Preparation and X-Ray Structure of 4-N,N'-Bis(trimethylsilyl)-amino-3,5-diisopropylphenylselenium Trichloride

Arto Maaninen[a], René T. Boeré*,[b], Tristram Chivers[c], and Masood Parvez[c]

[a] Department of Chemistry, University of Oulu, Linnanmaa, FIN-90570, Finland
[b] Department of Chemistry and Biochemistry, University of Lethbridge,
Lethbridge, Alberta, Canada T1K 3M4
[c] Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

* Reprint requests to Prof. Dr. R. T. Boeré. Fax: 001-403-329-2057. E-mail: boere@uleth.ca

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Crystal Structure, 2,6-Diisopropylaniline, Aryl Selenium Trichloride, Bridging Chloride, NMR Data

The reaction of $SeCl_4$ or $SeCl_2$ with *N,N'*-bis(trimethylsilyl)-2,6-diisopropylaniline occurs not at the nitrogen atom but by electrophilic aromatic substitution at C-4 of the phenyl ring to give $[(CH_3)_3Si]_2NC_6H_2(^iPr_2)SeCl_3$, which crystallizes as the chloro-bridged dimer in the triclinic system, space group $P\bar{1}$, a = 10.2598(17), b = 13.665(3), c = 9.7838(10) Å, α = 90.056(13), β = 102.439(11), γ = 70.922(14)°, V = 1262.3(4) Å^3, Z = 1. The dimer contains an essentially planar $Cl_2Se(\mu\text{-}Cl)_2SeCl_2$ unit, with *trans* apical $(Me_3Si)_2NC_6H_2(^iPr)_2$ groups, resulting in approximately square pyramidal geometry at Se. The bridging Se-Cl distances are unequal at 2.587(2) and 2.749(2) Å.

Introduction

The reactions of selenium halides, in particular $SeCl_2$, with primary amines are being investigated in our laboratories [1]. The preparation of cyclic or linear selenium imides is one goal of this research. We have examined the reactions of a number of amines and their trimethylsilylated derivatives, and find that the silylated analogues give cleaner reactions, presumably because of the absence of side reactions due to generated HCl. 2,6-Diisopropylaniline ($DipNH_2$) is a sterically congested primary amine, which may be expected to produce unusual selenium imide structures compared to the less bulky amines investigated so far. Although the monosilylated N-trimethylsilyl-2,6-diisopropylaniline has been reported [2], and its lithium derivative has been prepared and structurally characterized [3], the fully silylated analogue has not been reported to our knowledge. In this work we report on the preparation of *N,N'*-bis(trimethylsilyl)-2,6-diisopropylaniline (**1**) and studies of its reactions with $SeCl_2$ and $SeCl_4$. The initial product of the reaction with $SeCl_4$ is a yellow crystalline solid $[(CH_3)_3Si]_2NC_6H_2(^iPr_2)SeCl_3$ (**2**), shown by crystallography to have an $SeCl_3$ group at the C-4 position of the aromatic ring. The structure of **2** is only the third reported for $RSeCl_3$ compounds, each of which has a different type of dimeric structure.

Results and Discussion

The silylated aniline was prepared in a straightforward manner from the corresponding aniline using two equivalents of nBuLi, followed by refluxing the anilide with excess $ClSi(CH_3)_3$ in diethyl ether, according to (1) and (2).

$$DipNH_2 + 2\ n\text{BuLi} \rightarrow [Li^+]_2DipN^{2-} \quad (1)$$

$$[Li^+]_2DipN^{2-} + 2\ ClSi(CH_3)_3 \rightarrow DipN[Si(CH_3)_3]_2 + 2\ LiCl \quad (2)$$

$DipN[Si(CH_3)_3]_2$ (**1**) is easily purified by vacuum sublimation to give colourless crystals that have been fully characterized by elemental analysis, mass spectrometry and solution NMR. The structure of **1** has been calculated using AM1 semi-empirical MO techniques, and is presented with relevant MO's in Fig. 1. Of particular note is the perpendicular orientation of the aromatic ring to the Si-N-Si plane. This structural feature is also found in the crystal structure of **2**. A co-planar structure, which is predicted by AM1 calculations for the parent $DipNH_2$, is not stable to structure minimization for **1**, but a

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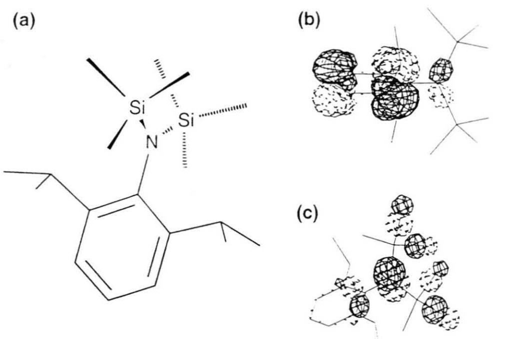

