14)
C(21)-C(20)-H(20)	120.4	C(66)-C(61)-B(1)	123.1(3)	F(19B)-C(83)-F(20B)	99.6(8)
C(19)-C(20)-H(20)	120.4	C(62)-C(61)-B(1)	120.5(4)	F(21)-C(83)-F(20B)	88.6(12)
C(22)-C(21)-C(20)	120.3(4)	C(63)-C(62)-C(61)	122.7(4)	F(19)-C(83)-F(20B)	138.1(7)
C(22)-C(21)-H(21)	119.8	C(63)-C(62)-H(62)	118.7	F(20)-C(83)-C(79)	121.1(8)
C(20)-C(21)-H(21)	119.8	C(61)-C(62)-H(62)	118.7	F(21B)-C(83)-C(79)	115.4(15)
C(23)-C(22)-C(21)	120.4(4)	C(64)-C(63)-C(62)	120.2(4)	F(19B)-C(83)-C(79)	112.1(6)
C(23)-C(22)-H(22)	119.8	C(64)-C(63)-C(67)	119.9(5)	F(21)-C(83)-C(79)	113.7(12)
C(21)-C(22)-H(22)	119.8	C(62)-C(63)-C(67)	119.9(6)	F(19)-C(83)-C(79)	108.4(6)
C(22)-C(23)-C(24)	120.4(4)	C(63)-C(64)-C(65)	119.0(4)	F(20B)-C(83)-C(79)	107.5(7)
C(22)-C(23)-H(23)	119.8	C(63)-C(64)-H(64)	120.5	F(24)-C(84)-F(23)	106.2(7)
C(24)-C(23)-H(23)	119.8	C(65)-C(64)-H(64)	120.5	F(24)-C(84)-F(22)	107.9(8)
C(23)-C(24)-C(19)	120.1(4)	C(64)-C(65)-C(66)	120.1(5)	F(23)-C(84)-F(22)	98.7(8)
C(23)-C(24)-H(24)	119.9	C(64)-C(65)-C(68)	120.7(5)	F(24)-C(84)-C(81)	115.7(6)
C(19)-C(24)-H(24)	119.9	C(66)-C(65)-C(68)	119.2(6)	F(23)-C(84)-C(81)	115.7(7)
C(30)-C(25)-C(26)	118.6(4)	C(61)-C(66)-C(65)	122.0(4)	F(22)-C(84)-C(81)	111.0(7)
C(30)-C(25)-N(1)	119.6(4)	C(61)-C(66)-H(66)	119.0	C(51)-O(2)-Zn(1)	107.0(3)
C(26)-C(25)-N(1)	121.8(3)	C(65)-C(66)-H(66)	119.0	C(51)-O(4)-C(52)	116.0(4)
C(27)-C(26)-C(25)	120.2(5)	F(9)-C(67)-F(8B)	72.2(12)	C(77)-B(1)-C(61)	112.5(3)

C(27)-C(26)-H(26)	119.9	F(9)-C(67)-F(7B)	116.6(15)	C(77)-B(1)-C(53)	113.4(3)
C(25)-C(26)-H(26)	119.9	F(8B)-C(67)-F(7B)	111.9(17)	C(61)-B(1)-C(53)	104.2(3)
C(26)-C(27)-C(28)	120.2(5)	F(9)-C(67)-F(7)	109.1(9)	C(77)-B(1)-C(69)	101.5(3)
C(26)-C(27)-H(27)	119.9	F(8B)-C(67)-F(7)	42.9(12)	C(61)-B(1)-C(69)	113.3(3)
C(28)-C(27)-H(27)	119.9	F(7B)-C(67)-F(7)	76.2(16)	C(53)-B(1)-C(69)	112.3(3)
C(29)-C(28)-C(27)	120.0(5)	F(9)-C(67)-F(8)	105.5(11)	C(2S)-C(1S)-C(6S)	120.0
C(29)-C(28)-H(28)	120.0	F(8B)-C(67)-F(8)	132.5(14)	C(2S)-C(1S)-Br(1)	116.5(5)
C(27)-C(28)-H(28)	120.0	F(7B)-C(67)-F(8)	25.1(18)	C(6S)-C(1S)-Br(1)	123.4(5)
C(28)-C(29)-C(30)	120.2(5)	F(7)-C(67)-F(8)	101.2(11)	C(1S)-C(2S)-C(3S)	120.0
C(28)-C(29)-H(29)	119.9	F(9)-C(67)-F(9B)	32.7(11)	C(1S)-C(2S)-H(2S)	120.0
C(30)-C(29)-H(29)	119.9	F(8B)-C(67)-F(9B)	104.8(13)	C(3S)-C(2S)-H(2S)	120.0
C(25)-C(30)-C(29)	120.8(5)	F(7B)-C(67)-F(9B)	101.8(14)	C(2S)-C(3S)-C(4S)	120.0
C(25)-C(30)-H(30)	119.6	F(7)-C(67)-F(9B)	136.9(10)	C(2S)-C(3S)-H(3S)	120.0
C(29)-C(30)-H(30)	119.6	F(8)-C(67)-F(9B)	81.8(15)	C(4S)-C(3S)-H(3S)	120.0
C(32)-C(31)-C(36)	120.3(4)	F(9)-C(67)-C(63)	118.9(9)	C(5S)-C(4S)-C(3S)	120.0
C(32)-C(31)-P(2)	119.5(3)	F(8B)-C(67)-C(63)	113.9(9)	C(5S)-C(4S)-H(4S)	120.0
C(36)-C(31)-P(2)	119.2(3)	F(7B)-C(67)-C(63)	115.6(12)	C(3S)-C(4S)-H(4S)	120.0
C(31)-C(32)-C(33)	119.7(5)	F(7)-C(67)-C(63)	112.2(6)	C(4S)-C(5S)-C(6S)	120.0
C(31)-C(32)-H(32)	120.2	F(8)-C(67)-C(63)	108.3(10)	C(4S)-C(5S)-H(5S)	120.0
C(33)-C(32)-H(32)	120.2	F(9B)-C(67)-C(63)	107.3(9)	C(6S)-C(5S)-H(5S)	120.0
C(34)-C(33)-C(32)	119.4(6)	F(12)-C(68)-F(10B)	130.5(17)	C(5S)-C(6S)-C(1S)	120.0
C(34)-C(33)-H(33)	120.3	F(12)-C(68)-F(12B)	34.7(15)	C(5S)-C(6S)-H(6S)	120.0
C(32)-C(33)-H(33)	120.3	F(10B)-C(68)-F(12B)	116.4(15)	C(1S)-C(6S)-H(6S)	120.0
C(33)-C(34)-C(35)	122.1(5)	F(12)-C(68)-F(11)	114.3(17)	C(2SB)-C(1SB)-C(6SB)	120.0
C(33)-C(34)-H(34)	119.0	F(10B)-C(68)-F(11)	39.7(12)	C(2SB)-C(1SB)-Br(1B)	120.2(8)
C(35)-C(34)-H(34)	119.0	F(12B)-C(68)-F(11)	127.5(15)	C(6SB)-C(1SB)-Br(1B)	119.8(8)
C(34)-C(35)-C(36)	119.3(6)	F(12)-C(68)-F(10)	107.4(16)	C(1SB)-C(2SB)-C(3SB)	120.0
C(34)-C(35)-H(35)	120.4	F(10B)-C(68)-F(10)	60.6(12)	C(1SB)-C(2SB)-H(2SB)	120.0
C(36)-C(35)-H(35)	120.4	F(12B)-C(68)-F(10)	73.4(13)	C(3SB)-C(2SB)-H(2SB)	120.0
C(35)-C(36)-C(31)	119.2(5)	F(11)-C(68)-F(10)	99.5(14)	C(2SB)-C(3SB)-C(4SB)	120.0
C(35)-C(36)-H(36)	120.4	F(12)-C(68)-C(65)	116.0(13)	C(2SB)-C(3SB)-H(3SB)	120.0
C(31)-C(36)-H(36)	120.4	F(10B)-C(68)-C(65)	113.4(15)	C(4SB)-C(3SB)-H(3SB)	120.0
C(42)-C(37)-C(38)	119.5(4)	F(12B)-C(68)-C(65)	118.4(9)	C(5SB)-C(4SB)-C(3SB)	120.0
C(42)-C(37)-P(2)	117.9(3)	F(11)-C(68)-C(65)	113.9(12)	C(5SB)-C(4SB)-H(4SB)	120.0
C(38)-C(37)-P(2)	122.4(3)	F(10)-C(68)-C(65)	103.5(11)	C(3SB)-C(4SB)-H(4SB)	120.0
C(37)-C(38)-C(39)	119.0(5)	F(12)-C(68)-F(11B)	64.1(18)	C(4SB)-C(5SB)-C(6SB)	120.0
C(37)-C(38)-H(38)	120.5	F(10B)-C(68)-F(11B)	100.6(11)	C(4SB)-C(5SB)-H(5SB)	120.0
C(39)-C(38)-H(38)	120.5	F(12B)-C(68)-F(11B)	97.0(15)	C(6SB)-C(5SB)-H(5SB)	120.0
C(40)-C(39)-C(38)	119.8(6)	F(11)-C(68)-F(11B)	62.3(11)	C(5SB)-C(6SB)-C(1SB)	120.0
C(40)-C(39)-H(39)	120.1	F(10)-C(68)-F(11B)	148.7(9)	C(5SB)-C(6SB)-H(6SB)	120.0
C(38)-C(39)-H(39)	120.1	C(65)-C(68)-F(11B)	107.2(8)	C(1SB)-C(6SB)-H(6SB)	120.0
C(41)-C(40)-C(39)	119.6(5)				

Table A.125: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **26**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	35(1)	38(1)	35(1)	9(1)	14(1)	-1(1)
P(1)	31(1)	30(1)	37(1)	2(1)	12(1)	-4(1)
P(2)	34(1)	41(1)	34(1)	1(1)	17(1)	-3(1)
O(1)	32(1)	36(1)	28(1)	5(1)	12(1)	-5(1)
N(1)	33(2)	34(2)	35(2)	2(1)	14(1)	-4(1)
O(3)	87(2)	43(2)	44(2)	2(1)	34(2)	-7(2)
N(2)	36(2)	65(2)	32(2)	11(2)	14(1)	-5(2)
C(1)	41(2)	26(2)	30(2)	3(1)	10(2)	-4(2)
C(2)	34(2)	33(2)	35(2)	4(2)	7(2)	-6(2)
C(3)	41(2)	50(2)	46(2)	11(2)	6(2)	-2(2)
C(4)	50(3)	57(3)	39(2)	14(2)	-1(2)	-1(2)
C(5)	65(3)	43(2)	31(2)	9(2)	11(2)	0(2)
C(6)	55(2)	28(2)	29(2)	2(1)	15(2)	-5(2)
C(7)	55(2)	26(2)	33(2)	3(1)	23(2)	-1(2)
C(8)	70(3)	35(2)	42(2)	9(2)	35(2)	6(2)
C(9)	70(3)	47(2)	58(3)	12(2)	49(2)	6(2)
C(10)	53(2)	46(2)	54(2)	10(2)	37(2)	8(2)
C(11)	42(2)	33(2)	37(2)	3(2)	23(2)	-1(2)
C(12)	47(2)	25(2)	33(2)	1(1)	23(2)	-3(2)
C(13)	34(2)	35(2)	43(2)	0(2)	12(2)	0(2)
C(14)	43(2)	45(2)	48(2)	5(2)	22(2)	1(2)
C(15)	46(2)	67(3)	54(3)	5(2)	24(2)	6(2)
C(16)	40(2)	71(3)	64(3)	-10(2)	13(2)	14(2)
C(17)	69(3)	39(3)	147(6)	-17(3)	46(4)	4(2)
C(18)	51(3)	39(3)	138(5)	-10(3)	43(3)	-5(2)
C(19)	34(2)	34(2)	44(2)	0(2)	17(2)	-5(2)
C(20)	59(3)	40(2)	52(2)	3(2)	30(2)	-6(2)
C(21)	72(3)	43(2)	81(3)	11(2)	49(3)	-7(2)
C(22)	53(3)	39(2)	97(4)	-7(3)	31(3)	-17(2)
C(23)	54(3)	45(3)	70(3)	-13(2)	6(2)	-11(2)
C(24)	40(2)	40(2)	51(2)	-1(2)	12(2)	-2(2)
C(25)	36(2)	47(2)	39(2)	-4(2)	17(2)	-8(2)
C(26)	85(3)	52(3)	61(3)	-18(2)	41(3)	-27(2)
C(27)	111(5)	72(4)	98(4)	-41(3)	61(4)	-49(3)
C(28)	100(5)	98(5)	92(4)	-57(4)	55(4)	-37(4)
C(29)	79(4)	109(5)	58(3)	-27(3)	42(3)	-22(3)
C(30)	56(3)	73(3)	50(2)	-9(2)	30(2)	-13(2)
C(31)	49(2)	47(2)	46(2)	-9(2)	30(2)	-9(2)
C(32)	72(3)	51(3)	64(3)	-7(2)	45(3)	-8(2)
C(33)	133(6)	54(3)	94(4)	-24(3)	79(4)	-28(3)

C(34)	123(5)	88(5)	66(4)	-35(3)	49(4)	-58(4)
C(35)	81(4)	99(5)	57(3)	-23(3)	24(3)	-42(3)
C(36)	51(3)	70(3)	54(3)	-11(2)	24(2)	-16(2)
C(37)	51(2)	45(2)	31(2)	7(2)	16(2)	9(2)
C(38)	62(3)	71(3)	55(3)	6(2)	34(2)	20(2)
C(39)	77(4)	120(5)	60(3)	16(3)	37(3)	53(4)
C(40)	139(6)	85(5)	60(3)	16(3)	35(4)	77(5)
C(41)	127(6)	53(3)	79(4)	8(3)	28(4)	35(4)
C(42)	79(3)	42(3)	57(3)	11(2)	17(2)	14(2)
C(43)	28(2)	143(5)	38(2)	20(3)	10(2)	-12(3)
C(44)	45(3)	205(8)	69(4)	78(5)	18(3)	13(4)
C(45)	64(4)	351(17)	69(5)	90(8)	28(4)	29(7)
C(46)	49(4)	480(20)	55(5)	81(9)	15(4)	-2(8)
C(47)	51(4)	366(16)	51(4)	-46(6)	26(3)	-44(6)
C(48)	55(3)	188(7)	40(3)	-30(4)	26(2)	-35(4)
C(49A)	233(9)	44(3)	76(4)	-11(3)	91(5)	-19(4)
C(50A)	67(7)	61(6)	63(6)	-5(5)	34(5)	-6(5)
C(49B)	233(9)	44(3)	76(4)	-11(3)	91(5)	-19(4)
C(50B)	79(7)	55(6)	65(6)	-5(5)	35(6)	10(5)
C(51)	105(4)	34(2)	72(3)	14(2)	55(3)	10(2)
C(52)	321(13)	63(4)	92(5)	40(4)	116(7)	43(6)
C(53)	26(2)	30(2)	40(2)	3(2)	13(2)	0(1)
C(54)	30(2)	34(2)	45(2)	4(2)	18(2)	1(2)
C(55)	29(2)	35(2)	42(2)	7(2)	11(2)	-3(2)
C(56)	36(2)	27(2)	48(2)	5(2)	12(2)	0(2)
C(57)	30(2)	30(2)	45(2)	-1(2)	12(2)	0(1)
C(58)	33(2)	30(2)	40(2)	1(2)	17(2)	-1(1)
C(59)	49(2)	42(2)	61(3)	9(2)	27(2)	-2(2)
C(60)	60(3)	35(2)	64(3)	1(2)	34(2)	9(2)
C(61)	37(2)	24(2)	51(2)	3(2)	15(2)	6(2)
C(62)	43(2)	36(2)	67(3)	13(2)	21(2)	8(2)
C(63)	39(2)	39(2)	93(4)	10(2)	22(2)	6(2)
C(64)	43(3)	60(3)	79(4)	-14(3)	-1(2)	7(2)
C(65)	55(3)	83(4)	58(3)	-22(3)	5(2)	12(3)
C(66)	41(2)	58(3)	52(3)	-11(2)	14(2)	8(2)
C(67)	53(4)	83(5)	138(7)	24(5)	40(4)	16(3)
C(68)	80(6)	225(13)	47(4)	-36(6)	1(4)	16(7)
C(69)	45(2)	26(2)	26(2)	-4(1)	19(2)	-2(2)
C(70)	43(2)	31(2)	37(2)	-1(2)	19(2)	-4(2)
C(71)	50(2)	47(2)	52(2)	-9(2)	27(2)	-11(2)
C(72)	66(3)	58(3)	64(3)	0(2)	39(3)	-21(2)
C(73)	76(3)	47(2)	48(2)	11(2)	31(2)	-8(2)
C(74)	55(2)	39(2)	37(2)	6(2)	23(2)	1(2)

C(75)	43(3)	78(4)	105(5)	-11(4)	34(3)	-15(3)
C(76)	110(6)	88(5)	93(5)	44(4)	33(5)	-22(5)
C(77)	46(2)	34(2)	46(2)	6(2)	30(2)	7(2)
C(78)	50(2)	39(2)	48(2)	8(2)	34(2)	9(2)
C(79)	58(3)	62(3)	42(2)	6(2)	32(2)	10(2)
C(80)	88(4)	73(3)	56(3)	-8(2)	44(3)	22(3)
C(81)	86(4)	65(3)	60(3)	-2(2)	35(3)	35(3)
C(82)	63(3)	49(2)	47(2)	6(2)	28(2)	22(2)
C(83)	80(4)	103(5)	42(3)	7(3)	36(3)	15(3)
C(84)	150(7)	75(5)	104(5)	-4(4)	53(5)	58(5)
O(2)	64(2)	37(2)	50(2)	10(1)	28(1)	8(1)
O(4)	254(6)	43(2)	101(3)	21(2)	115(4)	23(3)
B(1)	34(2)	29(2)	40(2)	4(2)	19(2)	4(2)
F(1)	139(3)	60(2)	154(3)	35(2)	122(3)	21(2)
F(2)	81(2)	74(2)	56(2)	23(1)	27(1)	3(2)
F(3)	81(2)	78(2)	79(2)	6(2)	32(2)	-43(2)
F(4)	61(3)	104(4)	131(4)	-44(4)	62(3)	0(2)
F(5)	112(5)	83(3)	50(2)	-5(2)	36(3)	31(3)
F(6)	182(8)	33(2)	140(7)	12(3)	117(7)	30(4)
F(4B)	160(20)	38(8)	121(15)	-1(11)	108(16)	7(12)
F(5B)	66(11)	112(17)	130(20)	-83(16)	37(12)	-13(13)
F(6B)	127(19)	110(20)	67(11)	47(13)	55(13)	113(17)
F(7)	62(5)	211(14)	190(9)	113(9)	67(6)	23(6)
F(8)	107(8)	178(13)	213(15)	21(10)	111(9)	32(8)
F(9)	38(4)	217(15)	149(8)	37(8)	7(4)	-37(7)
F(7B)	65(10)	132(15)	184(18)	-38(16)	81(11)	-28(11)
F(8B)	112(13)	40(5)	400(30)	14(12)	161(17)	0(7)
F(9B)	57(9)	240(20)	197(17)	90(16)	69(10)	80(12)
F(10)	199(14)	238(16)	135(12)	-105(12)	93(11)	-8(14)
F(11)	83(7)	320(30)	64(7)	16(15)	-15(5)	42(13)
F(12)	250(30)	220(20)	55(7)	23(10)	62(15)	-10(20)
F(10B)	230(20)	234(19)	71(9)	-66(11)	-15(11)	-23(15)
F(11B)	213(14)	212(13)	94(8)	49(8)	74(9)	57(12)
F(12B)	98(8)	370(30)	51(5)	-22(12)	26(5)	73(13)
F(13)	71(4)	169(7)	86(4)	1(5)	3(3)	39(4)
F(14)	53(3)	109(5)	191(9)	18(6)	54(5)	-25(3)
F(15)	63(3)	82(4)	170(8)	-14(5)	51(5)	9(3)
F(13B)	40(10)	140(20)	170(30)	-59(18)	-12(13)	-11(12)
F(14B)	80(20)	220(30)	130(20)	40(20)	77(18)	69(19)
F(15B)	35(10)	100(20)	200(30)	100(20)	31(18)	7(15)
F(16)	145(10)	123(12)	83(7)	62(6)	28(6)	-3(8)
F(17)	203(10)	39(3)	117(6)	23(4)	97(6)	25(4)
F(18)	133(9)	90(8)	175(13)	69(8)	129(10)	15(7)

F(16B)	141(12)	78(9)	193(17)	91(11)	139(13)	67(9)
F(17B)	243(15)	205(13)	151(10)	137(10)	145(11)	136(12)
F(18B)	194(14)	111(12)	260(20)	93(13)	59(14)	-64(10)
F(19)	168(9)	156(8)	76(6)	63(6)	17(5)	-60(8)
F(20)	142(11)	191(15)	49(5)	-30(8)	32(5)	76(11)
F(21)	70(5)	111(7)	48(6)	14(5)	21(4)	26(5)
F(19B)	76(5)	120(8)	48(5)	34(5)	33(4)	-1(6)
F(20B)	134(11)	88(6)	41(6)	-5(4)	16(5)	-9(6)
F(21B)	130(20)	136(17)	39(7)	-4(10)	17(11)	85(15)
F(22)	319(11)	110(4)	427(13)	103(6)	235(11)	143(6)
F(23)	233(6)	234(7)	122(4)	-44(4)	-5(4)	197(6)
F(24)	222(5)	177(4)	98(3)	-34(3)	42(3)	139(4)
Br(1)	76(2)	78(2)	73(2)	3(1)	27(2)	19(2)
C(1S)	171(12)	55(6)	290(20)	-36(9)	182(14)	-12(7)
C(2S)	193(13)	59(6)	266(16)	-28(8)	197(14)	-23(7)
C(3S)	270(20)	176(15)	250(20)	87(14)	220(20)	139(15)
C(4S)	117(11)	160(14)	147(12)	49(10)	49(10)	22(10)
C(5S)	144(12)	183(15)	235(17)	83(14)	154(13)	68(11)
C(6S)	158(12)	72(9)	269(19)	-5(10)	160(14)	17(8)
Br(1B)	109(5)	127(6)	480(17)	58(9)	-25(8)	25(4)
C(1SB)	148(16)	89(19)	369(17)	20(20)	90(16)	31(14)
C(2SB)	170(20)	150(30)	462(19)	-20(30)	194(19)	27(19)
C(3SB)	230(30)	120(20)	390(18)	-40(20)	219(19)	20(20)
C(4SB)	220(20)	57(14)	270(20)	-58(17)	172(19)	5(16)
C(5SB)	215(19)	44(14)	230(20)	-45(17)	113(15)	-21(17)
C(6SB)	179(17)	27(13)	260(20)	29(16)	57(15)	-12(14)

Table A.126: Crystal data and structure refinement for **L3**.

Empirical formula	$C_{34}H_{40}N_2OP_2$	
Formula weight	554.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8628(14) Å	α= 72.3880(10)°.
	b = 11.1264(15) Å	β= 88.627(2)°.
	c = 13.9234(18) Å	γ = 69.7920(10)°.
Volume	1499.1(3) $Å^3$	
Z	2	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.174 mm^{-1}	
F(000)	592	
Crystal size	0.32 x 0.32 x 0.12 mm^3	
Theta range for data collection	2.05 to 26.37°.	
Index ranges	-13<=h<=13, -13<=k<=13, -17<=l<=17	
Reflections collected	20286	
Independent reflections	6118 [R(int) = 0.0225]	
Completeness to theta = 26.37°	99.60%	
Max. and min. transmission	0.9794 and 0.9458	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6118 / 0 / 356	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0885	
R indices (all data)	R1 = 0.0445, wR2 = 0.0940	
Largest diff. peak and hole	0.393 and -0.296 $e.Å^{-3}$	

Table A.127: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **L3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
P(1)	3251(1)	3563(1)	3771(1)	20(1)	C(16)	1767(2)	3907(2)	2050(2)	48(1)
O(1)	3801(1)	6353(1)	2787(1)	21(1)	C(17)	3029(2)	1227(2)	4525(2)	46(1)
N(1)	2627(1)	2623(1)	4529(1)	29(1)	C(18)	2623(2)	341(2)	5428(1)	32(1)
C(1)	2651(1)	6392(1)	3251(1)	20(1)	C(19)	3020(2)	202(2)	6407(2)	40(1)
P(2)	6237(1)	6990(1)	1604(1)	23(1)	C(20)	2686(2)	-673(2)	7227(2)	47(1)
N(2)	7052(1)	7699(1)	870(1)	30(1)	C(21)	1953(2)	-1405(2)	7068(2)	46(1)
C(2)	2330(1)	5269(1)	3749(1)	21(1)	C(22)	1556(2)	-1267(2)	6104(2)	42(1)
C(3)	1123(2)	5548(2)	4168(1)	28(1)	C(23)	1884(2)	-398(2)	5294(1)	35(1)
C(4)	297(2)	6858(2)	4090(1)	32(1)	C(24)	6998(2)	5965(2)	2871(1)	31(1)

C(5)	641(2)	7951(2)	3578(1)	27(1)	C(25)	8366(2)	4946(2)	2869(2)	44(1)
C(6)	1839(1)	7715(1)	3148(1)	21(1)	C(26)	5804(2)	5932(2)	1015(1)	31(1)
C(7)	2521(1)	8565(2)	2562(1)	22(1)	C(27)	5277(2)	6689(2)	-86(2)	45(1)
C(8)	2228(2)	9953(2)	2157(1)	28(1)	C(28)	7941(2)	8295(2)	1124(1)	31(1)
C(9)	3137(2)	10399(2)	1589(1)	32(1)	C(29)	9254(2)	7863(2)	683(1)	25(1)
C(10)	4324(2)	9497(2)	1434(1)	28(1)	C(30)	10207(2)	8387(2)	816(1)	32(1)
C(11)	4657(1)	8100(2)	1832(1)	23(1)	C(31)	11406(2)	8013(2)	414(1)	39(1)
C(12)	3703(1)	7691(1)	2376(1)	21(1)	C(32)	11670(2)	7112(2)	-128(1)	40(1)
C(13)	4982(2)	3226(2)	4035(1)	27(1)	C(33)	10728(2)	6593(2)	-274(1)	38(1)
C(14)	5341(2)	3081(3)	5118(2)	58(1)	C(34)	9532(2)	6963(2)	136(1)	30(1)
C(15)	3162(2)	3596(2)	2465(1)	30(1)					

Table A.128: Bond lengths [Å] for **L3**.

