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Synthesis and Characterization of Chelating Triamide Complexes of Bismuth and Antimony

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Introduction

Triamides of bismuth and antimony have been proposed as potential MOCVD precursors to thin films of bismuth- or antimony-containing materials.[1−4] The absence of M−C bonds in these precursors is anticipated to minimize carbon incorporation in the resulting films,[2] and the low M−N bond strengths should allow deposition at relatively low temperatures. Indeed, the triamides $M(NMe_2)_3$ (M = Bi, Sb) do exhibit sufficient volatility for the deposition of M_2Te_3 films.[3] In addition, they have been used for the low-temperature synthesis of polycrystalline M_2Te_3 and BiP powders via a solution precipitation method.[3,4] $Bi(NMe_2)_3$ is also light-sensitive,[1] suggesting that facile photolytic Bi−N bond cleavage may make triamides of bismuth suitable photo-CVD precursors.[5]

Despite their potential utility, triamides of bismuth and antimony are relatively rare. Structurally characterized homoleptic triamides of bismuth are limited to $Bi(NMe_2)_3$,[1,6] $Bi(NPh_2)_3$,[7] and $Bi[N(H)C_6H_2{}^tBu_3]_3$,[8] although the syntheses of $Bi[N(Me)SiMe_3]_3$,[9] $Bi(NEt_2)_3$,[10] $Bi(N^nPr_2)_3$,[10] and $Bi[N(SiMe_3)_2]_3$[6,11] have also been reported. $Sb(NMe_2)_3$[12] and $Sb[N(H)C_6H_2{}^tBu_3]_3$[8] are the only known homoleptic triamides of antimony. A few related polyimido anions of antimony[13] and cyclic imido dimers of antimony, $[(Me_2N)Sb(\mu\text{-NDipp})]_2$ (Dipp = 2,6-$^iPr_2C_6H_3$),[14] and of bismuth, $[(DippHN)Bi(\mu\text{-NDipp})]_2$,[15] are also known.

The virtual absence of bismuth and antimony complexes stabilized by chelating amides is surprising, since chelating frameworks may potentially be used in tailoring the thermal, photolytic, and hydrolytic stability of these compounds. Veith and coworkers have reported the chelating diamide complexes $Me_2Si(N^tBu)_2MCl$ and $Me_2Si(N^tBu)_2MW(CO)_3Cp$ (M = Bi, Sb),[16] and Raston's group has reported a bismuth and an antimony complex of the chelating amidoamine $[\{2\text{-}(6\text{-Me})\text{-}C_5H_3N\}NSiMe_3]^-$.[17] The diamidoamine complex $[MeN(CH_2CH_2NSiMe_3)_2]BiCl$ was recently prepared by Bertrand.[18] An antimony complex with chelating triisopropylguanidine mono- and dianions has also been reported.[19] However, we are aware of no complexes of bismuth or antimony containing a chelating tridentate triamido ligand, despite the present interest in chelating triamido and triamidoamine frameworks for coordination to a variety of main group and transition elements.[20,21] Here, we report the synthesis and structural characterization of the first chelating triamido complexes of bismuth and antimony, $Bi[N(^tBu)SiMe_2]_3CH$ (**1**) and $Sb[N(^tBu)SiMe_2]_3CH$ (**2**).

Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Pentane and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. Benzene-d_6 was dried by storage over activated molecular sieves. $HC[Me_2SiN(Li)^tBu]_3$ was prepared as previously described.[22] All other reagents were purchased from Aldrich and used without further purification. Solution NMR spectra were recorded on a Bruker AMX-500 spectrometer using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS. High-resolution mass spectrometric analyses were conducted at the Nebraska Center for Mass Spectrometry. Elemental analyses were performed at Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of $Bi[N(^tBu)SiMe_2]_3CH$ (1). A solution of $HC[Me_2SiN(Li)^tBu]_3$ (0.35 g, 0.84 mmol) in pentane (40 mL) was added dropwise to a stirred solution of $BiCl_3$ (0.30 g, 0.95 mmol) in THF (40 mL) at −55 °C. The temperature was slowly raised to room temperature, and the resulting dark mixture was stirred for 2 days. Volatiles were removed in vacuo, and the resulting residue was extracted with pentane. The extract was filtered through Celite, reduced in volume, and cooled at −20 °C to give clear, colorless crystals of **1** in approximately 50% yield.

