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Note

Synthesis and characterization of single-source precursors to nanocrystalline GaP, GaP_xAs_{1-x}, and GaP_xSb_{1-x}. X-ray crystal structures of $[Et_2GaP(SiMe_3)_2]_2$, $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$, and $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$

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Abstract

The 1:1 mole ratio reaction of Et_2GaCl with $P(SiMe_3)_3$ resulted in the formation of $[Et_2GaP(SiMe_3)_2]_2$ (**1**). The mixed-pnicogen compounds $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$ (**2**) and $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**) were prepared from the 2:1:1 mole ratio reactions of Et_2GaCl with $P(SiMe_3)_3$ and $As(SiMe_3)_3$ and $P(SiMe_3)_3$ and $Sb(SiMe_3)_3$, respectively. Compounds **2** and **3** were also synthesized by comproportionation reactions of **1** and $[Et_2GaAs(SiMe_3)_2]_2$, and **1** and $[Et_2GaSb(SiMe_3)_2]_2$, respectively. Characterization of **1**, **2**, and **3** was accomplished using multinuclear NMR, elemental analysis, mass spectrometry, and single-crystal X-ray crystallographic analysis and the X-ray crystal structure of **3** is reported. Thermolysis of **1**, **2**, and **3** results in the formation of nanocrystalline GaP, GaP_xAs_{1-x}, or GaP_xSb_{1-x}, respectively. Compound **3** represents the first example of a compound containing a $P(\mu\text{-}Ga)_2Sb$ core. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nanocrystalline; Gallium phosphide; Gallium phosphorus clusters

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1. Introduction

Recently the research in our laboratories has been aimed at the synthesis of precursors containing ligands that have the potential for β-hydride elimination to form nanocrystalline 13–15 materials [1–4]. Additionally, it has been observed by Cowley and coworkers that β-hydride elimination can be a lower-energy decomposition pathway relative to Ga–C bond homolysis [5]. Our interest in this aspect of precursor design was sparked by the superior quality of GaSb produced by the thermolysis of $[^tBu_2GaSb(SiMe_3)_2]_2$ [1] when compared with that produced by the thermolysis of the material formed from the 1:1 mole ratio reaction of GaX_3 and $Sb(SiMe_3)_3$ [6]. The elimination products from the thermolysis of $[^tBu_2GaSb(SiMe_3)_2]_2$ were isolated and characterized as isobutylene and trimethylsilane — consistent with the hypothesis of β-hydride elimination and dehydrosilylation as proposed elimination pathways.

Our success with $[^tBu_2GaSb(SiMe_3)_2]_2$ led us to expand our research in the area of precursors with the capacity for β-hydride elimination with the syntheses of the ethyl-containing precursors $[Et_2GaAs(SiMe_3)_2]_2$, $[Et_2GaSb(SiMe_3)_2]_2$ and $(Me_3Si)_2As[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ [2]. These compounds were shown to undergo complete elimination of their alkyl and silyl substituents upon thermolysis to produce nanocrystalline GaAs, GaSb and $GaAs_xSb_{1-x}$, respectively.

As we noted in our previous report [2], compounds that could serve as precursors to gallium-containing

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ternary materials have only cursorily been investigated. The only reported examples of compounds with such a potential are $(Me_3Si)_2P[\mu\text{-}GaI_2]_2As(SiMe_3)_2$ [7], $Ga_2(As/P)Cl_3$ [8], and the aforementioned $(Me_3Si)_2As[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ [2]. Preliminary studies of the decomposition of these compounds showed that they did form nanocrystalline GaP_xAs_{1-x}, and $GaAs_xSb_{1-x}$, respectively. Inspection of the literature regarding precursors to gallium-containing ternary materials shows that there are no gallium-containing mixed pnicogen compounds containing P and Sb.

In an attempt to further explore the potential of gallium-containing single-source precursors for the formation of ternary nanocrystalline 13–15 materials, we have prepared the dimeric compound $[Et_2GaP(SiMe_3)_2]_2$ (**1**) and the mixed-pnicogen compounds $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$ (**2**) and $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**). The X-ray crystal structure of **3** is presented. In addition, preliminary thermolysis experiments of **1**, **2**, and **3** have been conducted for the purpose of determining their utility as precursors to nanocrystalline GaP, GaP_xAs_{1-x}, and GaP_xSb_{1-x}. Compound **3** is the first example of a mixed-pnicogen compound containing phosphorus and antimony.

2. Experimental

2.1. 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. Solvents were distilled from sodium–potassium alloy under dry dinitrogen. $P(SiMe_3)_3$ [9], $As(SiMe_3)_3$ [9], $Sb(SiMe_3)_3$ [10], $[Et_2GaAs(SiMe_3)_2]_2$ [2] and $[Et_2GaSb(SiMe_3)_2]_2$ [2] were prepared from methods described in the literature. $P(SiMe_3)_3$ was also purchased from Strem Chemicals as were Et_3Ga and $GaCl_3$. All were used as received. Et_2GaCl was obtained from the 2:1 comproportionation reaction of Et_3Ga with $GaCl_3$. All ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Varian Inova 400 NMR spectrometer operating at 399.937, 100.577, and 161.901 MHz, respectively, in 5 mm tubes septum-sealed under argon and referenced using generally accepted methods. 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., Parsippany, NJ. Mass spectra were collected using a JEOL JMS-SX 102A spectrometer operating in the EI + mode at 20 eV; the assignment of the ion fragments was supported by comparisons with theoretical ion distributions. Powder X-ray diffraction (XRD) data were collected on a Phillips XRG-3000 diffractometer using Cu–K_α radiation. Single-crystal X-ray diffraction studies were performed at the University of Delaware on a Siemens P4/CCD diffractometer.

2.2. Preparation of $[Et_2GaP(SiMe_3)_2]_2$ (**1**)

A 100 ml round-bottom flask equipped with a stirbar and a Teflon valve was charged with Et_2GaCl (0.490 g; 3.0 mmol) and 10 ml of hexane. A solution of $P(SiMe_3)_3$ (0.752 g; 3.0 mmol) in 10 ml of hexane was then added via pipette at room temperature (r.t.) in a dry box. The flask was sealed and removed from the dry box and the clear, colorless solution stirred for 12 h. The volume of the solution was then reduced in vacuo, and storage at −30°C for 7 days afforded colorless crystals of **1** (0.884 g, 97% yield). M.p.: 265–272°C. Anal. Found: C, 39.64; H, 10.33. Calc. for $Ga_2P_2Si_4C_{20}H_{56}$: C, 39.35; H, 9.25%. ^1H-NMR: δ 0.38 [t, 36H, $-SiMe_3$ ($^3J_{P-H} = 3$ Hz)], δ 0.90 [q, 8H, $-CH_2CH_3$ ($J_{H-H} = 8.0$ Hz)], δ 1.32 [t, 12H, $-CH_2CH_3-$ ($J_{H-H} = 8.0$ Hz)]. $^{13}C\{^1H\}$-NMR: δ 4.41 (t, $^2J_{P-C} = 4.4$ Hz; $-SiMe_3$) δ 7.93 (t, $^2J_{P-C} = 9.8$ Hz; $-CH_2CH_3$) δ 10.76 (t, $^3J_{P-C} = 3.2$ Hz $-CH_2CH_3$). $^{31}P\{^1H\}$-NMR: δ −227.8 [s, $P(SiMe_3)_2$]. MS (*m*/*e*, ion): 581 $(M{-}C_2H_5)^*$.

2.3. Preparation of $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$ (**2**)

A 100 ml round-bottom flask equipped with a stirbar and a Teflon valve was charged with Et_2GaCl (0.653 g; 4.0 mmol) and 10 ml of hexane. A solution of $P(SiMe_3)_3$ (0.501 g; 2.0 mmol) and $As(SiMe_3)_3$ (0.589 g; 2.0 mmol) in 10 ml of hexane was added via pipette at r.t. in a dry box. The flask was sealed and removed from the dry box and the clear, light yellow solution was stirred for 12 h. The volume of the solution was then reduced in vacuo, and storage at −30°C for 3 days afforded colorless blocks of **2** (1.220 g, 93.2% yield). M.p.: 175–182°C. Anal. Found: C, 36.07; H, 9.15. Calc. for $Ga_2PAsSi_4C_{20}H_{56}$: C, 36.71; H, 8.63%. ^1H-NMR: δ 0.37 [d, 18H, $-P(SiMe_3)_2$ ($^3J_{P-H} = 4.8$ Hz)], δ 0.42 [s, 18H, $-As(SiMe_3)_2$], δ 0.94 [q, 8H, $-CH_2CH_3$ ($J_{H-H} = 8.0$ Hz)], δ 1.31 [t, 12H, $-CH_2CH_3$ ($J_{H-H} = 8.0$ Hz)]. $^{13}C\{^1H\}$-NMR: δ 4.34 [d, $-PSiMe_3$ ($^2J_{P-C} = 8.4$ Hz)], δ 4.64 [s, $-AsSiMe_3$], δ 8.59 [s, $-CH_2CH_3$], δ 10.93 [s, $-CH_2CH_3$]. $^{31}P\{^1H\}$-NMR: δ −227.7 [s, $P(SiMe_3)_2$]. MS (*m*/*e*, ion): 654, M^*; 625, $[M{-}C_2H_5]^*$; 349, $[Et_2GaAs(SiMe_3)_2]^*$; 319, $[Et_2GaAs(SiMe)_2{-}Et{-}H]^*$; 305, $[Et_2GaP(SiMe_3)_2]^*$; 275, $[Et_2GaP(SiMe)_2{-}Et{-}H]^*$.

2.4. *In situ preparation of **2** by comproportionation of **1** and $[Et_2GaAs(SiMe_3)_2]_2$*