P(1)-N(1)	1.5678(13)	C(10)-C(11)	1.398(2)	C(23)-H(23)	0.9500
P(1)-C(2)	1.8053(15)	C(10)-H(10)	0.9500	C(24)-C(25)	1.527(2)
P(1)-C(13)	1.8098(16)	C(11)-C(12)	1.390(2)	C(24)-H(24A)	0.9900
P(1)-C(15)	1.8118(16)	C(13)-C(14)	1.513(3)	C(24)-H(24B)	0.9900
O(1)-C(1)	1.3857(16)	C(13)-H(13A)	0.9900	C(25)-H(25A)	0.9800
O(1)-C(12)	1.3902(17)	C(13)-H(13B)	0.9900	C(25)-H(25B)	0.9800
N(1)-C(17)	1.462(2)	C(14)-H(14A)	0.9800	C(25)-H(25C)	0.9800
C(1)-C(2)	1.388(2)	C(14)-H(14B)	0.9800	C(26)-C(27)	1.521(3)
C(1)-C(6)	1.3959(19)	C(14)-H(14C)	0.9800	C(26)-H(26A)	0.9900
P(2)-N(2)	1.5498(13)	C(15)-C(16)	1.519(2)	C(26)-H(26B)	0.9900
P(2)-C(26)	1.8067(16)	C(15)-H(15A)	0.9900	C(27)-H(27A)	0.9800
P(2)-C(24)	1.8150(17)	C(15)-H(15B)	0.9900	C(27)-H(27B)	0.9800
P(2)-C(11)	1.8216(15)	C(16)-H(16A)	0.9800	C(27)-H(27C)	0.9800
N(2)-C(28)	1.448(2)	C(16)-H(16B)	0.9800	C(28)-C(29)	1.518(2)
C(2)-C(3)	1.396(2)	C(16)-H(16C)	0.9800	C(28)-H(28A)	0.9900
C(3)-C(4)	1.395(2)	C(17)-C(18)	1.506(2)	C(28)-H(28B)	0.9900
C(3)-H(3)	0.9500	C(17)-H(17A)	0.9900	C(29)-C(34)	1.384(2)
C(4)-C(5)	1.380(2)	C(17)-H(17B)	0.9900	C(29)-C(30)	1.391(2)
C(4)-H(4)	0.9500	C(18)-C(23)	1.383(2)	C(30)-C(31)	1.384(2)
C(5)-C(6)	1.394(2)	C(18)-C(19)	1.386(3)	C(30)-H(30)	0.9500
C(5)-H(5)	0.9500	C(19)-C(20)	1.391(3)	C(31)-C(32)	1.381(3)
C(6)-C(7)	1.448(2)	C(19)-H(19)	0.9500	C(31)-H(31)	0.9500
C(7)-C(12)	1.391(2)	C(20)-C(21)	1.383(3)	C(32)-C(33)	1.381(3)
C(7)-C(8)	1.395(2)	C(20)-H(20)	0.9500	C(32)-H(32)	0.9500
C(8)-C(9)	1.382(2)	C(21)-C(22)	1.368(3)	C(33)-C(34)	1.386(2)
C(8)-H(8)	0.9500	C(21)-H(21)	0.9500	C(33)-H(33)	0.9500
C(9)-C(10)	1.393(2)	C(22)-C(23)	1.376(3)	C(34)-H(34)	0.9500
C(9)-H(9)	0.9500	C(22)-H(22)	0.9500		

Table A.129: Bond angles [°] for **L₃**

N(1)-P(1)-C(2)	107.09(7)	O(1)-C(12)-C(7)	111.38(12)	C(18)-C(23)-H(23)	119.2
N(1)-P(1)-C(13)	116.84(8)	C(11)-C(12)-C(7)	124.50(13)	C(25)-C(24)-P(2)	112.64(12)
C(2)-P(1)-C(13)	108.54(7)	C(14)-C(13)-P(1)	113.11(12)	C(25)-C(24)-H(24A)	109.1
N(1)-P(1)-C(15)	116.14(8)	C(14)-C(13)-H(13A)	109.0	P(2)-C(24)-H(24A)	109.1
C(2)-P(1)-C(15)	105.17(7)	P(1)-C(13)-H(13A)	109.0	C(25)-C(24)-H(24B)	109.1
C(13)-P(1)-C(15)	102.33(8)	C(14)-C(13)-H(13B)	109.0	P(2)-C(24)-H(24B)	109.1
C(1)-O(1)-C(12)	105.60(11)	P(1)-C(13)-H(13B)	109.0	H(24A)-C(24)-H(24B)	107.8
C(17)-N(1)-P(1)	117.13(11)	H(13A)-C(13)-H(13B)	107.8	C(24)-C(25)-H(25A)	109.5
O(1)-C(1)-C(2)	125.00(12)	C(13)-C(14)-H(14A)	109.5	C(24)-C(25)-H(25B)	109.5
O(1)-C(1)-C(6)	111.24(12)	C(13)-C(14)-H(14B)	109.5	H(25A)-C(25)-H(25B)	109.5
C(2)-C(1)-C(6)	123.76(13)	H(14A)-C(14)-H(14B)	109.5	C(24)-C(25)-H(25C)	109.5
N(2)-P(2)-C(26)	107.30(8)	C(13)-C(14)-H(14C)	109.5	H(25A)-C(25)-H(25C)	109.5
N(2)-P(2)-C(24)	117.57(8)	H(14A)-C(14)-H(14C)	109.5	H(25B)-C(25)-H(25C)	109.5
C(26)-P(2)-C(24)	108.22(8)	H(14B)-C(14)-H(14C)	109.5	C(27)-C(26)-P(2)	111.27(12)
N(2)-P(2)-C(11)	115.54(7)	C(16)-C(15)-P(1)	112.43(12)	C(27)-C(26)-H(26A)	109.4
C(26)-P(2)-C(11)	104.04(7)	C(16)-C(15)-H(15A)	109.1	P(2)-C(26)-H(26A)	109.4
C(24)-P(2)-C(11)	103.22(7)	P(1)-C(15)-H(15A)	109.1	C(27)-C(26)-H(26B)	109.4
C(28)-N(2)-P(2)	126.87(12)	C(16)-C(15)-H(15B)	109.1	P(2)-C(26)-H(26B)	109.4
C(1)-C(2)-C(3)	115.09(13)	P(1)-C(15)-H(15B)	109.1	H(26A)-C(26)-H(26B)	108.0
C(1)-C(2)-P(1)	125.22(11)	H(15A)-C(15)-H(15B)	107.8	C(26)-C(27)-H(27A)	109.5
C(3)-C(2)-P(1)	119.36(11)	C(15)-C(16)-H(16A)	109.5	C(26)-C(27)-H(27B)	109.5
C(4)-C(3)-C(2)	122.52(14)	C(15)-C(16)-H(16B)	109.5	H(27A)-C(27)-H(27B)	109.5
C(4)-C(3)-H(3)	118.7	H(16A)-C(16)-H(16B)	109.5	C(26)-C(27)-H(27C)	109.5
C(2)-C(3)-H(3)	118.7	C(15)-C(16)-H(16C)	109.5	H(27A)-C(27)-H(27C)	109.5
C(5)-C(4)-C(3)	120.78(14)	H(16A)-C(16)-H(16C)	109.5	H(27B)-C(27)-H(27C)	109.5
C(5)-C(4)-H(4)	119.6	H(16B)-C(16)-H(16C)	109.5	N(2)-C(28)-C(29)	112.27(13)
C(3)-C(4)-H(4)	119.6	N(1)-C(17)-C(18)	112.51(14)	N(2)-C(28)-H(28A)	109.2
C(4)-C(5)-C(6)	118.46(14)	N(1)-C(17)-H(17A)	109.1	C(29)-C(28)-H(28A)	109.2
C(4)-C(5)-H(5)	120.8	C(18)-C(17)-H(17A)	109.1	N(2)-C(28)-H(28B)	109.2
C(6)-C(5)-H(5)	120.8	N(1)-C(17)-H(17B)	109.1	C(29)-C(28)-H(28B)	109.2
C(5)-C(6)-C(1)	119.37(13)	C(18)-C(17)-H(17B)	109.1	H(28A)-C(28)-H(28B)	107.9
C(5)-C(6)-C(7)	134.71(14)	H(17A)-C(17)-H(17B)	107.8	C(34)-C(29)-C(30)	118.42(15)
C(1)-C(6)-C(7)	105.91(12)	C(23)-C(18)-C(19)	118.36(16)	C(34)-C(29)-C(28)	121.63(14)
C(12)-C(7)-C(8)	119.07(14)	C(23)-C(18)-C(17)	120.24(17)	C(30)-C(29)-C(28)	119.95(14)
C(12)-C(7)-C(6)	105.85(12)	C(19)-C(18)-C(17)	121.35(17)	C(31)-C(30)-C(29)	120.77(16)
C(8)-C(7)-C(6)	135.03(14)	C(18)-C(19)-C(20)	120.26(18)	C(31)-C(30)-H(30)	119.6
C(9)-C(8)-C(7)	118.09(14)	C(18)-C(19)-H(19)	119.9	C(29)-C(30)-H(30)	119.6
C(9)-C(8)-H(8)	121.0	C(20)-C(19)-H(19)	119.9	C(32)-C(31)-C(30)	120.13(16)
C(7)-C(8)-H(8)	121.0	C(21)-C(20)-C(19)	120.02(19)	C(32)-C(31)-H(31)	119.9
C(8)-C(9)-C(10)	121.44(15)	C(21)-C(20)-H(20)	120.0	C(30)-C(31)-H(31)	119.9
C(8)-C(9)-H(9)	119.3	C(19)-C(20)-H(20)	120.0	C(31)-C(32)-C(33)	119.71(16)
C(10)-C(9)-H(9)	119.3	C(22)-C(21)-C(20)	119.92(17)	C(31)-C(32)-H(32)	120.1

C(9)-C(10)-C(11)	122.15(14)	C(22)-C(21)-H(21)	120.0	C(33)-C(32)-H(32)	120.1
C(9)-C(10)-H(10)	118.9	C(20)-C(21)-H(21)	120.0	C(32)-C(33)-C(34)	119.98(17)
C(11)-C(10)-H(10)	118.9	C(21)-C(22)-C(23)	119.89(18)	C(32)-C(33)-H(33)	120.0
C(12)-C(11)-C(10)	114.70(14)	C(21)-C(22)-H(22)	120.1	C(34)-C(33)-H(33)	120.0
C(12)-C(11)-P(2)	125.89(11)	C(23)-C(22)-H(22)	120.1	C(29)-C(34)-C(33)	120.99(15)
C(10)-C(11)-P(2)	119.40(11)	C(22)-C(23)-C(18)	121.55(18)	C(29)-C(34)-H(34)	119.5
O(1)-C(12)-C(11)	124.11(13)	C(22)-C(23)-H(23)	119.2	C(33)-C(34)-H(34)	119.5

Table A.130: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{L_3}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	20(1)	18(1)	22(1)	-6(1)	6(1)	-5(1)
O(1)	19(1)	18(1)	25(1)	-6(1)	8(1)	-7(1)
N(1)	32(1)	19(1)	35(1)	-7(1)	14(1)	-8(1)
C(1)	16(1)	22(1)	20(1)	-7(1)	6(1)	-6(1)
P(2)	22(1)	25(1)	26(1)	-9(1)	9(1)	-11(1)
N(2)	28(1)	37(1)	29(1)	-11(1)	10(1)	-18(1)
C(2)	20(1)	19(1)	22(1)	-6(1)	5(1)	-5(1)
C(3)	26(1)	23(1)	32(1)	-6(1)	12(1)	-9(1)
C(4)	24(1)	27(1)	40(1)	-10(1)	17(1)	-7(1)
C(5)	24(1)	22(1)	32(1)	-8(1)	8(1)	-3(1)
C(6)	22(1)	19(1)	21(1)	-6(1)	4(1)	-7(1)
C(7)	23(1)	22(1)	21(1)	-7(1)	4(1)	-8(1)
C(8)	28(1)	20(1)	32(1)	-7(1)	5(1)	-6(1)
C(9)	36(1)	19(1)	37(1)	-4(1)	6(1)	-10(1)
C(10)	31(1)	25(1)	29(1)	-6(1)	8(1)	-15(1)
C(11)	23(1)	24(1)	23(1)	-7(1)	5(1)	-10(1)
C(12)	23(1)	18(1)	21(1)	-4(1)	2(1)	-8(1)
C(13)	21(1)	24(1)	34(1)	-11(1)	2(1)	-4(1)
C(14)	36(1)	86(2)	55(1)	-43(1)	-8(1)	-5(1)
C(15)	33(1)	29(1)	26(1)	-11(1)	4(1)	-7(1)
C(16)	43(1)	52(1)	44(1)	-20(1)	-12(1)	-5(1)
C(17)	66(1)	24(1)	49(1)	-12(1)	28(1)	-16(1)
C(18)	36(1)	17(1)	36(1)	-7(1)	13(1)	-4(1)
C(19)	45(1)	28(1)	49(1)	-17(1)	8(1)	-11(1)
C(20)	64(1)	33(1)	31(1)	-10(1)	6(1)	-3(1)
C(21)	57(1)	24(1)	46(1)	-2(1)	24(1)	-9(1)
C(22)	36(1)	28(1)	59(1)	-10(1)	13(1)	-12(1)
C(23)	33(1)	26(1)	38(1)	-7(1)	2(1)	-3(1)
C(24)	28(1)	34(1)	29(1)	-7(1)	6(1)	-11(1)
C(25)	35(1)	39(1)	48(1)	-8(1)	1(1)	-4(1)
C(26)	32(1)	35(1)	38(1)	-19(1)	16(1)	-19(1)
C(27)	51(1)	66(1)	39(1)	-25(1)	11(1)	-38(1)

C(28)	32(1)	34(1)	35(1)	-16(1)	13(1)	-19(1)
C(29)	26(1)	26(1)	23(1)	-5(1)	3(1)	-12(1)
C(30)	34(1)	40(1)	31(1)	-14(1)	5(1)	-20(1)
C(31)	29(1)	56(1)	40(1)	-16(1)	5(1)	-24(1)
C(32)	25(1)	54(1)	41(1)	-16(1)	10(1)	-13(1)
C(33)	35(1)	42(1)	41(1)	-21(1)	11(1)	-13(1)
C(34)	28(1)	32(1)	35(1)	-13(1)	5(1)	-14(1)

Table A.131: Crystal data and structure refinement for **30**.

Empirical formula	$C_{70}H_{59}BF_{24}N_2O_4P_2Zn$	
Formula weight	1586.31	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.0190(19) Å	α= 104.9790(10)°.
	b = 15.4530(19) Å	β= 101.2910(10)°.
	c = 16.072(2) Å	γ = 95.3630(10)°.
Volume	3492.5(8) $Å^3$	
Z	2	
Density (calculated)	1.508 Mg/m^3	
Absorption coefficient	0.512 mm^{-1}	
F(000)	1612	
Crystal size	0.52 x 0.33 x 0.27 mm^3	
Theta range for data collection	2.66 to 26.37°.	
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=20	
Reflections collected	47147	
Independent reflections	14217 [R(int) = 0.0184]	
Completeness to theta = 26.37°	99.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8725 and 0.7757	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14217 / 231 / 1056	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0868	
R indices (all data)	R1 = 0.0398, wR2 = 0.0904	
Largest diff. peak and hole	0.660 and -0.427 $e.Å^{-3}$	

Table A.132: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **30**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
Zn(1)	4700(1)	2441(1)	2147(1)	27(1)	C(46)	9705(1)	3237(1)	4473(1)	34(1)
P(1)	6000(1)	1575(1)	3397(1)	26(1)	C(47)	9723(1)	1405(1)	6926(1)	25(1)
O(1)	4525(1)	737(1)	1817(1)	26(1)	C(48)	9153(1)	939(1)	6101(1)	26(1)
N(1)	5889(1)	2394(1)	2957(1)	28(1)	C(49)	9044(1)	1(1)	5767(1)	27(1)
C(1)	5262(1)	266(1)	1862(1)	24(1)	C(50)	9484(1)	-521(1)	6251(1)	28(1)
B(1)	9753(1)	2485(1)	7417(1)	26(1)	C(51)	10046(1)	-74(1)	7077(1)	27(1)
P(2)	2607(1)	1398(1)	1439(1)	30(1)	C(52)	10169(1)	863(1)	7397(1)	27(1)
N(2)	3387(1)	2115(1)	2192(1)	29(1)	C(53)	8403(1)	-450(1)	4887(1)	34(1)
C(2)	6007(1)	526(1)	2580(1)	26(1)	C(54)	10516(1)	-614(1)	7632(1)	37(1)

C(3)	6690(1)	-31(1)	2525(1)	31(1)
C(4)	6603(1)	-773(1)	1787(1)	34(1)
C(5)	5850(1)	-999(1)	1079(1)	30(1)
C(6)	5153(1)	-464(1)	1119(1)	25(1)
C(7)	4273(1)	-444(1)	555(1)	25(1)
C(8)	3754(1)	-965(1)	-271(1)	29(1)
C(9)	2917(1)	-718(1)	-581(1)	33(1)
C(10)	2585(1)	10(1)	-91(1)	32(1)
C(11)	3091(1)	551(1)	740(1)	27(1)
C(12)	3929(1)	291(1)	1020(1)	25(1)
C(13)	5028(1)	1415(1)	3861(1)	30(1)
C(14)	5013(2)	634(2)	4278(2)	48(1)
C(15)	7025(1)	1736(1)	4256(1)	38(1)
C(16)	7032(2)	2500(2)	5078(1)	49(1)
C(17)	6696(1)	2703(1)	2644(1)	31(1)
C(18)	7093(1)	3693(1)	3065(1)	29(1)
C(19)	7808(1)	4062(2)	2762(1)	42(1)
C(20)	8204(2)	4961(2)	3133(2)	52(1)
C(21)	7897(2)	5502(1)	3806(2)	50(1)
C(22)	7186(2)	5152(1)	4112(2)	45(1)
C(23)	6786(1)	4249(1)	3740(1)	36(1)
C(24)	1843(1)	754(1)	1884(2)	42(1)
C(25)	2329(2)	195(2)	2426(2)	47(1)
C(26)	1846(2)	1887(2)	728(2)	46(1)
C(27)	2346(2)	2426(2)	244(2)	66(1)
C(28)	3018(1)	2834(1)	2800(1)	37(1)
C(29)	3496(1)	2990(1)	3756(1)	36(1)
C(30)	4289(2)	3622(1)	4139(1)	40(1)
C(31)	4749(2)	3735(2)	5007(2)	47(1)
C(32)	4417(2)	3225(2)	5501(2)	52(1)
C(33)	3618(2)	2611(2)	5134(2)	51(1)
C(34)	3161(2)	2495(1)	4272(1)	42(1)
O(2)	4917(1)	2414(1)	1001(1)	37(1)
C(35)	4832(3)	3179(2)	730(2)	32(1)
C(36)	5714(3)	3524(2)	498(3)	51(1)
O(4)	4448(3)	4662(4)	1220(3)	45(1)
C(38)	4250(2)	5397(2)	1918(2)	60(1)
C(35B)	5292(9)	3384(7)	1019(8)	37(2)
C(36B)	5028(9)	3451(6)	96(6)	52(3)
O(4B)	4775(11)	4807(10)	1463(10)	48(3)
C(38B)	4250(2)	5397(2)	1918(2)	60(1)
O(3)	4611(1)	3852(1)	2215(1)	36(1)
C(37)	4667(2)	3945(1)	1494(2)	44(1)
C(55)	9032(1)	2445(1)	8058(1)	27(1)
C(56)	8083(1)	2333(1)	7726(1)	30(1)
C(57)	7455(1)	2225(1)	8239(1)	32(1)
C(58)	7754(1)	2221(1)	9111(1)	35(1)
C(59)	8690(1)	2327(1)	9453(1)	33(1)
C(60)	9313(1)	2427(1)	8933(1)	30(1)
C(61)	6452(1)	2081(2)	7833(2)	43(1)
C(62)	9066(2)	2323(2)	10387(1)	48(1)
C(63)	10783(1)	2999(1)	7971(1)	28(1)
C(64)	10904(1)	3768(1)	8691(1)	33(1)
C(65)	11765(2)	4273(1)	9114(1)	41(1)
C(66)	12536(2)	4040(1)	8824(2)	44(1)
C(67)	12437(1)	3290(1)	8103(1)	37(1)
C(68)	11577(1)	2776(1)	7689(1)	32(1)
C(69)	11840(2)	5069(2)	9907(2)	69(1)
C(70)	13272(2)	3070(2)	7764(2)	50(1)
F(1)	8386(7)	5792(5)	6335(7)	76(2)
F(2)	8347(8)	5464(7)	7536(4)	84(3)
F(3)	7340(4)	4847(6)	6385(6)	79(2)
F(1B)	8776(15)	5712(10)	7477(9)	135(6)
F(2B)	7482(11)	4909(8)	6820(17)	129(6)
F(3B)	8199(10)	5688(8)	6215(7)	80(3)
F(4)	10489(1)	2889(1)	4477(1)	47(1)
F(5)	9790(1)	3937(1)	4145(1)	58(1)
F(6)	9060(1)	2606(1)	3871(1)	62(1)
F(7)	8539(1)	-54(1)	4268(1)	56(1)
F(8)	7524(1)	-410(1)	4917(1)	58(1)
F(9)	8461(1)	-1320(1)	4579(1)	67(1)
F(10)	10069(1)	-1445(1)	7473(1)	40(1)
F(11)	10592(1)	-222(1)	8505(1)	62(1)
F(12)	11357(1)	-714(1)	7522(1)	76(1)
F(13)	6232(4)	2457(7)	7197(5)	82(2)
F(14)	5957(4)	2415(4)	8412(4)	65(1)
F(15)	6082(4)	1216(3)	7532(6)	76(2)
F(13B)	6246(9)	2653(8)	7369(10)	79(4)
F(14B)	5932(9)	2120(20)	8360(10)	129(6)
F(15B)	6229(11)	1335(14)	7156(19)	120(7)
F(16)	9824(1)	2923(1)	10779(1)	67(1)
F(17)	8462(1)	2496(1)	10897(1)	68(1)
F(18)	9301(1)	1521(1)	10433(1)	74(1)
F(19)	12574(3)	5655(3)	10120(4)	86(2)
F(20)	11146(4)	5505(4)	9858(5)	115(3)
F(21)	11869(5)	4791(2)	10661(2)	108(2)

C(39)	9445(1)	3082(1)	6734(1)	27(1)	F(19B)	12002(18)	5813(5)	9560(9)	156(7)
C(40)	8995(1)	3832(1)	6968(1)	30(1)	F(20B)	11142(9)	5222(13)	10152(12)	145(10)
C(41)	8784(1)	4379(1)	6414(1)	33(1)	F(21B)	12604(12)	5185(13)	10431(11)	186(10)
C(42)	9011(1)	4201(1)	5598(1)	33(1)	F(22)	13117(1)	2293(1)	7108(1)	76(1)
C(43)	9474(1)	3475(1)	5361(1)	29(1)	F(23)	13950(1)	2965(1)	8379(1)	68(1)
C(44)	9689(1)	2931(1)	5918(1)	28(1)	F(24)	13618(1)	3712(1)	7456(2)	94(1)
C(45)	8265(2)	5144(2)	6697(2)	48(1)					

Table A.133: Bond lengths [Å] for **30**.

Zn(1)-O(2)	1.9233(13)	C(22)-H(22)	0.9500	C(45)-F(1)	1.298(6)
Zn(1)-N(2)	2.0093(15)	C(23)-H(23)	0.9500	C(45)-F(1B)	1.363(9)
Zn(1)-N(1)	2.0126(15)	C(24)-C(25)	1.516(3)	C(45)-F(3)	1.372(6)
Zn(1)-O(3)	2.1729(13)	C(24)-H(24A)	0.9900	C(46)-F(5)	1.327(2)
P(1)-N(1)	1.6077(15)	C(24)-H(24B)	0.9900	C(46)-F(4)	1.338(2)
P(1)-C(13)	1.7887(18)	C(25)-H(25A)	0.9800	C(46)-F(6)	1.340(2)
P(1)-C(15)	1.8043(19)	C(25)-H(25B)	0.9800	C(47)-C(48)	1.398(2)
P(1)-C(2)	1.8061(18)	C(25)-H(25C)	0.9800	C(47)-C(52)	1.399(2)
O(1)-C(12)	1.3775(19)	C(26)-C(27)	1.519(4)	C(48)-C(49)	1.391(2)
O(1)-C(1)	1.3812(19)	C(26)-H(26A)	0.9900	C(48)-H(48)	0.9500
N(1)-C(17)	1.486(2)	C(26)-H(26B)	0.9900	C(49)-C(50)	1.383(2)
C(1)-C(6)	1.385(2)	C(27)-H(27A)	0.9800	C(49)-C(53)	1.498(2)
C(1)-C(2)	1.385(2)	C(27)-H(27B)	0.9800	C(50)-C(51)	1.390(2)
B(1)-C(39)	1.636(3)	C(27)-H(27C)	0.9800	C(50)-H(50)	0.9500
B(1)-C(63)	1.638(3)	C(28)-C(29)	1.509(3)	C(51)-C(52)	1.387(2)
B(1)-C(55)	1.641(3)	C(28)-H(28A)	0.9900	C(51)-C(54)	1.495(2)
B(1)-C(47)	1.644(2)	C(28)-H(28B)	0.9900	C(52)-H(52)	0.9500
P(2)-N(2)	1.6047(16)	C(29)-C(30)	1.392(3)	C(53)-F(9)	1.325(2)
P(2)-C(11)	1.8002(18)	C(29)-C(34)	1.395(3)	C(53)-F(7)	1.334(2)
P(2)-C(26)	1.811(2)	C(30)-C(31)	1.388(3)	C(53)-F(8)	1.338(2)
P(2)-C(24)	1.815(2)	C(30)-H(30)	0.9500	C(54)-F(12)	1.326(2)
N(2)-C(28)	1.503(2)	C(31)-C(32)	1.381(3)	C(54)-F(10)	1.329(2)
C(2)-C(3)	1.400(2)	C(31)-H(31)	0.9500	C(54)-F(11)	1.355(2)
C(3)-C(4)	1.395(3)	C(32)-C(33)	1.381(3)	C(55)-C(60)	1.395(2)
C(3)-H(3)	0.9500	C(32)-H(32)	0.9500	C(55)-C(56)	1.398(3)
C(4)-C(5)	1.383(3)	C(33)-C(34)	1.379(3)	C(56)-C(57)	1.393(3)
C(4)-H(4)	0.9500	C(33)-H(33)	0.9500	C(56)-H(56)	0.9500
C(5)-C(6)	1.394(2)	C(34)-H(34)	0.9500	C(57)-C(58)	1.388(3)
C(5)-H(5)	0.9500	O(2)-C(35)	1.371(3)	C(57)-C(61)	1.492(3)
C(6)-C(7)	1.457(2)	O(2)-C(35B)	1.543(10)	C(58)-C(59)	1.383(3)
C(7)-C(12)	1.391(2)	C(35)-C(36)	1.530(5)	C(58)-H(58)	0.9500
C(7)-C(8)	1.395(2)	C(35)-C(37)	1.546(4)	C(59)-C(60)	1.394(3)
C(8)-C(9)	1.383(3)	C(35)-H(35)	1.0000	C(59)-C(62)	1.499(3)
C(8)-H(8)	0.9500	C(36)-H(36A)	0.9800	C(60)-H(60)	0.9500

C(9)-C(10)	1.392(3)	C(36)-H(36B)	0.9800	C(61)-F(14B)	1.253(10)
C(9)-H(9)	0.9500	C(36)-H(36C)	0.9800	C(61)-F(13)	1.305(5)
C(10)-C(11)	1.402(2)	O(4)-C(37)	1.339(6)	C(61)-F(13B)	1.317(9)
C(10)-H(10)	0.9500	O(4)-C(38)	1.474(6)	C(61)-F(15)	1.324(5)
C(11)-C(12)	1.384(2)	C(38)-H(38A)	0.9800	C(61)-F(15B)	1.328(10)
C(13)-C(14)	1.525(3)	C(38)-H(38B)	0.9800	C(61)-F(14)	1.333(4)
C(13)-H(13A)	0.9900	C(38)-H(38C)	0.9800	C(62)-F(16)	1.331(3)
C(13)-H(13B)	0.9900	C(35B)-C(36B)	1.492(16)	C(62)-F(18)	1.336(3)
C(14)-H(14A)	0.9800	C(35B)-C(37)	1.518(10)	C(62)-F(17)	1.338(3)
C(14)-H(14B)	0.9800	C(35B)-H(35B)	1.0000	C(63)-C(64)	1.397(3)
C(14)-H(14C)	0.9800	C(36B)-H(36D)	0.9800	C(63)-C(68)	1.399(3)
C(15)-C(16)	1.524(3)	C(36B)-H(36E)	0.9800	C(64)-C(65)	1.392(3)
C(15)-H(15A)	0.9900	C(36B)-H(36F)	0.9800	C(64)-H(64)	0.9500
C(15)-H(15B)	0.9900	O(4B)-C(37)	1.340(16)	C(65)-C(66)	1.375(3)
C(16)-H(16A)	0.9800	O(3)-C(37)	1.222(2)	C(65)-C(69)	1.502(3)
C(16)-H(16B)	0.9800	C(39)-C(44)	1.398(2)	C(66)-C(67)	1.384(3)
C(16)-H(16C)	0.9800	C(39)-C(40)	1.401(2)	C(66)-H(66)	0.9500
C(17)-C(18)	1.513(2)	C(40)-C(41)	1.391(3)	C(67)-C(68)	1.393(3)
C(17)-H(17A)	0.9900	C(40)-H(40)	0.9500	C(67)-C(70)	1.495(3)
C(17)-H(17B)	0.9900	C(41)-C(42)	1.385(3)	C(68)-H(68)	0.9500
C(18)-C(23)	1.384(3)	C(41)-C(45)	1.498(3)	C(69)-F(20B)	1.214(9)
C(18)-C(19)	1.395(3)	C(42)-C(43)	1.385(3)	C(69)-F(21B)	1.249(9)
C(19)-C(20)	1.385(3)	C(42)-H(42)	0.9500	C(69)-F(19)	1.287(4)
C(19)-H(19)	0.9500	C(43)-C(44)	1.392(2)	C(69)-F(20)	1.294(6)
C(20)-C(21)	1.372(4)	C(43)-C(46)	1.495(3)	C(69)-F(21)	1.380(5)
C(20)-H(20)	0.9500	C(44)-H(44)	0.9500	C(69)-F(19B)	1.423(9)
C(21)-C(22)	1.382(3)	C(45)-F(2B)	1.265(9)	C(70)-F(24)	1.325(3)
C(21)-H(21)	0.9500	C(45)-F(3B)	1.281(7)	C(70)-F(23)	1.328(3)
C(22)-C(23)	1.392(3)	C(45)-F(2)	1.287(6)	C(70)-F(22)	1.344(3)

Table A.134: Bond angles [°] for **30**

O(2)-Zn(1)-N(2)	116.10(6)	C(24)-C(25)-H(25A)	109.5	C(48)-C(47)-C(52)	115.48(15)
O(2)-Zn(1)-N(1)	109.06(6)	C(24)-C(25)-H(25B)	109.5	C(48)-C(47)-B(1)	124.08(15)
N(2)-Zn(1)-N(1)	131.36(6)	H(25A)-C(25)-H(25B)	109.5	C(52)-C(47)-B(1)	119.60(15)
O(2)-Zn(1)-O(3)	82.01(5)	C(24)-C(25)-H(25C)	109.5	C(49)-C(48)-C(47)	122.28(16)
N(2)-Zn(1)-O(3)	95.47(6)	H(25A)-C(25)-H(25C)	109.5	C(49)-C(48)-H(48)	118.9
N(1)-Zn(1)-O(3)	108.05(6)	H(25B)-C(25)-H(25C)	109.5	C(47)-C(48)-H(48)	118.9
N(1)-P(1)-C(13)	108.12(8)	C(27)-C(26)-P(2)	113.29(16)	C(50)-C(49)-C(48)	121.12(16)
N(1)-P(1)-C(15)	115.40(9)	C(27)-C(26)-H(26A)	108.9	C(50)-C(49)-C(53)	119.79(16)
C(13)-P(1)-C(15)	108.03(9)	P(2)-C(26)-H(26A)	108.9	C(48)-C(49)-C(53)	119.03(16)
N(1)-P(1)-C(2)	111.43(8)	C(27)-C(26)-H(26B)	108.9	C(49)-C(50)-C(51)	117.67(16)
C(13)-P(1)-C(2)	107.35(8)	P(2)-C(26)-H(26B)	108.9	C(49)-C(50)-H(50)	121.2
C(15)-P(1)-C(2)	106.21(9)	H(26A)-C(26)-H(26B)	107.7	C(51)-C(50)-H(50)	121.2

C(12)-O(1)-C(1)	105.46(12)	C(26)-C(27)-H(27A)	109.5	C(52)-C(51)-C(50)	120.88(16)
C(17)-N(1)-P(1)	115.40(12)	C(26)-C(27)-H(27B)	109.5	C(52)-C(51)-C(54)	119.73(16)
C(17)-N(1)-Zn(1)	111.60(11)	H(27A)-C(27)-H(27B)	109.5	C(50)-C(51)-C(54)	119.39(16)
P(1)-N(1)-Zn(1)	121.11(8)	C(26)-C(27)-H(27C)	109.5	C(51)-C(52)-C(47)	122.53(16)
O(1)-C(1)-C(6)	112.09(14)	H(27A)-C(27)-H(27C)	109.5	C(51)-C(52)-H(52)	118.7
O(1)-C(1)-C(2)	121.81(15)	H(27B)-C(27)-H(27C)	109.5	C(47)-C(52)-H(52)	118.7
C(6)-C(1)-C(2)	126.11(16)	N(2)-C(28)-C(29)	111.65(15)	F(9)-C(53)-F(7)	107.16(17)
C(39)-B(1)-C(63)	103.63(13)	N(2)-C(28)-H(28A)	109.3	F(9)-C(53)-F(8)	106.13(16)
C(39)-B(1)-C(55)	111.83(14)	C(29)-C(28)-H(28A)	109.3	F(7)-C(53)-F(8)	104.83(16)
C(63)-B(1)-C(55)	112.73(14)	N(2)-C(28)-H(28B)	109.3	F(9)-C(53)-C(49)	113.41(16)
C(39)-B(1)-C(47)	113.84(14)	C(29)-C(28)-H(28B)	109.3	F(7)-C(53)-C(49)	112.60(15)
C(63)-B(1)-C(47)	113.21(14)	H(28A)-C(28)-H(28B)	108.0	F(8)-C(53)-C(49)	112.10(16)
C(55)-B(1)-C(47)	101.96(13)	C(30)-C(29)-C(34)	118.4(2)	F(12)-C(54)-F(10)	106.24(16)
N(2)-P(2)-C(11)	111.79(8)	C(30)-C(29)-C(28)	120.76(18)	F(12)-C(54)-F(11)	107.06(17)
N(2)-P(2)-C(26)	114.91(10)	C(34)-C(29)-C(28)	120.81(19)	F(10)-C(54)-F(11)	104.98(16)
C(11)-P(2)-C(26)	107.52(10)	C(31)-C(30)-C(29)	120.6(2)	F(12)-C(54)-C(51)	112.93(17)
N(2)-P(2)-C(24)	113.04(9)	C(31)-C(30)-H(30)	119.7	F(10)-C(54)-C(51)	113.57(15)
C(11)-P(2)-C(24)	104.41(9)	C(29)-C(30)-H(30)	119.7	F(11)-C(54)-C(51)	111.49(16)
C(26)-P(2)-C(24)	104.35(11)	C(32)-C(31)-C(30)	120.0(2)	C(60)-C(55)-C(56)	115.76(16)
C(28)-N(2)-P(2)	113.96(12)	C(32)-C(31)-H(31)	120.0	C(60)-C(55)-B(1)	122.66(16)
C(28)-N(2)-Zn(1)	114.91(12)	C(30)-C(31)-H(31)	120.0	C(56)-C(55)-B(1)	121.27(15)
P(2)-N(2)-Zn(1)	126.90(8)	C(33)-C(32)-C(31)	119.9(2)	C(57)-C(56)-C(55)	122.27(17)
C(1)-C(2)-C(3)	114.55(16)	C(33)-C(32)-H(32)	120.0	C(57)-C(56)-H(56)	118.9
C(1)-C(2)-P(1)	115.57(13)	C(31)-C(32)-H(32)	120.0	C(55)-C(56)-H(56)	118.9
C(3)-C(2)-P(1)	129.65(13)	C(34)-C(33)-C(32)	120.2(2)	C(58)-C(57)-C(56)	120.74(18)
C(4)-C(3)-C(2)	120.86(16)	C(34)-C(33)-H(33)	119.9	C(58)-C(57)-C(61)	119.86(17)
C(4)-C(3)-H(3)	119.6	C(32)-C(33)-H(33)	119.9	C(56)-C(57)-C(61)	119.37(18)
C(2)-C(3)-H(3)	119.6	C(33)-C(34)-C(29)	120.8(2)	C(59)-C(58)-C(57)	118.03(17)
C(5)-C(4)-C(3)	122.56(17)	C(33)-C(34)-H(34)	119.6	C(59)-C(58)-H(58)	121.0
C(5)-C(4)-H(4)	118.7	C(29)-C(34)-H(34)	119.6	C(57)-C(58)-H(58)	121.0
C(3)-C(4)-H(4)	118.7	C(35)-O(2)-C(35B)	28.8(4)	C(58)-C(59)-C(60)	120.83(17)
C(4)-C(5)-C(6)	117.94(16)	C(35)-O(2)-Zn(1)	117.45(14)	C(58)-C(59)-C(62)	121.19(18)
C(4)-C(5)-H(5)	121.0	C(35B)-O(2)-Zn(1)	108.4(4)	C(60)-C(59)-C(62)	117.97(18)
C(6)-C(5)-H(5)	121.0	O(2)-C(35)-C(36)	111.3(3)	C(59)-C(60)-C(55)	122.34(17)
C(1)-C(6)-C(5)	117.98(16)	O(2)-C(35)-C(37)	109.4(2)	C(59)-C(60)-H(60)	118.8
C(1)-C(6)-C(7)	105.21(14)	C(36)-C(35)-C(37)	106.7(3)	C(55)-C(60)-H(60)	118.8
C(5)-C(6)-C(7)	136.80(16)	O(2)-C(35)-H(35)	109.8	F(14B)-C(61)-F(13)	116.8(9)
C(12)-C(7)-C(8)	118.74(16)	C(36)-C(35)-H(35)	109.8	F(14B)-C(61)-F(13B)	108.0(12)
C(12)-C(7)-C(6)	105.64(14)	C(37)-C(35)-H(35)	109.8	F(13)-C(61)-F(13B)	15.3(8)
C(8)-C(7)-C(6)	135.62(16)	C(37)-O(4)-C(38)	113.3(4)	F(14B)-C(61)-F(15)	84.4(12)
C(9)-C(8)-C(7)	117.58(16)	C(36B)-C(35B)-C(37)	103.5(9)	F(13)-C(61)-F(15)	107.9(5)
C(9)-C(8)-H(8)	121.2	C(36B)-C(35B)-O(2)	107.2(9)	F(13B)-C(61)-F(15)	121.0(7)
C(7)-C(8)-H(8)	121.2	C(37)-C(35B)-O(2)	102.3(6)	F(14B)-C(61)-F(15B)	113.3(10)

C(8)-C(9)-C(10)	122.20(16)	C(36B)-C(35B)-H(35B)	114.2	F(13)-C(61)-F(15B)	81.4(13)
C(8)-C(9)-H(9)	118.9	C(37)-C(35B)-H(35B)	114.2	F(13B)-C(61)-F(15B)	96.5(13)
C(10)-C(9)-H(9)	118.9	O(2)-C(35B)-H(35B)	114.2	F(15)-C(61)-F(15B)	32.5(14)
C(9)-C(10)-C(11)	121.72(17)	C(35B)-C(36B)-H(36D)	109.5	F(14B)-C(61)-F(14)	18.9(15)
C(9)-C(10)-H(10)	119.1	C(35B)-C(36B)-H(36E)	109.5	F(13)-C(61)-F(14)	104.8(5)
C(11)-C(10)-H(10)	119.1	H(36D)-C(36B)-H(36E)	109.5	F(13B)-C(61)-F(14)	93.2(7)
C(12)-C(11)-C(10)	114.26(16)	C(35B)-C(36B)-H(36F)	109.5	F(15)-C(61)-F(14)	102.3(4)
C(12)-C(11)-P(2)	123.25(13)	H(36D)-C(36B)-H(36F)	109.5	F(15B)-C(61)-F(14)	128.3(12)
C(10)-C(11)-P(2)	121.87(13)	H(36E)-C(36B)-H(36F)	109.5	F(14B)-C(61)-C(57)	115.8(7)
O(1)-C(12)-C(11)	122.92(15)	C(37)-O(3)-Zn(1)	107.03(12)	F(13)-C(61)-C(57)	114.5(3)
O(1)-C(12)-C(7)	111.60(14)	O(3)-C(37)-O(4)	124.1(3)	F(13B)-C(61)-C(57)	111.5(6)
C(11)-C(12)-C(7)	125.48(15)	O(3)-C(37)-O(4B)	114.8(7)	F(15)-C(61)-C(57)	113.4(3)
C(14)-C(13)-P(1)	114.66(14)	O(4)-C(37)-O(4B)	23.7(5)	F(15B)-C(61)-C(57)	110.0(6)
C(14)-C(13)-H(13A)	108.6	O(3)-C(37)-C(35B)	116.4(4)	F(14)-C(61)-C(57)	113.0(3)
P(1)-C(13)-H(13A)	108.6	O(4)-C(37)-C(35B)	116.5(4)	F(16)-C(62)-F(18)	105.6(2)
C(14)-C(13)-H(13B)	108.6	O(4B)-C(37)-C(35B)	112.7(9)	F(16)-C(62)-F(17)	107.31(19)
P(1)-C(13)-H(13B)	108.6	O(3)-C(37)-C(35)	123.66(19)	F(18)-C(62)-F(17)	106.04(18)
H(13A)-C(13)-H(13B)	107.6	O(4)-C(37)-C(35)	111.4(3)	F(16)-C(62)-C(59)	112.69(17)
C(13)-C(14)-H(14A)	109.5	O(4B)-C(37)-C(35)	120.1(7)	F(18)-C(62)-C(59)	112.03(19)
C(13)-C(14)-H(14B)	109.5	C(35B)-C(37)-C(35)	28.0(4)	F(17)-C(62)-C(59)	112.70(19)
H(14A)-C(14)-H(14B)	109.5	C(44)-C(39)-C(40)	115.77(16)	C(64)-C(63)-C(68)	116.01(16)
C(13)-C(14)-H(14C)	109.5	C(44)-C(39)-B(1)	122.26(15)	C(64)-C(63)-B(1)	120.95(16)
H(14A)-C(14)-H(14C)	109.5	C(40)-C(39)-B(1)	121.70(15)	C(68)-C(63)-B(1)	122.52(16)
H(14B)-C(14)-H(14C)	109.5	C(41)-C(40)-C(39)	122.09(17)	C(65)-C(64)-C(63)	122.05(19)
C(16)-C(15)-P(1)	112.59(15)	C(41)-C(40)-H(40)	119.0	C(65)-C(64)-H(64)	119.0
C(16)-C(15)-H(15A)	109.1	C(39)-C(40)-H(40)	119.0	C(63)-C(64)-H(64)	119.0
P(1)-C(15)-H(15A)	109.1	C(42)-C(41)-C(40)	121.05(17)	C(66)-C(65)-C(64)	120.85(19)
C(16)-C(15)-H(15B)	109.1	C(42)-C(41)-C(45)	120.14(17)	C(66)-C(65)-C(69)	120.5(2)
P(1)-C(15)-H(15B)	109.1	C(40)-C(41)-C(45)	118.75(17)	C(64)-C(65)-C(69)	118.7(2)
H(15A)-C(15)-H(15B)	107.8	C(43)-C(42)-C(41)	117.88(17)	C(65)-C(66)-C(67)	118.47(18)
C(15)-C(16)-H(16A)	109.5	C(43)-C(42)-H(42)	121.1	C(65)-C(66)-H(66)	120.8
C(15)-C(16)-H(16B)	109.5	C(41)-C(42)-H(42)	121.1	C(67)-C(66)-H(66)	120.8
H(16A)-C(16)-H(16B)	109.5	C(42)-C(43)-C(44)	120.95(17)	C(66)-C(67)-C(68)	120.68(19)
C(15)-C(16)-H(16C)	109.5	C(42)-C(43)-C(46)	119.76(16)	C(66)-C(67)-C(70)	118.02(19)
H(16A)-C(16)-H(16C)	109.5	C(44)-C(43)-C(46)	119.20(16)	C(68)-C(67)-C(70)	121.3(2)
H(16B)-C(16)-H(16C)	109.5	C(43)-C(44)-C(39)	122.22(16)	C(67)-C(68)-C(63)	121.92(18)
N(1)-C(17)-C(18)	114.31(15)	C(43)-C(44)-H(44)	118.9	C(67)-C(68)-H(68)	119.0
N(1)-C(17)-H(17A)	108.7	C(39)-C(44)-H(44)	118.9	C(63)-C(68)-H(68)	119.0
C(18)-C(17)-H(17A)	108.7	F(2B)-C(45)-F(3B)	109.5(9)	F(20B)-C(69)-F(21B)	122.8(12)
N(1)-C(17)-H(17B)	108.7	F(2B)-C(45)-F(2)	75.5(9)	F(20B)-C(69)-F(19)	123.9(8)
C(18)-C(17)-H(17B)	108.7	F(3B)-C(45)-F(2)	118.8(6)	F(21B)-C(69)-F(19)	45.5(11)
H(17A)-C(17)-H(17B)	107.6	F(2B)-C(45)-F(1)	120.0(8)	F(20B)-C(69)-F(20)	33.4(12)
C(23)-C(18)-C(19)	118.33(18)	F(3B)-C(45)-F(1)	13.8(9)	F(21B)-C(69)-F(20)	135.2(6)

C(23)-C(18)-C(17)	123.21(16)	F(2)-C(45)-F(1)	110.8(6)	F(19)-C(69)-F(20)	107.5(4)
C(19)-C(18)-C(17)	118.46(17)	F(2B)-C(45)-F(1B)	107.5(7)	F(20B)-C(69)-F(21)	72.5(11)
C(20)-C(19)-C(18)	120.8(2)	F(3B)-C(45)-F(1B)	100.5(8)	F(21B)-C(69)-F(21)	62.5(12)
C(20)-C(19)-H(19)	119.6	F(2)-C(45)-F(1B)	32.9(9)	F(19)-C(69)-F(21)	102.8(3)
C(18)-C(19)-H(19)	119.6	F(1)-C(45)-F(1B)	88.3(9)	F(20)-C(69)-F(21)	104.5(5)
C(21)-C(20)-C(19)	120.2(2)	F(2B)-C(45)-F(3)	29.0(10)	F(20B)-C(69)-F(19B)	100.4(11)
C(21)-C(20)-H(20)	119.9	F(3B)-C(45)-F(3)	88.6(7)	F(21B)-C(69)-F(19B)	98.1(11)
C(19)-C(20)-H(20)	119.9	F(2)-C(45)-F(3)	103.2(5)	F(19)-C(69)-F(19B)	52.6(9)
C(20)-C(21)-C(22)	119.9(2)	F(1)-C(45)-F(3)	101.7(6)	F(20)-C(69)-F(19B)	68.5(9)
C(20)-C(21)-H(21)	120.0	F(1B)-C(45)-F(3)	132.9(9)	F(21)-C(69)-F(19B)	146.0(5)
C(22)-C(21)-H(21)	120.0	F(2B)-C(45)-C(41)	114.9(5)	F(20B)-C(69)-C(65)	117.6(7)
C(21)-C(22)-C(23)	119.9(2)	F(3B)-C(45)-C(41)	115.3(6)	F(21B)-C(69)-C(65)	110.6(6)
C(21)-C(22)-H(22)	120.0	F(2)-C(45)-C(41)	116.2(3)	F(19)-C(69)-C(65)	116.0(3)
C(23)-C(22)-H(22)	120.0	F(1)-C(45)-C(41)	113.9(4)	F(20)-C(69)-C(65)	113.9(4)
C(18)-C(23)-C(22)	120.77(19)	F(1B)-C(45)-C(41)	107.8(6)	F(21)-C(69)-C(65)	110.9(2)
C(18)-C(23)-H(23)	119.6	F(3)-C(45)-C(41)	109.5(4)	F(19B)-C(69)-C(65)	101.9(4)
C(22)-C(23)-H(23)	119.6	F(5)-C(46)-F(4)	106.36(16)	F(24)-C(70)-F(23)	106.02(19)
C(25)-C(24)-P(2)	113.51(14)	F(5)-C(46)-F(6)	106.26(17)	F(24)-C(70)-F(22)	106.7(2)
C(25)-C(24)-H(24A)	108.9	F(4)-C(46)-F(6)	105.25(16)	F(23)-C(70)-F(22)	104.7(2)
P(2)-C(24)-H(24A)	108.9	F(5)-C(46)-C(43)	113.49(16)	F(24)-C(70)-C(67)	112.5(2)
C(25)-C(24)-H(24B)	108.9	F(4)-C(46)-C(43)	113.05(16)	F(23)-C(70)-C(67)	113.0(2)
P(2)-C(24)-H(24B)	108.9	F(6)-C(46)-C(43)	111.81(16)	F(22)-C(70)-C(67)	113.28(18)
H(24A)-C(24)-H(24B)	107.7				

Table A.135: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **30**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zn(1)	28(1)	25(1)	28(1)	8(1)	9(1)	5(1)
P(1)	24(1)	27(1)	24(1)	6(1)	1(1)	0(1)
O(1)	21(1)	27(1)	25(1)	2(1)	0(1)	7(1)
N(1)	27(1)	26(1)	29(1)	7(1)	6(1)	0(1)
C(1)	21(1)	24(1)	28(1)	8(1)	5(1)	7(1)
B(1)	27(1)	24(1)	25(1)	6(1)	5(1)	3(1)
P(2)	23(1)	32(1)	36(1)	10(1)	7(1)	10(1)
N(2)	28(1)	28(1)	32(1)	7(1)	11(1)	9(1)
C(2)	24(1)	27(1)	26(1)	8(1)	3(1)	3(1)
C(3)	22(1)	35(1)	35(1)	14(1)	2(1)	6(1)
C(4)	28(1)	34(1)	43(1)	14(1)	9(1)	13(1)
C(5)	30(1)	26(1)	36(1)	7(1)	12(1)	8(1)
C(6)	23(1)	25(1)	27(1)	8(1)	6(1)	3(1)
C(7)	23(1)	25(1)	26(1)	7(1)	6(1)	3(1)
C(8)	32(1)	27(1)	25(1)	4(1)	7(1)	1(1)
C(9)	32(1)	35(1)	25(1)	6(1)	-1(1)	-2(1)

C(10)	24(1)	39(1)	31(1)	11(1)	-1(1)	3(1)
C(11)	21(1)	29(1)	29(1)	8(1)	4(1)	4(1)
C(12)	22(1)	27(1)	22(1)	6(1)	2(1)	2(1)
C(13)	32(1)	31(1)	27(1)	9(1)	6(1)	2(1)
C(14)	53(1)	46(1)	52(1)	26(1)	15(1)	2(1)
C(15)	31(1)	44(1)	32(1)	9(1)	-5(1)	0(1)
C(16)	49(1)	50(1)	32(1)	3(1)	-9(1)	-5(1)
C(17)	30(1)	30(1)	32(1)	6(1)	9(1)	0(1)
C(18)	28(1)	29(1)	29(1)	11(1)	2(1)	2(1)
C(19)	39(1)	43(1)	44(1)	14(1)	12(1)	-1(1)
C(20)	45(1)	44(1)	69(2)	25(1)	9(1)	-9(1)
C(21)	50(1)	29(1)	63(1)	14(1)	-4(1)	-7(1)
C(22)	52(1)	29(1)	48(1)	4(1)	2(1)	5(1)
C(23)	36(1)	32(1)	40(1)	10(1)	7(1)	2(1)
C(24)	28(1)	42(1)	56(1)	10(1)	18(1)	4(1)
C(25)	52(1)	39(1)	60(1)	18(1)	29(1)	8(1)
C(26)	35(1)	52(1)	53(1)	17(1)	2(1)	21(1)
C(27)	68(2)	75(2)	71(2)	46(2)	9(1)	27(1)
C(28)	37(1)	32(1)	44(1)	8(1)	19(1)	13(1)
C(29)	43(1)	28(1)	39(1)	5(1)	21(1)	11(1)
C(30)	51(1)	29(1)	42(1)	6(1)	23(1)	7(1)
C(31)	54(1)	36(1)	42(1)	-2(1)	16(1)	1(1)
C(32)	71(2)	47(1)	33(1)	2(1)	17(1)	10(1)
C(33)	74(2)	42(1)	41(1)	9(1)	30(1)	6(1)
C(34)	51(1)	32(1)	45(1)	4(1)	24(1)	4(1)
O(2)	50(1)	36(1)	31(1)	12(1)	17(1)	15(1)
C(35)	39(2)	31(2)	27(2)	9(1)	9(1)	3(1)
C(36)	58(3)	51(2)	56(2)	23(2)	31(2)	8(2)
O(4)	63(3)	31(2)	44(2)	15(2)	13(2)	11(2)
C(38)	78(2)	32(1)	76(2)	15(1)	29(1)	17(1)
C(35B)	40(6)	32(5)	39(5)	13(4)	5(5)	-1(4)
C(36B)	77(9)	39(5)	39(5)	10(4)	15(5)	9(5)
O(4B)	73(9)	32(5)	45(7)	20(5)	17(5)	11(6)
C(38B)	78(2)	32(1)	76(2)	15(1)	29(1)	17(1)
O(3)	43(1)	29(1)	36(1)	9(1)	14(1)	5(1)
C(37)	57(1)	33(1)	52(1)	20(1)	26(1)	12(1)
C(39)	25(1)	24(1)	29(1)	6(1)	4(1)	1(1)
C(40)	34(1)	26(1)	30(1)	5(1)	9(1)	4(1)
C(41)	36(1)	25(1)	38(1)	8(1)	10(1)	8(1)
C(42)	37(1)	27(1)	38(1)	14(1)	9(1)	6(1)
C(43)	30(1)	25(1)	32(1)	9(1)	9(1)	2(1)
C(44)	28(1)	23(1)	32(1)	8(1)	8(1)	4(1)
C(45)	67(2)	38(1)	50(1)	17(1)	25(1)	24(1)

C(46)	38(1)	32(1)	35(1)	12(1)	11(1)	5(1)
C(47)	24(1)	26(1)	26(1)	7(1)	6(1)	2(1)
C(48)	25(1)	27(1)	26(1)	11(1)	4(1)	5(1)
C(49)	25(1)	28(1)	25(1)	6(1)	4(1)	2(1)
C(50)	25(1)	24(1)	32(1)	6(1)	4(1)	4(1)
C(51)	22(1)	28(1)	32(1)	11(1)	4(1)	5(1)
C(52)	24(1)	29(1)	25(1)	6(1)	1(1)	1(1)
C(53)	33(1)	32(1)	32(1)	6(1)	0(1)	2(1)
C(54)	29(1)	36(1)	44(1)	15(1)	-2(1)	5(1)
C(55)	31(1)	20(1)	29(1)	5(1)	7(1)	2(1)
C(56)	33(1)	26(1)	29(1)	8(1)	7(1)	4(1)
C(57)	31(1)	26(1)	40(1)	9(1)	10(1)	4(1)
C(58)	39(1)	31(1)	37(1)	10(1)	17(1)	3(1)
C(59)	41(1)	29(1)	30(1)	9(1)	9(1)	1(1)
C(60)	31(1)	27(1)	31(1)	8(1)	6(1)	2(1)
C(61)	35(1)	44(1)	52(1)	16(1)	12(1)	6(1)
C(62)	49(1)	59(1)	36(1)	18(1)	11(1)	-3(1)
C(63)	30(1)	26(1)	28(1)	10(1)	4(1)	1(1)
C(64)	35(1)	26(1)	35(1)	7(1)	4(1)	1(1)
C(65)	44(1)	29(1)	41(1)	6(1)	-1(1)	-3(1)
C(66)	35(1)	39(1)	49(1)	13(1)	-4(1)	-10(1)
C(67)	31(1)	42(1)	42(1)	21(1)	5(1)	-1(1)
C(68)	32(1)	33(1)	30(1)	11(1)	5(1)	2(1)
C(69)	64(2)	40(1)	72(2)	-12(1)	-7(2)	-7(1)
C(70)	33(1)	63(2)	59(1)	29(1)	10(1)	2(1)
F(1)	96(4)	33(2)	137(7)	46(3)	79(4)	34(2)
F(2)	145(6)	83(4)	40(2)	16(2)	32(3)	85(4)
F(3)	43(3)	69(3)	122(5)	11(3)	27(3)	26(2)
F(1B)	180(11)	82(6)	90(6)	-43(4)	-31(5)	87(7)
F(2B)	147(9)	73(6)	248(15)	77(9)	163(10)	69(6)
F(3B)	126(7)	86(6)	57(3)	41(3)	33(4)	81(5)
F(4)	51(1)	56(1)	44(1)	16(1)	23(1)	22(1)
F(5)	89(1)	51(1)	57(1)	34(1)	39(1)	24(1)
F(6)	57(1)	76(1)	36(1)	-5(1)	13(1)	-15(1)
F(7)	59(1)	71(1)	30(1)	18(1)	-5(1)	-8(1)
F(8)	29(1)	78(1)	51(1)	3(1)	-4(1)	-5(1)
F(9)	87(1)	37(1)	49(1)	-10(1)	-24(1)	14(1)
F(10)	42(1)	33(1)	50(1)	20(1)	7(1)	9(1)
F(11)	89(1)	46(1)	39(1)	16(1)	-18(1)	11(1)
F(12)	27(1)	96(1)	134(2)	80(1)	18(1)	23(1)
F(13)	33(2)	166(6)	73(3)	79(3)	12(2)	13(3)
F(14)	41(2)	86(3)	70(2)	13(2)	25(2)	29(2)
F(15)	32(2)	43(2)	132(4)	4(2)	-2(2)	-2(1)

F(13B)	51(5)	52(5)	135(10)	41(4)	-5(5)	24(3)
F(14B)	33(4)	277(17)	121(10)	134(12)	26(5)	1(8)
F(15B)	38(5)	91(8)	157(13)	-57(8)	-28(6)	8(5)
F(16)	60(1)	94(1)	36(1)	20(1)	-3(1)	-21(1)
F(17)	69(1)	99(1)	35(1)	16(1)	21(1)	-3(1)
F(18)	94(1)	79(1)	60(1)	45(1)	8(1)	16(1)
F(19)	70(2)	52(2)	97(3)	-25(2)	6(2)	-27(2)
F(20)	87(4)	67(3)	134(6)	-49(3)	-11(3)	27(3)
F(21)	167(5)	83(2)	50(2)	-16(1)	28(2)	-12(3)
F(19B)	310(20)	39(4)	120(9)	-8(4)	90(11)	5(7)
F(20B)	82(10)	155(15)	120(12)	-104(10)	70(10)	-62(9)
F(21B)	181(14)	154(13)	109(10)	-74(9)	-101(10)	65(11)
F(22)	47(1)	110(1)	65(1)	7(1)	25(1)	12(1)
F(23)	43(1)	88(1)	79(1)	32(1)	5(1)	22(1)
F(24)	54(1)	120(2)	161(2)	102(2)	56(1)	26(1)

checkCIF/PLATON (standard)

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: L1Dipp

```
Bond precision:        C-C = 0.0035 A                  Wavelength=0.71073
Cell:        a=11.1269(7)      b=17.6285(11)     c=29.3704(18)
             alpha=90          beta=90           gamma=90
Temperature: 173 K
                     Calculated                        Reported
Volume               5761.0(6)                         5761.0(6)
Space group          P b c a                           Pbca
Hall group           -P 2ac 2ab                        ?
Moiety formula       C36 H34 N O P                     ?
Sum formula          C36 H34 N O P                     C36 H34 N O P
Mr                   527.61                            527.61
Dx,g cm-3            1.217                             1.217
Z                    8                                 8
Mu (mm-1)            0.125                             0.125
F000                 2240.0                            2240.0
F000'                2241.61
h,k,lmax             13,20,34                          13,20,34
Nref                 5083                              5077
Tmin,Tmax            0.969,0.979                       0.969,0.979
Tmin'                0.969
Correction method= MULTI-SCAN
Data completeness= 0.999           Theta(max)= 25.030
R(reflections)= 0.0486( 4019)         wR2(reflections)= 0.1202( 5077)
S = 1.101               Npar= 356
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 5.11
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 1

```
Bond precision:        C-C = 0.0021 A                  Wavelength=0.71073
Cell:        a=9.3247(4)       b=10.7683(4)      c=16.9837(7)
             alpha=78.3200     beta=83.5800      gamma=75.8900
```

Temperature: 173 K

	Calculated	Reported
Volume	1616.15(11)	1616.14(11)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C36 H34 Cl2 N O P Zn	?
Sum formula	C36 H34 Cl2 N O P Zn	C36 H34 Cl2 N O P Zn
Mr	663.90	663.88
Dx,g cm-3	1.364	1.364
Z	2	2
Mu (mm-1)	1.004	1.004
F000	688.0	688.0
F000'	689.55	
h,k,lmax	11,13,21	11,13,21
Nref	6624	6576
Tmin,Tmax	0.687,0.778	0.697,0.790
Tmin'	0.669	

Correction method= MULTI-SCAN

Data completeness= 0.993 Theta(max)= 26.370

R(reflections)= 0.0223(6212) wR2(reflections)= 0.0620(6576)

S = 1.068 Npar= 383

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT144_ALERT_4_C su on alpha Small or Missing ..... 0.0000 Deg.
PLAT145_ALERT_4_C su on beta Small or Missing ..... 0.0000 Deg.
PLAT146_ALERT_4_C su on gamma Small or Missing ..... 0.0000 Deg.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 56 A**3

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 2

Bond precision: C-C = 0.0042 A Wavelength=0.71073

Cell: a=9.5777(5) b=13.5073(7) c=14.8891(12)
alpha=114.568(1) beta=92.957(1) gamma=108.823(1)

Temperature: 173 K

	Calculated	Reported
Volume	1619.06(18)	1619.06(18)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C66 H56 Cl4 N2 O2 P2 Zn2, C7 H8	?
Sum formula	C73 H64 Cl4 N2 O2 P2 Zn2	C36.50 H32 Cl2 N O P Zn
Mr	1335.78	667.87
Dx,g cm-3	1.370	1.370
Z	1	2
Mu (mm-1)	1.003	1.003
F000	690.0	690.0
F000'	691.55	
h,k,lmax	11,16,18	11,16,18

Nref	6617	6586
Tmin,Tmax	0.815,0.887	0.798,0.892
Tmin'	0.786	

Correction method= MULTI-SCAN

Data completeness= 0.995 Theta(max)= 26.370

R(reflections)= 0.0377(5389) wR2(reflections)= 0.1051(6586)

S = 1.034 Npar= 407

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT094_ALERT_2_B Ratio of Maximum / Minimum Residual Density 4.26
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor 5.4

Alert level C

PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.1 Ratio

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Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C1S
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2
C7 H8
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 99

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2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 3

Bond precision: C-C = 0.0047 A Wavelength=0.71073

Cell: a=12.3644(7) b=13.2795(7) c=17.704(1)
alpha=70.327(1) beta=70.849(1) gamma=71.903(1)

Temperature: 173 K

	Calculated	Reported
Volume	2519.4(2)	2519.4(2)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C48 H34 F10 N O P Zn, C7 H8	?
Sum formula	C55 H42 F10 N O P Zn	C55 H42 F10 N O P Zn
Mr	1019.26	1019.24
Dx,g cm-3	1.344	1.344
Z	2	2
Mu (mm-1)	0.595	0.595
F000	1044.0	1044.0
F000'	1045.37	
h,k,lmax	14,15,21	14,15,21
Nref	8904	8863
Tmin,Tmax	0.837,0.867	0.844,0.870
Tmin'	0.837	

Correction method= MULTI-SCAN

Data completeness= 0.995 Theta(max)= 25.030

R(reflections)= 0.0353(7588) wR2(reflections)= 0.0979(8863)

S = 1.046 Npar= 627

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 232 A**3

Alert level C

PLAT231_ALERT_4_C Hirshfeld Test (Solvent) C5S -- C6S .. 7.7 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C1S -- C6S .. 0.17 Ang.
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C3S
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C4S
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C1S
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C2S
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C6S
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.2
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C37 -C42 1.37 Ang.

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 3
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 99

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8 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 4

Bond precision: C-C = 0.0046 A Wavelength=0.71073
Cell: a=15.2741(13) b=14.1963(12) c=21.3107(19)
alpha=90 beta=98.317(1) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	4572.3(7)	4572.3(7)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C45 H28 F10 N O P Zn, C5 H12	?
Sum formula	C50 H40 F10 N O P Zn	C50 H40 F10 N O P Zn
Mr	957.19	957.17
Dx,g cm-3	1.390	1.390
Z	4	4
Mu (mm-1)	0.651	0.651
F000	1960.0	1960.0
F000'	1962.69	
h,k,lmax	18,16,25	18,16,25
Nref	8088	8076
Tmin,Tmax	0.823,0.889	0.829,0.894
Tmin'	0.823	

Correction method= MULTI-SCAN
Data completeness= 0.999 Theta(max)= 25.030
R(reflections)= 0.0365(6473) wR2(reflections)= 0.0972(8076)
S = 1.025 Npar= 582

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.2 Ratio

Alert level C

PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.5 Ratio
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C2S
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C3S
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C34 -C39 1.37 Ang.
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C40 -C45 1.37 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C2S - C3S ... 1.39 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C4S - C5S ... 1.40 Ang.

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c P21/n
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 12

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 5b

```
Bond precision:        C-C = 0.0031 A                  Wavelength=0.71073
Cell:        a=9.2135(5)       b=10.9472(6)      c=18.2092(10)
             alpha=77.056(1)   beta=88.658(1)    gamma=87.161(1)
Temperature: 173 K
                    Calculated                          Reported
Volume              1787.61(17)                         1787.61(17)
Space group         P -1                                P-1
Hall group          -P 1                                ?
Moiety formula      C36 H35 N O P, 0.5(C6 H6), C F3 O3 S ?
Sum formula         C40 H38 F3 N O4 P S                 C40 H38 F3 N O4 P S
Mr                  716.75                              716.74
Dx,g cm-3           1.332                               1.332
Z                   2                                   2
Mu (mm-1)           0.194                               0.194
F000                750.0                               750.0
F000'               750.83
h,k,lmax            10,13,21                            10,13,21
Nref                6308                                6284
Tmin,Tmax           0.913,0.945                         0.910,0.946
Tmin'               0.908
Correction method= MULTI-SCAN
Data completeness= 0.996          Theta(max)= 25.030
R(reflections)= 0.0422( 5673)         wR2(reflections)= 0.1166( 6284)
S = 1.023               Npar= 472
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT231_ALERT_4_C Hirshfeld Test (Solvent) S1 -- C37 .. 6.1 su
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of S1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C37

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 21 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact C3 .. O2B .. 2.76 Ang.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 6

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4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 6b

```
Bond precision:        C-C = 0.0035 A                Wavelength=0.71073
Cell:          a=9.6030(9)       b=12.3790(12)     c=16.7009(16)
               alpha=75.159(1)   beta=83.315(1)    gamma=74.035(1)
Temperature: 173 K
                      Calculated                          Reported
Volume                1842.8(3)                           1842.8(3)
Space group           P -1                                P-1
Hall group            -P 1                                ?
Moiety formula        C39 H39 F3 N O4 P S Zn              ?
Sum formula           C39 H39 F3 N O4 P S Zn              C39 H39 F3 N O4 P S Zn
Mr                    771.14                              771.11
Dx,g cm-3             1.390                               1.390
Z                     2                                   2
Mu (mm-1)             0.823                               0.823
F000                  800.0                               800.0
F000'                 801.37
h,k,lmax              11,14,19                            11,14,19
Nref                  6503                                6479
Tmin,Tmax             0.854,0.913                         0.778,0.918
Tmin'                 0.768
Correction method= MULTI-SCAN
Data completeness= 0.996          Theta(max)= 25.030
R(reflections)= 0.0360( 4859)         wR2(reflections)= 0.0891( 6479)
S = 1.015               Npar= 591
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 2
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.4 Ratio

Alert level C

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for S
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C39

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 66
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?

PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 32 Perc.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 1
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 20
C2B -P -C2 1.555 1.555 1.555 7.30 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 34
ZN -N -ZNB 1.555 1.555 1.555 9.80 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 67
ZNB -O4 -ZN 1.555 1.555 1.555 9.50 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 1200

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: 7

```
Bond precision:        C-C = 0.0054 A                  Wavelength=0.71073
Cell:        a=12.7291(15)     b=13.8611(16)     c=14.2257(17)
             alpha=86.308(1)   beta=89.135(1)    gamma=84.456(1)
Temperature: 173 K
                    Calculated                        Reported
Volume              2493.0(5)                         2492.9(5)
Space group         P -1                              P-1
Hall group          -P 1                              ?
Moiety formula      C78 H74 F12 N2 O16 P2 S4 Zn3      ?
Sum formula         C78 H74 F12 N2 O16 P2 S4 Zn3      C39 H37 F6 N O8 P S2 Zn1.50
Mr                  1909.78                           954.84
Dx,g cm-3           1.272                             1.272
Z                   1                                 2
Mu (mm-1)           0.908                             0.908
F000                976.0                             976.0
F000'               978.07
h,k,lmax            15,16,16                          15,16,16
Nref                8812                              8770
Tmin,Tmax           0.776,0.889                       0.787,0.888
Tmin'               0.776
Correction method= MULTI-SCAN
Data completeness= 0.995          Theta(max)= 25.030
R(reflections)= 0.0408( 6013)         wR2(reflections)= 0.1102( 8770)
S = 1.023               Npar= 534
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure !

Alert level C

PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.5 Ratio
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C23
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for S1
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C39

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 32
O3 -ZN1 -O3 -S2 17.00 0.00 2.766 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 43
O4 -ZN1 -O4 -S1 15.00 0.00 2.766 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 54
O6 -ZN1 -O6 -C37 1.00 0.00 2.766 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 59
O6 -ZN1 -O6 -ZN2 18.00 0.00 2.766 1.555 1.555 1.555

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1 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: L2Mes

Bond precision: C-C = 0.0024 A Wavelength=0.71073
Cell: a=9.0464(6) b=16.3859(11) c=28.9463(19)
alpha=90 beta=95.491(1) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	4271.1(5)	4271.1(5)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C54 H48 N2 O P2	?
Sum formula	C54 H48 N2 O P2	C54 H48 N2 O P2
Mr	802.88	802.88
Dx,g cm-3	1.249	1.249
Z	4	4
Mu (mm-1)	0.144	0.144
F000	1696.0	1696.0
F000'	1697.39	
h,k,lmax	10,19,34	10,19,34
Nref	7548	7537
Tmin,Tmax	0.939,0.949	0.681,0.746
Tmin'	0.939	

Correction method= MULTI-SCAN
Data completeness= 0.999 Theta(max)= 25.030
R(reflections)= 0.0350(6550) wR2(reflections)= 0.0912(7537)
S = 1.036 Npar= 538

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.3 Ratio

---

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c P21/n

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 9

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=17.2935(9) b=20.5469(11) c=23.7107(13)
alpha=90 beta=90 gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	8425.1(8)	8425.1(8)
Space group	P b c n	Pbcn
Hall group	-P 2n 2ab	?
Moiety formula	C54 H50 N2 O P2, 2(C24 H20 B), C3 H6 O	?
Sum formula	C105 H96 B2 N2 O2 P2	C105 H96 B2 N2 O2 P2
Mr	1501.40	1501.40
Dx,g cm-3	1.184	1.184
Z	4	4
Mu (mm-1)	0.105	0.105
F000	3184.0	3184.0
F000'	3185.93	
h,k,lmax	20,24,28	20,24,28
Nref	7439	7433
Tmin,Tmax	0.975,0.979	0.691,0.746
Tmin'	0.957	

Correction method= MULTI-SCAN
Data completeness= 0.999 Theta(max)= 25.030
R(reflections)= 0.0466(4939) wR2(reflections)= 0.1183(7433)
S = 1.028 Npar= 516

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C2S
PLAT420_ALERT_2_C D-H Without Acceptor N1 - H1N ... ?
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 31 A**3

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 3

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 10b

Bond precision: C-C = 0.0068 A Wavelength=0.71073

Cell: a=11.4348(10) b=15.8183(14) c=19.2062(17)
alpha=86.685(1) beta=75.823(1) gamma=82.763(1)

Temperature: 173 K

	Calculated	Reported
Volume	3340.1(5)	3340.0(5)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C55 H51 N2 O P2 Zn, C24 H20 B	?
Sum formula	C79 H71 B N2 O P2 Zn	C81 H72 B N2 O P2 Zn
Mr	1202.52	1227.53
Dx,g cm-3	1.196	1.221
Z	2	2
Mu (mm-1)	0.462	0.463
F000	1264.0	1290.0
F000'	1265.36	
h,k,lmax	13,18,22	13,18,22
Nref	11811	11774
Tmin,Tmax	0.920,0.942	0.674,0.746
Tmin'	0.887	

Correction method= MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.030

R(reflections)= 0.0656(6563) wR2(reflections)= 0.1771(11774)

S = 1.023 Npar= 822

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT410_ALERT_2_A Short Intra H...H Contact H66 .. H74B .. 1.14 Ang.

Alert level B

PLAT213_ALERT_2_B Atom C53 has ADP max/min Ratio ..... 4.1 prola
PLAT213_ALERT_2_B Atom C79 has ADP max/min Ratio ..... 4.6 prola
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 8.9 Ratio
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.5 Ratio
PLAT222_ALERT_3_B Large Non-Solvent H Uiso(max)/Uiso(min) .. 9.4 Ratio
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C65
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C66

Alert level C

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ ?
PLAT043_ALERT_1_C Check Reported Molecular Weight 1227.53
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT213_ALERT_2_C Atom C65 has ADP max/min Ratio ..... 3.1 prola
PLAT213_ALERT_2_C Atom C66 has ADP max/min Ratio ..... 3.1 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.5 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference Zn1 -- C79 .. 0.19 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C72
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C61
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0068 Ang
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H44A .. H53B .. 2.10 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C81 H72 B1 N2 O1 P2 Zn1
Atom count from the _atom_site data: C79 H71 B1 N2 O1 P2 Zn1
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 93
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C73B
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 8 Perc.
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 133 A**3
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 16
C73B -B1 -C73 1.555 1.555 1.555 23.50 Deg.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 1469
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

1 **ALERT level A** = Most likely a serious problem - resolve or explain
7 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
15 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 11

```
Bond precision:        C-C = 0.0047 A                Wavelength=0.71073
Cell:          a=17.7836(9)      b=21.8185(11)     c=19.8868(10)
               alpha=90          beta=100.504(1)   gamma=90
Temperature: 173 K
                     Calculated                       Reported
Volume               7587.0(7)                        7587.0(7)
Space group          P 21/c                           P2(1)/c
Hall group           -P 2ybc                          ?
```

Moiety formula	C60 H53 N2 O P2 Zn, C24 H20 B, C6 H5 Br	?
Sum formula	C90 H78 B Br N2 O P2 Zn	C90 H78 B Br N2 O P2 Zn
Mr	1421.58	1421.57
Dx,g cm-3	1.245	1.245
Z	4	4
Mu (mm-1)	0.941	0.941
F000	2960.0	2960.0
F000'	2961.68	
h,k,lmax	21,25,23	21,25,23
Nref	13413	13399
Tmin,Tmax	0.596,0.693	0.653,0.746
Tmin'	0.585	

Correction method= MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.030

R(reflections)= 0.0492(10529) wR2(reflections)= 0.1410(13399)

S = 1.051 Npar= 877

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.7 Ratio

---

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 7.17
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 326 A**3
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 12

Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell: a=17.8781(11) b=21.6874(13) c=19.8464(12)
alpha=90 beta=101.083(1) gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	7551.5(8)	7551.5(8)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C56 H51 N2 O3 P2 Zn, C24 H20 B, C6 H6	?
Sum formula	C86 H77 B N2 O3 P2 Zn	C86 H77 B N2 O3 P2 Zn
Mr	1324.64	1324.62
Dx,g cm-3	1.165	1.165
Z	4	4
Mu (mm-1)	0.416	0.416
F000	2784.0	2784.0
F000'	2786.87	
h,k,lmax	21,25,23	21,25,23
Nref	13358	13330
Tmin,Tmax	0.905,0.988	0.675,0.746
Tmin'	0.840	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.030

R(reflections)= 0.0620(8079) wR2(reflections)= 0.1544(13330)

S = 1.019 Npar= 755

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.9 Ratio

---

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.122
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.03
PLAT213_ALERT_2_C Atom C56 has ADP max/min Ratio ..... 3.2 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 6.0 Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Zn1

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 4
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure !
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 251
N2 -ZN1 -C55 -C56 -158.00 22.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 252
N1 -ZN1 -C55 -C56 19.00 22.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 253
O3 -ZN1 -C55 -C56 108.00 22.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 254
O2 -ZN1 -C55 -C56 -75.00 22.00 1.555 1.555 1.555 1.555
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 48
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 15b

Bond precision: C-C = 0.0039 A Wavelength=0.71073
Cell: a=17.4192(12) b=21.5109(15) c=20.0888(14)
alpha=90 beta=99.329(1) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	7427.8(9)	7427.8(9)
Space group	P 21/c	?
Hall group	-P 2ybc	?
Moiety formula	C60 H49.90 F3.10 N2 O1.62 P2 Zn, C24 H20 B, 0.19(C2 H2 Cl6), C	?
Sum formula	C85.38 H71.28 B Cl4.14 F3.10 N2 O1.62 P2 Zn	C85.38 H71.28 B Cl4.14 F3.10 N2 O1.62 P2 Zn
Mr	1495.01	1494.99
Dx,g cm-3	1.337	1.337
Z	4	4
Mu (mm-1)	0.580	0.580
F000	3095.9	3095.0
F000'	3100.68	
h,k,lmax	21,26,25	21,26,25
Nref	15187	15175
Tmin,Tmax	0.752,0.906	0.615,0.909
Tmin'	0.583	

Correction method= ?
Data completeness= 0.999 Theta(max)= 26.370

```
R(reflections)= 0.0477( 12881)        wR2(reflections)= 0.1368( 15175)
S = 1.077                Npar= 994
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

SHFSU01_ALERT_2_A The absolute value of parameter shift to su ratio > 0.20
Absolute value of the parameter shift to su ratio given 0.354
Additional refinement cycles may be required.
PLAT080_ALERT_2_A Maximum Shift/Error 0.35
PLAT122_ALERT_1_A No _symmetry_space_group_name_H-M Given ..... ?

Alert level B

PLAT052_ALERT_1_B Info on Absorption Correction Method Missing ... ?
PLAT057_ALERT_3_B Correction for Absorption Required RT(exp) ... 1.21
PLAT093_ALERT_1_B No su's on H-atoms, but refinement reported as . mixed
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 7.3 Ratio

Alert level C

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.10
PLAT213_ALERT_2_C Atom C63 has ADP max/min Ratio ..... 3.8 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 6.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C57 -- C58 .. 0.18 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C91
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 39 A**3

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 8
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 5
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size .... 0.93 mm
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 7.82
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C58
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C62
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C64
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C92
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 10 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 43 Perc.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 48

3 **ALERT level A** = Most likely a serious problem - resolve or explain
4 **ALERT level B** = A potentially serious problem, consider carefully
8 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
15 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
12 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: L2Mipp

```
Bond precision:        C-C = 0.0084 A                Wavelength=0.71073
Cell:          a=11.5434(11)     b=14.8956(15)     c=15.1659(15)
               alpha=62.313(1)   beta=86.134(1)    gamma=78.115(1)
Temperature: 173 K
                      Calculated                        Reported
Volume                2258.4(4)                         2258.4(4)
Space group           P -1                              P-1
Hall group            -P 1                              ?
Moiety formula        C54 H48 N2 O P2, 0.2(C H2 Cl2)    ?
```

Sum formula	C54.20 H48.40 Cl0.40 N2 O P2	C54.20 H48.40 Cl0.40 N2 O P2
Mr	819.87	819.87
Dx,g cm-3	1.206	1.206
Z	2	2
Mu (mm-1)	0.161	0.161
F000	864.8	865.0
F000'	865.61	
h,k,lmax	13,17,18	13,17,18
Nref	7994	7960
Tmin,Tmax	0.958,0.979	0.681,0.746
Tmin'	0.911	

Correction method= MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.030

R(reflections)= 0.0646(4429) wR2(reflections)= 0.1827(7960)

S = 1.110 Npar= 563

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.8 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for C48 -- C49 .. 9.1 su
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C49

Alert level C

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.24
PLAT214_ALERT_2_C Atom C1S (Anion/Solvent) ADP max/min Ratio 4.2 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.5 Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C48
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C52
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0084 Ang

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Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C1S
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact C50 .. Cl1 .. 2.70 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C51 .. Cl1 .. 2.91 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 2
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 1

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
3 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: L2Tol

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=18.0198(9) b=14.0045(7) c=16.7584(9)
alpha=90 beta=109.646(1) gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	3982.9(4)	3982.9(4)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?

Moiety formula	C50 H40 N2 O P2	?
Sum formula	C50 H40 N2 O P2	C50 H40 N2 O P2
Mr	746.78	746.78
Dx,g cm-3	1.245	1.245
Z	4	4
Mu (mm-1)	0.150	0.150
F000	1568.0	1568.0
F000'	1569.35	
h,k,lmax	21,16,19	21,16,19
Nref	7019	7010
Tmin,Tmax	0.956,0.969	0.670,0.746
Tmin'	0.933	

Correction method= MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.020

R(reflections)= 0.0394(5933) wR2(reflections)= 0.1079(7010)

S = 1.081 Npar= 498

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C44 -- C45 .. 7.4 su

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Alert level C

PLAT230_ALERT_2_C Hirshfeld Test Diff for C49 -- C50 .. 6.5 su

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Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 72 A**3
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: L2Pipp

Bond precision: C-C = 0.0059 A Wavelength=0.71073

Cell: a=26.938(3) b=18.8282(18) c=10.2745(10)
alpha=90 beta=90 gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	5211.2(9)	5211.1(9)
Space group	P c a 21	Pca2(1)
Hall group	P 2c -2ac	?
Moiety formula	C54 H48 N2 O P2, C5 H12	?
Sum formula	C59 H60 N2 O P2	C59 H60 N2 O P2
Mr	875.03	875.03
Dx,g cm-3	1.115	1.115
Z	4	4
Mu (mm-1)	0.123	0.123
F000	1864.0	1864.0
F000'	1865.44	
h,k,lmax	32,22,12	32,22,12
Nref	4893[9209]	9201
Tmin,Tmax	0.978,0.983	0.683,0.746
Tmin'	0.942	

Correction method= MULTI-SCAN

Data completeness= 1.88/1.00 Theta(max)= 25.030

R(reflections)= 0.0517(8100) wR2(reflections)= 0.1238(9201)
S = 1.106 Npar= 613

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.2 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for C4 -- C5 .. 8.3 su

Alert level C

PLAT213_ALERT_2_C Atom C53 has ADP max/min Ratio ..... 3.3 prola
PLAT213_ALERT_2_C Atom C53B has ADP max/min Ratio ..... 3.1 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 5.6 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C49 -- C52B .. 0.20 Ang.
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C2S
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C3S
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0059 Ang
PLAT361_ALERT_2_C Long C(sp3)-C(sp3) Bond C4S - C5S ... 1.69 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C48 - C49 ... 1.38 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C49 - C50 ... 1.39 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 6
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C52
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C52B
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 5 Perc.
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 198 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 12
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 174
C52B -C49 -C52 1.555 1.555 1.555 15.60 Deg.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 77
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
11 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
12 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: L2Ph

Bond precision: C-C = 0.0068 A Wavelength=0.71073
Cell: a=9.373(11) b=13.769(17) c=17.95(2)
alpha=104.285(15) beta=90.990(14) gamma=92.535(15)
Temperature: 173 K

	Calculated	Reported
Volume	2242(5)	2242(5)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C48 H36 N2 O P2, 0.5(C6 H6)	?
Sum formula	C51 H39 N2 O P2	C51 H39 N2 O P2
Mr	757.78	757.78
Dx,g cm-3	1.123	1.123
Z	2	2
Mu (mm-1)	0.134	0.134
F000	794.0	794.0
F000'	794.68	
h,k,lmax	11,16,21	11,16,21
Nref	7926	7900

```
Tmin,Tmax            0.981,0.989                    0.965,0.990
Tmin'                0.964
Correction method= MULTI-SCAN
Data completeness= 0.997          Theta(max)= 25.030
R(reflections)= 0.0794( 3097)         wR2(reflections)= 0.2141( 7900)
S = 0.915               Npar= 433
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections too Low .... 39 Perc.
PLAT331_ALERT_2_B Small Average Phenyl C-C Dist. C1S -C3S_a 1.35 Ang.
PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of . 164 A**3

Alert level C

PLAT148_ALERT_3_C su on the a - Axis is (Too) Large ..... 0.011 Ang.
PLAT148_ALERT_3_C su on the b - Axis is (Too) Large ..... 0.017 Ang.
PLAT148_ALERT_3_C su on the c - Axis is (Too) Large ..... 0.020 Ang.
PLAT230_ALERT_2_C Hirshfeld Test Diff for P1 -- N1 .. 5.3 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for N2 -- C43 .. 5.8 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C19 -- C24 .. 7.0 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C25 -- C26 .. 6.8 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C38 -- C39 .. 6.0 su
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 2.7
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0068 Ang
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1
C48 H36 N2 O P2

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2
C6 H6

0 **ALERT level A** = Most likely a serious problem - resolve or explain
3 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 20b

```
Bond precision:        C-C = 0.0030 A                  Wavelength=0.71073
Cell:          a=14.3702(7)      b=15.2542(7)      c=17.2588(8)
               alpha=81.451(1)   beta=66.469(1)    gamma=76.867(1)
Temperature: 173 K
                      Calculated                          Reported
Volume                3370.8(3)                           3370.8(3)
Space group           P -1                                P-1
Hall group            -P 1                                ?
Moiety formula        C55 H51 N2 O P2 Zn, C24 H20 B, C6   ?
                      H6
Sum formula           C85 H77 B N2 O P2 Zn                C85 H77 B N2 O P2 Zn
Mr                    1280.63                             1280.61
Dx,g cm-3             1.262                               1.262
Z                     2                                   2
Mu (mm-1)             0.462                               0.462
F000                  1348.0                              1348.0
F000'                 1349.39
h,k,lmax              17,18,20                            17,18,20
Nref                  11915                               11879
Tmin,Tmax             0.758,0.916                         0.768,0.916
```

```
Tmin'                0.758
Correction method= MULTI-SCAN
Data completeness= 0.997          Theta(max)= 25.030
R(reflections)= 0.0302( 10320)        wR2(reflections)= 0.0825( 11879)
S = 1.016               Npar= 834
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT331_ALERT_2_B Small Average Phenyl C-C Dist. C1S -C6S 1.35 Ang.

Alert level C

PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 38 A**3

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 21b

```
Bond precision:        C-C = 0.0046 A                Wavelength=0.71073
Cell:        a=9.9214(8)       b=17.1175(13)     c=18.4747(14)
             alpha=86.754(1)   beta=78.725(1)    gamma=80.859(1)
Temperature: 173 K
                    Calculated                          Reported
Volume              3036.9(4)                           3036.9(4)
Space group         P -1                                P-1
Hall group          -P 1                                ?
Moiety formula      C52.20 H43.48 N2 O P2 Zn, C24 H20   ?
                    B
Sum formula         C76.20 H63.48 B N2 O P2 Zn          C76.18 H63.47 B N2 O P2 Zn
Mr                  1161.31                             1160.98
Dx,g cm-3           1.270                               1.270
Z                   2                                   2
Mu (mm-1)           0.505                               0.505
F000                1215.4                              1215.0
F000'               1216.71
h,k,lmax            11,20,21                            11,20,21
Nref                10717                               10686
Tmin,Tmax           0.881,0.980                         0.678,0.746
Tmin'               0.809
Correction method= MULTI-SCAN
Data completeness= 0.997          Theta(max)= 25.030
R(reflections)= 0.0445( 6972)         wR2(reflections)= 0.0987( 10686)
S = 1.012               Npar= 784
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ ?
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT213_ALERT_2_C Atom C75B has ADP max/min Ratio ..... 3.3 prola

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the _chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C76.18 H63.47 B1 N2 O1 P2 Zn1
Atom count from the _atom_site data: C76.2 H63.48 B1 N2 O1 P2 Zn1
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 6
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 3 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact C76B .. C77B .. 3.12 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C77B .. C77B .. 2.72 Ang.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 84

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 22b

Bond precision: C-C = 0.0054 A Wavelength=0.71073
Cell: a=9.878(7) b=17.426(11) c=21.932(14)
alpha=80.235(8) beta=82.751(8) gamma=80.160(8)
Temperature: 173 K

	Calculated	Reported
Volume	3647(4)	3647(4)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	2(C55.80 H51.32 N2 O P2 Zn), 2(C24 H20 B), C6 H6	?
Sum formula	C165.60 H148.64 B2 N4 O2 P4 Zn2	C79 H71 B N2 O P2 Zn
Mr	2503.00	1202.50
Dx,g cm-3	1.140	1.095
Z	1	2
Mu (mm-1)	0.425	0.423
F000	1316.2	1264.0
F000'	1317.62	
h,k,lmax	11,20,26	11,20,26
Nref	12890	12848
Tmin,Tmax	0.816,0.942	0.659,0.746
Tmin'	0.782	

Correction method= MULTI-SCAN
Data completeness= 0.997 Theta(max)= 25.030
R(reflections)= 0.0507(10448) wR2(reflections)= 0.1284(12848)
S = 1.035 Npar= 927

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT410_ALERT_2_A Short Intra H...H Contact H73 .. H63B .. 1.72 Ang.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.7 Ratio
PLAT413_ALERT_2_B Short Inter XH3 .. XHn H53B .. H57 .. 1.91 Ang.

Alert level C

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ ?
PLAT043_ALERT_1_C Check Reported Molecular Weight 1202.50
PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 0.50 Ratio

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.7 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.2 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C37 -- C38 .. 5.7 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C64 -- C65 .. 6.2 su
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C21
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C76
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C74
PLAT331_ALERT_2_C Small Average Phenyl C-C Dist. C1S -C3S_a 1.37 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact H10 .. H64B .. 2.11 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact H2S .. H64B .. 2.14 Ang.
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H53A .. H57 .. 2.10 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C79 H71 B1 N2 O1 P2 Zn1
Atom count from the _atom_site data: C82.8 H74.32 B1 N2 O1 P2 Zn1
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 18
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00800 Deg.
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C66B
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 16 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact C1S .. C66B .. 3.14 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C44 .. C63B .. 2.69 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C44 .. C64B .. 2.84 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C45 .. C64B .. 2.96 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C53 .. C57 .. 2.94 Ang.
PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 212 A**3
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 18
C13B -P1 -C13 1.555 1.555 1.555 19.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 39
C62B -B1 -C62 1.555 1.555 1.555 11.00 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 252
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

1 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
16 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
17 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
22 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: 23c

Bond precision: C-C = 0.0036 A Wavelength=0.71073
Cell: a=9.9023(5) b=16.8670(9) c=20.7112(11)
alpha=101.974(1) beta=91.114(1) gamma=95.296(1)
Temperature: 173 K

	Calculated	Reported
Volume	3366.9(3)	3366.9(3)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	2(C53.65 H40.86 N2 O P2 Zn), 2(C24 H20 B), C6 H6	?
Sum formula	C161.30 H127.72 B2 N4 O2 P4 Zn2	C80.65 H63.86 B N2 O P2 Zn
Mr	2430.27	1215.12
Dx,g cm-3	1.199	1.199
Z	1	2
Mu (mm-1)	0.459	0.459
F000	1269.5	1270.0
F000'	1270.89	
h,k,lmax	11,20,24	11,20,24
Nref	11906	11870

```
Tmin,Tmax            0.813,0.908                        0.687,0.746
Tmin'                0.813
Correction method= MULTI-SCAN
Data completeness= 0.997          Theta(max)= 25.030
R(reflections)= 0.0387( 10042)        wR2(reflections)= 0.1073( 11870)
S = 1.069               Npar= 829
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT230_ALERT_2_C Hirshfeld Test Diff for P1 -- C37 .. 6.3 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C19 -- C20 .. 5.2 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C23 -- C24 .. 6.0 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C41 -- C42 .. 7.0 su
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C1 - C2 ... 1.38 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C10 - C11 ... 1.39 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C11 - C12 ... 1.39 Ang.

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 11 Perc.
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure !
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 65
P1B -C2 -P1 1.555 1.555 1.555 21.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 101
P2 -C11 -P2B 1.555 1.555 1.555 22.68 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 110
P2B -C13 -P2 1.555 1.555 1.555 23.41 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 131
N2B -C19 -P2 1.555 1.555 1.555 43.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 152
N2 -C25 -P2B 1.555 1.555 1.555 43.35 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 173
P1 -C31 -P1B 1.555 1.555 1.555 21.62 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 194
N1B -C37 -P1 1.555 1.555 1.555 42.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 215
N1 -C43 -P1B 1.555 1.555 1.555 43.45 Deg.
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
10 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 24

```
Bond precision:        C-C = 0.0096 A                  Wavelength=0.71073
Cell:          a=11.4655(17)     b=19.564(3)       c=19.662(3)
               alpha=99.640(2)   beta=103.416(2)   gamma=92.916(2)
Temperature: 173 K
```

	Calculated	Reported
Volume	4210.9(11)	4210.9(11)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C54 H47 N2 O4 P2 Zn, C32 H12 B F24, 0.83(C H2 Cl2)	?

Sum formula	C86.83 H60.66 B Cl1.66 F24 N2 O4 P2 Zn	C86.83 H60.66 B Cl1.66 F24 N2 O4 P2 Zn
Mr	1848.98	1848.96
Dx,g cm-3	1.458	1.458
Z	2	2
Mu (mm-1)	0.487	0.487
F000	1873.6	1874.0
F000'	1876.46	
h,k,lmax	13,23,23	13,23,23
Nref	15053	14955
Tmin,Tmax	0.960,0.976	0.848,0.977
Tmin'	0.843	

Correction method= MULTI-SCAN

Data completeness= 0.993 Theta(max)= 25.120

R(reflections)= 0.0785(7374) wR2(reflections)= 0.2148(14955)

S = 1.020 Npar= 1170

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT213_ALERT_2_B Atom F13 has ADP max/min Ratio ..... 4.2 prola
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C62
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C86

Alert level C

PLAT026_ALERT_3_C Ratio Observed / Unique Reflections too Low .... 49 Perc.
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT165_ALERT_3_C Nr. of Status R Flagged Non-Hydrogen Atoms 2
PLAT213_ALERT_2_C Atom F5 has ADP max/min Ratio ..... 3.3 prola
PLAT213_ALERT_2_C Atom F6 has ADP max/min Ratio ..... 3.2 prola
PLAT213_ALERT_2_C Atom F22 has ADP max/min Ratio ..... 3.8 prola
PLAT213_ALERT_2_C Atom F24 has ADP max/min Ratio ..... 3.1 prola
PLAT214_ALERT_2_C Atom C87 (Anion/Solvent) ADP max/min Ratio 4.6 prola
PLAT220_ALERT_2_C Large Non-Solvent F Ueq(max)/Ueq(min) ... 3.4 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C35 -- C36 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F4 -- C62 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F10 -- C70 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F13 -- C77 .. 0.16 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C36
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for O3
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C53
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C61
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C69
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C70
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C77
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C78
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C85
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0096 Ang
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 38 A**3
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1
C54 H47 N2 O4 P2 Zn

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 20
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 18
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00200 Deg.
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C52A
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 7 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact C6 .. F11B .. 2.87 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 264
F12B -C70 -F11 1.555 1.555 1.555 36.20 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 274
F10 -C70 -F10B 1.555 1.555 1.555 41.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 335
F21B -C85 -F21 1.555 1.555 1.555 27.10 Deg.

PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2
C32 H12 B F24
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 3
C H2 Cl2
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 225

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
3 **ALERT level B** = A potentially serious problem, consider carefully
26 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
23 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
12 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 25

```
Bond precision:        C-C = 0.0115 A                  Wavelength=0.71073
Cell:        a=19.0867(15)     b=26.603(2)       c=19.5381(15)
             alpha=90          beta=116.133(1)   gamma=90
Temperature: 173 K
```

	Calculated	Reported
Volume	8906.6(12)	8906.6(12)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C58 H55 N2 O4 P2 Zn, C32 H12 B F24, C6 H6	?
Sum formula	C96 H73 B F24 N2 O4 P2 Zn	C96 H73 B F24 N2 O4 P2 Zn
Mr	1912.70	1912.68
Dx,g cm-3	1.426	1.426
Z	4	4
Mu (mm-1)	0.415	0.415
F000	3904.0	3904.0
F000'	3908.58	
h,k,lmax	19,26,19	19,26,19
Nref	9323	9322
Tmin,Tmax	0.928,0.963	0.896,0.963
Tmin'	0.894	

```
Correction method= MULTI-SCAN
Data completeness= 1.000           Theta(max)= 20.810
R(reflections)= 0.0761( 7605)         wR2(reflections)= 0.1665( 9322)
S = 1.275               Npar= 1297
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4999

Alert level B

REFNR01_ALERT_3_B Ratio of reflections to parameters is < 8 for a
centrosymmetric structure
sine(theta)/lambda 0.4999
Proportion of unique data used 1.0000
Ratio reflections to parameters 7.1874
PLAT088_ALERT_3_B Poor Data / Parameter Ratio 7.19
PLAT213_ALERT_2_B Atom F16 has ADP max/min Ratio ..... 4.3 prola
PLAT213_ALERT_2_B Atom F18 has ADP max/min Ratio ..... 4.7 prola
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.9 Ratio
PLAT220_ALERT_2_B Large Non-Solvent O Ueq(max)/Ueq(min) ... 4.3 Ratio
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.0 Ratio
PLAT220_ALERT_2_B Large Non-Solvent F Ueq(max)/Ueq(min) ... 4.5 Ratio
PLAT234_ALERT_4_B Large Hirshfeld Difference F18 -- C82 .. 0.30 Ang.
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C82

Alert level C

PLAT213_ALERT_2_C Atom O4 has ADP max/min Ratio ..... 3.4 prola
PLAT213_ALERT_2_C Atom C33 has ADP max/min Ratio ..... 3.2 prola
PLAT213_ALERT_2_C Atom C58 has ADP max/min Ratio ..... 3.8 prola
PLAT213_ALERT_2_C Atom C54B has ADP max/min Ratio ..... 3.5 oblat
PLAT213_ALERT_2_C Atom F1 has ADP max/min Ratio ..... 3.8 prola
PLAT213_ALERT_2_C Atom F2 has ADP max/min Ratio ..... 3.5 prola
PLAT213_ALERT_2_C Atom F8B has ADP max/min Ratio ..... 3.8 prola
PLAT213_ALERT_2_C Atom F9B has ADP max/min Ratio ..... 3.9 prola
PLAT213_ALERT_2_C Atom F13 has ADP max/min Ratio ..... 3.3 prola
PLAT213_ALERT_2_C Atom F15 has ADP max/min Ratio ..... 4.0 prola
PLAT213_ALERT_2_C Atom C82 has ADP max/min Ratio ..... 3.1 prola
PLAT213_ALERT_2_C Atom F4B has ADP max/min Ratio ..... 3.6 prola
PLAT213_ALERT_2_C Atom F5B has ADP max/min Ratio ..... 3.2 prola
PLAT213_ALERT_2_C Atom F6B has ADP max/min Ratio ..... 3.4 prola
PLAT213_ALERT_2_C Atom F7 has ADP max/min Ratio ..... 4.0 prola
PLAT213_ALERT_2_C Atom F19B has ADP max/min Ratio ..... 3.6 oblat
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.9 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C16 -- C17 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F13 -- C81 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F16 -- C82 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C61 -- C62 .. 0.17 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for O4
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for O2
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C31
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C57
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C65
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C66
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C73
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C79
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C81
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C89
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C90
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.5
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.5
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0115 Ang
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C48 - C49 ... 1.37 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C49 - C50 ... 1.38 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1
C58 H55 N2 O4 P2 Zn

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 24
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 56
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 54.61
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C52
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C56B
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C52B
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 14 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 12
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 190
C52 -C49 -C52B 1.555 1.555 1.555 23.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 261
F2 -C65 -F1B 1.555 1.555 1.555 44.30 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 263
F3B -C65 -F1 1.555 1.555 1.555 37.50 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 282
F4 -C66 -F4B 1.555 1.555 1.555 25.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 284
F5B -C66 -F5 1.555 1.555 1.555 35.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 322
F7 -C73 -F9B 1.555 1.555 1.555 22.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 324
F8B -C73 -F9 1.555 1.555 1.555 41.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 327
F8 -C73 -F7B 1.555 1.555 1.555 43.50 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 394
F20B -C89 -F20 1.555 1.555 1.555 44.00 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 699

1 **ALERT level A** = Most likely a serious problem - resolve or explain
10 **ALERT level B** = A potentially serious problem, consider carefully
38 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
21 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
44 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
17 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: 26

```
Bond precision:        C-C = 0.0074 A                  Wavelength=0.71073
Cell:        a=18.7810(11)     b=27.1179(16)     c=18.6506(11)
             alpha=90          beta=116.785(1)   gamma=90
Temperature: 173 K
                     Calculated                          Reported
Volume               8479.6(9)                           8479.6(9)
Space group          P 21/c                              P2(1)/c
Hall group           -P 2ybc                             ?
Moiety formula       C52 H43 N2 O4 P2 Zn, C32 H12 B      ?
                     F24, C6 H5, 0.38(Br)
Sum formula          C90 H60 B Br0.38 F24 N2 O4 P2 Zn    C90 H60 B Br0.38 F24 N2 O4 P2 Zn
Mr                   1857.90                             1857.89
Dx,g cm-3            1.455                               1.455
Z                    4                                   4
Mu (mm-1)            0.612                               0.612
F000                 3760.5                              3761.0
F000'                3765.28
h,k,lmax             22,32,22                            22,32,22
Nref                 14982                               14960
Tmin,Tmax            0.773,0.843                         0.761,0.849
Tmin'                0.750
Correction method= MULTI-SCAN
Data completeness= 0.999           Theta(max)= 25.030
R(reflections)= 0.0613( 11787)        wR2(reflections)= 0.1617( 14960)
S = 1.117               Npar= 1339
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT213_ALERT_2_A Atom F6B has ADP max/min Ratio ..... 6.7 prola

Alert level B

PLAT213_ALERT_2_B Atom F18 has ADP max/min Ratio ..... 4.5 prola
PLAT213_ALERT_2_B Atom F23 has ADP max/min Ratio ..... 4.1 prola
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 6.0 Ratio
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.1 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for F17 -- C76 .. 11.9 su
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C46
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C84
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor 4.4

Alert level C

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT213_ALERT_2_C Atom C46 has ADP max/min Ratio ..... 3.6 prola
PLAT213_ALERT_2_C Atom C52 has ADP max/min Ratio ..... 3.2 prola
PLAT213_ALERT_2_C Atom F20 has ADP max/min Ratio ..... 3.1 prola
PLAT213_ALERT_2_C Atom F22 has ADP max/min Ratio ..... 3.6 prola
PLAT213_ALERT_2_C Atom F24 has ADP max/min Ratio ..... 3.6 prola
PLAT213_ALERT_2_C Atom F8B has ADP max/min Ratio ..... 3.3 prola
PLAT213_ALERT_2_C Atom F9B has ADP max/min Ratio ..... 3.7 prola
PLAT213_ALERT_2_C Atom F16B has ADP max/min Ratio ..... 3.1 prola
PLAT213_ALERT_2_C Atom F17B has ADP max/min Ratio ..... 3.3 prola

PLAT213_ALERT_2_C Atom F18B has ADP max/min Ratio ..... 3.6 prola
PLAT220_ALERT_2_C Large Non-Solvent O Ueq(max)/Ueq(min) ... 3.7 Ratio
PLAT220_ALERT_2_C Large Non-Solvent F Ueq(max)/Ueq(min) ... 3.6 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.4 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C45 -- C46 .. 6.8 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for F18 -- C76 .. 5.5 su
PLAT234_ALERT_4_C Large Hirshfeld Difference F8 -- C67 .. 0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F9 -- C67 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F11B -- C68 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F19 -- C83 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F22 -- C84 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F23 -- C84 .. 0.18 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C17
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for O3
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C48
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C51
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C59
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C60
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C67
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C68
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C75
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C76
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C83
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.7
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0074 Ang

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Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 56
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 49
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 15.47
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C50A
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C50B
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C2S
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C4S
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C4SB
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 17 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1 .. C1S .. 1.70 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1 .. C2S .. 2.63 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1 .. C6S .. 2.72 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1 .. C50B .. 2.85 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1B .. C4S .. 1.06 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1B .. C3S .. 1.50 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1B .. C5S .. 2.35 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1B .. C2S .. 2.79 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact Br1B .. C6S .. 3.32 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact F19 .. C73 .. 2.89 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C50B .. F9B .. 2.92 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 11
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 220
F6B -C60 -F6 1.555 1.555 1.555 38.20 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 230
F5 -C60 -F5B 1.555 1.555 1.555 40.40 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 262
F8B -C67 -F7 1.555 1.555 1.555 42.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 266
F7B -C67 -F8 1.555 1.555 1.555 25.10 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 268
F9 -C67 -F9B 1.555 1.555 1.555 32.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 280
F12 -C68 -F12B 1.555 1.555 1.555 34.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 283
F10B -C68 -F11 1.555 1.555 1.555 39.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 324
F15B -C75 -F15 1.555 1.555 1.555 30.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 329
F14 -C75 -F14B 1.555 1.555 1.555 32.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 341
F18 -C76 -F18B 1.555 1.555 1.555 38.20 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 342
F16B -C76 -F16 1.555 1.555 1.555 30.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 382

F21B -C83 -F21 1.555 1.555 1.555 16.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 388
F20 -C83 -F20B 1.555 1.555 1.555 35.50 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 815

1 **ALERT level A** = Most likely a serious problem - resolve or explain
8 **ALERT level B** = A potentially serious problem, consider carefully
36 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
38 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
51 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
25 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: L3

```
Bond precision:        C-C = 0.0026 A                Wavelength=0.71073
Cell:        a=10.8628(14)     b=11.1264(15)     c=13.9234(18)
             alpha=72.388(1)   beta=88.627(2)    gamma=69.792(1)
Temperature: 173 K
                     Calculated                          Reported
Volume               1499.1(3)                           1499.1(3)
Space group          P -1                                P-1
Hall group           -P 1                                ?
Moiety formula       C34 H40 N2 O P2                     ?
Sum formula          C34 H40 N2 O P2                     C34 H40 N2 O P2
Mr                   554.62                              554.62
Dx,g cm-3            1.229                               1.229
Z                    2                                   2
Mu (mm-1)            0.174                               0.174
F000                 592.0                               592.0
F000'                592.60
h,k,lmax             13,13,17                            13,13,17
Nref                 6140                                6118
Tmin,Tmax            0.946,0.979                         0.946,0.979
Tmin'                0.946
Correction method= MULTI-SCAN
Data completeness= 0.996          Theta(max)= 26.370
R(reflections)= 0.0357( 5164)         wR2(reflections)= 0.0940( 6118)
S = 1.025               Npar= 356
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C17

