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Synthesis and Characterization of Potential Single-Source Precursors to Group 13−Antimonides

Ryan A. Baldwin, Edward E. Foos, and Richard L. Wells*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

Peter S. White

Department of Chemistry, Venable Hall, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

Arnold L. Rheingold and Glenn P. A. Yap

Department of Chemistry, Drake Hall, University of Delaware, Newark, Delaware 19716

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The independent 1:1 reactions of Et_3Ga and $(Me_3SiCH_2)_3In$ with $Sb(SiMe_3)_3$ yield the simple Lewis acid−base adducts $Et_3Ga{\cdot}Sb(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3In{\cdot}Sb(SiMe_3)_3$ (**2**), respectively. Reaction of $(Me_3CCH_2)_2GaCl$ or $(Me_3SiCH_2)_2InCl$ with $Sb(SiMe_3)_3$ in a 1:1 mole ratio affords the dehalosilylation products $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ (**3**) and $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$ (**4**), respectively. These new compounds were characterized by multinuclear solution NMR (^1H and ^{13}C), partial elemental analysis, and, for **1**, **2**, and **4**, single crystal X-ray analysis.

Introduction

The bulk of our recent studies in the area of single-source precursors to 13−15 semiconducting materials has focused primarily on group 13−phosphides and −arsenides.[1] This work has led not only to the isolation and characterization of many new potential precursor compounds (*vide supra*) but also to the facile synthesis of nanocrystalline 13−15 materials.[2] A review of this general area, however, reveals that little investigation has been done in the area of group 13−antimonides, especially pertaining to the isolation of potential single-source precursors. In addition, only a handful of compounds containing a gallium or indium atom directly bonded to antimony have been characterized in the solid state.[3−5] In an attempt to explore this uncharted area, we have synthesized and characterized four new compounds containing the group 13−antimony linkage. Herein, we report the synthesis and characterization, including solid-state structures, of $Et_3Ga{\cdot}Sb(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3In{\cdot}Sb(SiMe_3)_3$ (**2**), the first examples of compounds containing group 13−antimony dative bonds to be characterized in the solid state, as well as the compounds $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ (**3**) and $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$ (**4**).

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by standard Schlenk techniques. Pentane, hexane, and toluene were distilled over sodium/potassium alloy under dry dinitrogen. $(Me_3SiCH_2)_3In$,[6] $(Me_3SiCH_2)_2InCl$,[6] $(Me_3CCH_2)_2GaCl$,[7] and $Sb(SiMe_3)_3$[8] were prepared by literature procedures. Et_3Ga was purchased from Aldrich Chemicals and used as received. The integrity of all starting materials was confirmed using ^1H NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity XL-400 spectrometer operating at 400 and 100.6 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or δ 128.0, respectively. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, using capillaries that were flame-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of $Et_3Ga{\cdot}Sb(SiMe_3)_3$ (1). Et_3Ga (0.314 g, 2.00 mmol) in 20 mL of pentane was added to a single-necked 250 mL round-bottomed flask equipped with a stir bar and Teflon valve. $Sb(SiMe_3)_3$ (0.682 g, 2.00 mmol) in 20 mL of pentane was added slowly via pipet, and the clear, colorless solution was stirred overnight at room temperature. The

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* To whom correspondence should be addressed.

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Table 1. Crystallographic Data and Measurements for $Et_3Ga·Sb(SiMe_3)_3$ (1), $(Me_3SiCH_2)_3In·Sb(SiMe_3)_3$ (2), and $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$ (4)

