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Preparation and Characterization of Arsine Derivatives: X-ray Crystal Structures of $As(Si^tBuMe_2)_3$, $As(SiMe_3)_2(SiPh_3)$, $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$, and $As(SePh)_3$

Ryan A. Baldwin, Hamid Rahbarnoohi, Leonidas J. Jones III, Andrew T. McPhail, 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, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

Arnold L. Rheingold and Glenn P. A. Yap

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

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ABSTRACT

*$As(Si^tBuMe_2)_3$ (**1**) was prepared by the salt-elimination reaction between $(Na/K)_3As$ and $^tBuMe_2SiCl$. Mixing $LiAs(SiMe_3)_2$ with Ph_3SiCl (1:1) yielded $As(SiMe_3)_2(SiPh_3)$ (**2**) in a good crystalline yield. Reaction of **2** (1:1) with Et_3Ga gave the expected Lewis acid-base adduct $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$ (**3**). The 1:1 mole ratio reaction of $In(SePh)_3$ with $As(SiMe_3)_3$ resulted in a ligand redistribution around the indium and arsenic centers to afford $As(SePh)_3$ (**4**) in a low yield. The solid-state structures of **1**–**4** have been established by single-crystal X-ray analysis. Crystal data for **1**, monoclinic space group $P\,2_1/c$, with $a = 11.112(2)$, $b = 17.453(2)$, $c = 14.199(2)$ Å, $\beta = 114.89°$ for $Z = 4$; **2**, orthorhombic space group $P\,c2_1n$, with $a = 9.236(1)$, $b = 16.612(2)$, $c = 16.803(4)$ Å for $Z = 4$; **3**, monoclinic space group $P\,2_1/c$, with $a = 16.799(1)$, $b = 11.199(2)$, $c = 19.413(3)$ Å, $\beta = 112.22(1)$ for $Z = 4$; **4**, trigonal space group $R\,\bar{3}$, with $a = 12.863(5)$, $c = 18.96(1)$ Å for $Z = 6$.*

INTRODUCTION

For the last decade, our laboratory has had great interest in the chemistry of silylarsines [1]. These compounds, in combination with group-13 alkyl or halogen derivatives, have been shown to be excellent starting reagents for preparing compounds that contain the group-13 element–arsenic bond. Although the reactivity of silylarsines is well documented *(vide supra)*, structural characterization data for these

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the Department of Chemistry of the University of Massachusetts at Amherst.

*To whom correspondence should be addressed.

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species has been limited to solution- and gas-phase measurements [2] due to their noncrystallinity. As a result, unambiguous structural information for these compounds is scant and appears to be limited to lithium–arsenide salts coordinated to donor solvents [3]. Therefore, we became interested in preparing organosilylarsines that could find utility in our ongoing investigations of group-13 element–arsenic compounds and be characterized in the solid state. In addition to this chemistry, we wished to study systems that focused on the reactions of organosilylarsines with group-13 and group-16 derivatives. Through our efforts, we have been able to observe some interesting chemical phenomena and isolate several new compounds (this work).

Herein, we report the synthesis and structural characterization of three new organosilylarsine derivatives $As(Si^tBuMe_2)_3$ (**1**), $As(SiMe_3)_2(SiPh_3)$ (**2**), and $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$ (**3**). The X-ray crystal structure of $As(SePh)_3$ (**4**), previously unreported [4], is also detailed.

EXPERIMENTAL

Synthesis

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 general Schlenk techniques. Toluene and pentane were distilled over sodium–potassium alloy under dry dinitrogen. Dimethoxyethyl ether (DME) and diethyl ether were distilled from sodium benzophenone ketyl under dry dinitrogen. $In(SePh)_3$ [5] and $As(SiMe_3)_3$ [6] were synthesized by literature procedures. $LiAs(SiMe_3)_2$ [6] was prepared via the 1:1 mole reaction of $As(SiMe_3)_3$ and MeLi. Sodium–potassium alloy (44%:56%), triphenylsilyl chloride, and triethylgallium were purchased from Strem chemicals. Arsenic powder was purchased from Atomergic Chemetals. *tert*-Butyldimethylsilyl chloride was purchased from Aldrich Chemicals and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively, and a Varian Unity 400 spectrometer operating at 400 and 100.6 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively, or the upfield pentet of C_7D_8 at δ 2.09 ppm for the ^1H NMR spectra. All NMR samples were prepared in 5-mm tubes that were flame-sealed under vacuum or septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas–Hoover Uni-melt apparatus, and capillaries were flame-sealed under argon. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Mass spectral data were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. X-ray crystallographic data were obtained as described *(vide infra)*.