A solution of equivalent molar amounts of **1** (0.0063 g, 0.010 mmol) and $[\mathrm{Et_2GaAs(SiMe_3)_2}]_2$ (0.0072 g, 0.010 mmol) was prepared in 0.75 ml of toluene-d_8. This solution was then placed in a 5 mm NMR tube and flame-sealed under partial vacuum. Spectra, taken at 25°C, were obtained immediately after preparation and after 24 h of agitation. ^{1}H-NMR: immediately following solution preparation: δ 0.38 [t, $^3J_{\mathrm{P-H}} =$ 3 Hz; 36H, $-\mathrm{Si}Me_3$, **1**], δ 0.42 [s, 36H, $-\mathrm{Si}Me_3$, $[\mathrm{Et_2GaAs(SiMe_3)_2}]_2$], δ 0.90 [q, 8H, $-CH_2\mathrm{CH_3}$ ($J_{\mathrm{H-H}} =$ 8.0 Hz) **1**], δ 0.95 [q, 8H, $-CH_2\mathrm{CH_3}$ ($J_{\mathrm{H-H}} = 8.0$ Hz) $[\mathrm{Et_2GaAs(SiMe_3)_2}]_2$], δ 1.32 [t, 12H, $-\mathrm{CH_2}CH_3-$ ($J_{\mathrm{H-}}$ $\mathrm{H} = 8.0$ Hz) **1**], δ 1.34 [t, 12H, $-\mathrm{CH_2}CH_3-$ ($J_{\mathrm{H-H}} = 8.0$ Hz) $[\mathrm{Et_2GaAs(SiMe_3)_2}]_2$]. After 24 h: δ 0.37 [d, 18H, $-\mathrm{P(Si}Me_3)_2$ ($^3J_{\mathrm{P-H}} = 4.8$ Hz) **2**], δ 0.42 [s, 18H, $-\mathrm{As(Si}Me_3)_2$, **2**], δ 0.94 [q, 8H, $-CH_2\mathrm{CH_3}$ ($J_{\mathrm{H-H}} = 8.0$ Hz) **2**], δ 1.31 [t, 12H, $-\mathrm{CH_2}CH_3$ ($J_{\mathrm{H-H}} = 8.0$ Hz) **2**].

2.5. *Preparation of $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**)*

A 100 ml round-bottom flask equipped with a stirbar and a Teflon valve was charged with $\mathrm{Et_2GaCl}$ (0.653 g; 4.0 mmol) and 20 ml of hexane. A solution of $\mathrm{P(SiMe_3)_3}$ (0.501 g; 2.0 mmol) and $\mathrm{Sb(SiMe_3)_3}$ (0.682 g; 2.0 mmol) in 25 ml of hexane was added via pipette at r.t. in a dry box. The solution became cloudy and dark gray upon addition. The flask was sealed and removed from the dry box and the solution was stirred for 12 h in the dark after which time it was light yellow and completely clear. The volume of the solution was reduced in vacuo, and storage at −30°C for 8 days afforded thick, colorless blocks of **3** (0.468 g, 63% yield). M.p.: 165–171°C. Anal. Found: C, 35.64; H, 9.44. Calc. for $\mathrm{Ga_2PSbSi_4C_{20}H_{56}}$: C, 34.26; H, 8.05%. ^{1}H-NMR: δ 0.35 [d, $-\mathrm{P(Si}Me_3)_2$, **3**, ($^3J_{\mathrm{P-H}} = 4.8$ Hz)], δ 0.37 [t, $-\mathrm{P(Si}Me_3)_2$, **1**, ($^3J_{\mathrm{P-H}} = 2.4$ Hz)], δ 0.50 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$], δ 0.51 [s, $-\mathrm{Sb(Si}Me_3)_2$, **3**], δ 0.57 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$], δ 0.87–0.97 [m, $-CH_2\mathrm{CH_3}$], δ 1.37–1.29 [m, $-\mathrm{CH_2}CH_3$]. ^{13}C{^{1}H}-NMR: δ 4.20 [d, $-\mathrm{PSi}Me_3$, **3**, ($^2J_{\mathrm{P-C}} = 7.6$ Hz)], δ 4.13 [t, $-\mathrm{PSi}Me_3$, **1**, ($^2J_{\mathrm{P-C}} =$ 4.6 Hz)], δ 5.38 [s, $-\mathrm{SbSi}Me_3$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$], δ 5.52 [s, $-\mathrm{SbSi}Me_3$, **3**], δ 5.74 [s, $-\mathrm{SbSi}Me_3$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$], δ 7.93 [t, $^2J_{\mathrm{P-C}} = 10$ Hz; $-CH_2\mathrm{CH_3}$, **1**], δ 8.67 [d, $^2J_{\mathrm{P-C}} = 9.6$ Hz; $-CH_2\mathrm{CH_3}$, **3**], δ 7.93 [s, $-CH_2\mathrm{CH_3}$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$/$[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$], δ 10.75 [t, $^3J_{\mathrm{P-C}} = 3.2$ Hz; $-\mathrm{CH_2}CH_3$, **1**], δ 11.53 [d, $^3J_{\mathrm{P-C}} = 4.2$ Hz; $-\mathrm{CH_2}CH_3$, **3**], δ 12.19 [s, $-\mathrm{CH_2}CH_3$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$/$[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$]. MS ($m/e$, ion): 700 M^*; 653 $[M\mathrm{-Et-Me-2H}]^*$; 623 $[M\mathrm{-2Et-Me-3H}]^*$.

2.6. *In situ preparation of **3** by comproportionation of **1** and $[Et_2GaSb(SiMe_3)_2]_2$*

A solution of equivalent molar amounts of **1** (0.0123 g, 0.020 mmol) and $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$ (0.0159 g, 0.020 mmol) was prepared with ca. 0.75 ml of toluene-d_8. This solution was then placed in a 5 mm NMR tube and flame-sealed under partial vacuum. Spectra, taken at 25°C, were obtained immediately after preparation, after 15 h of agitation, and after 24 h of agitation. To avoid the complexity of the peaks associated with the ethyl moieties comparisons were made using the peaks associated with the trimethylsilyl moieties on P and Sb. ^{1}H-NMR: immediately following solution preparation: δ 0.38 [t, $^3J_{\mathrm{P-H}} = 3$ Hz; 36H, $-\mathrm{Si}Me_3$, **1**], δ 0.50 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$], δ 0.51 [s, $-\mathrm{Sb(Si}Me_3)_2$, **3**], δ 0.57 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$]. After 15 h: δ 0.35 [d, $-\mathrm{P(Si}Me_3)_2$, **3**, ($^3J_{\mathrm{P-H}} = 4.8$ Hz)], δ 0.38 [t, $-\mathrm{P(Si}Me_3)_2$, 1, ($^3J_{\mathrm{P-H}} = 2.4$ Hz)], δ 0.50 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$], δ 0.51 [s, $-\mathrm{Sb(Si}Me_3)_2$, **3**], δ 0.57 [s, $-\mathrm{Sb(Si}Me_3)_2$, $[\mathrm{Et_2GaSb(SiMe_3)_2}]_3$].