	1	2	4
mol formula	$C_{15}H_{42}GaSbSi_3$	$C_{21}H_{60}InSbSi_6$	$C_{14}H_{40}InSbSi_4$
fw	498.22	717.79	1114.77
cryst syst	monoclinic	trigonal	monoclinic
space group	$P2_1/c$	$R3$	$P2_1/n$
a, Å	15.013(8)	16.509(3)	13.060(3)
b, Å	9.959(8)	16.509(3)	18.738(5)
c, Å	17.025(5)	12.5893(13)	21.8376(21)
β, deg	91.68(3)	90.00(−)	90.443(12)
V, Å^3	2544(3)	2971.5(7)	5343.9(19)
Z	4	3	4
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	22.6	14.53	20.4
temp, °C	−135	25	−135
D_{calcd}, g cm^{-3}	1.301	1.203	1.386
crystal dimens, mm	0.25 × 0.25 × 0.30	0.40 × 0.30 × 0.30	0.25 × 0.25 × 0.20
T_{max}; T_{min}	0.653; 0.470	0.616; 0.443	0.686; 0.424
scan type	ω	ω	ω
$2\theta_{max}$, deg	46	60	46
no. of rflns recorded	3403	3531	8391
no. of nonequiv rflns recorded	3310	2106	7448
R_{merg} (on I)	0.046	0.024	0.029
no. of rflns retained,	1486[a]	2106[b]	5227[a]
no. of params refined	181	88	221
R; R_w[c]	0.074; 0.074	0.029; 0.064	0.103; 0.117
goodness of fit[d]	1.90	1.01	4.51
max shift/esd in final least-squares cycle	0.018	0.001	0.223
final max, min $\Delta\rho$, e Å^{-3}	1.770; −1.210	0.273; −0.421	4.210; −7.810

[a] $I > 2.5\sigma(I)$. [b] $F = 4.0\sigma(F)$. [c] $R = \Sigma(||F_o| - |Fc||)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$. [d] Goodness of fit $= [\Sigma w\Delta^2/(N_{observns} - N_{params})]^{1/2}$.

volatiles were removed *in vacuo* to yield a yellow, waxy solid. Extraction of this solid with a small amount of warm pentane, followed by cooling to −30 °C, produced clear, colorless prismatic crystals of **1**, suitable for X-ray analysis (0.705 g, 71% yield). These crystals quickly redissolved upon warming to room temperature. Mp: 120−125 °C. Anal. Calcd (found) for $C_{15}H_{42}GaSbSi_3$: C, 36.16 (36.11); H, 8.50 (8.42). ^{1}H NMR: δ 0.38 (s, 27H, $-SiMe_3$), δ 0.74 (q, 6H, $-CH_2$), δ 1.42 (t, 9H, $-CH_3$). ^{13}C {^{1}H} NMR: δ 4.26 (s, $-SiMe_3$), δ 7.35 (s, $-CH_2$), δ 12.26 (s, $-CH_3$).

Preparation of $(Me_3SiCH_2)_3In·Sb(SiMe_3)_3$ (2). $(Me_3SiCH_2)_3In$ (0.438 g, 1.16 mmol) was dissolved in 25 mL of pentane and added to a single-necked 250 mL round-bottomed flask fitted with a stir bar and Teflon valve. To this solution was added $Sb(SiMe_3)_3$ (0.398 g, 1.16 mmol) in 25 mL of pentane. The resulting clear, slightly gray solution was stirred at room temperature for 2 d. The volatiles were removed *in vacuo* to yield an off-white crystalline solid, which was extracted with warm pentane. Cooling of the extract to −30 °C afforded clear, colorless crystals of **2** suitable for single-crystal X-ray analysis (0.574 g, 80% yield). Mp: 105−112 °C dec (brown liquid). Anal. Calcd (found) for $C_{21}H_{60}InSbSi_6$: C, 35.11 (35.21); H, 8.42 (8.36). ^{1}H NMR: δ −0.04 (s, 6H, $-CH_2$), δ 0.27 (s, 27H, $-SiMe_3$), δ 0.37 (s, 27H, Me_3SiCH_2-). ^{13}C{^{1}H} NMR: δ 3.14 (s, $-SiMe_3$), δ 4.59 (s, Me_3SiCH_2-), δ 6.31 (s, $-CH_2$). The electron ionization mass spectrum shows peaks for $(C_{11}H_{30}InSi_3)^+$ at m/z 361.1 and $(C_9H_{27}SbSi_3)^+$ at m/z 340.1. These ions correspond to the fragments $(Me_3SiCH_2)_3In$ (with loss of a methyl group) and $Sb(SiMe_3)_3$, respectively.