*Preparation of $As(Si^tBuMe_2)_3$ (**1**)*

Sodium–potassium alloy (2.514 g, 84.08 mmol) was transferred via pipet to a 50 mL addition bulb, which was attached to a 1 L round-bottomed screw-top flask equipped with a Teflon valve and magnetic stirbar. A second 50 mL addition bulb attached to the 1 L flask was charged with $^tBuMe_2SiCl$ (12.666 g, 84.08 mmol) dissolved in 40 mL of DME. Arsenic powder (2.000 g, 26.69 mmol) was added to the 1 L reaction bulb along with 450 mL of DME. The flask was removed from the dry box and placed in an oil bath. The arsenic suspension was heated to 65°C with stirring, and the sodium–potassium alloy was added over a 2 minute period. The resulting black suspension was heated at 65°C for 6.5 hours, followed by cooling to room temperature and addition of the $^tBuMe_2SiCl$ solution dropwise over a 1.5 hour period. The black mixture was heated at 82°C for 22 hours where a black to olive-green color change was observed. Cooling the reaction mixture, followed by filtration and concentration of volatiles in vacuo, afforded several colorless X-ray–quality crystals of **1**. Complete recovery of **1** was achieved by removal of the remaining volatiles, followed by sublimation and recrystallization of the white solid obtained. Yield (1.23 g, 10.9%). Mp 156–158°C. Anal. calcd. (found) for $C_{18}H_{45}AsSi_3$: C, 51.39 (51.41); H, 10.78 (10.79). ^1H NMR (C_6D_6): δ 0.39 (s, $-Me_2$), 1.05 [s, $-CMe_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.85 [s, $-Si(\underline{C}H_3)_3$] 27.82 [s, $-C(\underline{C}H_3)_3$].

*Preparation of $As(SiMe_3)_2(SiPh_3)$ (**2**)*

Ph_3SiCl (2.944 g, 10.00 mmol) dissolved in 25 mL of diethyl ether was added via pipet to a 50 mL addition bulb, which was attached to a 500 mL round-bottomed screw-top flask equipped with a Teflon valve and magnetic stirbar. $LiAs(SiMe_3)_2$ (2.282 g, 10.00 mmol) was added to the 500 mL reaction bulb along with 50 mL of diethyl ether. The flask was removed from the dry box and placed into an ice bath. The Ph_3SiCl solution was added dropwise to the stirring $LiAs(SiMe_3)_2$ solution over a 1 hour period, resulting in the formation of a white precipitate from solution.

The cloudy mixture was stirred at room temperature for 24 hours. Filtering the solution and removing the volatiles in vacuo afforded a pale yellow solid that was extracted into 10 mL of warm pentane. Cooling the extract to −30°C for 2 days afforded colorless crystals of **2** suitable for X-ray analysis (4.210 g, 87.4%). Mp 81–85°C. Anal. calcd. (found) for $C_{24}H_{33}AsSi_3$: C, 59.97 (60.06); H, 6.92 (6.89). ^{1}H NMR (C_6D_6): δ 0.21 (s, $-SiMe_3$), 7.08 (m, $-SiPh_3$), 7.86 (m, $-SiPh_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 4.30 (s, $-SiMe_3$); 128.10, 129.66, 136.72 (s, $-SiPh_3$).