Fig. 1. (a) Line drawing of AM1 calculated structure of **1** and topological sketch of (b) the HOMO and (c) the HOMO-3 orbitals, the latter corresponding to the "nitrogen lone pair".

static calculation places it several hundred kJ mol^{-1} higher in energy than the perpendicular form. The origin of this conformational preference seems to be steric crowding by the 2,6-diisopropyl groups. As a consequence the HOMO of **1** is one of the occupied π-orbitals of the aromatic ring, rather than the nitrogen atom lone pair. The planar N p_z orbital is fully delocalized into the Si-C anti-bonding orbitals in an MO that is highly reminiscent of the HOMO of $N[Si(CH_3)_3]_3$, and is the third-highest orbital in the stack, located 0.46 eV below the HOMO.

The $SeCl_3$ derivative **2** was first obtained from a reaction of **1** with $SeCl_2$, which implies that $SeCl_2$ disproportionates into $SeCl_4$ and Se_2Cl_2 under the reaction conditions. Indeed, the concomitant formation of Se_2Cl_2 is evidenced by a peak at δ 1279 in the ^{77}Se NMR spectrum in CH_2Cl_2 solution (*cf.* δ 1279.5 in the same solvent relative to external $(CH_3)_2Se$) [4]. The ^{77}Se NMR spectrum of **2** displays a peak at δ 940. The same product was obtained more cleanly when $SeCl_4$ was used instead of $SeCl_2$. The ^{1}H NMR spectrum of **2** revealed that the $Si(CH_3)_2$ groups have been retained, and the single aromatic resonance integrating to 2H suggested that *para* substitution of the aromatic ring has taken place. Slow crystallization of **2** from pentane provided X-ray quality crystals, and the crystal structure confirmed that electrophilic aromatic substitution has occurred to give 4-N,N'-bis(trimethylsilyl)-amino-3,5-diisopropylphenylselenium trichloride:

$$\begin{aligned}&\mathrm{DipN[Si(CH_3)_3]_2 + SeCl_4}\\ &\rightarrow \mathrm{[(CH_3)_3Si]_2NC_6H_2(^{i}Pr_2)SeCl_3 + HCl.} \qquad (3)\end{aligned}$$

In the solid state at 25 °C and in CH_2Cl_2 solution, even at –20 °C, the trichloride **2** decomposes to give the corresponding monochloride, $[(CH_3)_3Si]_2NC_6H_2(^iPr_2)SeCl$ (**3**):

$$\begin{aligned}&\mathrm{[(CH_3)_3Si]_2NC_6H_2(^{i}Pr_2)SeCl_3}\\ &\rightarrow \mathrm{[(CH_3)_3Si]_2NC_6H_2(^{i}Pr_2)SeCl + Cl_2.} \qquad (4)\end{aligned}$$

Although both $TeCl_4$ and $SeCl_4$ undergo *para*-directed electrophilic aromatic substitution in reactions with $CH_3OC_6H_5$ to give 4-$CH_3OC_6H_5TeCl_3$ [5] and (4-$CH_3OC_6H_5)_2SeCl_2$ [6], respectively, the preference for this reaction pathway over Si-N bond cleavage with **1** was unexpected. A reasonable explanation for this preference is the fact that the N lone-pair orbital of **1** (Fig. 1c) is buried below the two higher lying π orbitals of the aromatic ring, one of which is the HOMO (Fig. 1b). The AM1 calculations show that the highest charge density on the aromatic ring is at C-4. Normally, amino groups are *o,p*-directing (leading to substitution at C-4, as observed), while alkyl groups are also *o,p* directors, but of weaker activating character (consistent with non-substitution at C-3,5). However, most of the activating character of the amino group is usually attributed to π-delocalization into the N lone pair orbital. This mechanism cannot operate in **1** because of its twisted structure. It is known, however, that large alkyl substituents can exert considerable steric influence over the regioselectivity of electrophilic aromatic substitution. Certainly in the crystal structure of **2** (see below) the isopropyl groups overhang the two *meta* sites of the substituted benzene ring.