^1H NMR (C_6D_6, 500 MHz): δ 1.26 (s, 27H, ^tBu), 0.47 (s, 18H, $SiMe_2$), −0.81 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 55.49

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Table 1. Crystallographic Data for Bi[N(^{t}Bu)SiMe$_2$]$_3$CH (**1**) and Sb[N(^{t}Bu)SiMe$_2$]$_3$CH (**2**)

	1	**2**
formula	$C_{19}H_{46}Si_3N_3Bi$	$C_{19}H_{46}Si_3N_3Sb$
fw	609.83	522.60
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.158(5)	11.120(3)
b, Å	11.003(5)	10.978(3)
c, Å	22.109(8)	22.086(6)
β, deg	99.18(3)	99.07(2)
V, Å^3	2679(1)	2662(1)
Z	4	4
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
ρ_{calcd}, g cm^{-3}	1.512	1.304
μ, cm^{-1}	67.1	11.8
T, K	296(2)	296(2)
R (R_w)^a	0.037 (0.040)	0.031 (0.032)

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$.

(s, C(CH$_3$)$_3$), 36.58 (s, C(CH$_3$)$_3$), 18.59 (s, CH), 10.17 (s, SiMe$_2$). MS (EI) m/z (assignment, relative intensity): 609 (M$^+$, 5), 594 (M$^+$ − CH$_3$, 100). HRMS (EI) m/z for $C_{19}H_{46}Si_3N_3Bi$ (M$^+$): calcd, 609.2803; found, 609.2812. Anal. Calcd for $C_{19}H_{46}Si_3N_3Bi$: C, 37.42; H, 7.60; N, 6.89; Bi, 34.27. Found: C, 37.28; H, 7.23; N, 6.50; Bi, 34.64.

Preparation of Sb[N(^{t}Bu)SiMe$_2$]$_3$CH (2). Equimolar reaction of HC[Me$_2$SiN(Li)^{t}Bu]$_3$ and SbCl$_3$ via the procedure described above gave compound **2** as a colorless, crystalline solid in approximately 50% yield. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 1.33 (s, 27H, ^{t}Bu), 0.42 (s, 18H, SiMe$_2$), −0.87 (s, 1H, CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.5 MHz): δ 55.72 (s, C(CH$_3$)$_3$), 35.38 (s, C(CH$_3$)$_3$), 13.51 (s, CH), 9.56 (s, SiMe$_2$).

X-ray Crystallography. Crystal data and experimental details are listed in Table 1. Data for **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator) using the $\omega-2\theta$ scan technique to a maximum 2θ of 50°. All computations were performed on a Silicon Graphics Iris Indigo workstation utilizing the teXsan crystallographic software package.[23] Data were corrected for Lorentz and polarization effects as well as absorption (ψ scans). No decay correction was necessary. Scattering and anomalous dispersion factors were taken from Cromer and Waber.[24] Structures were refined by full-matrix, least-squares methods based on F minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F)]^{-1}$. The methine hydrogen atom was located from difference maps, while the methyl hydrogen atoms were included as fixed contributions with B set to $1.2B_{eq}$ of the carbon atom to which they were bonded.

A colorless crystal of **1** with dimensions of 0.50 × 0.50 × 0.40 mm was obtained from pentane at −20 °C, mounted on a glass fiber, and used for data collection. The structure was solved by Patterson methods[25] and expanded using Fourier techniques.[26] Of the 5253 reflections measured, 5004 were unique (R_{int} = 0.050). The final residuals for 236 parameters refined against 3507 unique, observed reflections with $I > 3\sigma(I)$ were R = 0.037 and R_w = 0.040. Selected bond lengths and angles for **1** are listed in Table 2, while the ORTEP diagram is shown in Figure 1.

For **2**, 5079 data (4992 unique, R_{int} = 0.028) were collected on a colorless crystal measuring 0.43 × 0.35 × 0.30 mm. The structure was solved by direct methods (SIR 92),[27] and the remaining non-hydrogen atoms (in addition to the C−H hydrogen atom) were located from a series of difference Fourier maps. For the 3707 unique, observed reflections with $I > 3\sigma(I)$ and 236 parameters, the discrepancy indices were R = 0.031 and R_w = 0.032. Selected crystallographic results for **2** are listed in Table 3, while an ORTEP diagram looking down the Sb−CH axis of the structure is shown in Figure 2.