Preparation of $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$ (**3**)

Et_3Ga (0.157 g, 1.00 mmol) dissolved in 25 mL of pentane was added via pipet to a 250 mL round-bottomed screw-top flask equipped with a Teflon valve and magnetic stirbar. Compound **2** (0.482 g, 1.00 mmol) dissolved in 25 mL of pentane was added via pipet to the stirring Et_3Ga solution. The resulting cloudy solution was stirred at room temperature for 4 days. Removal of the volatiles in vacuo yielded a white-crystalline solid that was dissolved in 5 mL of warm toluene. Cooling the extract to −30°C for several days afforded colorless hexagonal crystals of **3** suitable for X-ray analysis (0.447 g, 70%). Mp 107–110°C. Anal. calcd. (found) for $C_{30}H_{48}AsGaSi_3$: C, 56.51 (56.72); H, 7.59 (7.67). ^{1}H NMR (C_6D_6): δ 0.21 (s, $-SiMe_3$), 0.58 [q, $-CH_2$ ($^3J_{H-H}$ = 8 Hz)], 1.27 [t, $-CH_3$ ($^3J_{H-H}$ = 8 Hz)], 7.08 (m, $-SiPh_3$), 7.81 (m, $-SiPh_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 4.01 (s, $-Si(\underline{C}H_3)_3$), 9.04 (s, $-CH_2$), 10.54 (s, $-CH_3$); 127.64, 129.71, 136.61 (s, $-SiPh_3$).

Preparation of $As(SePh)_3$ (**4**)

$In(SePh)_3$ (1.07 g, 1.84 mmol) dissolved in 50 mL of toluene was added to a 250 mL round-bottomed flask equipped with a ground-glass valve and a magnetic stirbar. $As(SiMe_3)_3$ (0.54 g, 1.84 mmol) was added dropwise via syringe to the stirring $In(SePh)_3$ suspension. After complete addition of the $As(SiMe_3)_3$, a red precipitate formed from solution. The resulting red mixture was allowed to stir outside of the dry box for 24 hours at room temperature. After 24 hours, the stirring was stopped, and the red precipitate settled to the bottom of the flask, leaving a yellow solution. The yellow solution was transferred via canula to an empty 250 mL round-bottomed flask, and the volatiles were removed in vacuo, yielding a yellow solid that was extracted with 30 mL of pentane. Cooling the extract to −4°C for 12 hours afforded yellow crystals of **4** suitable for X-ray analysis (0.099 g, 10% yield based on As). The ^{1}H NMR, mass spectral, and melting point data for **4** matched exactly with data reported in a previous literature preparation of $As(SePh)_3$ [4], thereby confirming its identity.

TABLE 1 Crystallographic Data and Measurements for $As(Si^tBuMe_2)_3$ (**1**), $As(SiMe_3)_2(SiPh_3)$ (**2**), $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$ (**3**), and $As(SePh)_3$ (**4**)

	1	**2**
Mol formula	$C_{18}H_{45}AsSi_3$	$C_{24}H_{33}AsSi_3$
fw	420.74	480.70
Cryst. syst.	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pc2_1n$
a, Å	11.112(2)	9.236(1)
b, Å	17.453(2)	16.612(2)
c, Å	14.199(2)	16.803(4)
β, deg	114.89(1)	90.00(−)
V, Å^3	2498(1)	2578.0(8)
Z	4	4
Radiation (wavelength, Å)	Cu-Kα (1.5418)	Mo-Kα (0.71073)
μ, cm^{-1}	32.2	14.6
Temp, °C	25	−120
D_{calcd}, g cm^{-3}	1.119	1.239
Crystal Dimens., mm	0.16 × 0.24 × 0.52	0.30 × 0.25 × 0.15
T_{max}; T_{min}	1.00:0.72 (relative)	0.76:0.58
Scan type	ω–2Θ	ω
$2\Theta_{max}$, deg	37.5	50
No. of rflns recorded	5320	2728
No. of nonequiv. Rflns recorded	5108	2701
R_{merg} (on I)	0.038	0.015
No. of rflns retained	2913	2102
No. of params. Refined	200	252
R; R_w^a	0.068; 0.092	0.033; 0.035
Goodness-of-fit^b	2.18	1.04
Max shift/esd. in final Least-squares cycle	0.03	0.001
Final max, min $\Delta\rho$, e/Å^{-3}	1.2; −0.8	0.34; −0.30

[a] $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.
[b] Goodness-of-fit $= [\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

X-ray Crystal Structure Determination

[Crystallographic data for compounds 1–4 are summarized in Table 1.]