In the solid state, **2** exists as a chloro-bridged dimer (Fig. 2 and Table I). In a tetra-substituted $RSe^{(IV)}X_3$ derivative the geometry at Se is expected to be trigonal bipyramidal with the aryl ring in one of the equatorial sites. However, in the dimer there is an essentially planar $Cl_2Se(\mu\text{-}Cl)_2SeCl_2$ unit with *trans* apical $(Me_3Si)_2NC_6H_2(^iPr)_2$ groups, resulting in an approximately square pyramidal geometry at Se. The central $(\mu\text{-}Cl)_2$ bridge is unsymmetrical, with short and long Se-Cl distances of 2.587(2) and 2.749(2) Å. Although $ArSeCl_3$ compounds are well-known [7 and references therein], there are only two for which structures are listed in the Cambridge Crystallographic Database (Fig. 3) [8]. Both **4** and **5** have folded $Se(\mu\text{-}Cl)_2Se$ units. In **4** the Se-C bonds are arranged *cis* and inward-pointing, as required by the *ortho*-disubstituted benzene ring [9], whereas in

Table I. Selected bond lengths (Å) and angles (deg) for **2**.

Bond lengths:			
Se(1)-Cl(1)	2.206(2)	Se(1)-Cl(2)	2.257(2)
Se(1)-Cl(3)	2.587(2)	Se(1)-Cl(3*)	2.749(2)
Se(1)-C(4)	1.955(6)	Si(1)-N(1)	1.764(5)
Si(2)-N(1)	1.736(5)	Si(1)-C(13)	1.868(7)
Si(1)-C(14)	1.861(8)	Si(1)-C(15)	1.834(8)
Si(2)-C(16)	1.858(8)	Si(2)-C(17)	1.855(8)
Si(2)-C(18)	1.851(8)	N(1)-C(1)	1.442(7)
Bond angles:			
Cl(1)-Se(1)-Cl(2)	93.79(9)	Cl(1)-Se(1)-Cl(3)	89.67(9)
Cl(1)-Se(1)-Cl(3*)	170.61(8)	Cl(1)-Se(1)-C(4)	96.3(2)
Cl(2)-Se(1)-Cl(3)	175.39(9)	Cl(2)-Se(1)-Cl(3*)	90.73(8)
Cl(2)-Se(1)-C(4)	92.7(2)	Cl(3)-Se(1)-Cl(3*)	85.42(7)
Cl(3)-Se(1)-C(4)	90.0(2)	Cl(3*)-Se(1)-C(4)	91.7(2)
Se(1)-Cl(3)-Se(1)	94.58(7)	Si(1)-N(1)-Si(2)	124.5(3)
Si(1)-N(1)-C(1)	117.0(4)	Si(2)-N(1)-C(1)	118.5(4)
Se(1)-C(4)-C(3)	119.0(5)	Se(1)-C(4)-C(5)	118.8(5)

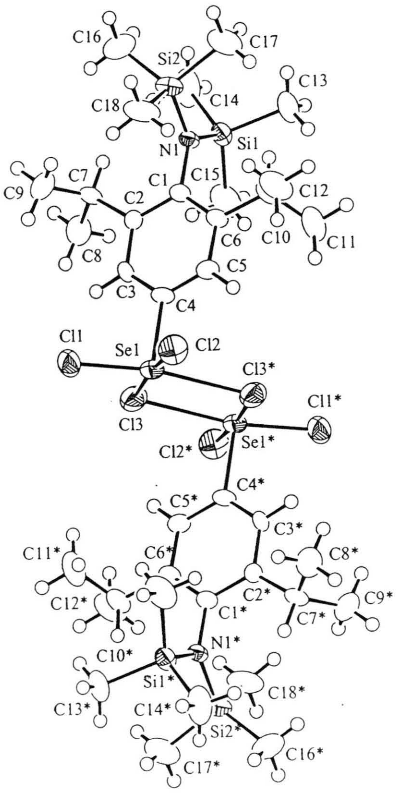

Fig. 2. ORTEP drawing of the dimeric structure of **2**.

5 the *cis* CF_3 groups point outward [10]. In **4**, the distances to the bridging Cl atoms are also unequal at 2.497(3) and 2.697(4) Å, on average 0.07 Å shorter than in **2**, which may be attributed to the constraint of the benzene backbone in **4**. The bridge in **5** is symmetrical on one side (Se-Cl distances 2.65(2) Å) and asymmetrical on the other (2.51(2), 2.75(2) Å), but on average they are only marginally shorter than in **2**. The iminophosphine derivative $Ph_3P=NSeCl_3$ (**6**) exhibits a dimeric structure similar to that of **2** in the solid state [11]. The $Ph_3P=N$ groups are in *trans* positions and the bridging Se-Cl distances in the almost planar $Cl_2Se(\mu\text{-}Cl)_2SeCl_2$ unit are 2.634(2) and 2.983(2) Å.

