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Triamidoamine-supported zirconium: hydrogen activation, Lewis acidity, and rac-lactide polymerization†

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Investigation of a triamidoamine-supported zirconium hydride intermediate, important to a range of catalytic reactions, revealed the potential Lewis acidity of [k5-N,N,N,N,C-(Me3SiNCH2CH2)2NCH2CH2NSiMe2CH2]Zr (1). A preliminary study of 1 as a precursor for the polymerization of rac-lactide showed modest activity but indicated that five-coordinate zirconium complexes with tetra-N donor ligands may be an avenue for further development in group 4 metal lactide polymerization catalysis.

Introduction

The transfer of hydrogen is an essential step impacting a range of catalytic reactions from commodity (e.g., hydrogenation) to specialty chemical synthesis, with broad impact on energy and environmental issues.1,2 It has been observed that hydrogen transfer from triamidoamine-supported zirconium compounds frequently arises from C–H bond activation of a trimethylsilyl substituent. Such cyclometalation reactions are a pivotal step in transformations catalyzed by (N3N)ZrX derivatives including dehydrocoupling, hydrogenation, and heterofunctionalization reactions.3–10 The commonly observed product, [k5-N,N,N,N,N,-(Me3SiNCH2CH2)2NCH2CH2NSiMe2CH2]Zr (1), is therefore a key intermediate in these catalytic reactions. In hydrophosphination, for instance, cyclometalation has been proposed to be the product-elimination step.7 In dehydrocoupling catalysis, H2 loss is proposed from a putative hydride intermediate, (N,N)ZrH (2), via cyclometalation and formation of 1.10 Computational analysis of 2 with respect to related derivatives (e.g., (N,N)ZrMe) has been reported. Based on that analysis, the Zr–H bond dissociation energy of 2 is greater than that calculated for (N,N)ZrMe.9

Hydride compounds of group 4 metals supported by triamidoamine ligands are rare and unstable. Schrock and coworkers previously reported the observation of a titanium(iv) hydride complex, (N2)TiH, with a hydride resonance at δ 8.29 in the 1H NMR spectrum.11 However, the complex was not isolable due to a cyclometalation process involving a trimethylsilyl substituent. In analogous zirconium chemistry, Scott and coworkers reported that a benzyl complex, [N,N′]Zr(CH2Ph) (N,N′=N(CH2CH2NSiMe2Bu)3), reacts with H2 or by sublimation to afford the cyclometalated product [k5-(Me2BuSiNCH2-CH2)2NCH2CH2NSiBuMeCH2]Zr,12 which was the inspiration for the preparation of 1. Notably, the expected hydride intermediate was not observed in those studies. In a later effort to avert cyclometalation, Scott and coworkers replaced the trialkylsilyl ligand substituents with aryl groups, which did not afford the targeted family of tetradentate compounds.13 Interestingly, four coordinate tris(amide) hydride derivatives of group 4 metals are isolable.14

Efforts to better understand compounds 1 and 2 provided evidence of potential Lewis acidity of 1. In an attempt to leverage this behavior, 1 was tested as a pre-catalyst for the polymerization of rac-lactide. These initial studies revealed moderate activity for rac-lactide polymerization. More important, these results demonstrate that lower coordination number triamidoamine-supported zirconium compounds may be a viable catalyst type for lactide polymerizations.

Results and discussion

Reactions with hydrogen and Lewis bases

Reaction of 1 with approximately 3 atm of hydrogen in benzene-d6 solution resulted in the equilibrium formation of (N,N)ZrH (2) and 1 (in an approximate 1 : 2 ratio, eqn (1)). As an average of three trials, an equilibrium constant, Keq = 0.54(2), for the formation of 2 was measured by integration of 3H NMR

**References**

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5. Electronic supplementary information (ESI) available: Plots and spectra from polymerization reactions and X-ray data. CCDC 1471864. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ra15617g
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resonances against an internal standard of ferrocene. The most
telling feature of 2 is the hydride resonance at $\delta$ 10.59 in the $^1$H
NMR spectrum, which is downfield of the resonance observed
by Schrock and coworkers for (N$_3$N)TiH at $\delta$ 8.29 and that for
Cp*$_2$Zr(H)$_2$ at $\delta$ 7.46. An NOE experiment revealed magnetiza-
tion transfer between the hydride resonance and that of
hydrogen gas, illustrating the equilibrium formation of 2 and
confirming the hydride resonance originates from hydrogen
addition (Fig. 1). The small equilibrium formation of 2 is likely
a contributing reason for the limited hydrogenation reactivity of
1 with molecular hydrogen rather than sacrificial donors like
amine boranes.  

