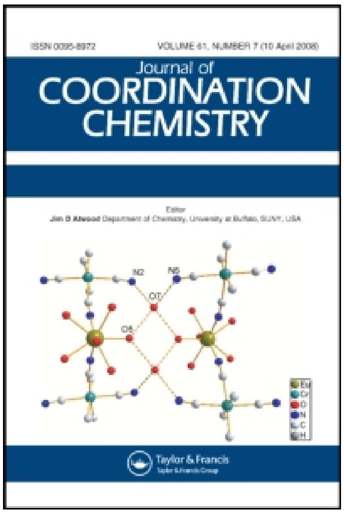

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X-RAY CRYSTAL STRUCTURE OF A MONOMERIC TRIS(ARSINO)GALLANE, $[(Me_3Si)_2As]_3Ga$

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NOTE

X-RAY CRYSTAL STRUCTURE OF A MONOMERIC TRIS(ARSINO)GALLANE, $[(Me_3Si)_2As]_3Ga$

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The solid-state structure of $[(Me_3Si)_2As]_3Ga$ (**1**) has been established by single-crystal X-ray analysis. Triclinic crystals of **1** belong to the space group $P\bar{1}$, with $a = 10.7529(23)$, $b = 10.7899(23)$, $c = 17.55(6)$ Å, $\alpha = 88.077(23)°$, $\beta = 84.537(23)°$, $\gamma = 60.282(16)°$ for $Z = 2$. Refinement of atomic parameters converged at $R = 0.058$ ($R_w = 0.064$) for 2378 observed reflections with $I>2.5\sigma(I)$. The monomeric molecule adopts a trigonal planar configuration with Ga-As = 2.4171(23), 2.4250(22) and 2.4213(24) Å, and As-Ga-As (av.) = 120.00(1)°. Compound **1** is only the second example of a monomeric tris(arsino)gallane to be structurally characterized in this manner.

KEYWORDS: arsinogallane, gallium salt, X-ray structure

INTRODUCTION

Early efforts in organogallium-arsenic synthetic chemistry centered on the utilization of alkane elimination reactions, as evidenced by the work of Coates and co-workers in the 1960s.[1] Through their efforts, they were able to isolate mono(arsino)gallanes of the type $(R_2AsGaMe_2)_n$ (R = Me; n = 3, R = Ph; n = 2) and show that intermolecular As-Ga bonding to form four-coordinate gallium and arsenic dominates the structural properties of these compounds. We tried to obtain sterically hindered arsinogallanes by this method; however, we discovered that the practicality of alkane elimination was severely diminished as the steric bulk of the substituents was increased.[2] Subsequently, we employed a coupling reaction involving a lithium arsenide and a chlorogallane to successfully isolate the first

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example of a tris(arsino)gallane, $(Mes_2As)_3Ga$ (**2**)[3] (Mes = mesityl = $Me_3C_6H_2$), which was shown by X-ray analysis to be a monomer containing three-coordinate gallium and arsenic. This coupling method was also used in the formation of the tris(arsino)gallanes $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (**3**)[4], synthesized in our laboratory, and $(Bu^t_2As)_3Ga$ (**4**)[5], reported by others. It is interesting to note that only compounds **2** and **3** have been characterized by X-ray crystallographic analysis. To this end, we report herein the fortuitous isolation of $[Me_3Si)_2As]_3Ga$ (**1**), and its solid-state structure which represents only the second example in the literature of a monomeric tris(arsino)gallane whose solid-state structure has been determined by X-ray crystallography and the first compound of this type containing silyl-substituted arsenic atoms.

EXPERIMENTAL

Materials and Measurements

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 diethyl ether were distilled from sodium benzophenone ketyl under dry dinitrogen. Pentane was distilled over $LiAlH_4$ under dry dinitrogen. $[Cl_2GaP(SiMe_3)_2]_2$[6] and $As(SiMe_3)_3$[7] were synthesized by literature procedures. $LiAs(SiMe_3)_2$[8] was prepared *via* the 1:1 mole reaction of $As(SiMe_3)_3$ and MeLi. The integrity of all materials used was confirmed via ^1H NMR spectra. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ7.15 or 128 ppm. All NMR samples were prepared in 5-mm tubes which were flame sealed under vacuum. X-ray crystallographic data were obtained at −170°C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation in the Single Crystal X-ray Structure Centre at the University of North Carolina at Chapel Hill.