2.7. *Thermolysis of **1***

Compound **1** (0.884 g, 2.90 mmol based on the monomeric unit) was loaded into a sublimator and evacuated for 1 h. The sublimator was then heated to 425°C for 4 h under static vacuum. During this time, significant sublimation of **1** (later identified by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy) was observed as white crystals that formed on the walls of the sublimator above the heat source. A dull gray metallic mirror, GaP, formed on the sides of the sublimator as well as the cold finger during thermolysis. This material was scraped from the sides and collected (0.023 g, 22.8%) and its identity verified by comparison of the d-spacings and line intensities obtained by XRD analysis with those of GaP (JCPDS file 32-397). The approximate average particle size of 6.4 nm was calculated using the Scherrer equation. Anal. Found: C, 5.84; H, 0.46; Ga, 62.60; P, 31.50. Calc. for GaP: C, 0.00; H, 0.00; Ga, 69.24; P, 30.76%.

2.8. *Thermolysis of **2***

Thermolysis of **2** (0.448 g, 0.68 mmol) was identical to the procedure described for compound **1**. Significant sublimation of **2** (later identified by ^{1}H-NMR spectroscopy) was observed as white crystals, which formed on the walls of the sublimator above the heat source. The material, $\mathrm{GaP}_x\mathrm{As}_{1-x}$, formed as a dark gray mirror on the sides of the sublimator during thermolysis. This material was scraped from the sides and collected (0.048 g, 28.6%) and its identity verified by comparison of the d-spacings and line intensities obtained by XRD analysis with those of both GaP (JCPDS file 32-397) and GaAs (JCPDS file 14-450). The approximate average particle size of 6.7 nm was calculated using the Scherrer equation. Anal. Found: C, 1.73; H, 0.00; As, 33.43; Ga, 52.30; P, 12.72. Calc. for GaP_xAs_{1-x}: C, 0.00; H, 0.00; As, 30.54; Ga, 56.84; P, 12.62%.

*2.9. Thermolysis of **3***

Thermolysis of **3** was conducted in two parts. A solution of Et_2GaCl (0.327 g; 2.0 mmol) and 50 ml of decane was prepared and to it was added a solution of $P(SiMe_3)_3$ (0.251 g; 1.0 mmol) and $Sb(SiMe_3)_3$ (0.341 g; 1.0 mmol) at r.t. The resulting light yellow solution was stirred at r.t. overnight. It was then heated to reflux at 174°C for 10 h. The solution turned rust-brown and finally black at 100°C. The solvent was then removed in vacuo and the sticky black material was transferred to a sublimator. It was then evacuated for 2 h and heated under dynamic vacuum to 425°C for 4 h. The material GaP_xSb_{1-x} was collected as black chunks on the bottom of the sublimator (0.172 g, 58.9%) and its identity verified by comparison of the d-spacings and line intensities obtained by XRD analysis with those of both GaP (JCPDS file 32-397) and GaSb (JCPDS file 7-215). The approximate average particle size of 9.3 nm was calculated using the Scherrer equation. Anal. Found: C, 2.10; H, 0.00; Ga, 44.82; P, 10.54; Sb, 42.52. Calc. for $GaP_xSb_{(1-x)}$: C, 0.00; H, 0.00; Ga, 47.73; P, 10.60; Sb, 41.67%.

2.10. X-ray structural solution and refinement

Crystal, data collection, and refinement parameters for **1**–**3** are given in Table 1, while selected bond lengths and angles are presented in Table 2. An ORTEP diagram showing the solid-state conformation of **3** can be found in Fig. 1. Suitable crystals for data collection were selected and mounted in nitrogen-flushed thin-walled capillaries. All data were collected with a Siemens P4 diffractometer equipped with a SMART/CCD detector. The systematic absences in the diffraction data of **1**, **2**, and **3**, are consistent for the C-centered monoclinic space groups, *Cc* and *C2/c*. The *E*-statistic suggested the centrosymmetric space group, which yielded chemically reasonable and computationally stable results of refinement. These isomorphous structures were solved using direct methods or initiated from analog coordinates, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The molecules for all three structures lie on twofold rotation axes. There is arsenic–phosphorus compositional disorder in **2** (70/30). There is a crystallographically imposed disorder between the phosphorus and antimony atoms of **3**; the unique atom was refined as an undersized antimony atom and labeled SbP(1). 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 (5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

3. Results and discussion

The 1:1 mole ratio reaction of Et_2GaCl with $P(SiMe_3)_3$ leads to the isolation of the dimeric compound $[Et_2GaP(SiMe_3)_2]_2$ (**1**). Compounds **2** and **3** were prepared from the direct reaction of two equivalents of Et_2GaCl with one equivalent each of $P(SiMe_3)_3$ and $As(SiMe_3)_3$ for **2** and one equivalent each of $P(SiMe_3)_3$ and $Sb(SiMe_3)_3$ for **3**. This method was employed for

Table 1
Crystallographic data for $[Et_2GaP(SiMe_3)_2]_2$ (**1**) $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$ (**2**) and $(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**)

Formula	$C_{20}H_{56}Ga_2P_2Si_4$	$C_{20}H_{56}As_{1.44}Ga_2P_{0.56}Si_4$	$C_{20}H_{56}Ga_2PSbSi_4$
Formula weight	610.39	673.68	701.17
Space group	*C2/c*	*C2/c*	*C2/c*
a (Å)	17.9864(3)	18.1212(2)	18.1221(3)
b (Å)	9.3513(2)	9.3971(2)	9.5418(2)
c (Å)	20.1239(3)	20.3337(4)	20.6748(2)
β (°)	100.66(2)	100.4686(4)	99.7066(5)
V (Å³)	3326.18(7)	3404.92(15)	3523.85(8)
Z	4	4	4
Crystal color, habit	Colorless, rod	Colorless, block	Dark brown, block
D_{calc} (g cm^{-3})	1.219	1.314	1.322
μ(Mo–K$_\alpha$) (cm^{-1})	18.67	31.45	24.67
Temperature (K)	203(2)	173(2)	203(2)
Diffractometer	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
$R(F)$ (%) [a]	5.00	2.92	5.17
$R(wF^2)$ (%) [a]	15.86	7.80	19.70

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

Table 2
Selected bond lengths (Å) and angles (°)

$[Et_2GaP(SiMe_3)_2]_2$ (**1**)			
Ga(1)–P(1)	2.4558(7)	P(1)–Si(1)	2.2602(11)
Ga(1)–C(7)	2.017(3)	P(1)–Si(2)	2.2634(10)
Ga(1)–C(9)	1.996(3)		
Ga(1)–P(1)–Ga(1A)	91.37(3)	Si(1)–P(1)–Ga(1)	111.44(3)
P(1)–Ga(1)–P(1A)	88.63(3)	Si(1)–P(1)–Ga(1A)	114.73(4)
C(7)–Ga(1)–P(1)	110.99(10)	Si(2)–P(1)–Ga(1)	117.51(4)
C(7)–Ga(1)–P(1A)	112.08(9)	Si(2)–P(1)–Ga(1A)	113.60(3)
C(9)–Ga(1)–P(1)	114.35(10)	C(7)–Ga(1)–C(9)	114.67(13)
C(9)–Ga(1)–P(1A)	113.42(10)	Si(1)–P(1)–Si(2)	107.77(4)
$(Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$ (**2**)			
Ga(1)–As/P(1)	2.5273(4)	Ga(1)–C(9)	1.999(3)
Ga(1A)–As/P(1)	2.5200(4)	As/P(1)–Si(1)	2.3334(8)
Ga(1)–As/P(1A)	2.5200(4)	As/P(1)–Si(2)	2.3347(8)
Ga(1)–C(7)	2.006(3)		
Ga(1)–As/P(1)–Ga(1A)	92.152(13)	Si(1)–As/P(1)–Ga(1)	111.18(2)
As/P(1)–Ga(1)–As/P(1A)	87.845(13)	Si(1)–AS/P(1)–Ga(1A)	114.50(2)
C(9)–Ga(1)–As/P(1)	114.06(9)	Si(2)–As/P(1)–Ga(1)	117.09(2)
C(9)–Ga(1)–As/P(1A)	113.41(9)	Si(2)–As/P(1)–Ga(1A)	114.28(2)
C(7)–Ga(1)–As/P(1)	110.83(8)	C(9)–Ga(1)–C(7)	115.65(12)
C(7)–Ga(1)–As/P(1A)	111.89(9)	Si(1)–As/P(1)–Si(2)	107.33(3)
$(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**)			
Ga(1)–Sb/P(1)	2.5683(13)	Ga(1)–C(9)	1.994(8)
Ga(1A)–Sb/P(1)	2.5761(11)	Sb/P(1)–Si(1)	2.445(2)
Ga(1)–Sb/P(1A)	2.5761(11)	Sb/P(1)–Si(2)	2.428(2)
Ga(1)–C(7)	1.995(8)		
Ga(1)–Sb/P(1)–Ga(1A)	92.77(3)	Si(1)–Sb/P(1)–Ga(1)	111.12(6)
Sb/P(1)–Ga(1)–Sb/P(1A)	87.23(3)	Si(1)–Sb/P(1)–Ga(1A)	114.37(6)
C(9)–Ga(1)–Sb/P(1)	114.0(3)	Si(2)–Sb/P(1)–Ga(1)	117.02(7)
C(9)–Ga(1)–Sb/P(1A)	112.8(3)	Si(2)–Sb/P(1)–Ga(1A)	115.31(6)
C(7)–Ga(1)–Sb/P(1)	110.4(3)	C(9)–Ga(1)–C(7)	116.3(4)
C(7)–Ga(1)–Sb/P(1A)	112.6(3)	Si(1)–Sb/P(1)–Si(2)	106.19(9)

the synthesis of the previously reported $(Me_3Si)_2As[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ [2], however **3** represents the first example of a compound with a core ring containing phosphorus and antimony.