![Diagram of structures 1 and 2](image)

Deuteration of the trimethylsilyl substituents of 1 was
successfully accomplished by repeatedly flushing a benzene-$d_6$
solution of 1 with deuterium gas. The reaction was monitored
over 4 days, and 83% of methyl proton intensity was lost from 1,
as measured by $^1$H NMR spectroscopy versus an internal stan-
dard. This value represents exchange of approximately 22 of the
27 hydrogen atoms. Further exposure to deuterium gas did not
result in additional exchange. H/D exchange of this kind is
known for (N$_3$N)Zr compounds, as reported by Scott.  

Mechanistic insight into bond-activations involving complex
1 was sought by reaction with para-hydrogen. However,
treatment of 1 with para-enriched hydrogen gas did not result in
an enhanced polarization. This negative result may indicate
that H$_2$ activation is not a concerted process, but rather,
involves one or more of a variety of other possibilities that
thwart polarization. One of the most intriguing possibilities is
rapid and reversible pre-coordination of H$_2$ at a vacant orbital
on zirconium prior to activation and ring opening. Such metal
interaction can catalyze the redistribution of the para-enriched
hydrogen sample back to a typical distribution of ortho and para
H$_2$. Hence, an effort to substantiate or disprove coordination to
1 without ring opening was undertaken.

Many candidate substrates for coordination to 1 have been
proven incompatible with the reactive metal–carbon bond. For
dexample, nitriles engage in 1,2-insertion reactions too rapidly
to provide evidence of pre-coordination. Accordingly, less reac-
tive ligands were sought. Only via X-ray crystallography was it
unambiguously demonstrated that Lewis bases inert toward
E–H bond activation and insertion could coordinate to zircon-
ium. Recrystallization of 1 from concentrated THF solution at
$-30$ °C afforded X-ray quality crystals of 1·THF (Fig. 2).

The molecular structure of 1·THF features a highly dis-
torted trigonal prismatic geometry with a weak axial amine
interaction to zirconium, Zr–N(4) = 2.4571(14) Å, analogous to
the (N$_3$N)ZrCH$_2$Ph complex by Scott and coworkers featuring
Zr–N$_{axial}$ = 2.548(4) Å as well as the larger family of (N$_3$N)ZrX
and (N$_3$N)ZrX(L) compounds that have been structurally
characterized. The most notable structural feature of
1·THF is the metallacycle, which is highly similar to that in
$[\kappa^5$-(Me$_3$SiNCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NSiMeBuMeCH$_2$]Zr (3). For
example, 1·THF has Zr–C(7) = 2.337(2) Å and N(1)–Zr–C(7) =
71.98(6), which compare favorably to the metallacycle of 3,
Zr–C = 2.613(11) Å and N–Zr–C = 67.8(2), where the shorter
bond length and more open angle are a result of the additional
ligand in 1·THF. Indeed, the Zr–C distance in 1·THF is similar
to Zr–C bonds (2.324(3) and 2.309(3) Å) in six-coordinate Zr
[CH$_2$SiMe$_2$N(SiMe)$_3$]$_2$(dmpe) (dmpe = 1,2-bis(dimethylphos-
phino)ethane).  

The THF of 1·THF is a weakly coordinated ligand as sug-
gested by the long Zr–O contact (Zr–O(1) = 2.3478(14) Å) and
the observed reaction chemistry. For example, extended periods of
reduced pressure quantitatively removed THF from 1·THF in
the solid state, but crystallinity of those samples was lost. NMR

![Molecular structure of 1·THF](image)