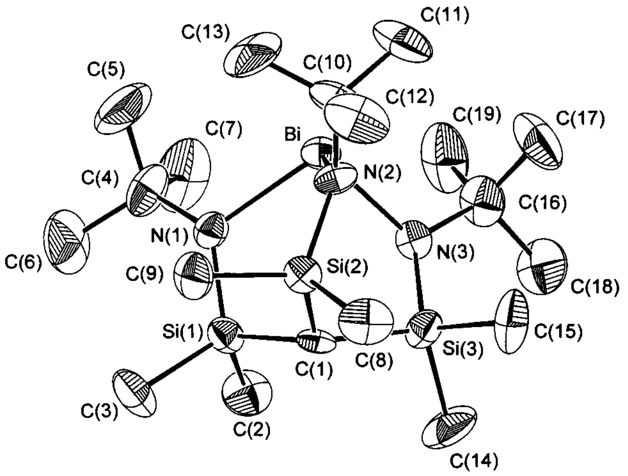

Figure 1. ORTEP drawing of Bi[N(^{t}Bu)SiMe$_2$]$_3$CH (**1**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Bi[N(^{t}Bu)SiMe$_2$]$_3$CH (**1**)

	Distances		
Bi−N(1)	2.162(7)	Si(3)−N(3)	1.739(8)
Bi−N(2)	2.182(7)	Si(1)−C(1)	1.895(9)
Bi−N(3)	2.149(7)	Si(2)−C(1)	1.852(9)
Si(1)−N(1)	1.714(8)	Si(3)−C(1)	1.901(9)
Si(2)−N(2)	1.704(7)		
	Angles		
N(1)−Bi−N(2)	97.5(3)	Bi−N(2)−C(10)	111.5(6)
N(1)−Bi−N(3)	97.2(3)	Bi−N(2)−Si(2)	114.9(4)
N(2)−Bi−N(3)	97.1(3)	Si(2)−N(2)−C(10)	127.7(6)
Bi−N(1)−C(4)	113.0(6)	Bi−N(3)−C(16)	113.7(6)
Bi−N(1)−Si(1)	115.4(4)	Bi−N(3)−Si(3)	114.4(3)
Si(1)−N(1)−C(4)	127.0(7)	Si(3)−N(3)−C(16)	126.4(7)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Sb[N(^{t}Bu)SiMe$_2$]$_3$CH (**2**)

	Distances		
Sb−N(1)	2.052(3)	Si(3)−N(3)	1.728(3)
Sb−N(2)	2.051(3)	Si(1)−C(1)	1.862(4)
Sb−N(3)	2.062(3)	Si(2)−C(1)	1.875(4)
Si(1)−N(1)	1.734(3)	Si(3)−C(1)	1.878(4)
Si(2)−N(2)	1.734(3)		
	Angles		
N(1)−Sb−N(2)	99.3(1)	Sb−N(2)−C(10)	114.7(3)
N(1)−Sb−N(3)	98.8(1)	Sb−N(2)−Si(2)	116.2(2)
N(2)−Sb−N(3)	99.1(1)	Si(2)−N(2)−C(10)	125.1(3)
Sb−N(1)−C(4)	114.9(3)	Sb−N(3)−C(16)	114.2(3)
Sb−N(1)−Si(1)	115.6(2)	Sb−N(3)−Si(3)	115.8(2)
Si(1)−N(1)−C(4)	125.6(3)	Si(3)−N(3)−C(16)	125.9(3)

Results and Discussion

We targeted the synthesis of bismuth and antimony complexes stabilized by chelating triamido ligands. Several known triamido frameworks derived from *cis*-1,3,5-triaminocyclohexane[28,29] and

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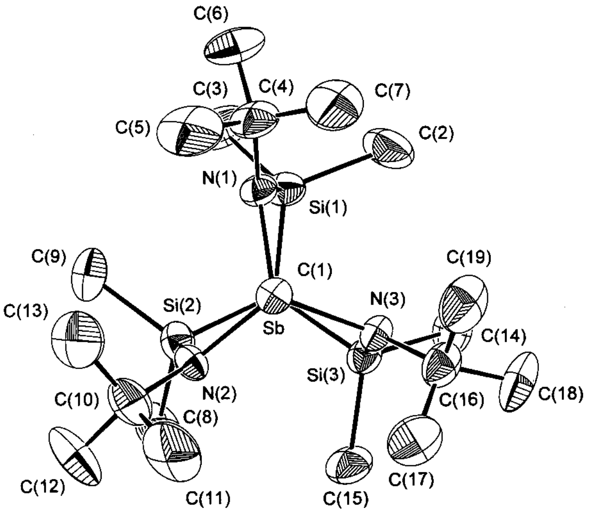
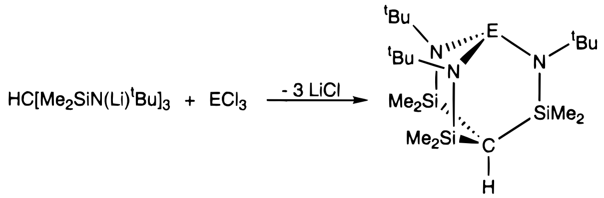