There are numerous $ArTeCl_3$ structures in the literature. The structural motifs observed are indicated by representative examples in Fig. 3. A *trans*-planar structure, very similar to that of **2**, is observed in **7** [12]. Like **2**, this compound crystallizes about an inversion centre, and it is likely that the planar structures of both compounds are determined by crystal symmetry. However, in **7** there are additional long contacts between the Te and Cl atoms of neighbouring dimers, thus completing a roughly octahedral coordination at Te. In **2** such tertiary interactions are prevented by the bulk of the aryl substituent. The other tellurium structural types include polymeric $C_6H_5TeCl_3$ (**8**), which shares the square pyramidal local geometry of **7**, but with approximately linear bridging Cl atoms in an infinite array [13]. In addition there are many examples of compounds internally chelated by aryl groups bearing N, O, S and even Se donor groups, of which **9** is a typical example [14]. Such compounds always crystallize as discrete molecules.

Experimental Section

General

Solvents were dried and distilled twice under an argon atmosphere from P_4O_{10} (dichloromethane and pentane) and sodium/benzophenone (ether). All reactions and the manipulations of air- and moisture-sensitive reagents were carried out under an argon atmosphere passed through P_4O_{10}. $DipNH_2$, $ClSiMe_3$ (Aldrich) and selenium tetrachloride (Alfa) were used without further purification. ^1H, ^{13}C and ^{77}Se NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400.135, 100.614 and 76.312 MHz, respectively. The spectral widths were 4.50, 23.81 and 100.00 kHz, yielding the respective resolutions of 0.55, 1.45 and 6.10 Hz/data point. The ^1H pulse width was 3.0 μs, for ^{13}C 3.5 μs and for ^{77}Se 9.0 μs. The ^1H accumulations contained 16, ^{13}C 400 - 1000 and ^{77}Se 5000 - 30000 transients. Relaxation times used were: ^1H 0 s, ^{13}C 5.0 s and ^{77}Se 2.0 s. The ^1H and ^{13}C chemical shifts δ [ppm] are referenced to TMS. The ^{77}Se

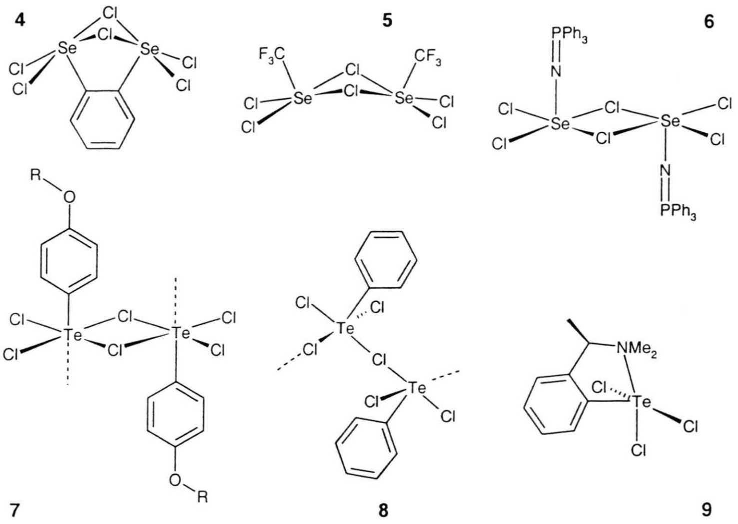

Fig. 3. Structural motifs of $RSeCl_3$ and $RTeCl_3$ as determined by X-ray crystallography.

Table II. Crystal data for **2**.

Formula	$C_{36}H_{68}N_4Cl_6Si_4Se_2$
Fw.	1039.94
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a [Å]	10.2598(10)
b [Å]	13.665(3)
c [Å]	9.7838(10)
α [deg]	90.056(13)
β [deg]	102.439(11)
γ [deg]	70.922(14)
V [Å^3]	1262.3(4)
Z	1
d_{calc} [g cm^{-3}]	1.368
Crystal dim. [mm]	0.40×0.35×0.30
Cell detn, refl	24
Cell detn, 2θ range, [deg]	18.5 - 24.5
Radiation, MoK_α [Å]	0.71069
Temperature [K]	170
μ [cm^{-1}]	18.91
Absorption correction	empirical
Absorptions, range	0.9385 - 1.0000
Total reflections	4735
Unique reflections	4461
Data with $I > 3\sigma(I)$	2256
Parameters refined	226
R; R_w	0.045; 0.036
GOF	1.91
Largest Δ/σ	0.01
Final diff. map [e Å^{-3}]	0.53, –0.47
F(000)	538

chemical shifts were measured relative to external SeO_2 (saturated aqueous solutions), but are reported relative to neat Me_2Se at room temperature $\{\delta(Me_2Se) = \delta(SeO_2) + 1302.6\}$. $CDCl_3$ and CD_2Cl_2 were used as internal ^2H lock solvents. Mass spectra and elemental analyses were undertaken in the Department of Chemistry, University of Calgary and in the Fachbereich Chemie, Universität Kaiserslautern (Germany).