**Fig. 1** 1D NOE spectrum of (N$_3$N)ZrH (2) illustrating magnetization transfer to dihydrogen (scale = -1 to 11 ppm).

**Fig. 2** Molecular structure of $[\kappa^5$-N$_3$N,N,N,C-(Me$_3$SiNCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NSiMeBuMeCH$_2$]Zr(THF) (1·THF). Thermal ellipsoids are drawn at the 35% level for optimal viewing. Hydrogen atoms except those on C(7) are omitted for clarity. Selected metrical parameters: Zr–C(7) 2.3373(18), Zr–C(7)–Si(1) 1.850(2), N(1)–Zr–N(2) 1.737(15), Zr–N(1) 2.100(8), Zr–N(2) 2.124(4), Zr–N(3) 2.134(4), Zr–N(4) 2.457(14), Zr–O(1) 2.3478(14), N(1)–Zr–O(1) 108.9(3), N(1)–Zr–N(2) 104.5(2), N(2)–Zr–N(3) 122.03(6), N(1)–Zr–C(7) 71.98(6), N(2)–Zr–C(7) 114.05(7), N(3)–Zr–C(7) 120.76(6), N(1)–Zr–O(1) 152.79(5), N(2)–Zr–O(1) 86.83(5), N(3)–Zr–O(1) 83.96(6), C(7)–Zr–O(1) 81.43(6), C(7)–Zr–N(4) 142.83(6), O(1)–Zr–N(4) 135.71(5).
spectra of complex 1 in the presence of THF, as well as spectra of isolated samples of 1·THF provided little evidence of Lewis base coordination in the solution state because the spectra are identical except for the presence of THF. Effort to establish purity by combustion analysis on isolated, dried samples of 1·THF afforded data consistent with 1 (e.g., found: C, 39.82; H, 8.55; N, 12.10). Regardless, the structure of 1·THF demonstrates coordination at zirconium without ring opening is indeed possible, and suggests that such latent Lewis acidity may reveal new reactivity for the [N,N]Zr fragment.

**rac-Lactide polymerization**

Lactide polymerization was chosen as a test reaction that might take advantage of the Lewis acidity of 1 because Lewis acids are known to polymerize lactide. Interest in biodegradable polymers from renewable precursors such as lactic acid has been tremendous,24 which has fueled global efforts to discover and understand catalysts for these reactions.25 There has been significant attention on group 4 metal compounds in these efforts for their unique reactivity and the relative abundance of metals like titanium and zirconium.26,27 Zirconium compounds supported by triamidoamine ligands have been studied as lactide polymerization catalysts and demonstrated good activities with low PDI values.28,29 For other systems, silyl-substituted amides have not proven an optimal ancillary substituent in this catalysis.26 This observation prompted the omission of an alcohol cocatalyst that might cleave N-Si bonds in this study, and excess alcohol decomposes 1.° Indeed, it is known that excess alcohol will decompose 1 and related derivatives.

Preliminary investigations of 1 for the ring-opening polymerization (ROP) of rac-lactide were undertaken on an NMR scale in toluene-d₈ solution at 70 °C. Using an initial concentration of 0.5 M rac-lactide and either 1% or 4% loading of 1, conversion to poly(lactide) (PLA) was determined by integration of the lactide methine resonance in the ¹H NMR spectra. Under these conditions linear relationships between ln[llactide] and time (pseudo-first-order kinetics) were established revealing observed rate constants of $k_{obs} = 1.61 \times 10^{-5}$ s⁻¹ and $k_{obs} = 3.43 \times 10^{-5}$ s⁻¹ for 100 and 25 equiv. of lactide, respectively. Compared to related zirconium and other group 4 metal initiators, 1 shows only modest activity.26 Importantly, however, these activities were obtained in the absence of a cocatalyst, such as isopropanol or benzyl alcohol.

Polymer samples isolated from ROP experiments were analyzed by gel-permeation chromatography (Table 1). These materials exhibited broad molecular weight distributions (PDI: 1.50–2.53) and substantially larger $M_n$ than calculated. Though the mechanism of polymerization remains unclear, the poor molecular weight control may be due to multiple active species and/or initiator degradation during the polymerization process. Likewise, slow initiation relative to propagation is also consistent with large PDI values and longer than anticipated polymer chains.

These observations confirm that five-coordinate zirconium compounds supported by triamidoamine ligands can effectively initiate the polymerization of rac-lactide. This observation compliments extensive lactide polymerization studies reported by Mountford that demonstrate the triamidoamine framework is an effective support for group 4 metal catalysts in lactide polymerization.28,29 It is, however, important to note that those studies involved zirconium compounds of sulfonyl-substituted derivatives, which are eight-coordinate.28 Interestingly, Mountford’s system exhibits substantially narrower PDI values than those of 1, despite comparable activities for the two systems.