Compound **1**. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer utilizing graphite-monochromated Cu-Kα (λ = 1.5418 Å) radiation. Colorless crystals of **1** suitable for X-ray diffraction

TABLE 1 (continued)

	3	4
Mol formula	$C_{30}H_{48}AsGaSi_3$	$C_{18}H_{15}AsSe_3$
fw	637.59	543.11
Cryst. syst.	monoclinic	trigonal
Space group	$P2_1/c$	R 3
a, Å	16.799(1)	12.863(5)
b, Å	11.199(2)	12.863(5)
c, Å	19.413(3)	18.96(1)
β, deg	112.22(1)	90.00(−)
V, Å^3	3381.0(7)	2717.0(2)
Z	4	6
Radiation (wavelength, Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
μ, cm^{-1}	19.1	78.3
Temp, °C	25	−120
D_{calcd}, g cm^{-3}	1.253	1.992
Crystal Dimens., mm	0.40 × 0.40 × 0.30	0.25 × 0.25 × 0.35
T_{max}; T_{min}	0.48:0.34	0.20:0.14
Scan type	ω	ω
$2\Theta_{max}$, deg	45	50
No. of rflns recorded	5387	1125
No. of nonequiv. Rflns recorded	4359	1083
R_{merg} (on I)	0.038	0.108
No. of rflns retained	2966	758
No. of params. Refined	317	68
R; R_w^a	0.044; 0.077	0.045; 0.054
Goodness-of-fit^b	1.05	1.67
Max shift/esd. in final Least-squares cycle	0.001	0.000
Final max, min $\Delta\rho$, e/Å^{-3}	0.28; −0.34	0.88; −1.10

[a] $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.
[b] Goodness-of-fit $= [\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

were mounted inside glass capillaries under argon. Preliminary unit-cell parameters and space-group information were derived from oscillation and Weissenberg photographs. The space group was defined uniquely by the systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$. Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections (35° < Θ < 40°) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects; an empirical absorption correction was also applied. The crystal structure was solved by the heavy-atom approach. Initial coordinates for the arsenic atom were derived from a Patterson map. A series of F_0 and difference-Fourier syntheses, phased successively by an increasing number of atoms, yielded coordinates for the silicon and carbon atoms. Atomic positional and thermal parameters of the nonhydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions (C–H = 1.05 Å) during the later iterations, and an extinction correction was included as a variable during the final cycles. The parameter refinement converged at R = 0.068 (R_w = 0.092). A final difference-Fourier synthesis contained no unusual features. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf–Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom-scattering factors and their anomalous dispersion corrections were taken from Ref. [7]. Selected interatomic distances and angles are given in Tables 2 and 3, respectively; selected fractional atomic coordinates are listed in Table 4. An ORTEP [8] diagram showing the solid-state conformation and atom numbering scheme of **1** is presented in Figure 1.

Compounds **2** *and* **4**. X-ray data were collected on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The crystals used were mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at −120°C, and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counter statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement that converged at R = 0.033 (R_w = 0.035) for **2** and R = 0.045 (R_w = 0.054) for **4**. A final difference-Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX [9] suite of structure determination programs. The space group choices for **2** and **4** were confirmed by the MISSYM [10] missing symmetry treatment program. For all structure-factor calculations, neutral atom-scattering factors and their anomalous dispersion corrections were taken from Ref. [7]. Selected interatomic distances and angles are given in Tables 2 and 3, respectively; selected fractional atomic coordinates are listed in Table 4. ORTEP [8] diagrams showing the solid-state conformations and atom numbering schemes of **2** and **4** are presented in Figures 2 and 4, respectively.