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 30

```
Bond precision:        C-C = 0.0029 A                  Wavelength=0.71073
Cell:        a=15.0190(19)     b=15.4530(19)     c=16.072(2)
             alpha=104.979(1)  beta=101.291(1)   gamma=95.363(1)
Temperature: 173 K
                     Calculated                          Reported
Volume               3492.5(8)                           3492.5(8)
Space group          P -1                                P-1
Hall group           -P 1                                ?
Moiety formula       C38 H47 N2 O4 P2 Zn, C32 H12 B F24  ?
Sum formula          C70 H59 B F24 N2 O4 P2 Zn           C70 H59 B F24 N2 O4 P2 Zn
Mr                   1586.33                             1586.31
Dx,g cm-3            1.508                               1.508
Z                    2                                   2
Mu (mm-1)            0.512                               0.512
F000                 1612.0                              1612.0
F000'                1614.16
h,k,lmax             18,19,20                            18,19,20
Nref                 14288                               14217
Tmin,Tmax            0.816,0.871                         0.776,0.873
Tmin'                0.766
Correction method= MULTI-SCAN
Data completeness= 0.995           Theta(max)= 26.370
R(reflections)= 0.0340( 12512)         wR2(reflections)= 0.0904( 14217)
S = 1.024                Npar= 1056
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT213_ALERT_2_B Atom F21B has ADP max/min Ratio ..... 4.2 prola
PLAT220_ALERT_2_B Large Non-Solvent F Ueq(max)/Ueq(min) ... 4.6 Ratio
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C69

Alert level C

PLAT213_ALERT_2_C Atom F1B has ADP max/min Ratio ..... 3.7 prola
PLAT213_ALERT_2_C Atom F2B has ADP max/min Ratio ..... 3.4 prola
PLAT213_ALERT_2_C Atom F14B has ADP max/min Ratio ..... 3.9 prola
PLAT213_ALERT_2_C Atom F15B has ADP max/min Ratio ..... 3.3 prola
PLAT213_ALERT_2_C Atom F19B has ADP max/min Ratio ..... 3.1 prola
PLAT213_ALERT_2_C Atom F20B has ADP max/min Ratio ..... 4.0 prola
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C45