*Preparation of N,N'-bis(trimethylsilyl)-2,6-diisopropylaniline (**1**)*

A solution of 5.0 g (28 mmol) diisopropylaniline in 100 ml of anhydrous diethyl ether was treated with 59.2 mmol of 2.5 M *n*BuLi in hexanes at 0 °C, and stirred for an additional 20 min at the same temperature. 7.66 g (70.5 mmol) $ClSiMe_3$ was added dropwise with stirring. After completion of the addition, the mixture was warmed to room temperature and then heated to reflux for 4 h, whereupon it was hot-filtered, the solvent removed under vacuum and the crude product sublimed (80 °C, 4 $\times$ 10^{-2} mbar) to give the product as colourless crystals, m. p. 141 - 143 °C. Yield: 7.2 g, 22 mmol, 80%.

Analysis for $C_{18}H_{35}NSi_2$ (321.66)
Calcd C 67.2 H 11.0 N 4.4%,
Found C 67.2 H 10.9 N 4.2%.

^1H NMR ($CDCl_3$): δ 0.11 (s, 18H), 1.21 (d, J(H-H) 6.8 Hz, 12H), 3.49 (sept, J(H-H) 6.8 Hz, 2H), δ 7.07 (m, 3H). ^{13}C NMR: δ 2.79, 25.28, 27.71, 123.76, 124.43, 143.47, 147.24. MS(70eV): *m/z* 306 ($M-CH_3^+$, 100%); 264 ($M-{}^iPr^+$, 20%); 232 ($M-Si[CH_3]_4^+$, 53%); 218 ($M-NSi[CH_3]_4^+$, 75%); 73 ($Si[CH_3]_3^+$, 33%).

*Preparation of 4-N,N'-bis(trimethylsilyl)amino-3,5-diisopropylphenyl selenium trichloride (**2**) and 4-N,N'-bis(trimethylsilyl)amino-3,5-diisopropylphenyl selenium chloride (**3**)*

A solution of **1** (0.643 g, 2.0 mmol) in CH_2Cl_2 was added to a slurry of selenium tetrachloride (0.442 g, 2.0 mmol) in CH_2Cl_2 (10 ml) at room temperature. The reaction mixture was stirred for 2 h, after which the reddish-brown solution was evaporated to dryness. The solid was extracted with pentane, filtered, and the extract cooled to –20 °C to give yellow crystals of **2** suitable for X-ray crystallography. Yield: 0.52 g, 1.0 mmol, 51%. ^1H NMR (CH_2Cl_2/CD_2Cl_2): δ 0.13 (s, 18H), 1.24 (d, J(H-H) 6.6 Hz, 12H), 3.55 (sept, J(H-H) 6.6 Hz, 2H), 7.98 (s, 2H). ^{13}C NMR (CH_2Cl_2/CD_2Cl_2): δ 2.45, 24.78, 28.65, 124.00, 145.03, 149.60. ^{77}Se NMR (CH_2Cl_2/CD_2Cl_2): δ 940 ppm.

Satisfactory CHN analyses for **2** could not be obtained owing to facile decomposition to the corresponding monochloride **3**.

Analysis for $C_{18}H_{34}ClNSeSi_2$ (435.06)
Calcd C 49.69 H 7.87 N 3.22%,
Found C 48.60 H 7.68 N 3.12%.

^1H NMR (CD_2Cl_2): δ 0.08 (s, 18H), 1.17 (d, 12H), 3.45 (sept, 2H), 7.03 (s, 2H). ^{13}C NMR (CD_2Cl_2): δ 2.79, 25.37, 28.00, 124.07, 131.96, 149.73. ^{77}Se NMR (CD_2Cl_2): δ 1060 ppm.

X-ray analysis

The crystal structure of **2** was determined using a Rigaku AFC6S diffractometer. Experimental details are summarized in Table II. The structure was solved by direct methods and expanded using Fourier techniques [15]. The non-hydrogen atoms were refined anisotropically, and the H atoms were constrained to idealized positions (C-H = 0.95 Å). Conventional atomic scattering factors, corrected for anomalous dispersion, were used [16]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 127456. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Electronic structure calculations

All calculations were performed using the AM1 method as implemented in HyperChem 5.1 running on a Pentium II computer under Windows95 [17].

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