Compound **3**. X-ray data were collected at 25°C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Colorless crystals of **3** suitable for X-ray diffraction

TABLE 2 Selected Bond Distances (Å) for **1–4**, with Estimated Standard Deviations in Parentheses

Bond Lengths			
1			
As–Si(1)	2.377(3)	Si(1)–C(11)	1.87(1)
As–Si(2)	2.378(2)	Si(2)–C(21)	1.89(1)
As–Si(3)	2.375(2)	Si(3)–C(31)	1.87(1)
2			
As–Si(1)	2.352(2)	Si(1)–C(1)	1.868(8)
As–Si(2)	2.364(2)	Si(2)–C(6)	1.856(8)
As–Si(3)	2.354(2)	Si(3)–C(31)	1.882(6)
3			
As–Si(1)	2.379(2)	As–Si(3)	2.376(2)
As–Si(2)	2.378(2)	As–Ga	2.694(1)
4			
As(1)–Se(1)	2.374(1)	Se(1)–C(11)	1.935(8)

TABLE 3 Selected Bond Angles (°) for **1–4**, with Estimated Standard Deviations in Parentheses

Bond Angles			
1			
Si(1)–As–Si(2)	106.7(1)	As–Si(1)–C(11)	112.1(3)
Si(1)–As–Si(3)	106.3(1)	As–Si(2)–C(21)	112.1(3)
Si(2)–As–Si(3)	106.6(1)	As–Si(3)–C(31)	111.7(3)
2			
Si(1)–As(1)–Si(2)	103.04(7)	As(1)–Si(2)–C(4)	107.3(2)
Si(1)–As(1)–Si(3)	105.84(6)	As(1)–Si(2)–C(5)	116.4(3)
Si(2)–As(1)–Si(3)	106.17(6)	As(1)–Si(2)–C(6)	106.6(3)
As(1)–Si(1)–C(1)	108.5(3)	As(1)–Si(3)–C(11)	106.6(2)
As(1)–Si(1)–C(2)	105.5(2)	As(1)–Si(3)–C(21)	106.5(2)
As(1)–Si(1)–C(3)	115.5(2)	As(1)–Si(3)–C(31)	119.5(2)
3			
Si(1)–As–Si(2)	105.42(6)	Si(2)–As–Ga	109.33(5)
Si(1)–As–Si(3)	106.75(6)	Si(3)–As–Ga	116.35(4)
Si(2)–As–Si(3)	108.84(6)	C(1)–Ga–As	105.0(2)
Si(1)–As–Ga	109.58(5)	C(5)–Ga–As	102.8(2)
4			
Se(1)–As(1)–Se(1a)	95.56(5)	As(1)–Se(1)–C(11)	96.4(2)

were mounted inside glass capillaries under argon. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections $(20^\circ < 2\,\Theta < 25^\circ)$. The structure was solved by direct methods, completed by subsequent difference-Fourier syntheses and refined by full-matrix least-squares procedures. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS [11] (4.2) and SHELXTL (5.3) program libraries. Selected interatomic distances and angles are given in Tables 2 and 3, re-