It was also shown, using ^{1}H-NMR, that the synthesis of compounds **2** and **3** was possible by equilibration of **1** with either of the two dimers, $[Et_2GaAs(SiMe_3)_2]_2$ for **2** or $[Et_2GaSb(SiMe_3)_2]_2$ for **3**. Equilibration of **1** and $[Et_2GaAs(SiMe_3)_2]_2$ in toluene-d_8 afforded **2** in 100% yield by ^{1}H-NMR. Comparison of the peaks for the trimethylsilyl moieties bound to P showed complete conversion of the triplet associated with **1** to the doublet associated with **2** after 24 h.

Compounds **1**, **2**, and **3** are isomorphous and crystallize in the monoclinic space group *C*2/*c*. The ORTEP diagram for **3** is depicted in Fig. 1. For **1** the average Ga–P bond length of 2.4558 (7) Å and the Ga–P–Ga and P–Ga–P endocyclic ring angles of 91.37(3)° and 88.63(3)°, respectively, fall well within the range of values associated with the numerous dimeric gallium–phosphorus compounds reported in the literature [11–13].

Compound **2** is structurally distinct from all similar previously reported mixed-pnicogen compounds [2,7,14,15] in that the compositional disorder associated with the pnicogen sites in the molecule is best solved

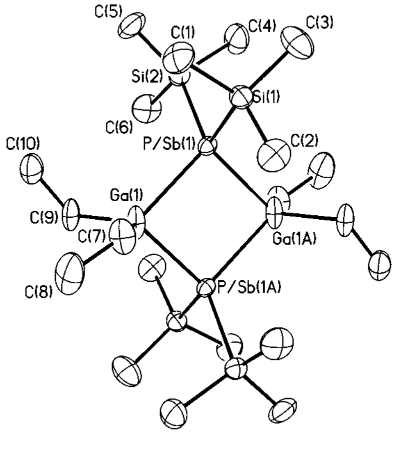
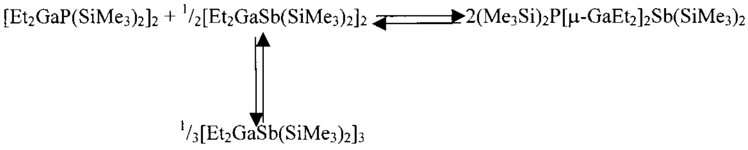


Fig. 1. ORTEP diagram of $(SiMe_3)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2$ (**3**). The Sb/P disordered atom is labeled as Sb/P(1). Thermal ellipsoids at 30% probability and hydrogen atoms are omitted for clarity.

$$[Et_2GaP(SiMe_3)_2]_2 + [Et_2GaAs(SiMe_3)_2]_2 \rightleftarrows (Me_3Si)_2P[\mu\text{-}GaEt_2]_2As(SiMe_3)_2$$

Scheme 1.



$$\begin{tikzcd}[Et_2GaP(SiMe_3)_2]_2 + {}^1/_2[Et_2GaSb(SiMe_3)_2]_2 \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & 2(Me_3Si)_2P[\mu\text{-}GaEt_2]_2Sb(SiMe_3)_2 \\ {}^1/_3[Et_2GaSb(SiMe_3)_2]_3 & \end{tikzcd}$$

Scheme 2.

with 70% As/30% P occupancy. This is in contrast with the solution phase ^{1}H-NMR of the material, which shows an approximately equal integrated area for the trimethylsilyl peaks, associated with the P and As atoms. As with all previously reported 'mixed pnicogen' compounds, X-ray crystallography is unable to distinguish between two different structural possibilities in the solid phase: (a) crystallization of discreet mixed-pnicogen molecules or (b) a cocrystallization of the corresponding dimers, namely **1** and $[Et_2GaAs(SiMe_3)_2]_2$. Indeed the nonequivalent occupancy of the P/As sites implies at least some sort of cocrystallization of compounds. The structure of **2** is also supported by EI MS evidence in which molecular ions of 654 and 625 mass units corresponding to **2*** and (**2**–Et)*, respectively, were observed. The use of multinuclear NMR allows determination of the solution phase structure of **2**, because of the characteristic splitting caused by P. In the case of **1**, a triplet is observed for exocyclic protons (and carbons) as is the case with all similar four-membered ring compounds containing P at opposing positions because of virtual coupling [16]. In the case of **2**, however, the protons (and carbons) of the trimethylsilyl moiety bound to P are split into a doublet indicating the presence of only one P in the ring and therefore discreet mixed pnicogen molecules. Doublet resonances are also observed for the ethyl moieties bound to Ga further establishing the presence of only one P atom in the molecule. The approximately equal integrated area of the doublet associated with the trimethylsilyl moieties bound to P and the singlet associated with the trimethylsilyl moieties bound to As in **2** is in conflict with the preponderance of As in the solid phase indicated by the crystal structure. This behavior seems to indicate the existence of an equilibrium in the solution phase according to Scheme 1.

This hypothesis is also supported by the fact that synthesis of **2** is possible via comproportionation of **1** and $[Et_2GaAs(SiMe_3)_2]_2$. It has been observed that $[Et_2GaAs(SiMe_3)_2]_2$ has a lower solubility in hexane when compared to **1**. This could explain the plurality of As in the crystal structure of **2** in that crystals falling out of solution early may have a higher As content while later crystals may have a higher P content.