Figure 2. ORTEP drawing looking down the Sb−CH axis of Sb[N(^{t}Bu)SiMe$_2$]$_3$CH (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

1,1,1-tris(aminomethyl)ethane[29,30] were initially contemplated, but after careful consideration of synthetic protocol, we chose HC[Me$_2$SiN(Li)^{t}Bu]$_3$ instead because of its relative ease of preparation without the use of potentially hazardous triazide intermediates. Furthermore, Gade has been successful in synthesizing monomeric complexes of several main group and transition metals using this ligand.[21]

Equimolar reactions of HC[Me$_2$SiN(Li)^{t}Bu]$_3$ with BiCl$_3$ or SbCl$_3$ in THF produced colorless Bi[N(^{t}Bu)SiMe$_2$]$_3$CH (**1**) or Sb[N(^{t}Bu)SiMe$_2$]$_3$CH (**2**), respectively.



(1)

1 E = Bi
2 E = Sb

Although variable, yields were often in the range of 40−50%. Solution NMR spectra (^{1}H, ^{13}C) for each compound exhibit a single resonance for methine, methyl, and *tert*-butyl substituents on the triamido framework, consistent with monomeric complexes of approximate C_3 symmetry. The ^{1}H NMR chemical shifts for **1** and **2** are very similar to those reported by Gade[21a] for the analogous tripodal stannane MeSn[N(^{t}Bu)SiMe$_2$]$_3$CH. Mass spectrometry revealed that **1** is monomeric in the gas phase. Exact mass measurement on the molecular ion, *m*/*z* 609, confirms the molecular formula of **1** to be $C_{19}H_{46}Si_3N_3Bi$. X-ray crystallography confirms that compounds **1** and **2** remain monomeric in the solid state.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure (Figure 1) features a trigonal pyramidal bismuth (sum of angles, 291.8°) coordinated by three amide nitrogens of the triamido framework. Nitrogen atoms deviate slightly from planarity (sums of angles for N(1), N(2), and N(3) are 355.4°, 354.1°, and 354.5°, respectively), as previously observed in Bi(NMe$_2$)$_3$ (sums of angles at N, 347.6° and 353.6°). Bi−N distances for **1** average 2.164 Å and are comparable to the average distances reported for Bi(NMe$_2$)$_3$ (2.185 Å),[1] Bi(NPh$_2$)$_3$ (2.20 Å),[5] and Bi[N(H)C$_6$H$_2$^{t}Bu$_3$]$_3$ (2.18 Å).[6]

X-ray crystallography revealed **2** (Figure 2) to be isostructural to **1**. Compound **2** similarly features a trigonal pyramidal antimony (sum of angles, 297.2°) connected to three nonplanar amide nitrogens (sums of angles for N(1), N(2), and N(3) are 356.1°, 356.0°, and 355.9°, respectively). The Sb−N distances (2.052(3), 2.051(3), and 2.062(3) Å) are comparable to those reported for Sb[N(H)C$_6$H$_2$^{t}Bu$_3$]$_3$ (2.041(6), 2.048(6), 2.064(6) Å). Both **1** and **2** exhibit a helical twist of the triamido framework about the E−CH axis (E = Bi, Sb), as previously observed about the Sn−CN axis of MeSn[N(^{t}Bu)SiMe$_2$]$_3$CH.[21a]

The stabilities of **1** and **2** qualitatively appear slightly greater than those of other homoleptic triamides of bismuth and antimony, which are moisture- and oxygen-sensitive, as well as light-sensitive in the case of Bi(NMe$_2$)$_3$. Although both **1** and **2** undergo facile Bi−N bond cleavage in the presence of moisture, benzene-d_6 solutions of each are stable to dry oxygen for several hours. Furthermore, both compounds can be handled in ordinary room light without observable photolytic decomposition. In fact, NMR spectroscopy showed no decomposition of a crystalline sample of **1** after 14 months in a capped, clear glass vial stored in an inert atmosphere glovebox. Under similar conditions, a sample of **2** showed approximately 20% decomposition over the same time period. Decomposition of **2** is attributed to hydrolysis, since ^{1}H NMR spectroscopy identified [HN(^{t}Bu)SiMe$_2$]$_3$CH as the only observable decomposition product.

Conclusions

The successful synthesis of oxygen- and light-stable **1** and **2** demonstrates that the stability of bismuth and antimony triamides can be increased with chelating triamido frameworks. Although we have not yet investigated the utility of these complexes as precursors to materials by MOCVD or solution precipitation methods, the synthesis of additonal complexes of bismuth and antimony stabilized by triamido frameworks more amenable to these applications appears worthy of future investigation.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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