Preparation of $[(Me_3Si)_2As]_3Ga$ **1**

$LiAs(SiMe_3)_2$ (0.130 g, 0.570 mmol) was dissolved in 15 mL of toluene with the aid of 8 drops of diethyl ether and transferred to a 50 mL addition bulb, which was attached to a 500 mL round-bottomed screw-top flask equipped with a Teflon valve. $[Cl_2GaP(SiMe_3)_2]_2$ (0.0837 g, 0.132 mmol) was dissolved in 75 mL of toluene and introduced into flask with a stir bar. The $[Cl_2GaP(SiMe_3)_2]_2$ solution was cooled to −78°C in a dry ice acetone bath for 20 min., and the $LiAs(SiMe_3)_2$ solution was added dropwise over a 10 min. period while the reaction was maintained at −78°C. The resulting bright yellow reaction mixture was stirred for 1 h in the cold and then allowed to warm to room temperature over a 24 h period. A bright yellow to deep orange color change was observed upon temperature increase. The volatiles were removed *in vacuo* leaving a dark red oily material. The material was dissolved in 15 mL of pentane and cooled to −30°C for several days. A fine white powder (LiCl) settled from the solution and the liquid was decanted into a small vial. Evaporation of the solvent under argon resulted in recovery of the red oily material as well as red crystals **1** suitable for X-ray analysis (yield, <1%). ${}^1H$ NMR: δ0.347 (s); ${}^{13}C\{{}^1H\}$ NMR: δ 4.292 (s).

X-Ray Crystal Structure Analysis of Compound 1

Crystallographic data are summarized in Table 1. The crystal used was a red block which was mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at - 170°C, and the structure was 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 riders model) in the later iterations of refinement which converged at $R = 0.058$ ($R_w = 0.064$). A final difference-Fourier synthesis revealed no unusual features (max. 1.15, min. - 1.11 e $Å^{-3}$). Crystallographic calculations were performed using the NRC VAX[9] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 10. Fractional atomic

Table 1 Crystallographic data and measurements for $[(Me_3Si)_2As]_3Ga$ (**1**)

	1
molecular formula	$C_{18}H_{54}GaAs_3Si_6$
formula weight	733.61
crystal system	triclinic
space group	$P\bar{1}$
a, Å	10.7529(23)
b, Å	10.7899(23)
c, Å	17.55(6)
α, deg	88.077(23)
β, deg	84.537(23)
γ, deg	60.282(16)
V, $Å^3$	1760(6)
Z	2
radiation (wavelength, Å)	Mo Kα(0.71073)
μ, cm^{-1}	37.8
temp, °C	- 170
^{D}calcd, g cm^{-3}	1.384
crystal dimens., mm	0.30 × 0.25 × 0.15
T_{max}:T_{min}	0.577:0.572
scan type	ω
scan width, deg	1.00
Q_{max}, deg	45
no. of rflns recorded	6346
no. of non-equiv. rflns recorded	4598
R_{merg} (on I)	0.048
no. of rflns retained, I>2.5σ(I)	2378
no. of params. refined	254
R;R_w[a]	0.058; 0.064
goodness-of-fit[b]	1.52
max shift/esd. in final least-squares cycle	0.006
final max, min Δρ, $e/Å^{-3}$	1.150; -1.110

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

coordinates are listed in Table 2; selected interatomic distances and angles are given in Table 3. An ORTEP[11] diagram showing the solid-state conformation and atom numbering scheme of **1** is presented in Figure 1.

RESULTS AND DISCUSSION

Recently, investigations in our laboratory have focused on the synthesis of potential single-source precursors to ternary semiconductor materials. The dimeric compound $[Cl_2GaP(SiMe_3)_2]_2$, recently isolated in our laboratory, was found by X-ray crystallographic analysis to contain a four-membered Ga—P—Ga—P ring with exocyclic chlorine atoms on the gallium centers.[6] We desired to replace the four exocyclic halogen atoms with arsenic-containing moieties, by salt elimination reactions, to produce mixed-pnicogen dimeric compounds. These compounds could then, upon thermal decomposition, lead to ternary materials containing one Group 13 metal and two different Group 15 pnicogens. However, when $[Cl_2GaP(SiMe_3)_2]_2$ and $LiAs(SiMe_3)_2$ were mixed in a 1:4 stoichiometric ratio (eq 1),

$$[Cl_2GaP(SiMe_3)_2]_2 + 4LiAs(SiMe_3)_2 \rightarrow [Me_3Si)_2As]_3Ga + \text{other products} \qquad (1)$$

ligand redistribution around the gallium center occurred to form compound **1**.

Table 2 Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **1**, with estimated standard deviations in parentheses.

Atom	*x*	*y*	*z*	$B_{iso}(Å^2)$
Ga1	0.67740(16)	0.65781(17)	0.24986(10)	1.02(9)
As1	0.41839(17)	0.79730(18)	0.25354(11)	1.41(9)
As2	0.81927(17)	0.77555(18)	0.25234(11)	1.45(9)
As3	0.79640(17)	0.39981(18)	0.24303(11)	1.52(9)
Si1	0.3749(5)	0.9312(5)	0.3655(3)	1.4(3)
Si2	0.3725(5)	0.9698(5)	0.1592(3)	1.3(3)
Si3	0.9687(4)	0.6873(5)	0.1385(3)	1.08(24)
Si4	0.9802(5)	0.6470(5)	0.3442(3)	1.4(3)
Si5	0.6963(5)	0.3374(5)	0.3515(3)	1.1(3)
Si6	0.6777(5)	0.3695(5)	0.1451(3)	1.3(3)
C11	0.1777(15)	1.0325(16)	0.3916(9)	1.2(8)
C12	0.4420(18)	1.0598(19)	0.3635(10)	2.7(11)
C13	0.4603(19)	0.7990(19)	0.4424(11)	3.0(12)
C21	0.4130(19)	0.8798(20)	0.0649(11)	3.3(12)
C22	0.1759(16)	1.0942(17)	0.1726(11)	2.5(10)
C23	0.4700(15)	1.0719(15)	0.1575(9)	1.1(9)
C31	0.8481(17)	0.7605(19)	0.0598(11)	2.7(11)
C32	1.0912(17)	0.7630(17)	0.1307(10)	2.2(10)
C33	1.0777(16)	0.4917(17)	0.1247(10)	2.0(10)
C41	0.8722(19)	0.6866(19)	0.4377(11)	3.2(12)
C42	1.1000(17)	0.7249(19)	0.3487(11)	2.9(12)
C43	1.0971(15)	0.4486(16)	0.3323(10)	1.9(9)
C51	0.7725(17)	0.3693(19)	0.4350(10)	2.6(11)
C52	0.7681(17)	0.1419(18)	0.3426(10)	2.1(10)
C53	0.4966(16)	0.4304(17)	0.3697(11)	2.1(10)
C61	0.7810(16)	0.1763(17)	0.1183(10)	1.9(10)
C62	0.4851(18)	0.4258(18)	0.1665(10)	2.5(11)
C63	0.6989(20)	0.4690(19)	0.0615(11)	3.2(12)