The X-ray crystal structure for compound **3** (Fig. 1) exhibits the more typical 50/50 occupancy of the ring pnicogen atoms, namely P and Sb. The mixed pnicogen structure of this species is again supported by EI MS evidence in which a molecular ion peak at 700 mass units corresponding to **3*** was observed. Again the same limitations of X-ray crystallography (vide supra) exist for **3** in that differentiation between the highly unlikely possibility of exact cocrystallization of the dimers **1** and $[Et_2GaSb(SiMe_3)_2]_2$ and crystallization of discreet mixed-pnicogen molecules is not possible. Again however, we can rely on multinuclear NMR for structural verification of **3**. The ^{1}H- and $^{13}C\{^1H\}$-NMR data for **3**, however, are rather complex in that peaks for **3**, **1**, $[Et_2GaSb(SiMe_3)_2]_2$, and $[Et_2GaSb(SiMe_3)_2]_3$ are observed. As with **2**, we are able to establish that **3** is, in fact, a discreet mixed-pnicogen molecule as evinced by the doublet peak observed for the trimethylsilyl moieties bound to P in **3**. The dimer/trimer equilibrium of $[Et_2GaSb(SiMe_3)_2]_3$ was described previously [2] and it seems that **3** is in equilibrium with all three compounds according to Scheme 2. Comparison of the relative integrated area of the trimethylsilyl peaks showed the concentration of **3** to be approximately four times that of **1** and $[Et_2GaSb(SiMe_3)_2]_2$/$[Et_2GaSb(SiMe_3)_2]_3$.

The $^{13}C\{^1H\}$-NMR for **3** in the trimethylsilyl region consists of a triplet at δ 4.13 corresponding to **1**, a doublet at δ 4.20 corresponding to the P-bound trimethylsilyl moieties in **3**, a singlet at δ 5.52 corresponding to the Sb-bound trimethylsilyl moieties in **3**, a singlet at δ 5.38 corresponding to $[Et_2GaSb(SiMe_3)_2]_2$ and a singlet at δ 5.74 corresponding to $[Et_2GaSb(SiMe_3)_2]_3$. Additionally, the peaks associated with the methylene and methyl carbons of the ethyl groups of the previous compounds are also observed. The P atom(s) split not only the carbons of the trimethylsilyl moieties directly bound to them, but also the carbons of the ethyl moieties attached to Ga in an identical fashion and we are, therefore, able to unequivocally assign the peaks of the ethyl moieties to **1**, **3**, or $[Et_2GaSb(SiMe_3)_2]_2$/$[Et_2GaSb(SiMe_3)_2]_3$. Thus, multinuclear NMR, EI MS, and the fact that an exact cocrys-

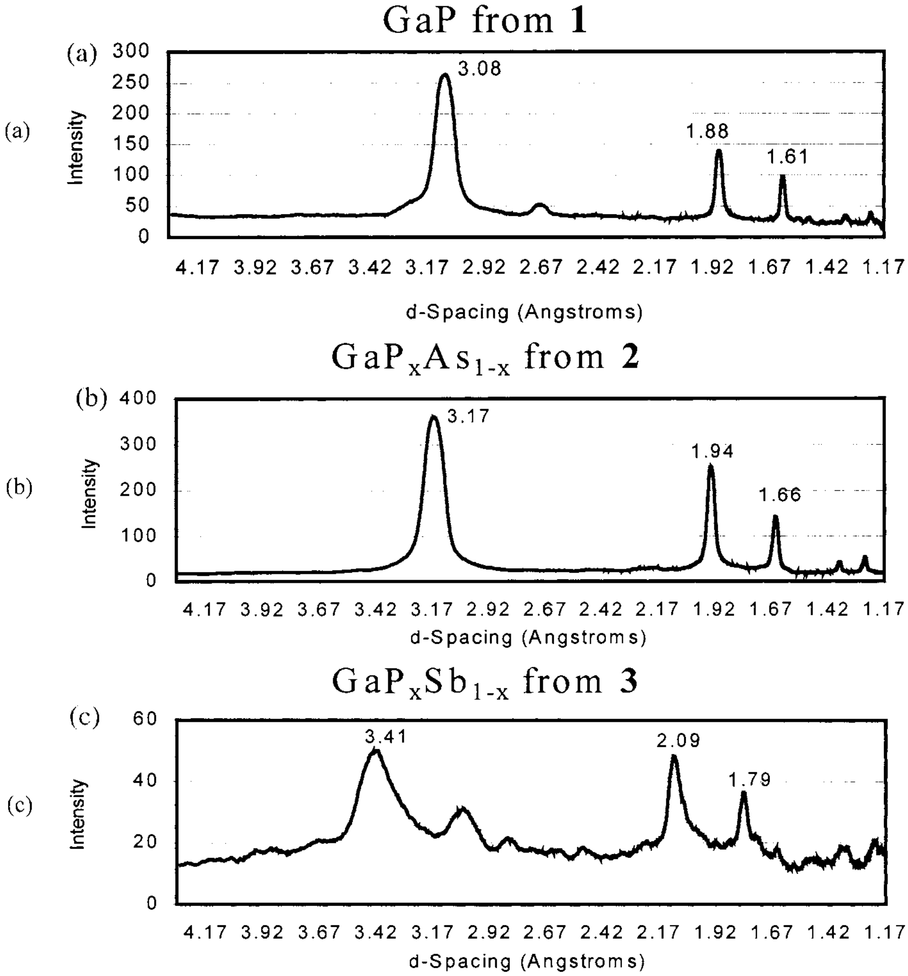


Fig. 2. XRD spectra of (a) GaP obtained from the thermolysis of **1** at 425°C. (b) GaP$_x$As$_{1-x}$ obtained from the thermolysis of **2** at 425°C. (c) GaP$_x$Sb$_{1-x}$ obtained from the thermolysis of **3** at 425°C.

tallization of dimers is improbable support the existence of the mixed-pnicogen compound.