Preparation of $[(Me_3CCH_2)_2GaSb(SiMe_3)_2]_x$ (3). $(Me_3CCH_2)_2GaCl$ (0.247 g, 1.00 mmol) was dissolved in 15 mL of pentane, and the solution was added to a single-necked 250 mL round-bottomed flask equipped with a stir bar and Teflon valve. $Sb(SiMe_3)_3$ (0.341 g, 1.00 mmol) in 10 mL of pentane was added slowly to the flask via pipet. The resulting clear, colorless solution was stirred at room temperature for 24 h, after which it had taken on a slight yellow color. The volatiles were removed *in vacuo* yielding a dark yellow solid which stuck to the bottom of the flask. Extraction with warm toluene followed by cooling to −30 °C produced clear, colorless crystals of **3** (0.120 g, 25% yield), which began to slowly take on a red-brown color after isolation. This discoloration continued as the crystals were warmed. Mp: 166−172 °C. Anal. Calcd (found) for $C_{16}H_{40}GaSbSi_2$: C, 40.02 (40.33); H, 8.41 (8.60); Sb, 25.35 (24.78). ^{1}H NMR: δ 0.58 (s, 18H, $-SiMe_3$), δ 1.29 (s, 18H, $-CMe_3$), δ 1.47 (s, 4H, $-CH_2$). ^{13}C{^{1}H} NMR: δ 5.01 (s, $-SiMe_3$), δ 5.71 (s, $-CH_2$), δ 34.63 (s, $-CMe_3$). The electron ionization mass spectrum shows a peak for $(C_{16}H_{40}GaSbSi_2)^+$ at m/z 480.1 corresponding to the monomeric unit of **3**.

Preparation of $[(Me_3SiCH_2)_2InSb(SiMe_3)_2]_2$ (4). $(Me_3SiCH_2)_2InCl$ (0.325 g, 1.00 mmol) dissolved in 25 mL of hexane was added to a single-necked 250 mL round-bottomed flask equipped with a stir bar and Teflon valve. $Sb(SiMe_3)_3$ (0.341 g, 1.00 mmol) dissolved in 25 mL of hexane was added to the flask dropwise via pipet, resulting in a clear, light yellow solution which was stirred for 24 h at room temperature. After 24 h, the solution had taken on a deep red color. The solution volume was reduced *in vacuo* and then stored at −30 °C for several days. Small colorless crystals of **4**, suitable for partial X-ray analysis, were isolated (0.167 g, 30% yield). Mp: 157−160 °C dec. Anal. Calcd (found) for $C_{14}H_{40}InSbSi_4$: C, 30.17 (30.24); H, 7.23 (7.51). ^{1}H NMR: δ 0.28 (s, 4H, $-CH_2$), δ 0.31 (s, 18H, $-SiMe_3$), δ 0.56 (s, 18H, Me_3SiCH_2-). ^{13}C{^{1}H} NMR: δ 3.31 (s, $-SiMe_3$), δ 5.78 (s, Me_3SiCH_2-), δ 35.05 (s, $-CH_2$).

X-ray Structure Solution and Refinement. Crystallographic data are summarized in Table 1, while Table 2 lists selected bond lengths and bond angles. The structural analyses were performed as follows:

Compounds 1 and 4. Single crystals of **1** and **4** were mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at −135 °C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counting statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at $R = 0.074$ ($R_w = 0.074$) for **1** and $R = 0.103$ ($R_w = 0.117$) for **4**. A final difference Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[9]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, and 4, with Estimated Standard Deviations in Parentheses

Compound **1**			
Bond Lengths			
Ga(1)−Sb(1)	2.846(5)	Sb(1)−Si(1)	2.570(8)
Ga(1)−C(41)	2.00(3)	Sb(1)−Si(2)	2.557(9)
Ga(1)−C(51)	1.96(3)	Sb(1)−Si(3)	2.569(9)
Ga(1)−C(61)	2.06(3)		
Bond Angles			
Ga(1)−Sb(1)−Si(1)	114.50(22)	Sb(1)−Ga(1)−C(41)	101.7(9)
Ga(1)−Sb(1)−Si(2)	116.10(24)	Sb(1)−Ga(1)−C(51)	99.7(9)
Ga(1)−Sb(1)−Si(3)	115.61(23)	Sb(1)−Ga(1)−C(61)	103.2(8)
Si(1)−Sb(1)−Si(2)	104.3(3)	C(41)−Ga(1)−C(51)	114.5(12)
Si(2)−Sb(1)−Si(3)	102.3(3)	C(51)−Ga(1)−C(61)	117.6(11)
Si(1)−Sb(1)−Si(3)	102.2(3)	C(41)−Ga(1)−C(61)	116.2(11)
Compound **2**			
Bond Lengths			
In−Sb	3.0078(6)	Sb−Si(2)	2.554(2)
In−C(4)	2.208(6)		
Bond Angles			
In−Sb−Si(2)	114.25(5)	Sb−In−C(4)	98.8(2)
Si(2)−Sb−Si(2a)	104.29(6)	C(4)−In−C(4a)	117.71(9)
Compound **4**			
Bond Length (Average)			
In−Sb		2.88	
Bond Angles (Average)			
In−Sb−In	95.2	Sb−In−Sb	84.8