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C53
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C61
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C70
PLAT303_ALERT_2_C Full Occupancy H-Atom H38A with # Connections 2
PLAT303_ALERT_2_C Full Occupancy H-Atom H38B with # Connections 2
PLAT303_ALERT_2_C Full Occupancy H-Atom H38C with # Connections 2

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 21
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 18
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00100 Deg.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Zn1 -- O3 .. 7.6 su
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 13 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact F23 .. C36B .. 2.78 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 164
C35 -O2 -C35B 1.555 1.555 1.555 28.80 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 189
O4 -C37 -O4B 1.555 1.555 1.555 23.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 196
C35B -C37 -C35 1.555 1.555 1.555 28.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 219
F3B -C45 -F1 1.555 1.555 1.555 13.80 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 223
F2 -C45 -F1B 1.555 1.555 1.555 32.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 225
F2B -C45 -F3 1.555 1.555 1.555 29.00 Deg.

PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 292
F13 -C61 -F13B 1.555 1.555 1.555 15.30 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 299
F15 -C61 -F15B 1.555 1.555 1.555 32.50 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 300
F14B -C61 -F14 1.555 1.555 1.555 18.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 338
F20B -C69 -F20 1.555 1.555 1.555 33.40 Deg.
PLAT793_ALERT_4_G The Model has Chirality at C35 (Verify) .... R
PLAT793_ALERT_4_G The Model has Chirality at C35B (Verify) .... S
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 231

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2 ALERT type 3 Indicator that the structure quality may be low
12 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

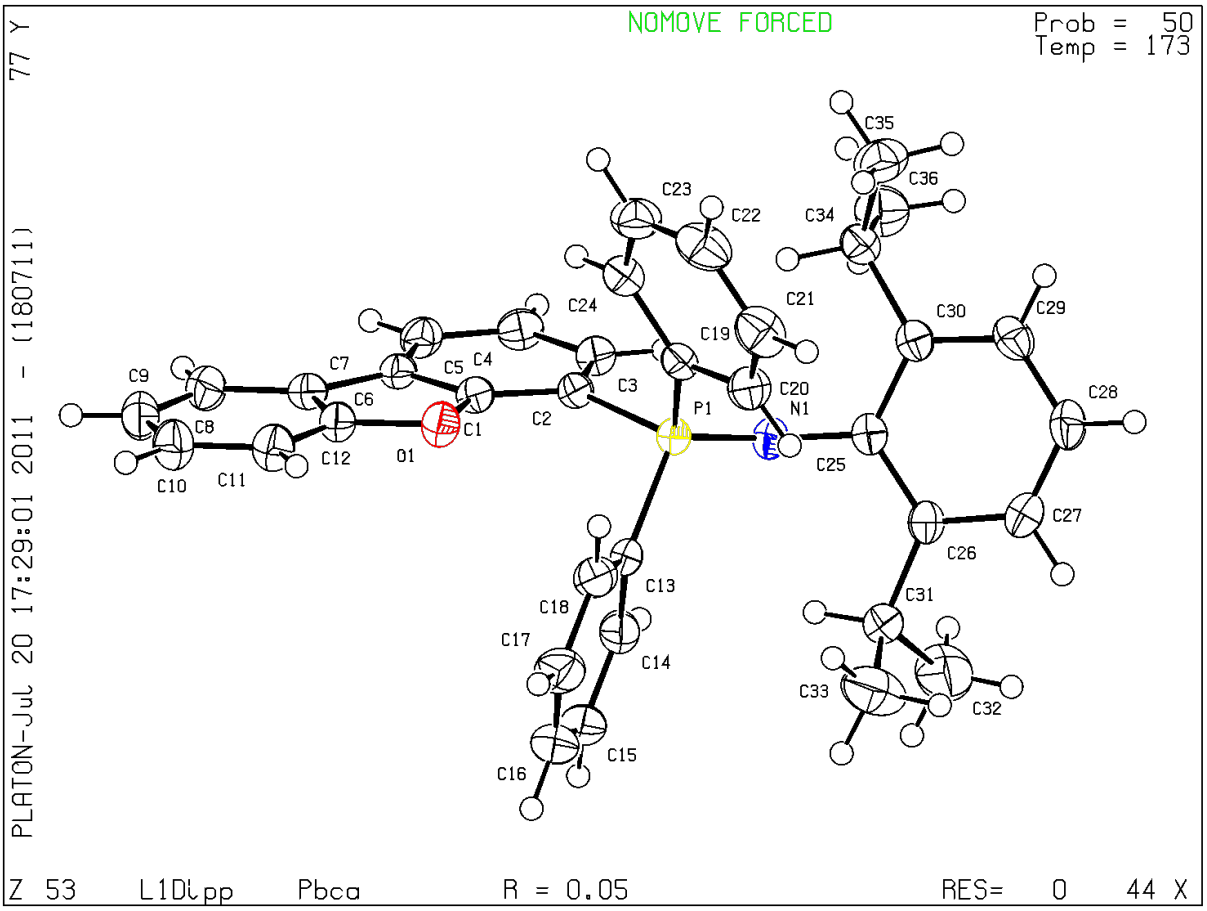
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