An equilibration study of **1** and [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$ conducted in toluene-*d*$_8$ resulted in the formation of **3** after 15 h of agitation at r.t. Comparison of the relative integrated area of the trimethylsilyl peaks showed the concentration of **3** to be approximately twice that of **1** and [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$/[Et$_2$GaSb(SiMe$_3$)$_2$]$_3$. Compound **3** exists in a dynamic equilibrium with **1** and [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$/[Et$_2$GaSb(SiMe$_3$)$_2$]$_3$ in toluene-*d*$_8$ and so therefore complete conversion from the two dimers to the mixed pnicogen does not occur. After 24 h however, the relative integration values for the peaks associated with the trimethylsilyl moieties on **1**, **3**, and [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$/[Et$_2$GaSb(SiMe$_3$)$_2$]$_3$ compared well with those obtained from the ^{1}H-NMR spectrum of **3**.

The average Ga–As/P bond length in **2** is 2.5273(4) Å and significantly larger than the average of the gallium–pnicogen bond lengths in **1** and [Et$_2$GaAs(SiMe$_3$)$_2$]$_2$. Similarly, the Ga–As/P–Ga and As/P–Ga–As/P bond angles of 92.152(13)° and 87.845(13)°, respectively, lie closer in value to the analogous bond angles in [Et$_2$GaAs(SiMe$_3$)$_2$]$_2$. This is no doubt the result of the preponderance of [Et$_2$GaAs(SiMe$_3$)$_2$]$_2$ in the crystal but it is interesting to note that very similar characteristics were observed in the case of the previously reported (Me$_3$Si)$_2$As[μ-GaEt$_2$]$_2$Sb(SiMe$_3$)$_2$ [2].

Conversely the average Ga–Sb/P bond length in **3** of 2.5683(13) Å is essentially equal to the average bond lengths of the analogous bonds in **1** and [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$. In addition, the Ga–Sb/P–Ga angle of 92.77(3) and the Sb/P–Ga–Sb/P angle of 87.23(3) are very similar to the analogous bond angles in [Et$_2$GaSb(SiMe$_3$)$_2$]$_2$. In the previously reported Al, Ga, and in mixed-pnicogen compounds, which were structurally characterized [2,7,14,15], the metal–pnicogen bond length was essentially the average of the lengths of the starting dimers.

In order to determine the suitability of **1**, **2**, and **3** as precursors to GaP, GaP$_x$As$_{1-x}$, and GaP$_x$Sb$_{1-x}$, respectively, preliminary thermolysis studies were conducted. The maximum temperature used for the pyrolyses was 425°C in all cases. In the case of **1**, the bulk powder produced from the pyrolysis was identified as GaP by XRD, produced in a 22.8% yield. The approximate average particle size of 6.4 nm was calculated using the Scherrer equation. Elemental analysis of this sample indicates that it is 94.10% GaP, with a total residual carbon and hydrogen contamination of 6.30%. The Ga:P ratio for this material was 1.00:1.13.

The material that was obtained from the pyrolysis of **2** amounted to a 28.6% yield and had an average particle size of 6.7 nm. The powder XRD spectrum for this material indicates the presence of GaP_xAs_{1-x}. This observation is based on the fact that the XRD spectrum contains three major peaks whose positions lie between the values associated with GaP and GaAs, thus following Vegard's Law [17]. Such average values are also associated with other compounds believed to be ternary materials [2,7,8]. Elemental analysis of this sample indicates that it is 98.45% GaP_xAs_{1-x}, with a small amount (1.53% total) of residual carbon with no detectable hydrogen, and a Ga:P:As ratio of 1.83:1.00:1.09.

Compound **3** is unstable at r.t. and decomposition was observed during its isolation and characterization. In an attempt to minimize the decomposition prior to pyrolysis, **3** was prepared and pyrolyzed in decane and then under vacuum at 425°C. This method produced material in a 58.9% yield. The XRD spectrum for the powder indicates that it contains GaP_xSb_{1-x} again by the same analogy as for the material produced from the decomposition of **2**. In this case the peak positions lie between the values for GaP and GaSb. Elemental analysis of this sample indicates that it is 97.88% GaP_xSb_{1-x}, with a small amount (2.10% total) of residual carbon and no detectable hydrogen. The Ga:P:Sb ratio for this material was 1.89:1.00:1.02. XRD plots for the materials obtained from **1**, **2**, and **3** can be found in Fig. 2.

For **1** and **2**, it is clear that while relatively clean nanocrystalline material is produced, the overall yields are low, ca. 20%. One contributing factor to these low yields is the high volatility of the compounds, both of which sublimed readily under the conditions of the experiment. This behavior may be attributable in part to the incorporation of the small alkyl group on the gallium. While this volatility is detrimental to the described studies, it does suggest that these compounds may be excellent candidates for OMCVD experiments.

4. Supplementary material

Crystallographic data (tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136999 for **1**, CCDC no. 137000 for **2**, CCDC no. 137001 for **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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