### Conclusions

The triamidoamine-supported zirconium hydride 2 is observable under H₂ pressure in an equilibrium with cyclometalated compound 1. This highly reversible reactivity with hydrogen allows for extensive deuteration of the trimethylethyl substituents of 1 under D₂ gas. In an effort to assess the relative Lewis acidity of 1, an ether adduct 1·THF was crystallographically characterized. Seeking to exploit this Lewis acidity, 1 was tested as an initiator for the ring-opening polymerization of rac-lactide. Compound 1 demonstrated comparable activity to related zirconium pre-catalysts from other researchers, but it provides less molecular-weight control than those systems. Most important, the rac-lactide polymerization activity demonstrated by 1 establishes that five-coordinate tetra-N donor group 4 compounds are a potentially viable class of initiators for further study.

### Experimental section

#### General considerations

Manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using a glove box or standard Schlenk techniques. NMR solvents were degassed and dried by conventional procedures. NMR spectra were recorded with a Varian 500 MHz or a Bruker Avance II NMR spectrometer in benzene-d₆ or toluene-d₈ solution and are reported with reference to the residual solvent resonance. Samples of para-enriched hydrogen were prepared from commercial H₂ using reported methods.17,18 GPC analyses were performed on a Waters 2695 equipped with a Waters 410 refractive index

### Table 1. Molecular weight data for PLA samples prepared using different concentrations of 1 as initiator

<table>
<thead>
<tr>
<th>[LA]₀/[1]</th>
<th>[Cat]</th>
<th>Time (h)</th>
<th>Calc. $M_n$ (×10³)</th>
<th>$M_n$ (×10³)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.020</td>
<td>14</td>
<td>3.4</td>
<td>97.1</td>
<td>245.1</td>
</tr>
<tr>
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<td>113.4</td>
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<tr>
<td>50</td>
<td>0.010</td>
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<td>6.6</td>
<td>56.5</td>
<td>91.3</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>24</td>
<td>6.6</td>
<td>32.7</td>
<td>68.1</td>
</tr>
<tr>
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<td>0.005</td>
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<td>11.6</td>
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</tr>
<tr>
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<tr>
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<td>0.005</td>
<td>24</td>
<td>11.6</td>
<td>34.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>

$^{a}$ [LA]₀ = 0.5 M, toluene, 70 °C. $^{b}$ Calculated using the formula $M_n = ([LA]₀/[1]) \times 144.13 \times$ conversion.
dissolved in minimal THF and was charged with excess D₂ using standard Schlenk techniques. 0.42 (s, 5H, C₁₁) via conversion from instrument.

The reaction proceeded for 4 days and additional D₂ was added. Crystallization of 1 as 1-H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, 1H (500.1 MHz): δ 10.59 (s, 1H, H₁), 3.60 (t, 6H, CH₂), 2.22 (t, 6H, CH₂), 0.31 (s, 36H, CH₃), 1.3C(¹H) (125.8 MHz): δ 62.8 (s, CH₂), 47.5 (s, CH₂), 0.5 (s, CH₃). The ¹H NMR NOE experiment was carried out using the standard Varian pulse sequence.

Polymerization reactions

Kinetic measurements. In a glovebox, an NMR tube was loaded with an appropriate amount of initiator (e.g. 2.2 mg for [LA][0][1] = 100) and 72.1 mg of rac-lactide, to which 0.50 mL of toluene-d₄ was then added. The tube was immediately sealed with a rubber septum, removed from the glove box, and inserted into the temperature stabilized (70 °C) and pre-shimmed spectrometer while data collected.

Polymer preparation. In a glove box with an ambient temperature of approximately 26 °C, a scintillation vial was loaded with 144.1 mg of rac-lactide and an appropriate amount of initiator (e.g. 4.3 mg of 1 for [LA][0][1] = 100). Toluene (1 mL) was added to the vial and the resulting solution was stirred for an appropriate period of time at 70 °C. Afterwards, the vial was removed from the glove box and exposed to the atmosphere. Cold (< −35 °C) wet methanol (10 mL) was added to the solution causing precipitation of the polymer. The vial was centrifuged and the solvent decanted. The isolated polymer was redissolved in 1 mL of CH₂Cl₂ and reprecipitated and isolated by the same procedure. The polymer sample was then dried in vacuo for no less than 24 h.

X-ray crystallography

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å) at 125 K. A suitable crystal of 1·THF, under paratone-N cryoprotectant oil, was mounted using a nylon loop. The structure 1·THF was solved using direct methods and standard difference map techniques with refinement using full-matrix least squares procedures on F² with SHELXTL (version 6.14). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. Extinction was refined to zero and was removed from the refinement. Crystal data and refinement details are presented in Table 2.

Notes and references

1 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus,