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Articles

Synthesis and Characterization of *tert*-Butylgallium−Antimony Compounds: X-ray Crystal Structures of t-Bu$_3$Ga·Sb(SiMe$_3$)$_3$, [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$, and t-Bu$_2$$\overline{\text{GaSb(SiMe}_3)_2\text{Ga(}t\text{-Bu)}_2\text{Cl}}$, the First Example of a Gallium−Antimony Mixed-Bridge Compound

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The 1:1 mol ratio reaction of t-Bu$_3$Ga with Sb(SiMe$_3$)$_3$ in hexane yields the expected Lewis acid−base adduct t-Bu$_3$Ga·Sb(SiMe$_3$)$_3$ (**1**). The 1:1 mol ratio dehalosilylation reaction of t-Bu$_2$GaCl with Sb(SiMe$_3$)$_3$ yields the dimeric compound [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (**2**). The mixed-bridge compound t-Bu$_2$$\overline{\text{GaSb(SiMe}_3)_2\text{Ga(}t\text{-Bu)}_2\text{Cl}}$ (**3**) was isolated from both the 2:1 reaction of t-Bu$_2$GaCl with Sb(SiMe$_3$)$_3$ and the 2:1 equilibration of t-Bu$_2$GaCl with **2**. These new gallium−antimony compounds have been characterized through multinuclear solution NMR spectroscopy, partial elemental analysis, and single-crystal X-ray structural analysis. In addition, compound **2** was found to produce nanocrystalline GaSb with an approximate average particle size of 9 nm upon thermolysis at 400 °C under vacuum.

Introduction

The bulk of our recent research into potential precursor compounds to group 13−group 15 materials has focused primarily on group 13 metals and the pnicogens phosphorus and arsenic.[1] These compounds have been isolated largely in the form of 1:1 Lewis acid−base adducts[2] and dimeric compounds containing an $\overline{\text{M−E−M−E}}$ type core.[1b,3] These dimeric compounds are generally obtained through either dehalosilylation or lithium halide elimination reactions by combining R$_2$MX (R = alkyl, aryl; X = Cl, Br) in a 1:1 ratio with E(SiMe$_3$)$_3$ or LiE(SiMe$_3$)$_2$ (E = P, As), respectively. Less common are compounds containing a mixed-bridge type core ring of the form $\overline{\text{M−E−M−X}}$ (X = Cl[3d,4] or Br[4b]), obtained from dehalosilylation of R$_2$MX and E(SiMe$_3$)$_3$ in a 2:1 ratio or equilibration of a dimeric compound with 2 equiv of R$_2$MX.

In an attempt to extend our methodologies to the formation of precursors to group 13−antimonides, we have recently reported the synthesis and characterization of the adducts Et$_3$Ga·Sb(SiMe$_3$)$_3$ and (Me$_3$SiCH$_2$)$_3$-In·Sb(SiMe$_3$)$_3$, as well as the oligomeric compounds [(Me$_3$CCH$_2$)$_2$GaSb(SiMe$_3$)$_2$]$_x$ and [(Me$_3$SiCH$_2$)$_2$InSb-

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(SiMe$_3$)$_2$]$_2$.[5] We, as well as others, have also demonstrated that nanocrystalline GaSb is obtained from the 1:1 dehalosilylation reaction of GaCl$_3$ and Sb(SiMe$_3$)$_3$ in pentane solution.[6] These results show that further study into this area is indeed warranted, as does the lack of known group-13–antimony compounds.[7–10] In an effort to further expand the library of known group-13–antimony compounds, herein we report the synthesis and complete characterization of t-Bu$_3$Ga·Sb(SiMe$_3$)$_3$ (**1**), [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (**2**), and t-Bu$_2$GaSb(SiMe$_3$)$_2$Ga(t-Bu)$_2$Cl (**3**), the first gallium–antimony mixed-bridge compound. In addition, the thermal decomposition of **2** was examined in order to assess the suitability of these compounds as precursors to GaSb.

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. Hexane and toluene were distilled over sodium/potassium alloy under dry dinitrogen. t-Bu$_3$Ga,[11] t-Bu$_2$GaCl,[11] and Sb(SiMe$_3$)$_3$[12] were prepared from literature procedures. GaCl$_3$ was purchased from Strem Chemicals and used as received. The integrity of all starting materials was confirmed using ^{1}H NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Unity XL-400 spectrometer operating at 400 and 100.6 MHz, respectively. ^{1}H and ^{13}C{^{1}H} spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or 128.0, respectively. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas-Hoover Unimelt apparatus, using capillaries that were flame-sealed under argon. Elemental analyses (EA) were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Powder X-ray diffraction (XRD) data were collected on a Phillips XRG-3000 diffractometer utilizing Cu Kα radiation. IR spectra of volatile gases were acquired using a gas cell on a BOMEM Michelson MB-100 FT-IR spectrometer. TGA/DTA analyses were obtained on a TA Instruments SDT 2960 simultaneous TGA/DTA apparatus.

Preparation of t-Bu$_3$Ga·Sb(SiMe$_3$)$_3$ (1). t-Bu$_3$Ga (0.241 g, 1.00 mmol) in 20 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir bar and Teflon valve. Sb(SiMe$_3$)$_3$ (0.341 g, 1.00 mmol) in 20 mL of pentane was added slowly via pipet, and the clear, slightly red solution was stirred overnight at room temperature. The solvent was reduced *in vacuo* to yield a red liquid, which was cooled to −30 °C to produce brown prismatic crystals of **1** suitable for X-ray analysis (0.533 g, 92%). Mp 103–107 °C. Anal. Calcd (found) for C$_{21}$H$_{54}$GaSbSi$_3$: C, 43.31 (43.13); H, 9.35 (9.27). ^{1}H NMR: δ 0.41 (s, 27H, −SiMe$_3$), 1.28 (s, 27H, −CH$_3$). ^{13}C NMR{^{1}H}: δ 4.86 (s, −SiMe$_3$), 32.11 (s, −CH$_3$).

Preparation of [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (2). t-Bu$_2$GaCl (0.242 g, 1.10 mmol) dissolved in 25 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir bar and Teflon valve. Sb(SiMe$_3$)$_3$ (0.375 g, 1.10 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 1 day at room temperature. After this period, the solution had taken on a dark yellow color. The solution volume was reduced *in vacuo* and then stored at −30 °C for several days. Colorless crystals of **2**, suitable for X-ray analysis were isolated (0.342 g, 45%). Mp 220 °C (dec to a red liquid). Anal. Calcd (found) for C$_{28}$H$_{72}$Ga$_2$Sb$_2$Si$_4$: C, 37.20 (37.10); H, 8.03 (7.95). ^{1}H NMR: δ 0.37 (s, 36H, −SiMe$_3$), 1.21 (s, 36H, CH$_3$−). ^{13}C{^{1}H} NMR: δ 4.79 (s, −SiMe$_3$), 30.77 (s, −CH$_3$).

Preparation of t-Bu$_2$GaSb(SiMe$_3$)$_2$Ga(t-Bu)$_2$Cl (3). Method 1. [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (0.174 g, 0.20 mmol) partially dissolved in 20 mL of hexane was added to a 250 mL Schlenk flask equipped with a stir bar and Teflon valve. A small amount of toluene (approximately 5 mL) was added to increase the solubility. t-Bu$_2$GaCl (0.084 g, 0.4 mmol) in 20 mL of toluene was added via pipet, resulting in a clear amber solution, which was allowed to stir at room temperature for 2.5 days. The solvent was reduced *in vacuo*, yielding a red liquid which was allowed to evaporate at −30 °C for 3 days, producing colorless, prismatic crystals of **3** suitable for X-ray analysis (0.097 g, 36%). Mp 174–182 °C (dec to a red liquid). Anal. Calcd (found) for C$_{22}$H$_{54}$Ga$_2$SbSi$_2$Cl: C, 39.35 (39.12); H, 8.11 (7.98). ^{1}H NMR: δ 0.49 (s, 18H, −SiMe$_3$), 1.32 (s, 36H, CH$_3$−). ^{13}C{^{1}H} NMR: δ 6.05 (s, −SiMe$_3$), 30.82 (s, −CH$_3$).

Method 2. t-Bu$_2$GaCl (0.316 g, 1.44 mmol) dissolved in 25 mL of hexane was added to a 250 mL Schlenk flask. Sb(SiMe$_3$)$_3$ (0.245 g, 0.72 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 5 days at room temperature. After 1 day, the solution began to take on a golden color and gradually continued to darken. The solution volume was reduced *in vacuo* and then evaporated at −30 °C. Colorless crystals of **3** formed, as confirmed by ^{1}H NMR analysis (0.099 g, 21%).

Thermal Decomposition of 2. (a) TGA Analysis. Figure 4 shows the weight loss of **2** under nitrogen flow with a 5 °C/min heating rate. Segment 1: 150–200 °C with 44% weight loss. Segment 2: 250–400 °C with 5% weight loss. Total observed weight loss: 52%. Total calculated weight loss for GaSb formation: 57.6%

(b) Pyrolysis at 400 °C. The sample (0.227 g, 0.50 mmol based on the monomeric unit) was loaded into a sublimator and heated under dynamic vacuum as follows: 175 °C, 15 min; 200 °C, 10 min; 400 °C, 12 h. A black residue was present on the cold finger, and a metallic mirror had formed on the base of the sublimator wall during this time. A gray/black powder was recovered (0.061g, 64% yield based on GaSb), and its identity was confirmed through comparison of the *d*-spacings and line intensities obtained by XRD analysis with those of GaSb (JCPDS file 7-215). The approximate average particle size of 9 nm was calculated using the Scherrer equation. Anal. Calcd (found) for GaSb: Ga, 36.41 (35.17); Sb, 63.59 (61.96). The Ga:Sb ratio was 1.00:1.01. A second sample of **2** (0.198 g, 0.44 mmol based on the monomeric unit) was decomposed as described above, with the exception that a static vacuum was used and a −196 °C cold trap was attached in an attempt to study the volatiles formed during decomposition. The results were as follows: noncondensable CH$_4$ and H$_2$, approximately 0.5 mmol total (0.3 mmol CH$_4$ and 0.2 mmol H$_2$); condensable HSiMe$_3$ and isobutylene, approximately 0.53 mmol total. CH$_4$, HSiMe$_3$, and isobutylene were identified by IR spectroscopy. The 0.023 g of black powder recovered (27% yield based on GaSb) was identified through XRD and analyzed for impurities. Anal. Calcd (found) for this second sample: C, 0.0 (2.28); H, 0.0 (0.99).

X-ray Structural Solution and Refinement. Crystal,

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Table 1. Crystallographic Data for t-$Bu_3Ga \cdot Sb(SiMe_3)_3$ (1), [t-$Bu_2GaSb(SiMe_3)_2$]$_2$ (2), and t-$Bu_2GaSb(SiMe_3)_2Ga(t$-$Bu)_2Cl$ (3)

	1	2	3
formula	$C_{21}H_{54}GaSbSi_3$	$C_{28}H_{72}Ga_2Sb_2Si_4$	$C_{22}H_{54}Ga_2SbSi_2Cl$
fw	582.38	904.15	671.47
space group	*Pnma*	*C*2/*c*	$P\bar{1}$
a, Å	17.504(3)	19.614(4)	10.0358(4)
b, Å	15.923(3)	13.280(3)	11.5969(5)
c, Å	11.522(5)	18.230(3)	16.3753(7)
α, deg			82.2250(1)
β, deg		116.912(12)	72.1790(1)
γ, deg			64.3690(1)
V, Å^3	3209(2)	4234.2(14)	1635.83(12)
Z	4	4	2
cryst color, habit	brown block	colorless block	colorless block
D(calc), g cm^3	1.206	1.418	1.363
μ(Mo Kα), cm^{-1}	17.98	26.5	26.2
temp, K	245(2)	138	138
radiation		Mo Kα (λ = 0.710 73 A)	
R(*F*), %	4.31[a]	3.2[b]	5.0[b]
R(*wF*^{2}), %	10.16[a]	4.1[b]	5.3[b]

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; ; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $\sum[w(F_o - F_c)^2]/\sum[(wF_o)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)$.

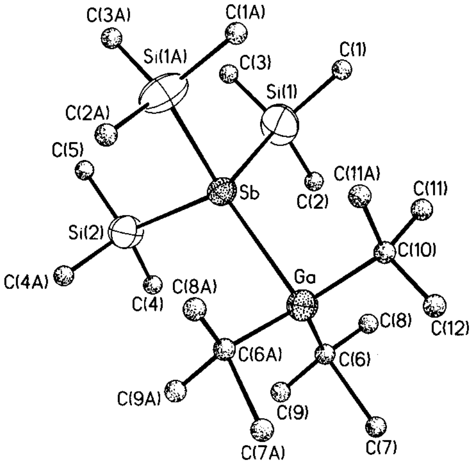

Figure 1. Molecular structure of **1** drawn with 30% probability ellipsoids. Methyl-group carbon atoms are rendered spherically due to their high thermal activity. Bond Lengths (Å): Ga−Sb 3.027(2); Sb−Si(1) 2.555(2); Ga−C(6) 2.007(8); Sb−Si(2) 2.566(3); Ga−C(10) 2.027(9). Bond Angles (deg): Ga−Sb−Si(1) 118.53(6); Sb−Ga−C(6) 98.7(3); Ga−Sb−Si(2) 114.68(7); Sb−Ga−C(10) 102.8(3); Si(1)−Sb−Si(2) 100.65(8); C(6)−Ga−C(10) 116.7(3); Si(1)−Sb−Si(1)A 100.75(13); C(6)−Ga−C(6)A: 117.5(5).

data collection, and refinement parameters are given in Table 1, while selected bond lengths and angles are presented in Figures 1, 2, and 3. ORTEP diagrams showing the solid state conformations of **1**−**3** can be found in Figures 1−3, respectively.

Compound **1.** A suitable crystal was selected and mounted in a nitrogen-flushed glass capillary. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data are consistent for the space groups $Pna2_1$ or *Pnma*. The *E*-statistics and the presence of a molecular mirror plane in the molecule suggested the centrosymmetric option, which was subsequently verified by chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Absorption corrections were not necessary because there was less than 10% variation in the integrated ψ-scan intensities. The molecule is located on a mirror plane. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

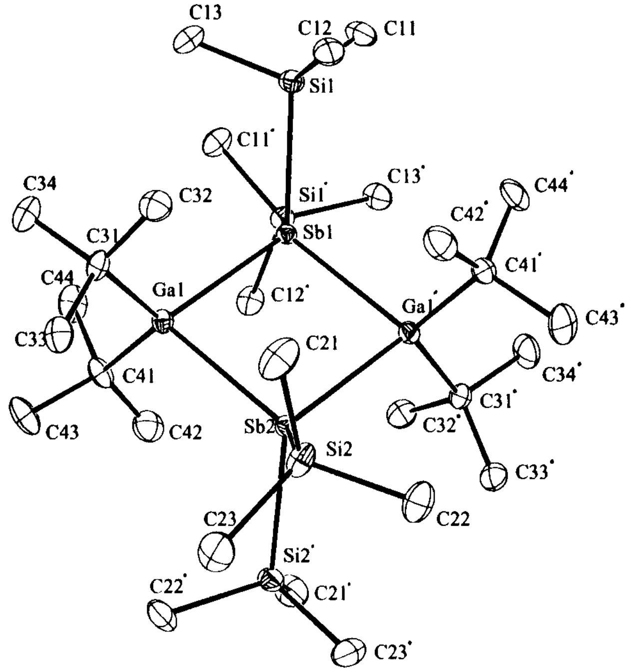

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**. Hydrogen atoms are omitted for clarity. Bond Lengths (Å): Ga1−Sb1 2.7684(7); Ga1−Sb2 2.7648(7); Ga1−C31 2.018(6); Sb1−Si1 2.5918(17); Ga1−C41 2.036(5); Sb2−Si2 2.5827(18). Bond Angles (deg): Ga1−Sb1−Ga1 94.37(3); Ga1−Sb2−Ga1 94.53(3); Sb1−Ga1−Sb2 85.549(24); C31−Ga1−Sb1 115.30(18); C41−Ga1−Sb1 109.61(16); C31−Ga1−Sb2 110.54(17); C41−Ga1−Sb2 112.76(18); Si1−Sb1−Ga1 115.83(4); Si2−Sb2−Ga1 118.74(4); C31−Ga1−C41 118.5(3); Si1−Sb1−Si1 96.52(6); Si2−Sb2−Si2 96.13(6); Si1A−Sb1−Ga1 117.98(4); Si2A−Sb2−Ga1 115.22(5).

Compounds 2 and 3. Single crystals of **2** and **3** 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 Siemens SMART CCD 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 $R = 0.032$ ($R_w = 0.041$) for **2** and $R = 0.050$ ($R_w = 0.053$) for **3**. A final difference Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[13] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 14.

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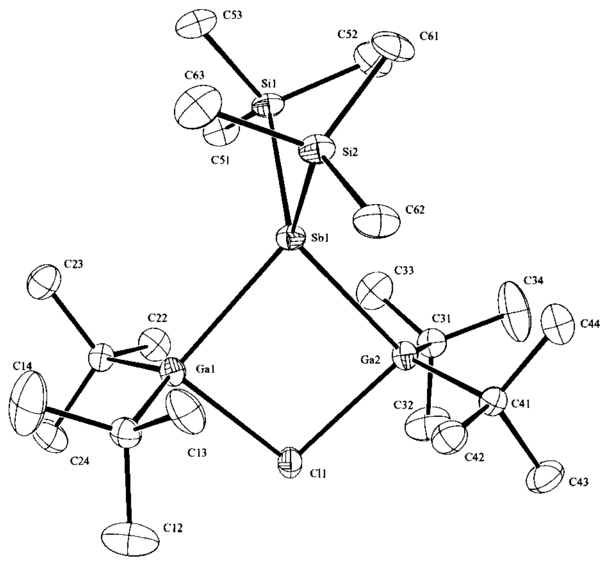


Figure 3. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **3**. Hydrogen atoms are omitted for clarity. Bond Lengths (Å): Ga1–Sb1 2.7336(12); Ga2–Sb1 2.7337(11); Ga1–Cl1 2.4568(24); Ga2–Cl1 2.462(3); Ga1–C11 2.032(9); Ga1–C21 2.007(9); Ga2–C31 2.019(8); Ga2–C41 2.007(9); Sb1–Si1 2.599(3); Sb1–Si2 2.599(3). Bond Angles (deg): Ga1–Sb1–Ga2 85.68(3); Ga1–Cl1–Ga2 98.18(9); Sb1–Ga1–Cl1: 88.12(6); Sb1–Ga2–Cl1 88.01(6); C11–Ga1–Sb1 117.4(3); C11–Ga1–Cl1 105.7(3); C21–Ga1–Sb1 111.8(3); C21–Ga1–Cl1 103.9(3); C11–Ga1–C21 122.5(4); C31–Ga2–C41 122.4(4); C31–Ga2–Sb1 117.4(3); C31–Ga2–Cl1 105.5(3); C41–Ga2–Sb1 112.09(25); C41–Ga2–Cl1 103.6(3); Si1–Sb1–Ga1 120.81(7); Si1–Sb1–Ga2 117.42(6); Si2–Sb1–Ga1 117.34(7); Si2–Sb1–Ga2 120.85(7); Si1–Sb1–Si2 96.93(8).

Results and Discussion

The 1:1 mol ratio reaction of t-Bu$_3$Ga and Sb(SiMe$_3$)$_3$ affords in high yield the expected Lewis acid–base adduct t-Bu$_3$Ga·Sb(SiMe$_3$)$_3$ (**1**). The 1:1 mol ratio dehalosilylation reaction of t-Bu$_2$GaCl with Sb(SiMe$_3$)$_3$ yielded the dimeric compound [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (**2**), while the 2:1 mol ratio reaction of t-Bu$_2$GaCl with Sb(SiMe$_3$)$_3$ resulted in the formation of t-Bu$_2$GaSb(SiMe$_3$)$_2$Ga(t-Bu)$_2$Cl (**3**) after 5 days. Initially, the reaction was stopped after 1 day and the only products isolated were **2** and t-Bu$_2$GaCl. Interestingly, the attempted formation of Ga–E–Ga–Cl core structures through 2:1 reactions yields a wide variety of results. The 2:1 reaction of (Me$_3$CCH$_2$)$_2$GaCl with P(SiMe$_3$)$_3$ fails to yield the mixed-bridge, instead forming [(Me$_3$CCH$_2$)(Cl)GaP(SiMe$_3$)$_2$]$_2$.[3d] In the case of (Me$_3$CCH$_2$)$_2$GaCl reacted 2:1 with As(SiMe$_3$)$_3$, the expected mixed-bridge was formed after 5 days,[4e] comparable to the time involved in the formation of **3**. Also noteworthy is the reaction of t-Bu$_2$GaCl with As(SiMe$_3$)$_3$, which failed to undergo dehalosilylation in 1:1 or 2:1 ratios, and the mixed-bridge was obtained only from reaction of [t-Bu$_2$GaAs(SiMe$_3$)$_2$]$_2$ with t-Bu$_2$GaCl.[15] The mixed-bridge **3** was also obtained from the equilibration reaction of t-Bu$_2$GaCl with **2** in a 2:1 mol ratio. These reactions are summarized in Scheme 1. Compound **3** is interesting due to the possibility of metathetical reactions involving the ring chlorine atom and a LiE(SiMe$_3$)$_2$ (E = P, As) salt to form the rare mixed-pnictogen structure. This possibility is currently under investigation. The solid-state structures of **1**, **2**, and **3** have been confirmed through single-crystal X-ray analysis.

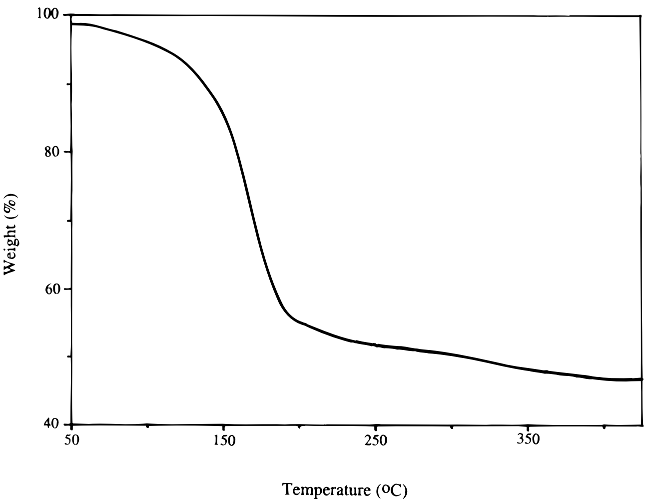
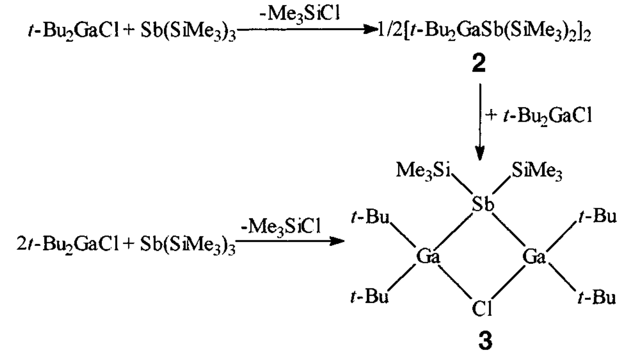


Figure 4. Thermogravimetric analysis (TGA) data for the decomposition of [t-Bu$_2$GaSb(SiMe$_3$)$_2$]$_2$ (**2**).