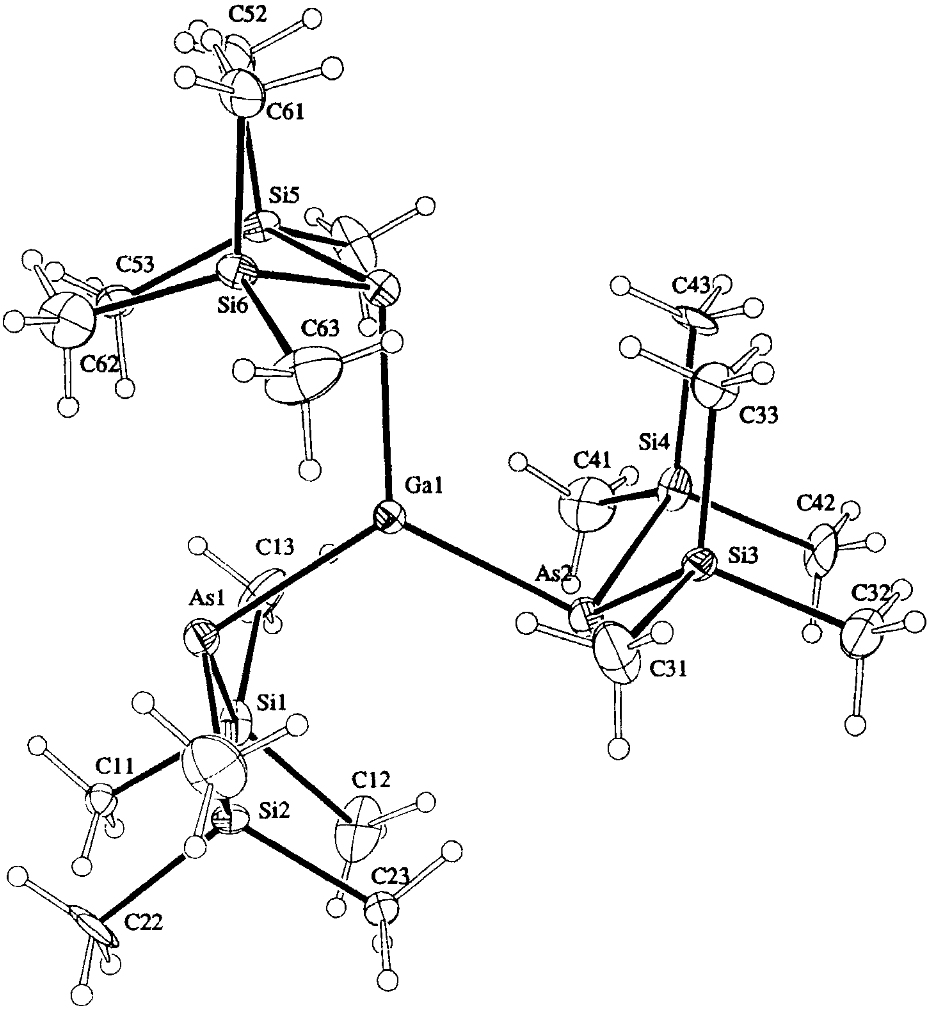

Figure 1 ORTEP diagram (30% probability ellipsoids) showing the solid-state conformation and partial atom numbering scheme of $[(Me_3Si)_2As]_3Ga$ **1**. The hydrogen atoms of the trimethylsilyl groups are shown but not designated.

Ligand redistributions are not without precedent in 13–15 systems, as the adducts $Me(Me_3CCH_2)_2In \cdot P(SiMe_3)_3$[12] $(Me_3SiCH_2)_3In \cdot As(SiMe_3)_3$[13] and $Ph_3Ga \cdot As(Sime_3)_3$[13] were formed in this manner. Though the formation of **1** was accomplished in a serendipitous manner, this does not diminish the fundamental value that the elucidation of its structure contributes to the general knowledge of organogallium-arsenic chemistry. The limited number of compounds of this type reported to date fuels the need for additional solid-state structural information. X-ray structural analysis finds that the gallium atom is bonded to the three arsenic atoms in a trigonal-planar configuration and is positioned exactly in the plane formed by the three arsenic atoms, whereas

Table 3 Bond distances (Å) and bond angles (°) for **1**, with estimated standard deviations in parentheses

Bond Lengths			
Ga1-As(1)	2.4171(23)	Si(2)-C(23)	1.856(14)
Ga1-As(2)	2.4250(22)	Si(3)-C(31)	1.861(18)
Ga1-As(3)	2.4213(24)	Si(3)-C(32)	1.857(15)
As(1)-Si(1)	2.348(7)	Si(3)-C(33)	1.848(17)
As(1)-Si(2)	2.343(6)	Si(4)-C(41)	1.850(21)
As(2)-Si(3)	2.341(7)	Si(4)-C(42)	1.863(15)
As(2)-Si(4)	2.349(6)	Si(4)-C(43)	1.876(15)
As(3)-Si(5)	2.341(7)	Si(5)-C(51)	1.865(16)
As(3)-Si(6)	2.358(6)	Si(5)-C(52)	1.859(17)
Si(1)-C(11)	1.858(15)	Si(5)-C(53)	1.864(16)
Si(1)-C(12)	1.853(16)	Si(6)-C(61)	1.863(16)
Si(1)-C(13)	1.873(20)	Si(6)-C(62)	1.849(17)
Si(2)-C(21)	1.850(20)	Si(6)-C(63)	1.852(21)
Si(2)-C(22)	1.855(15)		