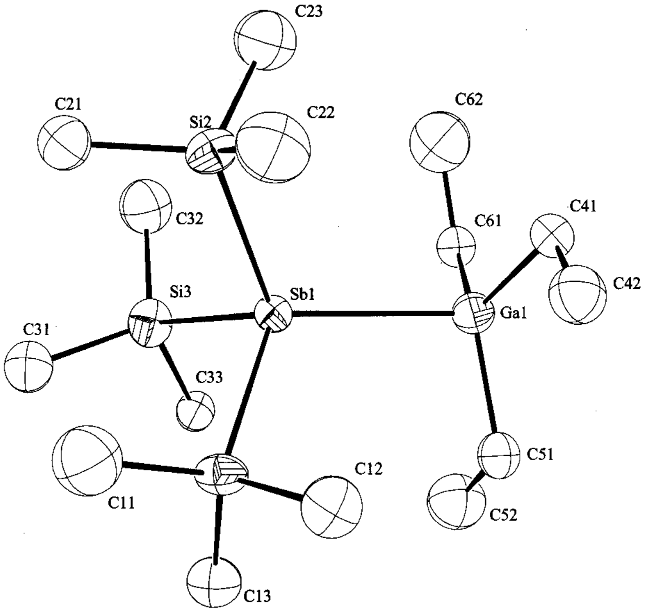

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **1**. Hydrogen atoms are omitted for clarity.

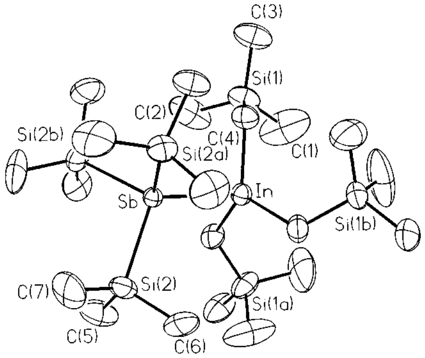

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**. Hydrogen atoms are omitted for clarity.

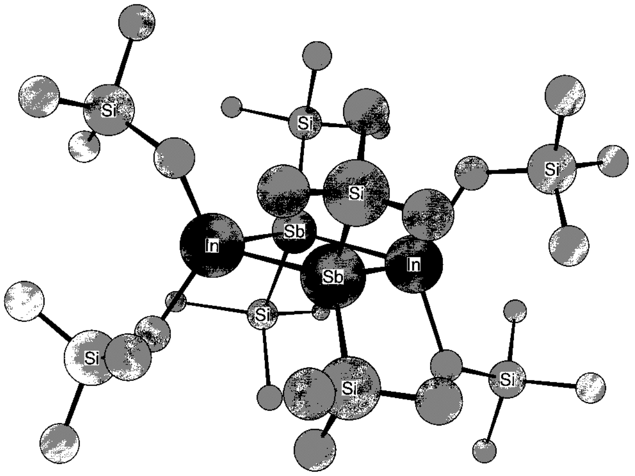

Figure 3. Chem-3D diagram showing the solid-state structure of **4**. Hydrogen atoms are omitted for clarity.

suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 10. An ORTEP[11] diagram showing the solid-state conformation and atom-numbering scheme for **1** is shown in Figure 1, while the Chem-3D plot of **4** is shown in Figure 3. Due to poor crystal quality, a full set of data could not be collected for **4**; hence, comprehensive structural data are not presented here. However, the plot shown in Figure 3 is generated from the partial data set, and the average In−Sb bond lengths and angles are given in Table 2.

Compound 2. Single crystals of **2** suitable for X-ray diffraction were mounted in glass capillaries under argon. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° < 2\theta < 25°$). The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures, yielding $R = 0.029$ ($R_w = 0.064$). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS[12] (4.2) and SHELXTL (5.3) program libraries. An ORTEP diagram showing the solid-state conformation and atom-numbering scheme of **2** is presented in Figure 2.