Scheme 1



Compound **1** crystallizes in the orthorhombic space group *Pnma*. The Ga–Sb bond length of 3.027(2) Å in this structure is significantly longer than the bond length of 2.846(5) Å reported for the adduct Et$_3$Ga·Sb(SiMe$_3$)$_3$.[5] This discrepancy can be explained by the extreme steric bulk of the *tert*-butyl group in comparison to the ethyl group, which prevents close approach of the Sb(SiMe$_3$)$_3$ moiety. It should also be noted that the ligands bound to the metal centers adopt a staggered conformation in relation to one another.

Crystals of the dimeric compound **2** belong to the monoclinic space group *C*2/*c* and lie on a 2-fold axis. The average Ga–Sb bond length of 2.7666(7) Å found in **2** is slightly longer than the average Ga–Sb bond length of 2.66 Å reported for the ring compound [Cl$_2$GaSb(t-Bu)$_2$]$_3$.[7] Again, this is probably due to the steric bulk exerted by the *tert*-butyl groups. The average endocyclic bond angles in **2** are 94.45(3)° for Ga–Sb–Ga and 85.549(24)° for Sb–Ga–Sb. The gallium and antimony atoms in this compound reside in distorted tetrahedral environments, and the core ring is planar.

The mixed-bridge compound **3** forms crystals belonging to the triclinic space group $P\bar{1}$. The average Ga–Sb bond length of 2.7336(11) Å compares well with the analogous bond length in **2** (*vide supra*). The core

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[15] Wells, R. L.; McPhail, A. T.; Alvanipour, A. *Polyhedron* **1992**, *11*, 839.

ring of this compound is again planar, with average endocyclic Ga−Sb−Ga, Ga−Cl−Ga, and Sb−Ga−Cl ring angles of 85.68(3)°, 98.18(9)°, and 88.07(6)°, respectively. The gallium and antimony atoms again reside in distorted tetrahedral environments, with the influence of the *tert*-butyl groups demonstrated in the appropriate bond angles.

In an attempt to assess the utility of these compounds as precursors to GaSb, the thermal decomposition behavior of **2** was closely examined. This compound was found to produce reasonably pure GaSb in moderate to low yield. In addition, analysis of the volatile products produced during decomposition suggests that the formation of GaSb occurs through a β-hydride elimination pathway. This is evidenced through the condensation of $HSiMe_3$ and isobutylene in the cold trap, the expected products of such an elimination process. Both compounds were identified by IR spectroscopy. If this elimination occurred cleanly, the theoretical amount of $HSiMe_3$ and isobutylene collected would be 1.76 mmol total (based on 0.44 mmol of starting material). The fact that approximately a third of this amount, 0.53 mmol, was observed suggests that the elimination was not complete and that a secondary process was also involved. Two other noncondensable gases were produced during the pyrolysis, namely CH_4 and H_2, presumably from decomposition of the $-SiMe_3$ groups. It is possible to envision a two-step mechanism for **2** undergoing β-hydride elimination and subsequently forming GaSb, with elimination of isobutylene as step 1 followed by elimination of trimethylsilane as step 2. However, the TGA plot for this process, shown in Figure 4, indicates only one major elimination occurring in the range of 150−200 °C. This suggests that steps 1 and 2 occur simultaneously. The small (approximately 5%), broad weight loss observed from 250−400 °C is probably due to evolution of residual silicon and carbon containing species not lost in the initial elimination and could account for the observed CH_4 and H_2 gas. It should be noted that initial pyrolysis experiments on **1** indicate that GaSb is also formed, however, the purity and yield are less than that observed for **2**, and the system is still under investigation.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**, **2**, and **3** (16 pages). Ordering information is given on any current masthead page.

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