Bond Angles			
As(1)-Ga(1)-As(3)	120.18(9)	Ga(1)-As(2)-Si(3)	100.92(13)
As(1)-Ga(1)-As(2)	120.11(8)	Ga(1)-As(2)-Si(4)	103.17(13)
As(2)-Ga(1)-As(3)	119.71(8)	Si(3)-As(2)-Si(4)	101.34(24)
Ga(1)-As(1)-Si(1)	98.50(13)	Ga(1)-As(3)-Si(5)	104.26(14)
Ga(1)-As(1)-Si(2)	105.22(14)	Ga(1)-As(3)-Si(6)	100.14(13)
Si(1)-As(1)-Si(2)	101.47(25)	Si(5)-As(3)-Si(6)	101.64(24)
As(1)-Si(1)-C(11)	108.4(5)	As(2)-Si(4)-C(43)	119.4(5)
As(1)-Si(1)-C(12)	117.7(6)	C(41)-Si(4)-C(42)	106.5(8)
As(1)-Si(1)-C(13)	106.3(6)	C(41)-Si(4)-C(43)	108.8(8)
C(11)-Si(1)-C(12)	107.6(7)	C(42)-Si(4)-C(43)	107.8(7)
C(11)-Si(1)-C(13)	108.4(8)	As(3)-Si(4)-C(51)	106.0(6)
C(12)-Si(1)-C(13)	108.3(8)	As(3)-Si(5)-C(52)	105.8(6)
As(1)-Si(2)-C(21)	107.7(6)	As(3)-Si(5)-C(53)	118.2(6)
As(1)-Si(2)-C(22)	105.1(6)	C(51)-Si(5)-C(52)	107.7(8)
As(1)-Si(2)-C(23)	118.2(5)	C(51)-Si(5)-C(53)	108.9(8)
C(21)-Si(2)-C(22)	107.7(8)	C(52)-Si(5)-C(53)	109.7(7)
C(21)-Si(2)-C(23)	107.9(8)	As(3)-Si(6)-C(61)	106.0(5)
C(22)-Si(2)-C(23)	109.8(7)	As(3)-Si(6)-C(62)	117.4(6)
As(2)-Si(3)-C(31)	105.9(6)	As(3)-Si(6)-C(63)	106.7(5)
As(2)-Si(3)-C(32)	107.7(6)	C(61)-Si(6)-C(62)	109.9(7)
As(2)-Si(3)-C(33)	118.0(6)	C(61)-Si(6)-C(63)	107.2(8)
C(31)-Si(3)-C(32)	108.2(8)	C(62)-Si(6)-C(63)	109.1(8)
C(31)-Si(3)-C(33)	108.1(8)		
C(32)-Si(3)-C(33)	108.6(7)		
As(2)-Si(4)-C(41)	106.7(6)		
As(2)-Si(4)-C(42)	107.0(6)		

the gallium atom in **2** lies 0.149 Å above the plane. Although the space group of **1** is $P\bar{1}$ the $[Me_3Si)_2As]_3Ga$ molecule possesses a non-crystallographic three-fold rotation axis and approximate C_{3h} symmetry. The mean Ga–As bond length of 2.421 Å in **1** is somewhat shorter than the corresponding lengths of 2.492 and 2.512 Å, respectively, in **2** and **3** which is most likely due to the lower steric bulk of the arsenic substituents. The mean As–Si bond length and Si–As–Si bond angle at 2.347Å and 101.5°, respectively, in **1** are unprecedented as this compound is the first of its type with direct silicon-arsenic bonds. The geometry at the arsenic atoms is considerably distorted from tetrahedral with Ga–As–Si angles ranging from 98.50(13) to 105.22(14)°. The As–Si–C angles were found to range from 105.1(6) to 119.4(5). The variation in the angles about As and about Si may be attributed to steric demands in the molecular structure. Compound **1** and its analogs find their greatest utility as potential single-source precursors to GaAs since they have the potential to eliminate a diarsine upon thermolysis.[4] Efforts are ongoing to produce **1** by the 3:1 mole reaction of $LiAs(SiMe_3)_2$ and $GaCl_3$ (eq 2)

$$3\ LiAs(SiMe_3)_2 + GaCl_3 \rightarrow 3LiCl + [(Me_3Si)_2As]_3Ga \qquad (2)$$

in hopes of obtaining the product in higher yield. To date, the above reaction has yielded a viscous red oil which, by ^1H NMR, contains **1**. However, we have not been able to isolate pure crystals of **1** from the reaction mixture.

Supplementary Data

Additional material consisting of H-atom coordinates, thermal parameters, and structure factors are available from R.L.W.

Acknowledgements

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