Results and Discussion

The independent room-temperature reactions of $Sb(SiMe_3)_3$ with Et_3Ga and $(Me_3SiCH_2)_3In$ (1:1) yield the simple Lewis acid−base adducts $Et_3Ga{\cdot}Sb(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3In{\cdot}Sb(SiMe_3)_3$ (**2**), respectively. Both of these compounds have been characterized by ^1H and $^{13}C\{^1H\}$ NMR, partial elemental analysis, and single-crystal X-ray analysis (*vide supra*). To the best of our knowledge, **1** and **2** are the first compounds containing gallium− and indium−antimony dative bonds to be fully characterized in the solid state. In addition, compound

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1 is potentially well suited to serve as a precursor to GaSb, due to the possibility of eliminating the organic substituents through a β-hydride elimination pathway.

The 1:1 mole ratio reactions of $(Me_3CCH_2)_2GaCl$ and $(Me_3SiCH_2)_2InCl$ with $Sb(SiMe_3)_3$ undergo facile room-temperature dehalosilylation to form compounds **3** and **4**, respectively. The identity of these compounds was established through ^1H and $^{13}C\{^1H\}$ NMR, partial elemental analysis, and single-crystal X-ray crystallography (*vide supra*). Unfortunately, crystals of **3** were very unstable and began to discolor when warmed to room temperature. This decomposition likely occurs due to photosensitivity, thermal instability, or a combination of the two. Because of this fact, determination of the oligomerization of **3** through X-ray analysis was not possible, although the monomeric unit of this compound was confirmed by NMR, EA, and EI mass spectral data.

Adduct **1** crystallizes in the monoclinic space group $P2_1/c$. The ethyl and trimethylsilyl substituents adopt a staggered conformation in relation to one another, and the gallium and antimony atoms reside in a distorted-tetrahedral coordination environment. Because this is the first example of a Ga−Sb dative bond to be characterized in the solid state, there is a lack of bond length data available for comparison. The average Ga−Sb bond length of 2.661(2) Å reported for the ring compound $[Cl_2GaSb(t\text{-}Bu)_2]_3$[3] is essentially the same as the value obtained from addition of the covalent radii of Ga and Sb, which is 2.66 Å. The gallium−antimony bond length of 2.846(5) Å in **1** is slightly longer than both the observed length in $[Cl_2GaSb(t\text{-}Bu)_2]_3$ and the calculated value. This is to be expected, however, due to the dative nature of the bond in **1**.

Crystals of compound **2** belong to the trigonal space group $R3$. Once again, the average In−Sb bond length of 2.844(1) Å reported for the ring compound $[(t\text{-}Bu_2Sb)(Cl)In(\mu\text{-}Sb\text{-}t\text{-}Bu_2)]_2$[4] (**5**) compares well with the expected length of 2.84 Å as determined from the covalent radii of indium and antimony. The In−Sb bond length of 3.0078(6) Å in **2** is once again slightly longer due to its dative nature. As in **1**, the ligands on the indium and antimony centers in **2** also adopt a staggered conformation in relation to one another with the indium and antimony atoms existing in distorted-tetrahedral environments.

The dimeric compound **4** crystallizes in the monoclinic space group $P2_1/n$; however, the poor quality of the crystals did not facilitate a complete data set collection. The data set collected did, however, confirm the presence of a planar $\overline{\mathrm{In{-}Sb{-}In{-}Sb}}$ four-membered ring in the molecule. The mean In−Sb bond length of 2.88 Å in **4** compares well with the analogous length found in the previously discussed dimeric compound **5**. The average In−Sb−In and Sb−In−Sb endocyclic ring angles of 95.2 and 84.8°, respectively, compare well with the analogous angle values of 94.93(2) and 85.07(2)° in **5**. These angles also indicate that the $\overline{\mathrm{In{-}Sb{-}In{-}Sb}}$ ring is indeed planar.

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Supporting Information Available: Tables of bond distances, bond angles, and anisotropic temperature factor parameters for **1** and **2** and of fractional coordinates for **1**, **2**, and **4** (9 pages). Ordering information is given on any current masthead page.

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