TABLE 4 Selected Nonhydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for **1–4**, with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	$B_{eq}(\text{Å}^2)^a$
1				
As	0.26144(6)	0.25011(4)	0.00607(6)	3.60(1)
Si(1)	0.0567(2)	0.2061(1)	0.0016(2)	4.45(4)
Si(2)	0.4300(2)	0.1704(1)	0.1258(2)	4.45(4)
Si(3)	0.2960(2)	0.3745(1)	0.0807(2)	4.40(4)
C11	−0.0648(7)	0.2858(6)	−0.0218(7)	6.2(2)
C12	0.0671(8)	0.1534(6)	0.1188(7)	6.5(2)
C13	−0.0178(7)	0.1417(5)	−0.1165(6)	5.2(2)
C14	−0.1539(9)	0.1105(6)	−0.1263(9)	7.8(3)
C15	0.075(1)	0.0726(5)	0.1097(7)	7.1(3)
C16	−0.040(1)	0.1867(6)	−0.2160(7)	7.2(3)
C21	0.3685(9)	0.0701(5)	0.1292(7)	6.8(2)
C22	0.504(1)	0.2036(7)	0.2638(7)	7.1(3)
C23	0.5641(7)	0.1619(5)	0.0751(7)	5.4(2)
C31	0.4764(9)	0.3948(6)	0.1592(7)	6.7(3)
C32	0.2108(9)	0.3949(6)	0.1681(7)	6.7(2)
C33	0.2363(7)	0.4448(5)	−0.0316(6)	5.2(2)
2				
As1	0.68254(5)	0.85868(−)	0.73107(3)	1.71(3)
Si1	0.8083(2)	0.8878(1)	0.8494(1)	2.15(7)
Si2	0.5281(2)	0.7518(1)	0.7688(1)	2.12(8)
Si3	0.5313(2)	0.9702(1)	0.7076(1)	1.72(7)
C1	0.8808(8)	0.9925(4)	0.8426(5)	3.5(3)
C2	0.9636(7)	0.8150(5)	0.8523(4)	3.3(3)
C3	0.7016(7)	0.8765(5)	0.9427(4)	3.2(3)
C4	0.6440(7)	0.6726(4)	0.8162(5)	3.1(3)
C5	0.3754(8)	0.7779(5)	0.8379(5)	3.1(3)
C6	0.4496(9)	0.7107(5)	0.6755(5)	4.3(4)
C11	0.3666(7)	0.9308(4)	0.6544(4)	1.8(3)
C21	0.6264(7)	1.0345(4)	0.6314(4)	2.0(3)
C31	0.4740(6)	1.0355(4)	0.7934(4)	1.79(2)
3				
As	0.2404(1)	0.7073(1)	0.3918(1)	2.68(1)
Ga	0.2498(1)	0.4854(1)	0.3419(1)	3.55(1)
Si(1)	0.1134(1)	0.8029(2)	0.3100(1)	3.55(1)
Si(2)	0.3563(1)	0.8239(2)	0.3864(1)	3.47(1)
Si(3)	0.2389(1)	0.7217(1)	0.5133(1)	2.76(1)
C1	0.3742(4)	0.4443(6)	0.3846(3)	5.05(2)
C2	0.3995(4)	0.3560(6)	0.3386(4)	7.19(3)
C3	0.2022(4)	0.5101(5)	0.2321(3)	4.74(2)
C4	0.1746(4)	0.3965(6)	0.1876(4)	6.71(2)
C5	0.1764(4)	0.3910(5)	0.3817(4)	5.21(2)
C6	0.2005(5)	0.2627(6)	0.3925(5)	8.37(3)
C18	0.3043(3)	0.8516(5)	0.5650(3)	2.92(1)
C24	0.1252(3)	0.7345(5)	0.5073(3)	3.08(1)
C25	0.2457(4)	0.5270(5)	0.6083(3)	4.18(2)
4				
As1	0	0	0.09866(7)	1.51(5)
Se1	0.17794(8)	0.12301(8)	0.16356(5)	1.84(5)
C11	0.2304(7)	0.2664(8)	0.1075(4)	1.5(4)
C12	0.2056(8)	0.3528(8)	0.1291(5)	1.8(5)
C13	0.2477(8)	0.4563(8)	0.0905(5)	1.9(4)
C14	0.3179(8)	0.4760(9)	0.0297(5)	2.2(5)
C15	0.3401(8)	0.3850(8)	0.0084(5)	2.1(4)
C16	0.2977(8)	0.2803(8)	0.0471(5)	2.0(5)

[a] B_{eq} = the mean of the principal axes of the thermal ellipsoid.

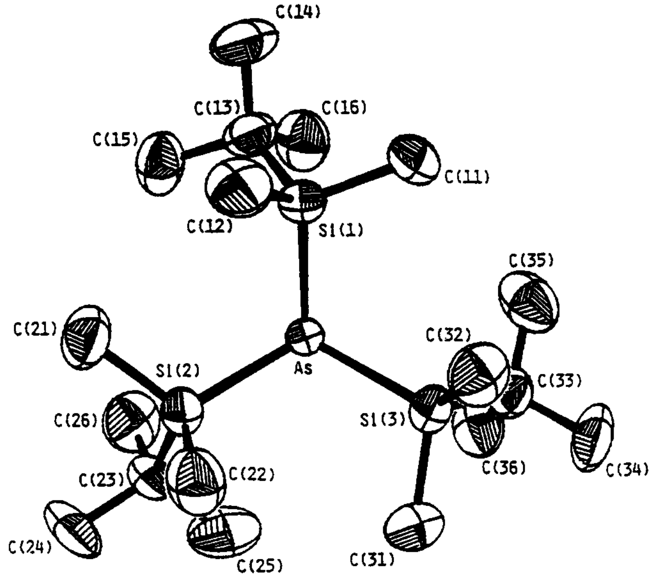

FIGURE 1 ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **1**. Hydrogen atoms are omitted for clarity.