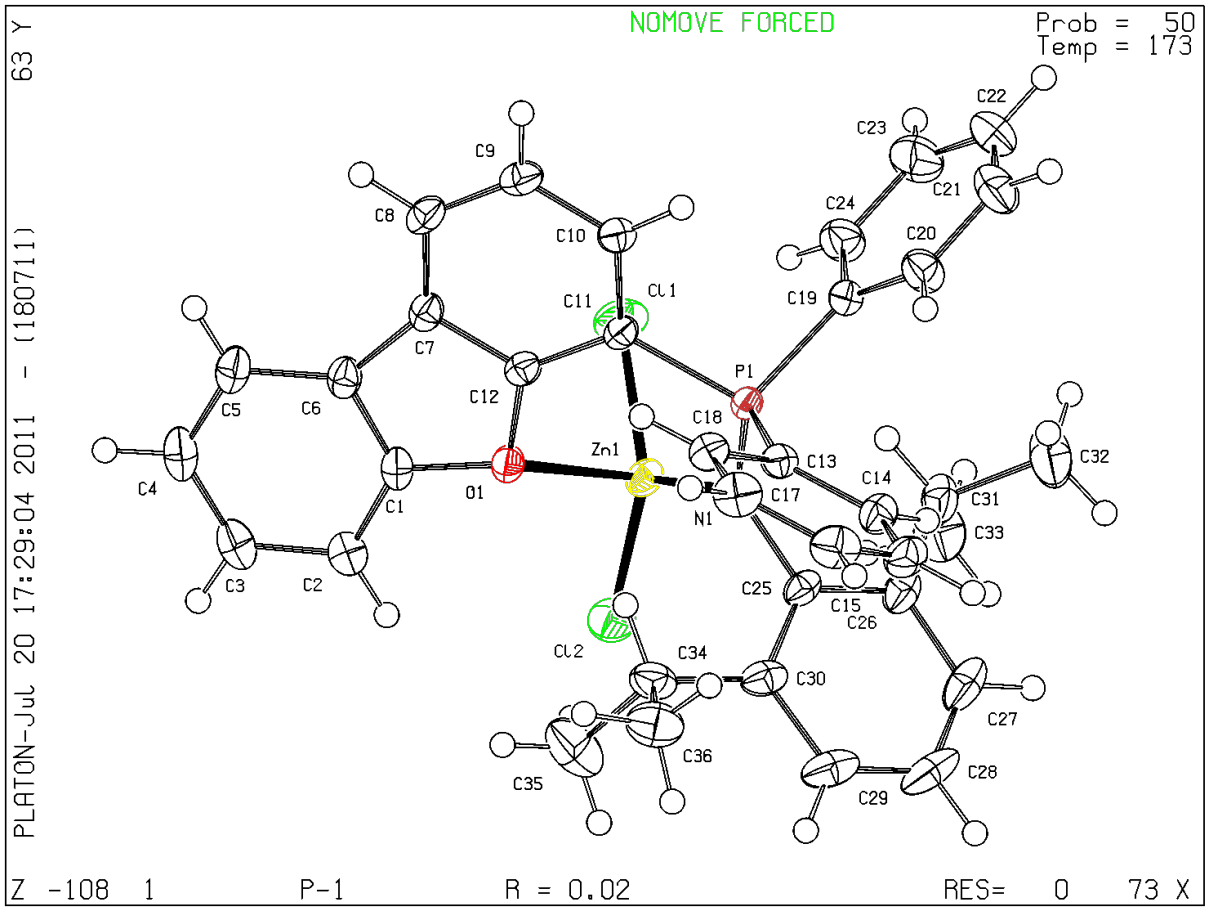
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/07/2011; check.def file version of 04/07/2011

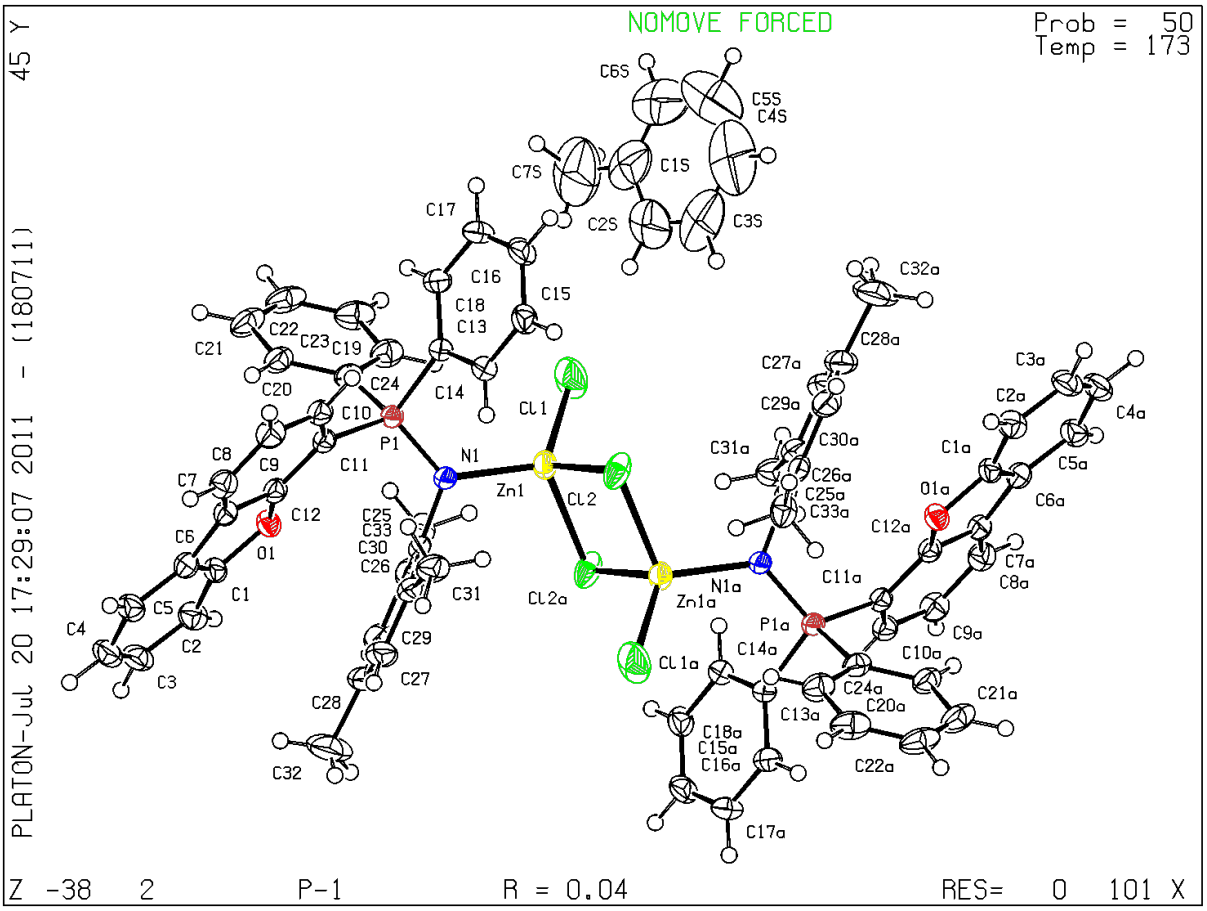
Datablock L1Dipp - ellipsoid plot



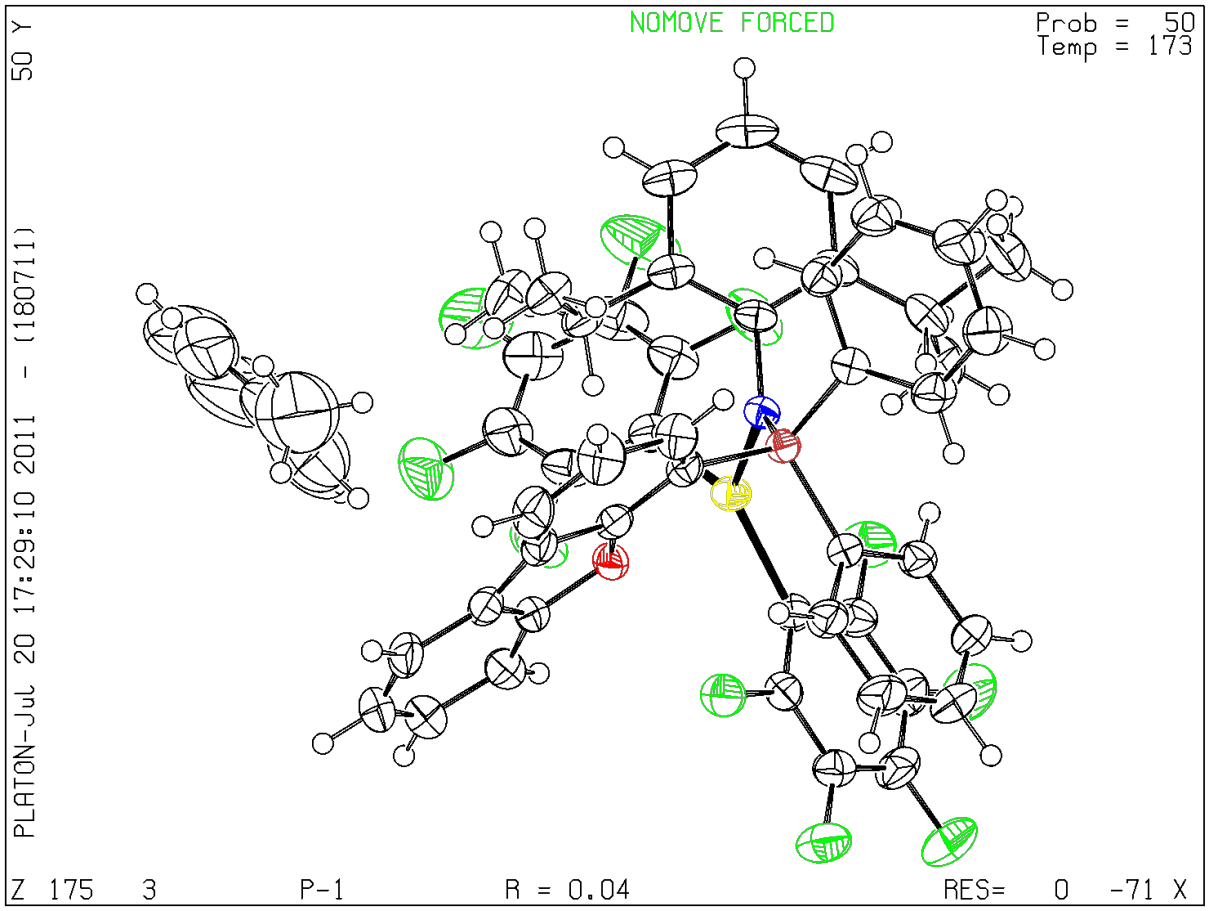
Datablock 1 - ellipsoid plot



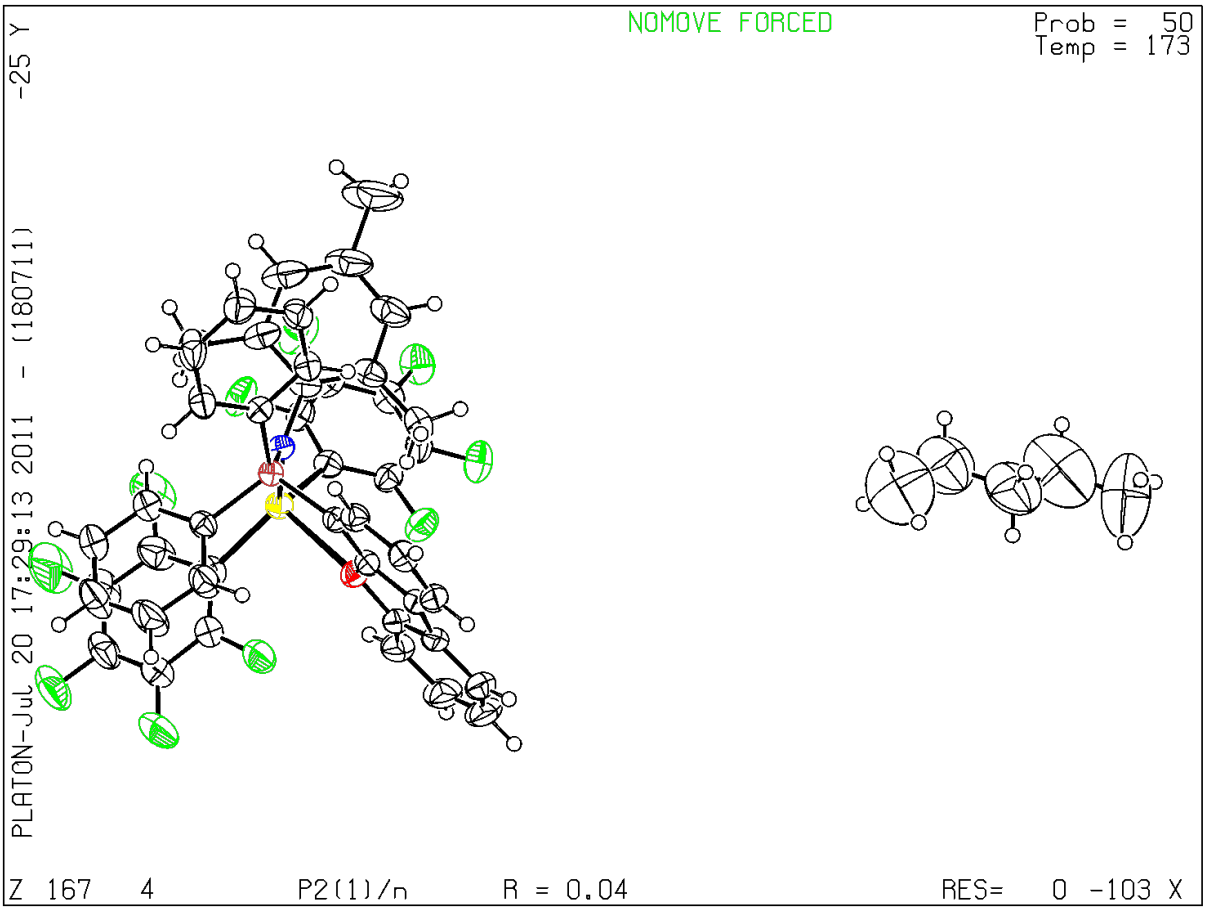
Datablock 2 - ellipsoid plot



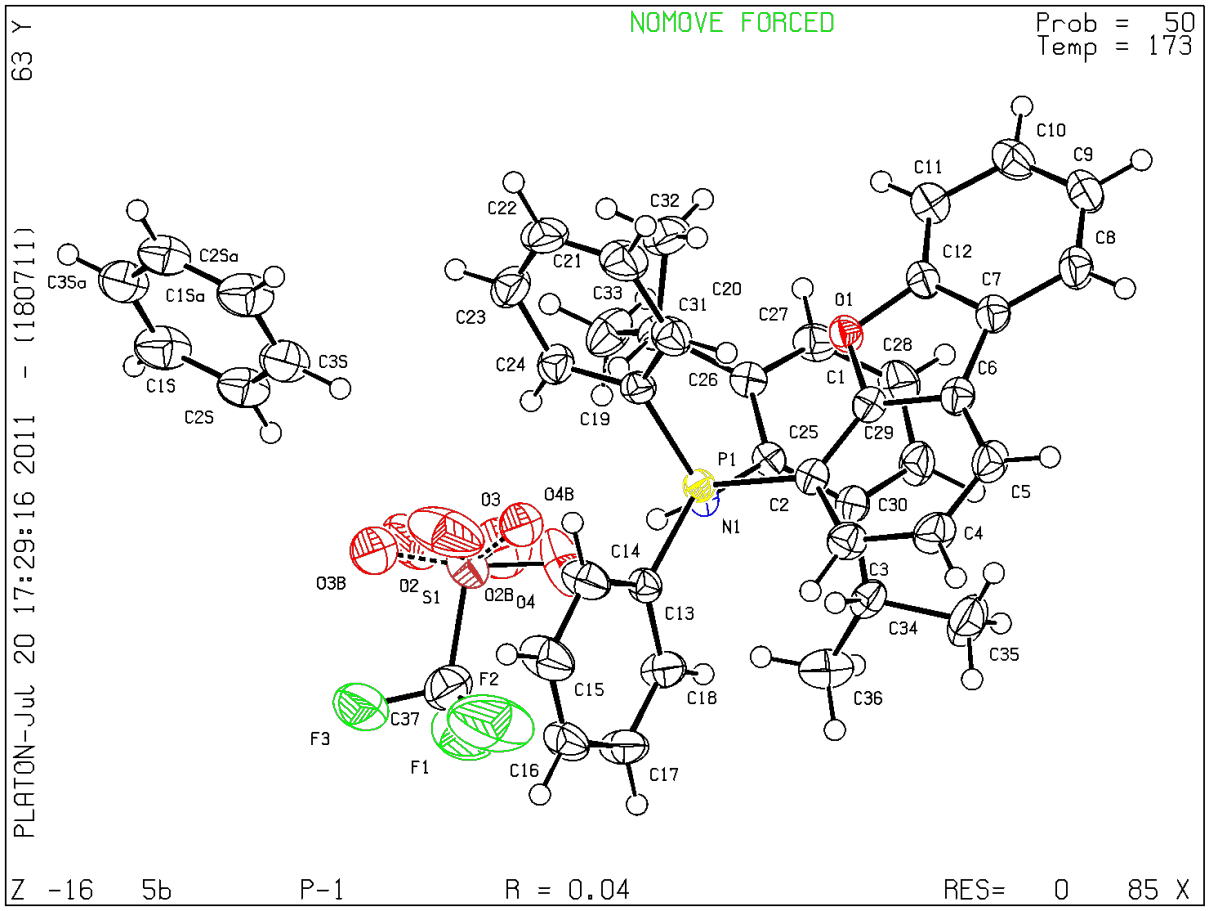
Datablock 3 - ellipsoid plot



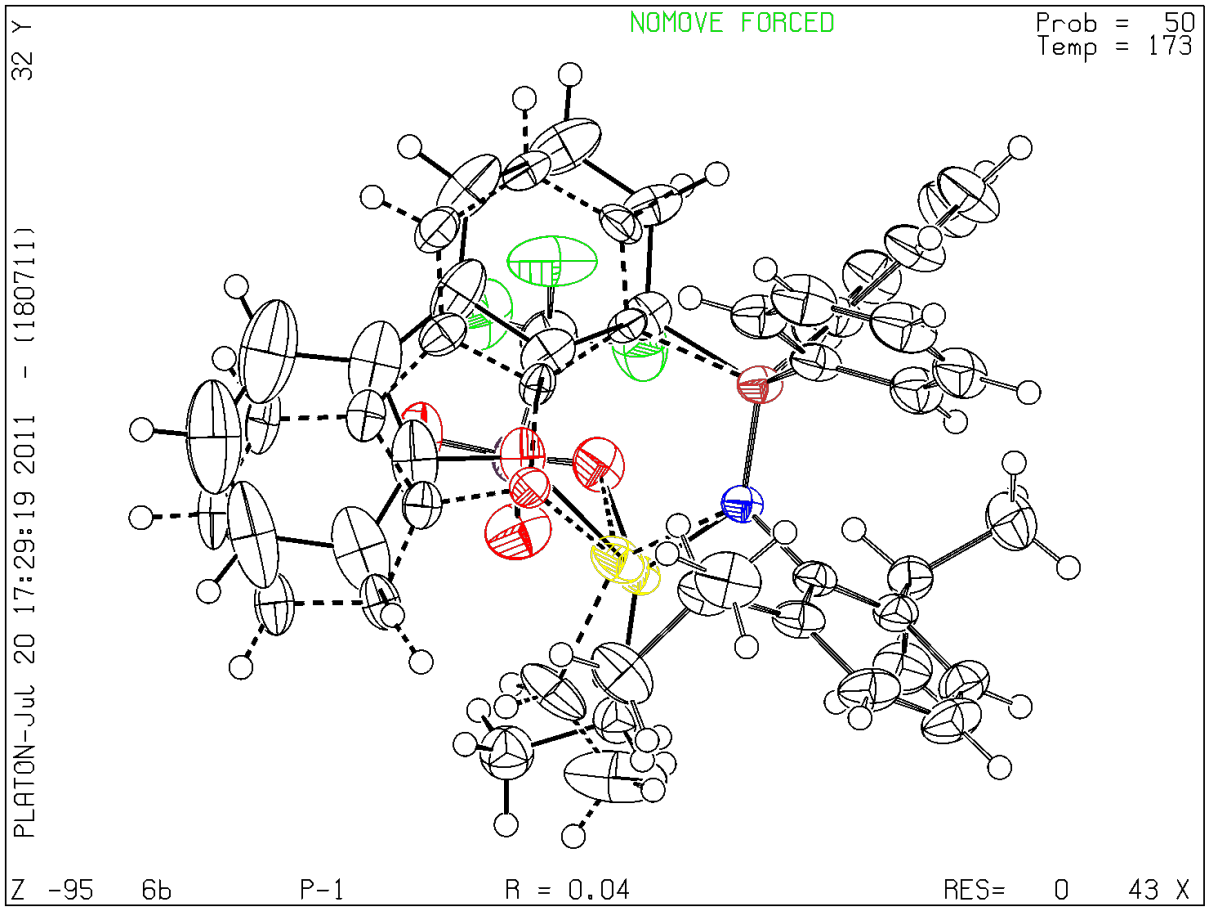
Datablock 4 - ellipsoid plot



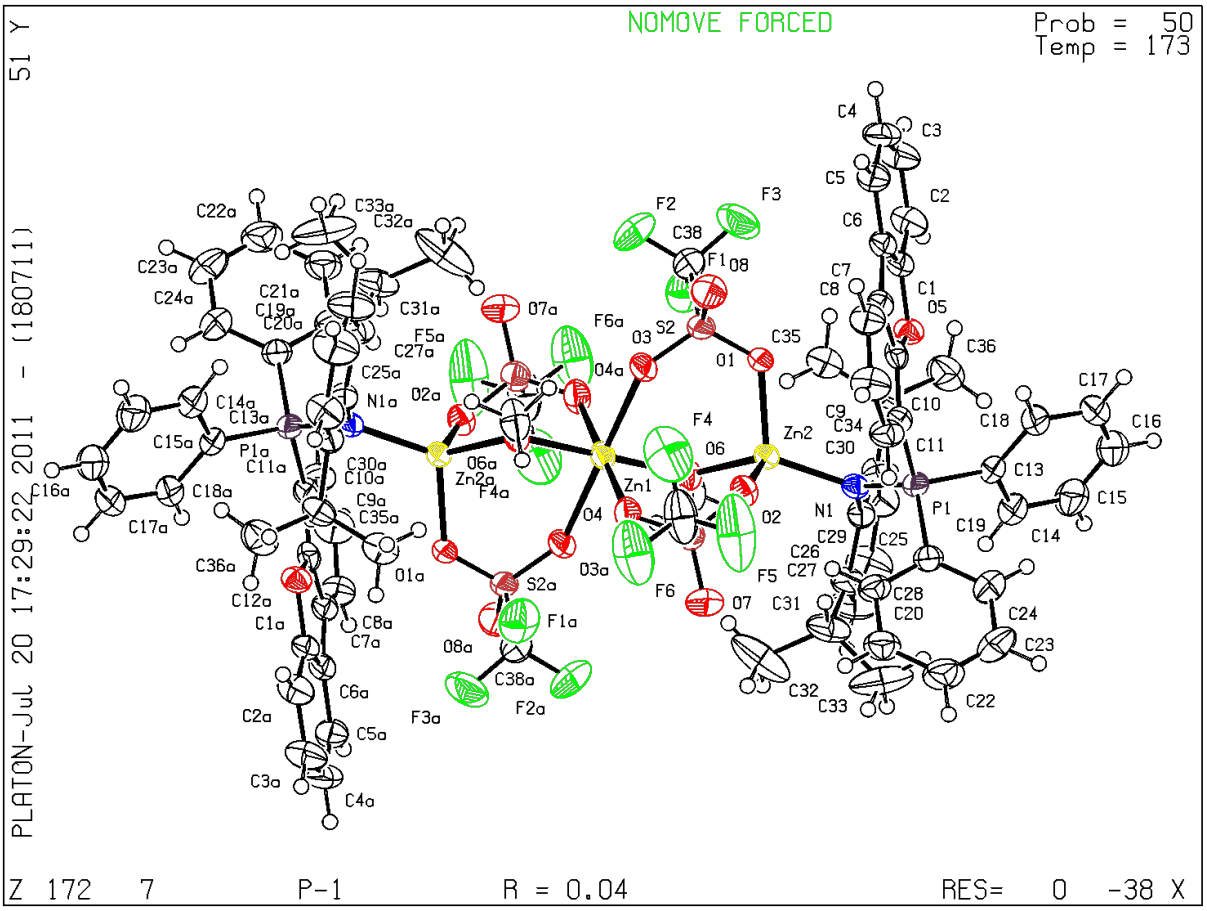
Datablock 5b - ellipsoid plot



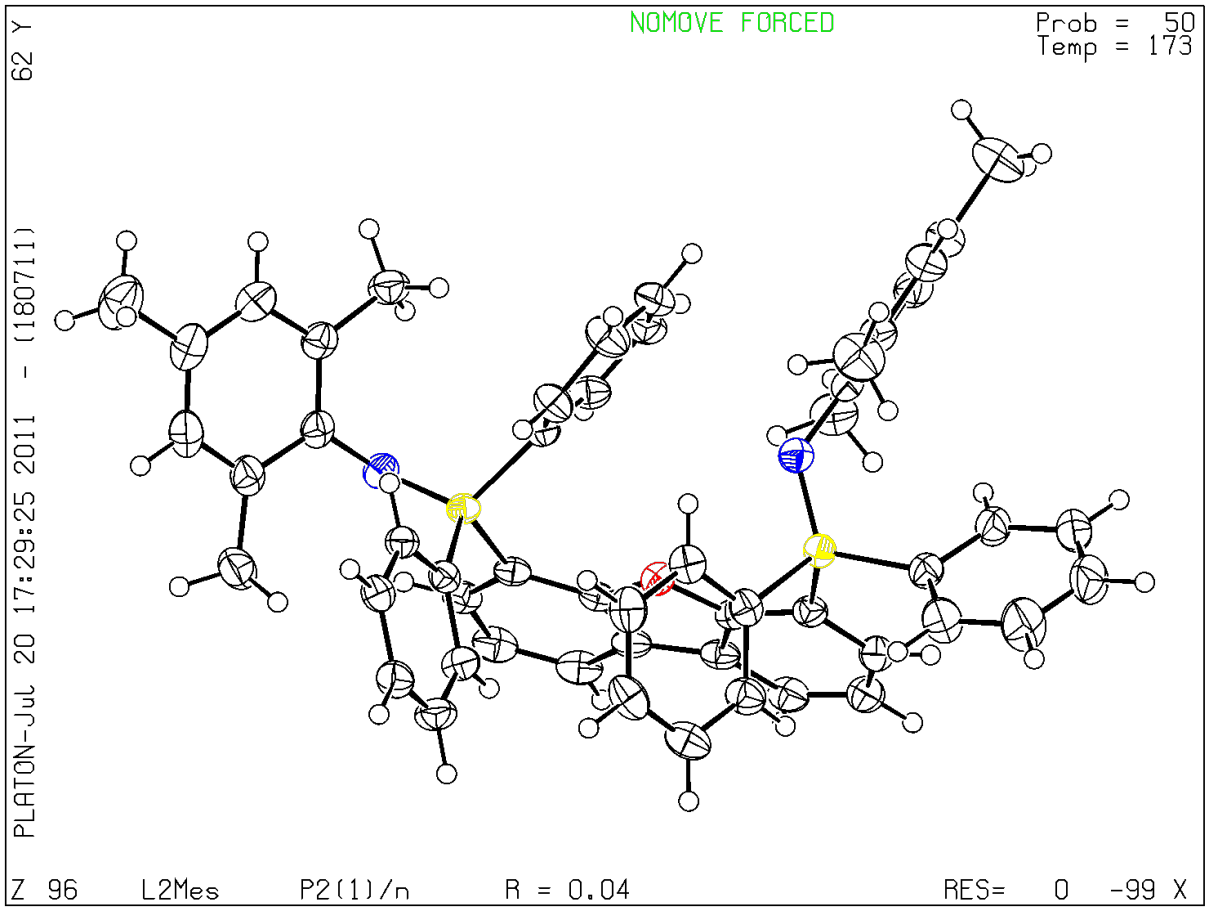
Datablock 6b - ellipsoid plot



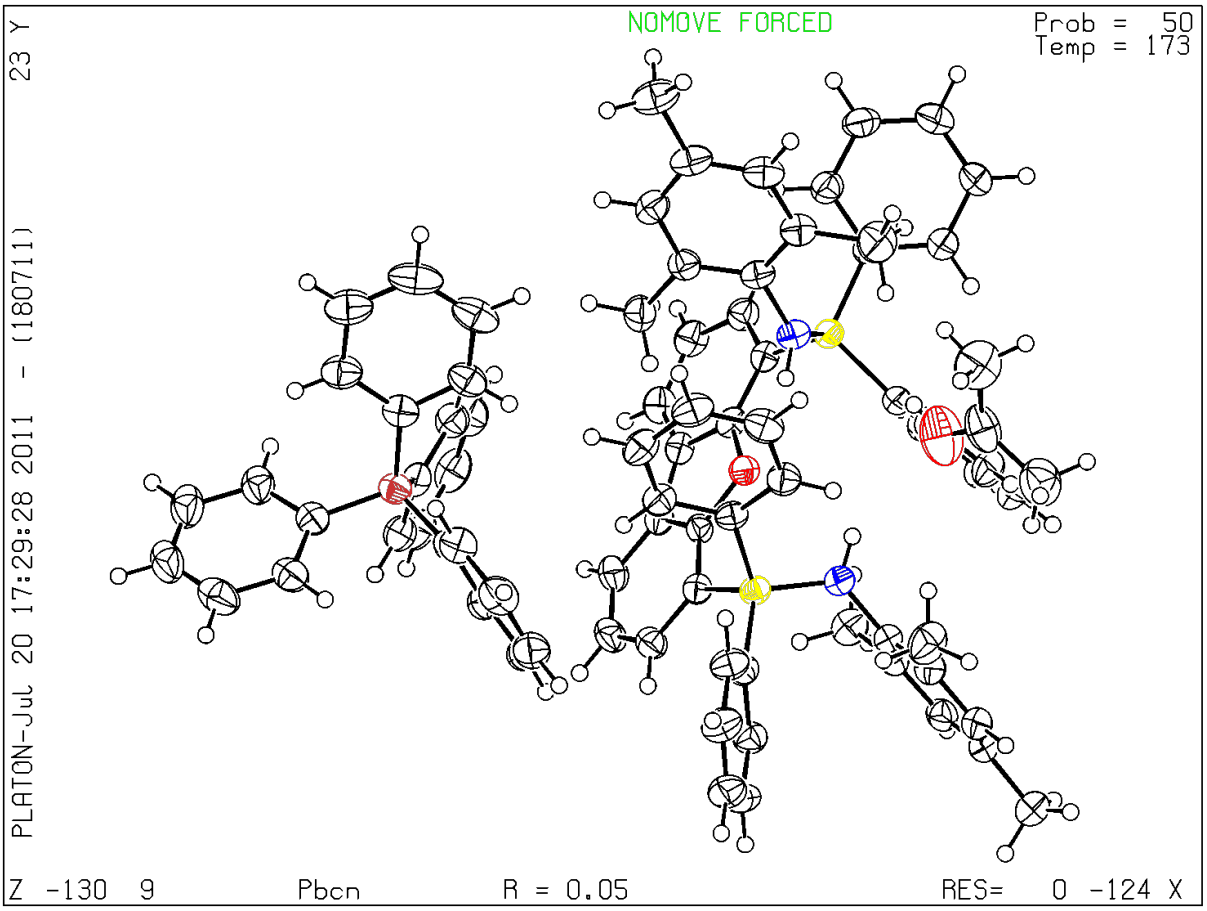
Datablock 7 - ellipsoid plot



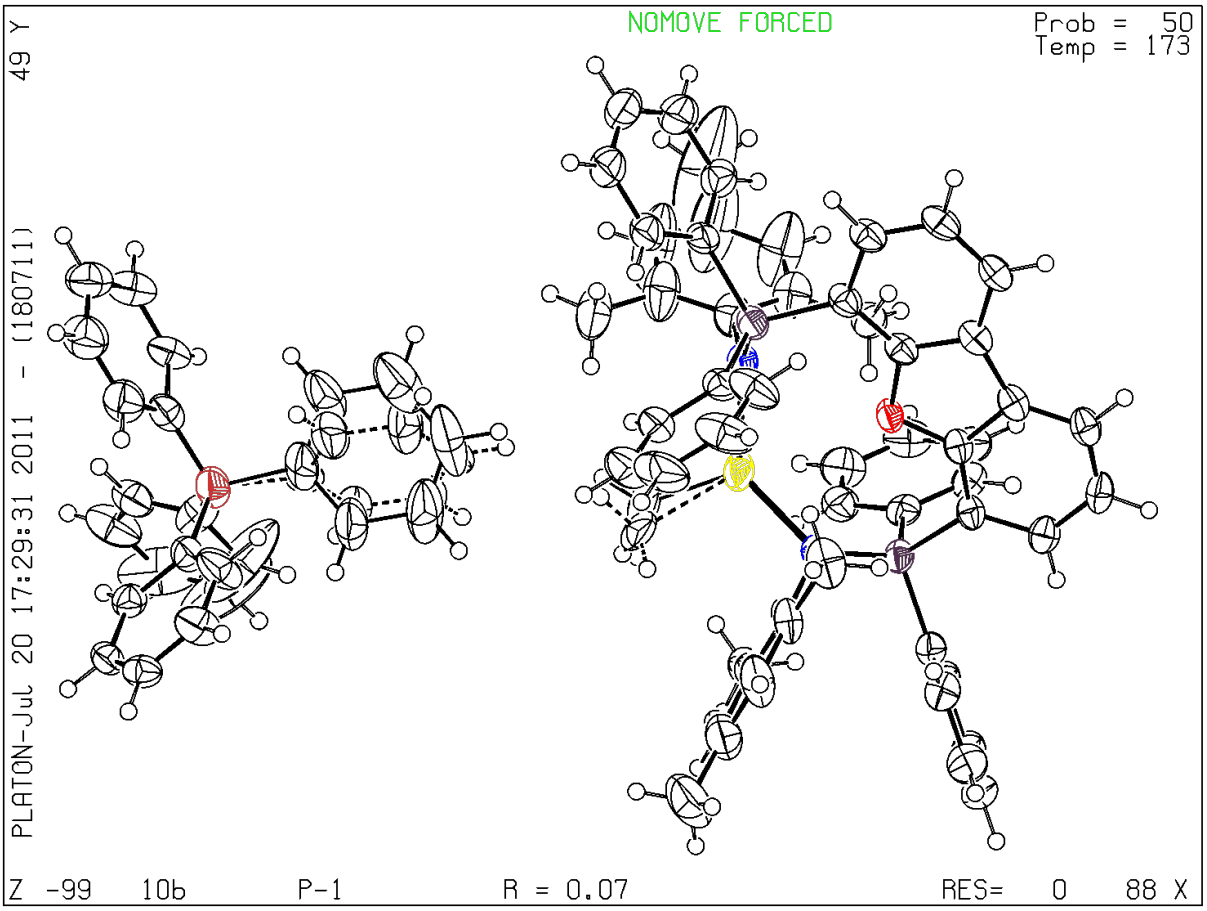
Datablock L2Mes - ellipsoid plot



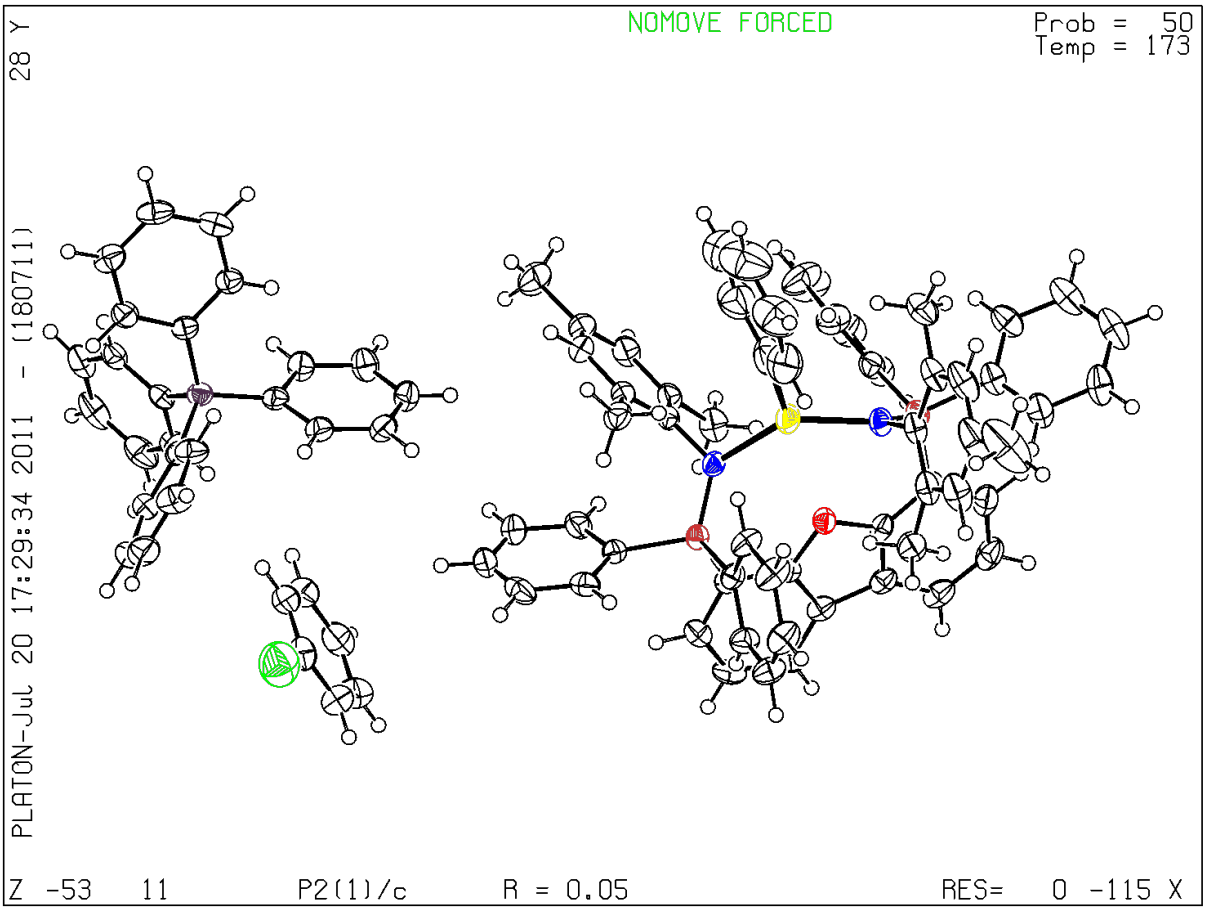
Datablock 9 - ellipsoid plot



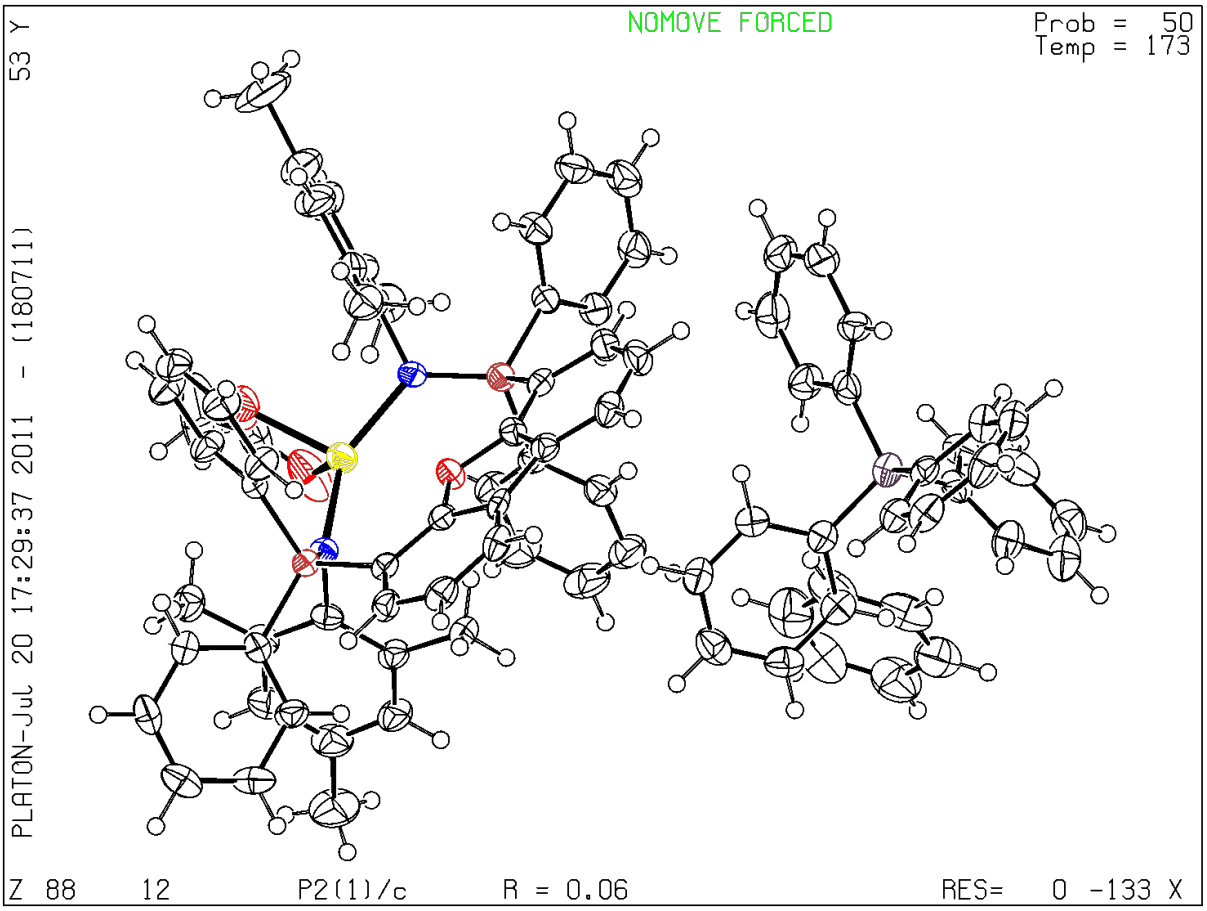
Datablock 10b - ellipsoid plot



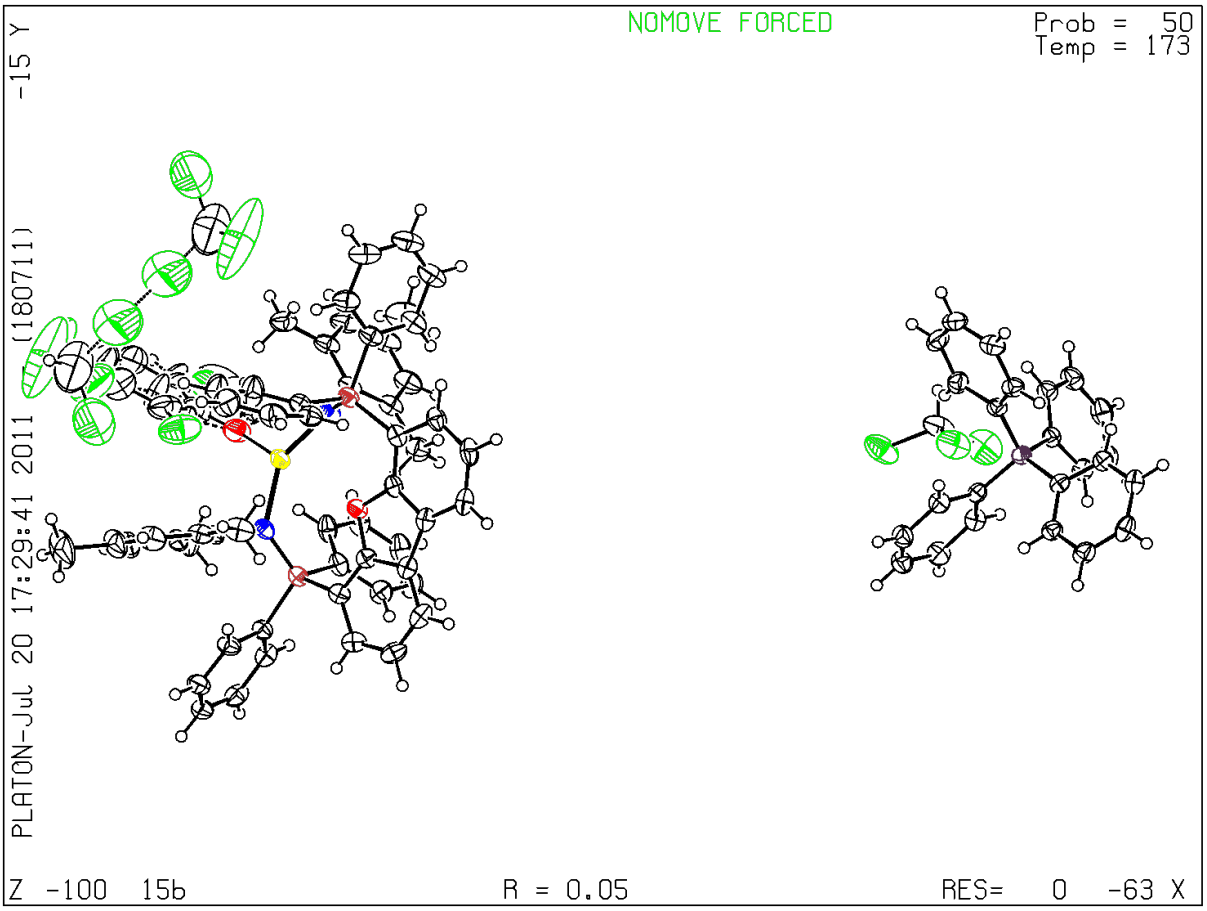
Datablock 11 - ellipsoid plot



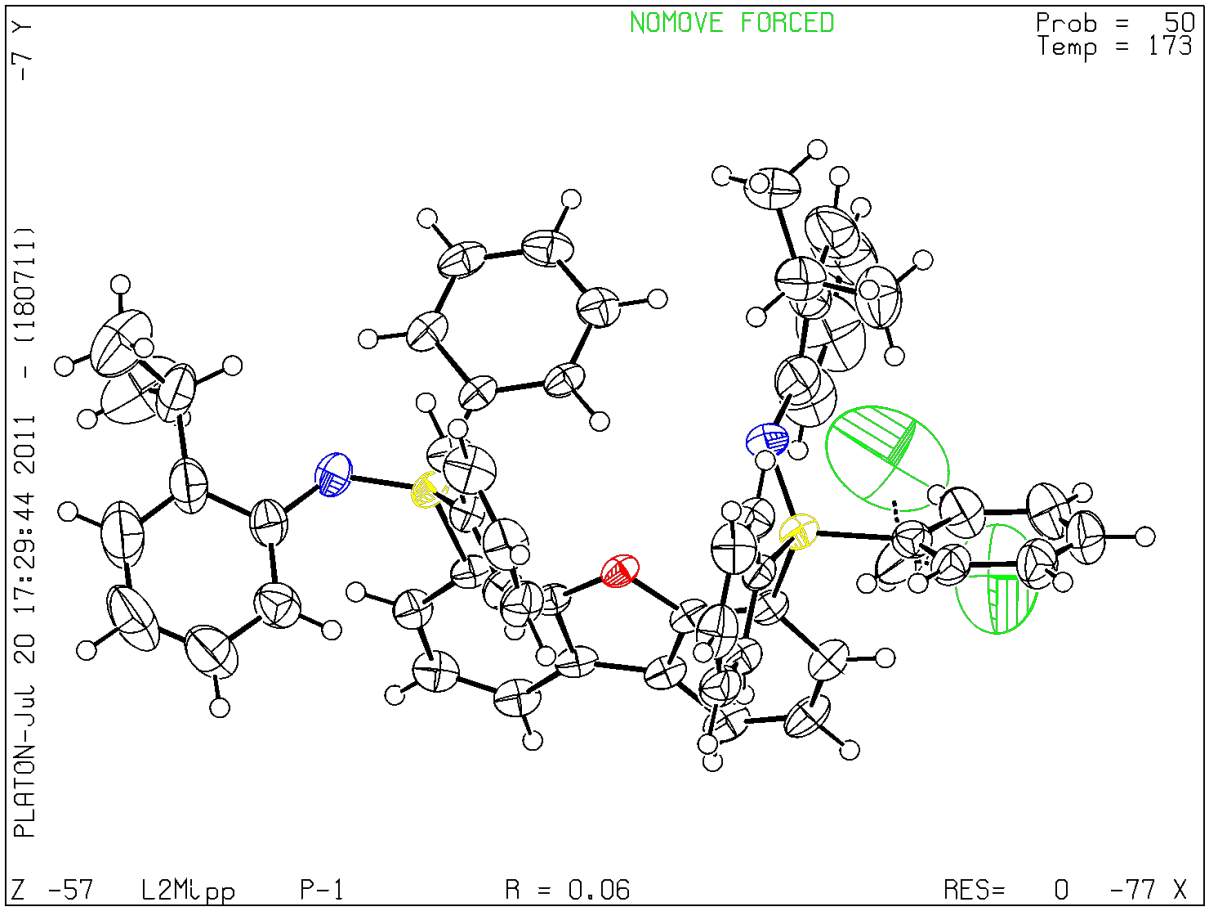
Datablock 12 - ellipsoid plot



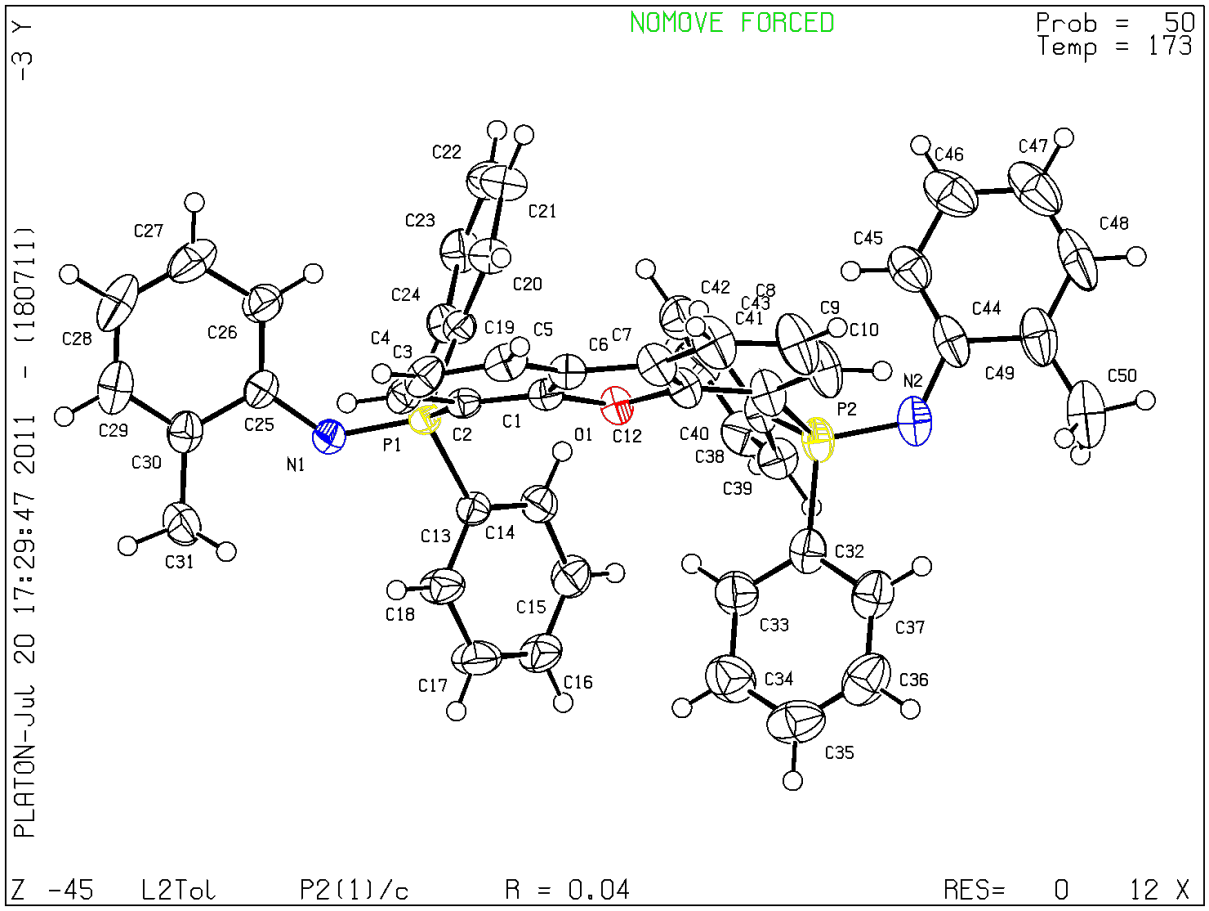
Datablock 15b - ellipsoid plot



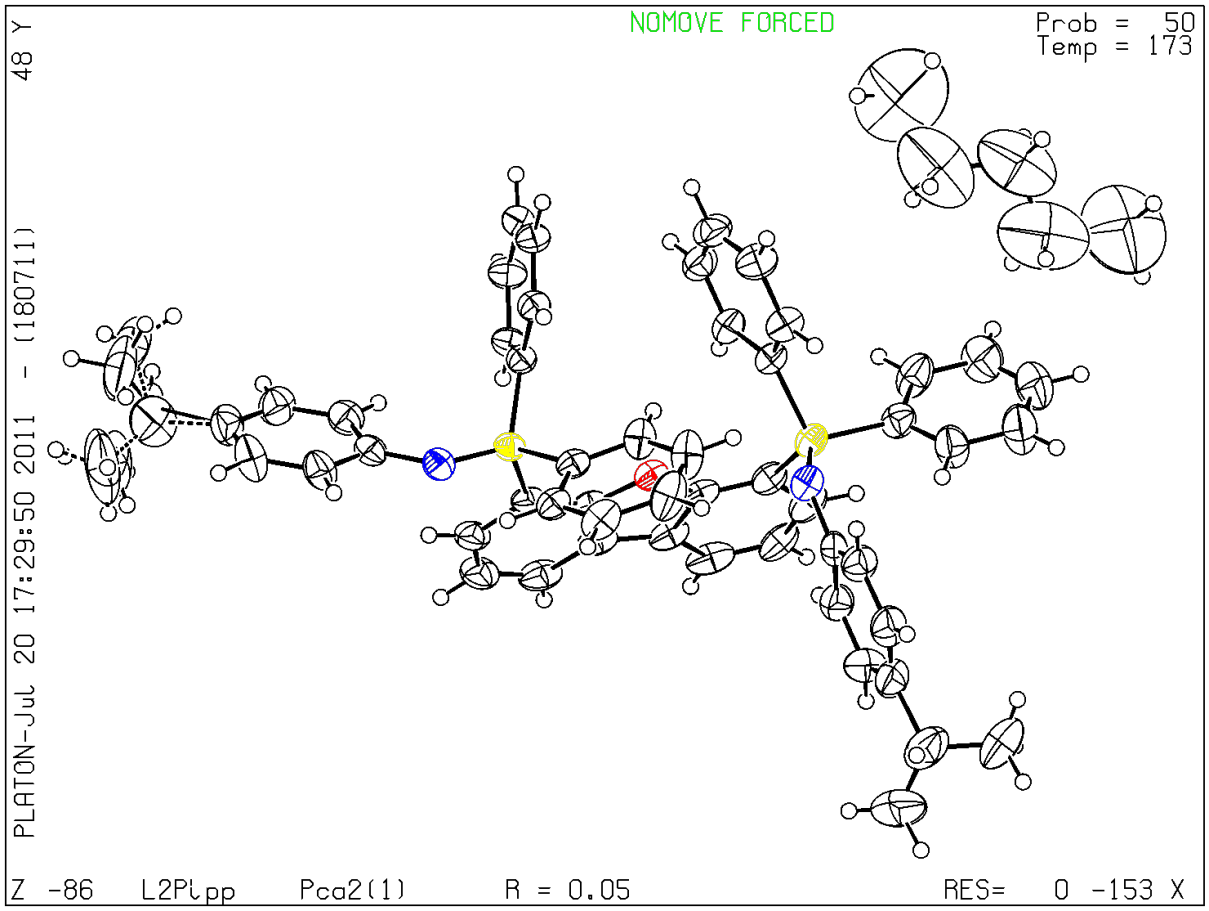
Datablock L2Mipp - ellipsoid plot



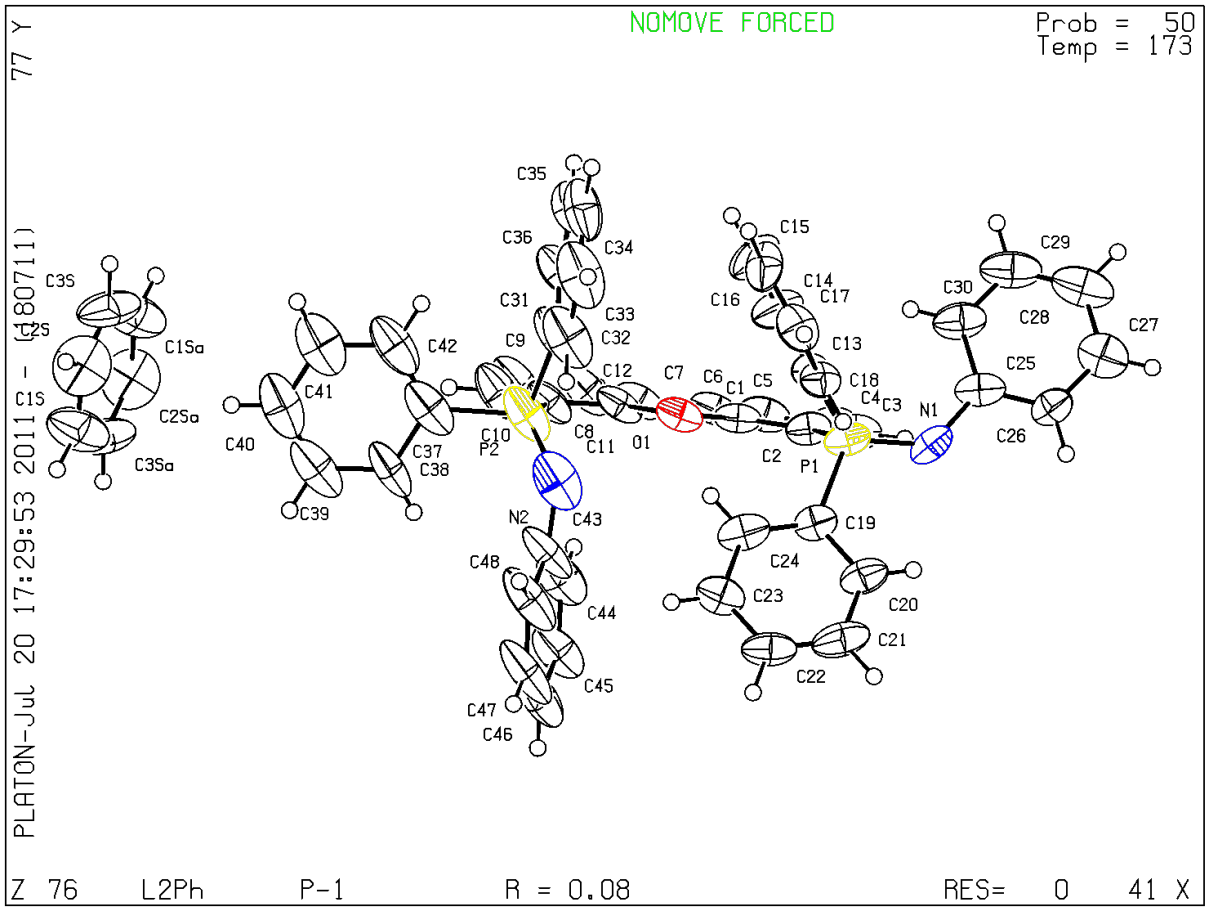
Datablock L2Tol - ellipsoid plot



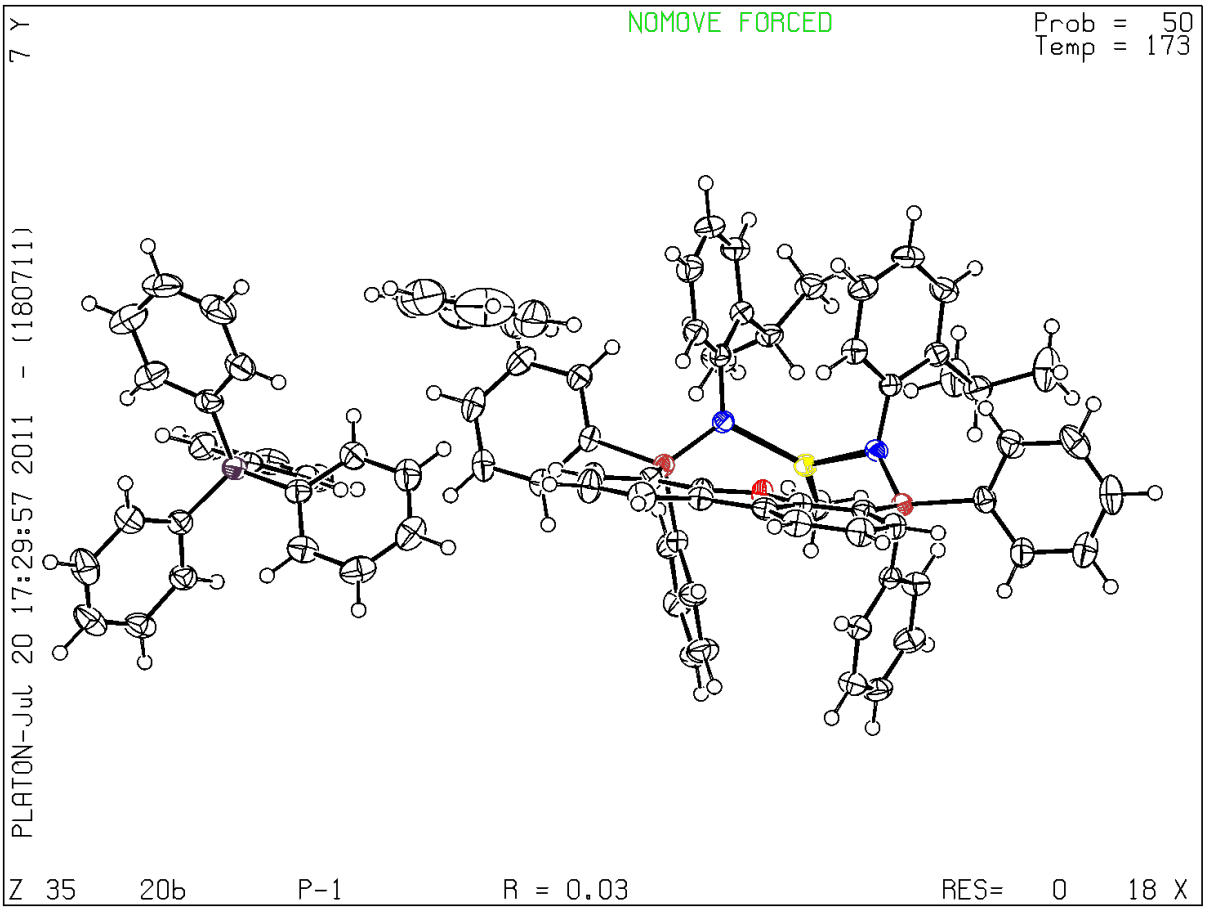
Datablock L2Pipp - ellipsoid plot



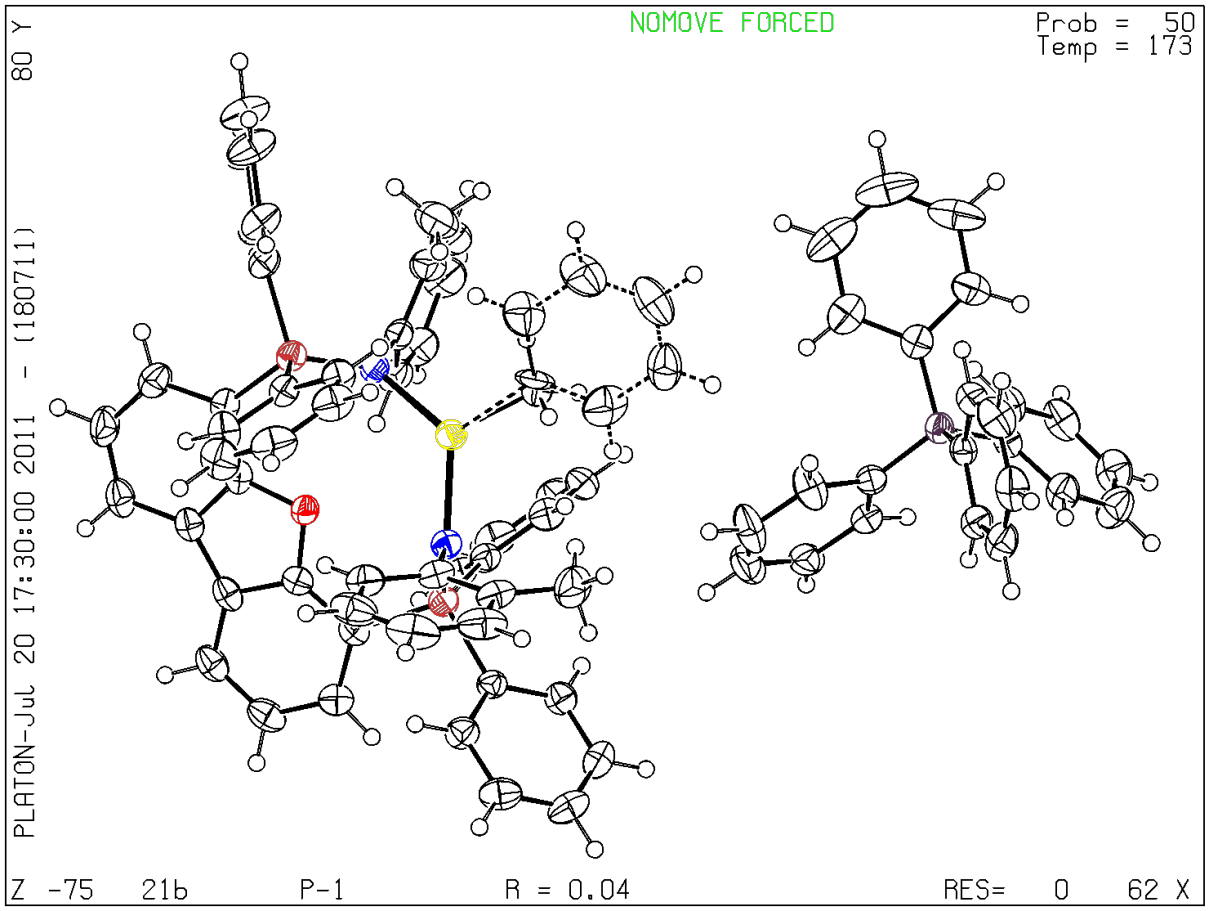
Datablock L2Ph - ellipsoid plot



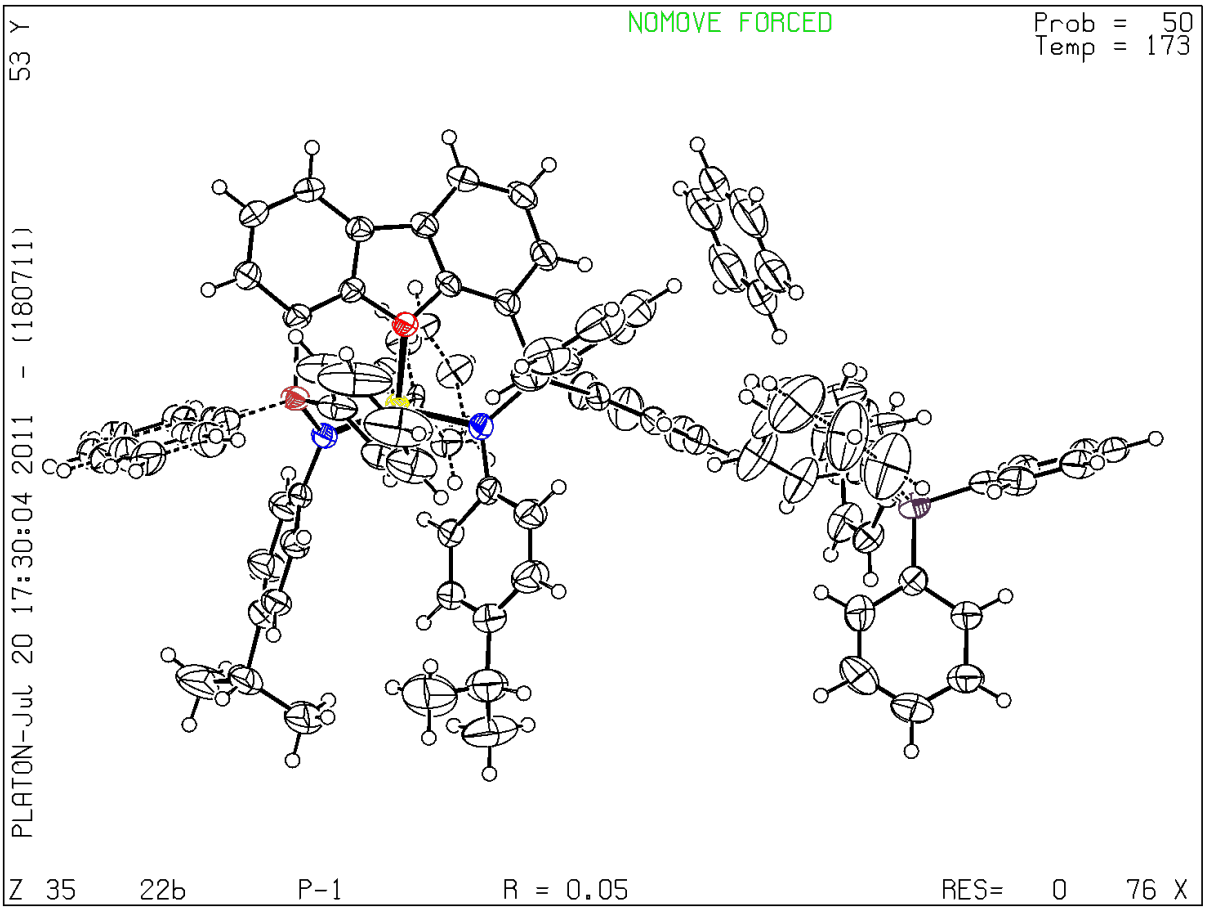
Datablock 20b - ellipsoid plot



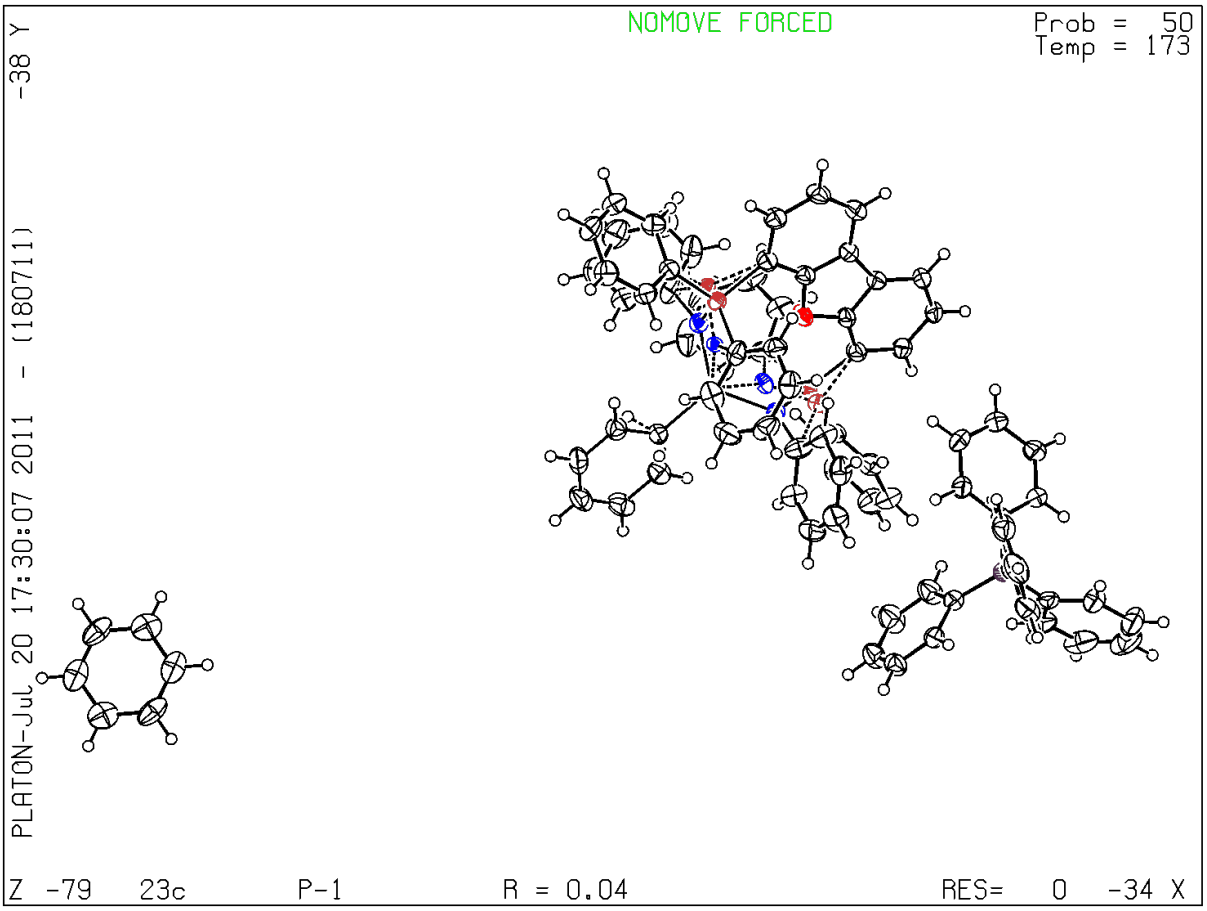
Datablock 21b - ellipsoid plot



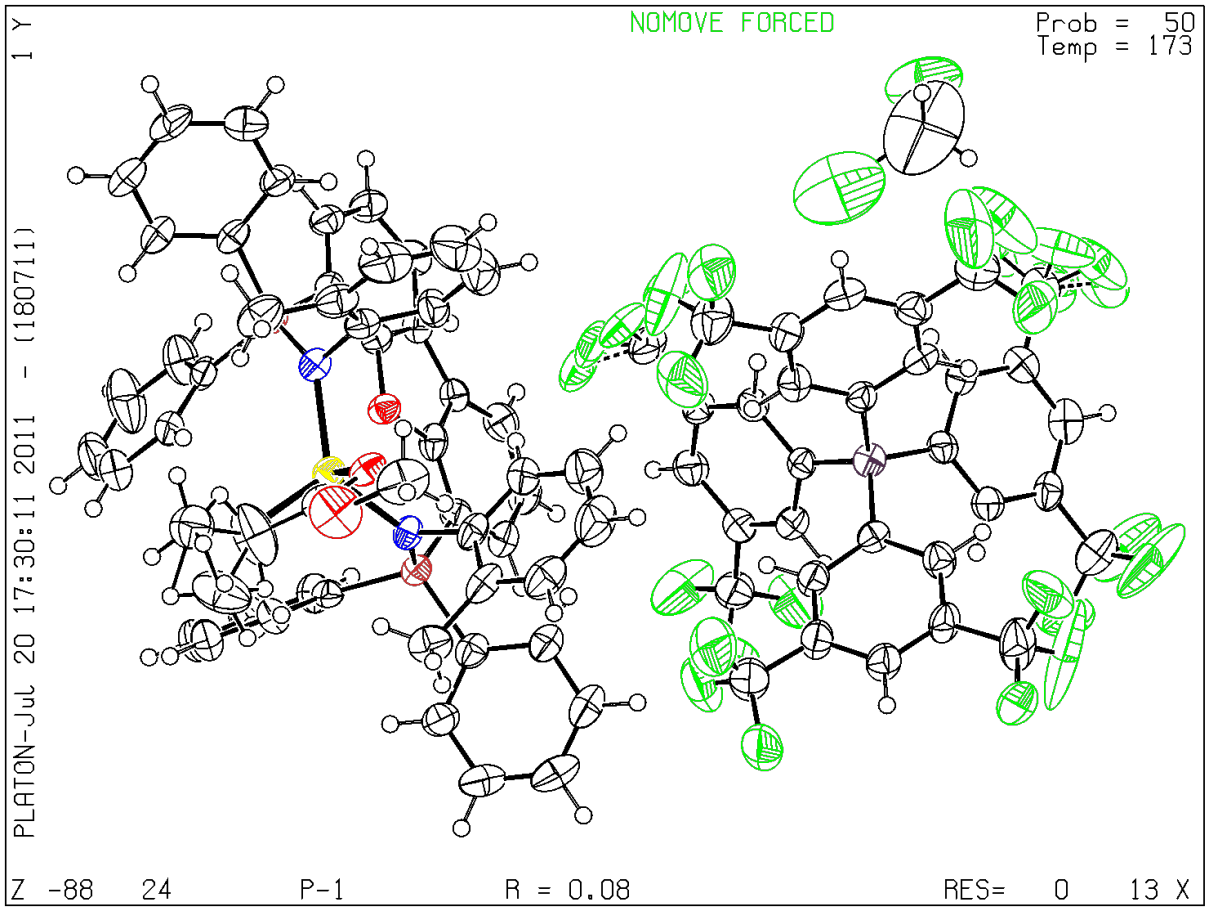
Datablock 22b - ellipsoid plot



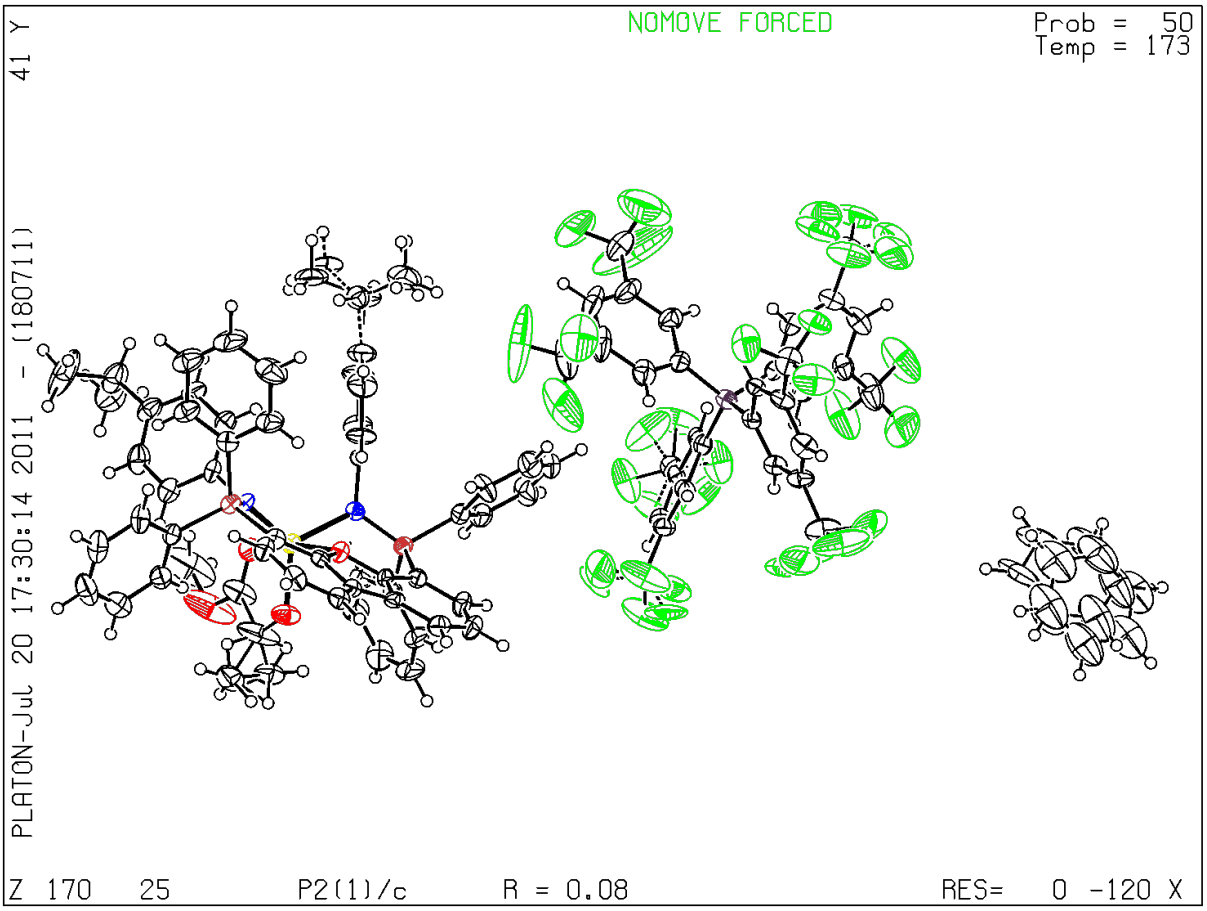
Datablock 23c - ellipsoid plot



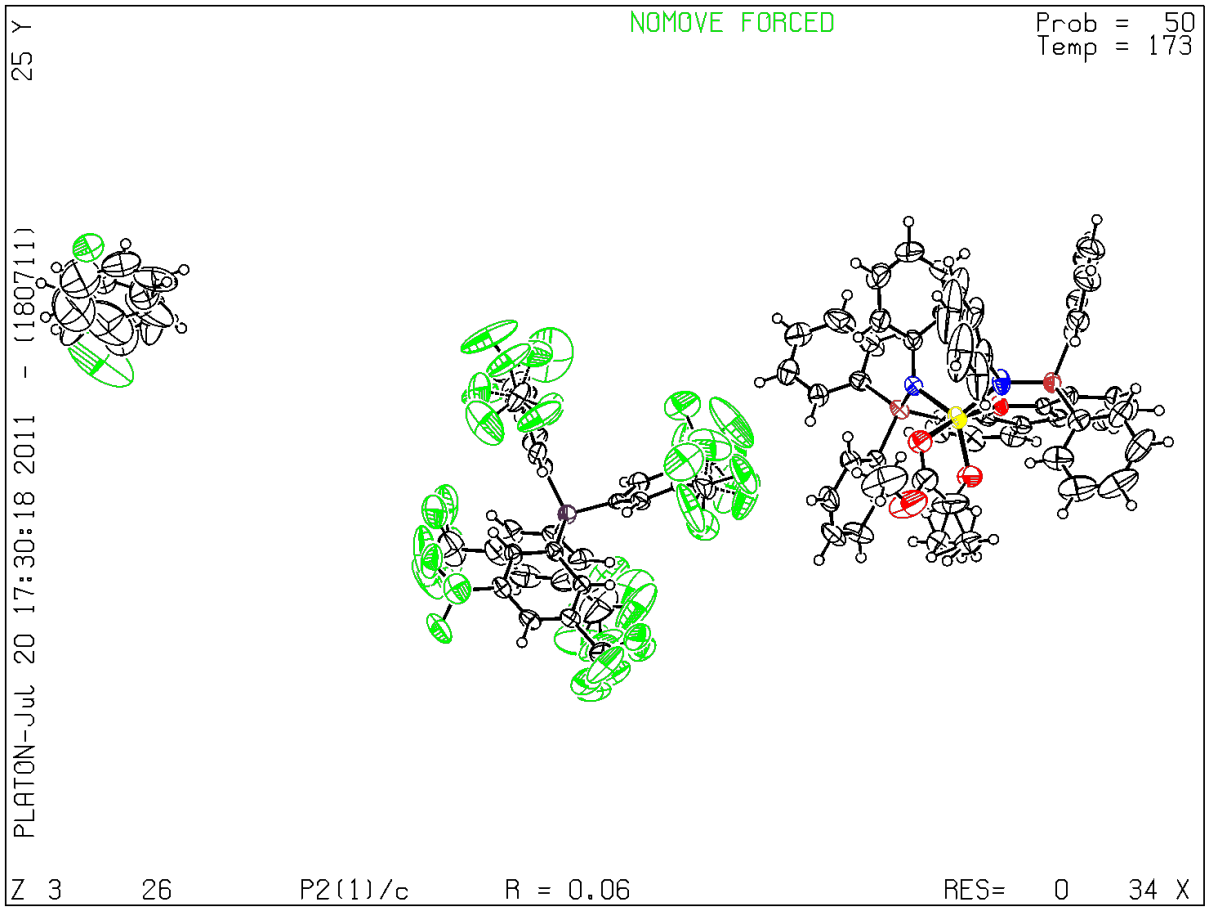
Datablock 24 - ellipsoid plot



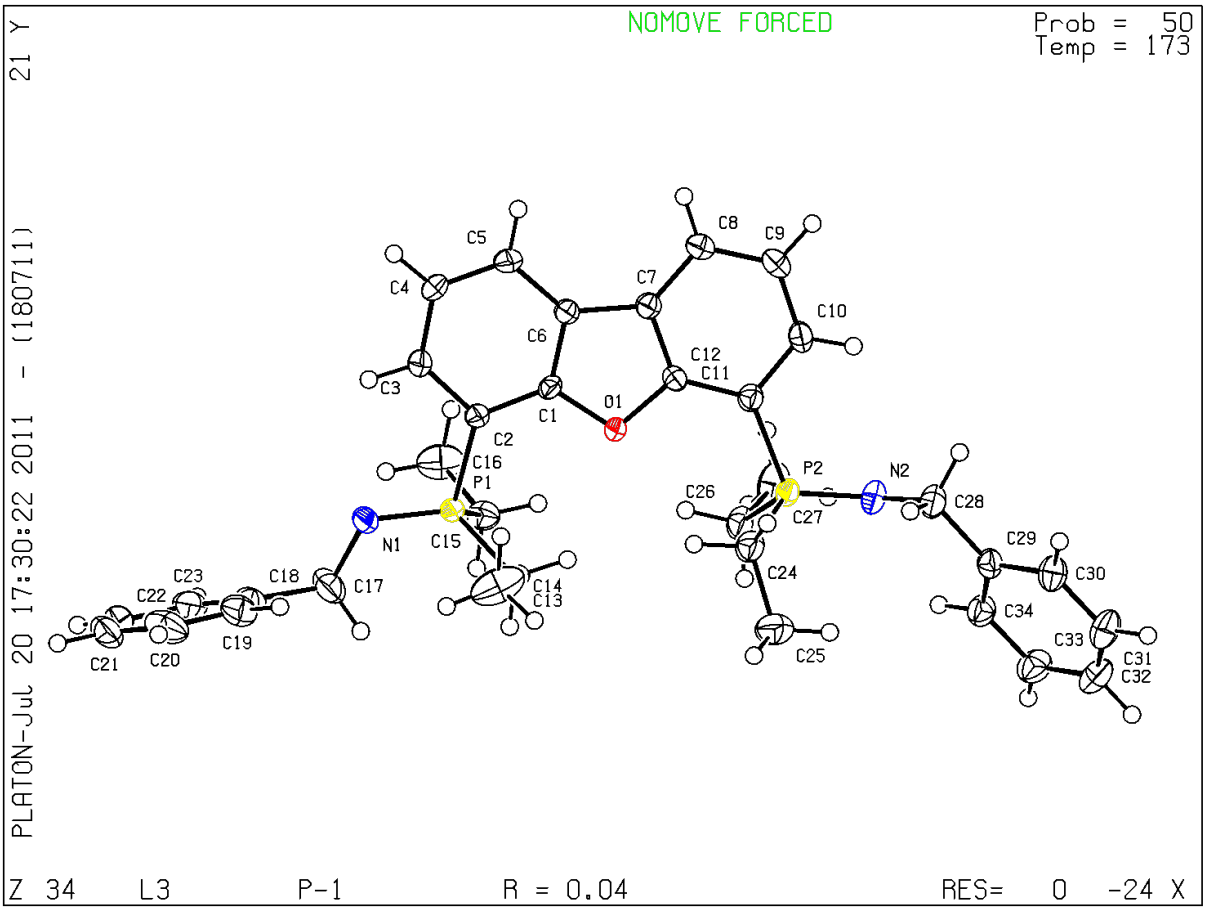
Datablock 25 - ellipsoid plot



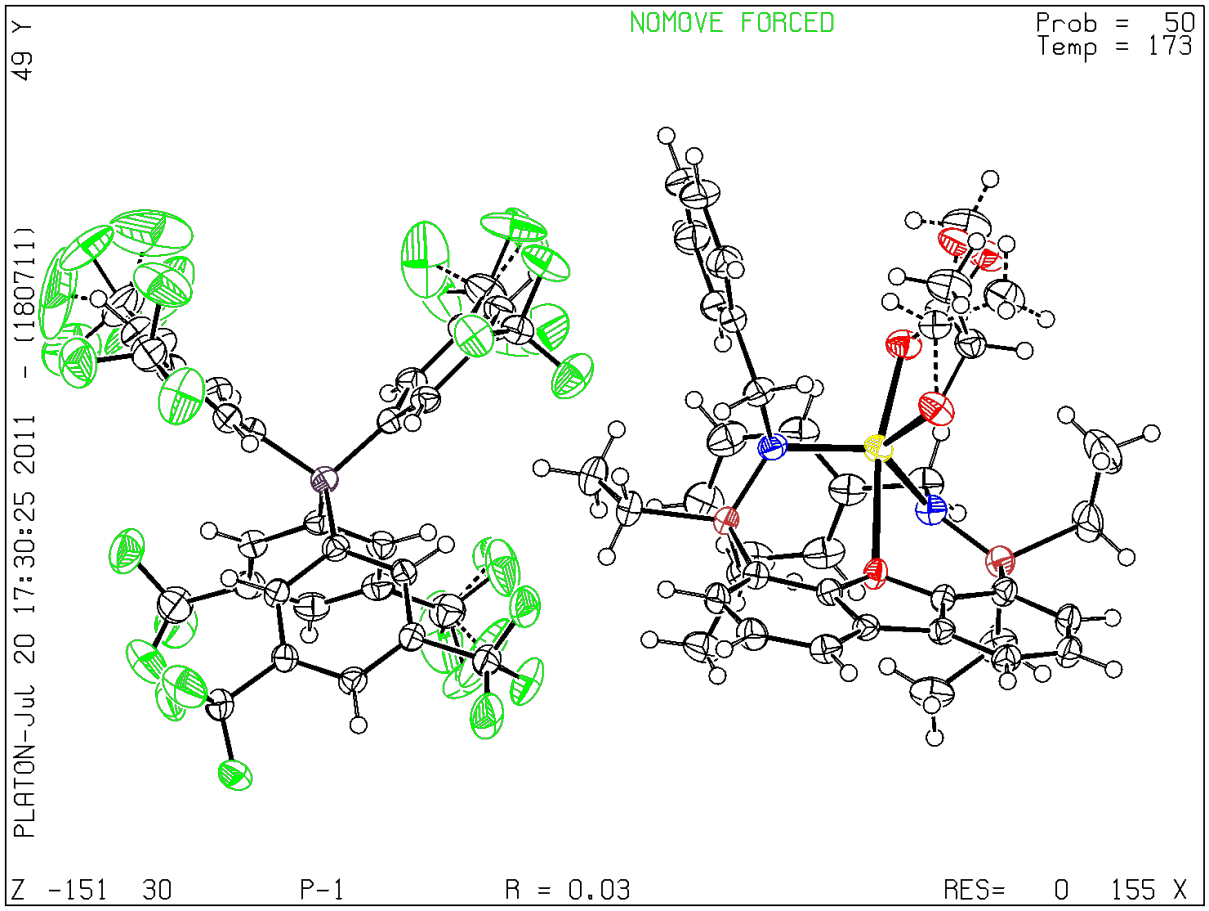
Datablock 26 - ellipsoid plot



Datablock L3 - ellipsoid plot



Datablock 30 - ellipsoid plot



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