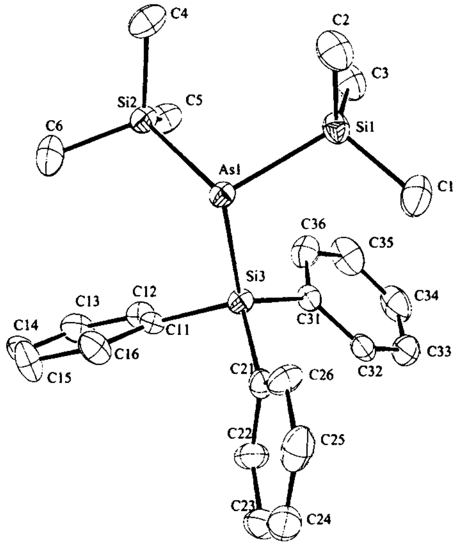

FIGURE 2 ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **2**. Hydrogen atoms are omitted for clarity.

spectively; selected fractional atomic coordinates are listed in Table 4. An ORTEP [8] diagram showing the solid-state conformation and atom numbering scheme of 3 is presented in Figure 3.

[Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, bond lengths and angles, thermal parameters, and observed and calculated structure factors for 1–4 have been deposited with the Cambridge Crystallographic Data Centre.]

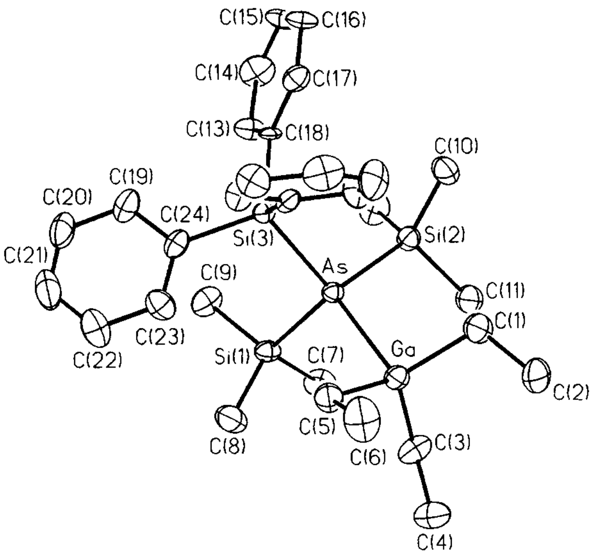

FIGURE 3 ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **3**. Hydrogen atoms are omitted for clarity.

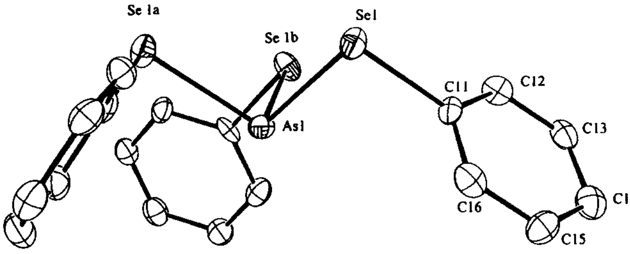

FIGURE 4 ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **4**. Hydrogen atoms are omitted for clarity.

RESULTS AND DISCUSSION

The 1:3 mole reaction of $(Na/K)_3As$ with $^tBuMe_2SiCl$ affords the crystalline silylarsine $As(Si^tBuMe_2)_3$ (1) in a low yield. A similar method was first used by Becker et al. to prepare $As(SiMe_3)_3$ [6a]; however, the product isolated is a liquid. By incorporating the bulky $^tBuMe_2Si$ groups around the As center, we were able to isolate compound 1 as a crystalline material, and it was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, partial elemental analysis, and single-crystal X-ray analysis (vide infra).

Reaction of $LiAs(SiMe_3)_2$ with Ph_3SiCl (1:1) yields $As(SiMe_3)_2(SiPh_3)$ (2) in a good crystalline yield. As is seen for 1, incorporating the relatively bulky Ph_3Si group around the As center allows the resulting trisilylarsine to exist as a crystalline compound. The phosphorus analog of 2 was previously reported by Petrie and Power [12], but they did not address any chemistry relating to the arsenic species.

To examine the reactivity of 2 toward group-13 metal compounds, the 1:1 mole reaction of 2 with Et_3Ga was carried out at room temperature, yielding the simple adduct $Et_3Ga \cdot As(SiMe_3)_2(SiPh_3)$ (3). This result is in contrast to those observed in similar reactions of 1, where attempted silyl-elimination and Lewis acid-base adduct formation reactions utilizing 1 and a group-13 metal compound were unsuccessful. In addition, during these studies, we noted that as the ligand size was increased on the group-13 center, compound 2 failed to form adducts analogous to 3. It is interesting to note that compound 3, with its ethyl substituents on the metal center, has great potential to serve as a single-source precursor to GaAs through a facile β-hydride/organosilane elimination pathway.

The tris(seleno)arsine $As(SePh)_3$ (4) was the only isolable crystalline product from the 1:1 reaction of $In(SePh)_3$ and $As(SiMe_3)_3$ and was recovered in a very low yield (~10%). The exact pathway to the formation of 4 is unclear; however, the low yield suggests the presence of other oligomeric species that we could not isolate and characterize. Ligand redistributions of this type are not without precedent in 13–15 chemistry and have been observed in a variety of systems [13]. Compound 4 was previously prepared by Barton et al. [4a] and by Arsenault and Dean [4b] by the direct 3:1 reaction of NaSePh and $AsCl_3$, but no solid-state structure was reported.

Compound 1 crystallizes in the monoclinic system with four molecules occupying the general positions of the centrosymmetric space group P $2_1/c$. In the solid state, this molecule adopts the conformation depicted in Figure 1. The most noteworthy structural feature of 1 is the pyramidal nature of the $AsSi_3$ core, which is evidenced by the average Si–As–Si angle of 106.5°. The average Si–As bond length of 2.376 Å in 1 is in accord with the sum of the covalent radii [14] for these two atoms.

Compound 2 crystallizes in the orthorhombic system with four molecules occupying the general positions of the unit cell. As in 1, the pyramidal geometry of the $AsSi_3$ core is evident as reflected in the average Si–As–Si angle of 105.0°. The greater deviation from ideal tetrahedral coordination geometry in 2 vs. 1 is likely a function of the steric requirements imposed by the Ph_3Si ligand. The average Si–As bond length of 2.357 Å in 2 is only slightly shorter than that observed in 1.

Crystals of adduct 3 belong to the monoclinic system space group P $2_1/c$. The Ga–As bond length of 2.694(1) Å in 3 is slightly longer than that usually observed for other adducts of this type [15]. This is not surprising due to the presence of the bulky Ph_3Si ligand. In the solid state, the ethyl substituents on the gallium center and the silyl substituents on the arsenic atom are in a staggered conformation to one another. As shown by the mean Si–As–Ga angle of 111.8° and mean C–Ga–As angle of 103.2° in 3, the metal and pnicogen centers reside in distorted tetrahedral coordination environments. It is important to note that, to our knowledge, compound 3 represents only the third example of a structurally characterized Ga–As Lewis acid-base adduct.

The tris(seleno)arsine 4 crystallizes in the trigonal system, space group R$\bar{3}$. Although structural data for this compound were previously unreported, the adduct $(PhSe)_3As \cdot MnCp'(CO)_2$ ($Cp' = C_5H_4Me$) (5) [16] was fully characterized. The pyramidal $AsSe_3$ core in 4 is greatly distorted from the ideal tetrahedral angle, as shown by the Se–As–Se angle of 95.56(5)°. The Se–As bond length of 2.374(1) Å in 4 is nearly identical to the sum of the covalent radii [14] for the two atoms as well as that observed in 5.

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