Journal of Organometallic Chemistry, 381 (1990) 15–27
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20415

Synthesis and characterization of four-membered gallium-arsenic ring compounds containing a bridging $As(SiMe_3)_2$ group: crystal structures of $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ and $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Br$

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(Received July 17th, 1989)

Abstract

The first organogallium four-membered ring compounds with arsenic, halogen mixed bridging to be characterized completely, $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2X$ (X = Cl (**1**) and X = Br (**2**)) were prepared by the reaction of $(Me_3Si)_3As$ (**3**) with Ph_2GaCl and Ph_2GaBr, respectively. X-ray crystallographic analyses show the compounds to be isostructural with each containing a non-planar Ga–As–Ga–X four membered ring. Isomorphous crystals of **1** and **2** belong to the monoclinic system, space group $P2_1/c$ (C_{2h}^5), with four molecules in unit cells of dimensions: a 10.560(3), b 15.797(3), c 20.591(4) Å, β 92.17(2)°, V 3433(2) $Å^3$ for **1**, and a 10.653(1), b 15.777(2), c 20.517(2) Å, β 91.97(1)°, V 3446(1) $Å^3$ for **2**. The non-planarity of the rings is manifested in the halogen atom displacements of 0.256 Å in **1** and 0.293 Å in **2** from the respective Ga–As–Ga′ planes. Deviations from overall C_{2v} symmetry serve to relieve unfavorable intramolecular bulky ring substituent interactions present in such a symmetric form. The dimer $[Ph_2GaAs(SiMe_3)_2]_2$ (**4**), obtained from the reaction of Ph_2GaCl and $LiAs(SiMe_3)_2$, has been characterized by partial elemental analysis, NMR spectroscopy and cryoscopic molecular weight determination. An alternative route to the synthesis of **1** by reaction of **4** and Ph_2GaCl was investigated via NMR spectroscopy.

Introduction

In the past few years, we have exploited two synthetic routes, both first employed by us, to form Ga–As bonds; namely, dehalosilylation between a silylarsine and a

0022-328X/90/$03.50

halogallane [1,2], and coupling using a lithium arsenide and a chlorogallane [3,4]. Others have also reported the use of the lithium arsenide method [5,6]. Some of our more recent studies involving dehalosilylation reactions have made use of $(Me_3Si)_3As$ and, as a result, we have prepared $[(THF)Br_2Ga]_3As$ [7], AlAs, GaAs and InAs [8,9], as well as $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (**1**) [10]. Although four-membered ring formation is known to occur via bridging of gallium centers by two arsenic atoms [2] or two halogen atoms [11*], there were no reports of this occurring through one of each of these atoms prior to our preliminary communication on **1** [10]. We now report the complete characterization, including crystal structures, of two compounds containing four-membered rings with arsenic, halogen mixed bridging of gallium centers, **1** and $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Br$ (**2**), both obtained by dehalosilylation reactions between $(Me_3Si)_3As$ (**3**) and Ph_2GaCl or Ph_2GaBr. Synthesis and characterization of $[Ph_2GaAs(SiMe_3)_2]_2$ (**4**), obtained from the coupling reaction of $LiAs(SiMe_3)_2$ and Ph_2GaCl, and its subsequent reaction with Ph_2GaCl to form **1** are also described.

Experimental

General comments

All manipulations and reactions were carried out under vacuum, or under an atmosphere of N_2 in a Vacuum/Atmospheres HE-43 Dri-Lab, or in standard Schlenk Apparatus. Organic solvents were distilled from sodium benzophenone ketyl under N_2. Tris(trimethylsilyl)arsine (**3**) was prepared by the published procedure and was vacuum distilled prior to use [12]. Lithium bis(trimethylsilyl)arsenide was prepared by heating, under vacuum, a sample of the corresponding THF adduct prepared by the literature method [12]. The diphenylgallium halides were prepared by heating stoichiometric mixtures of triphenylgallium, which was prepared by the published procedure [13], and the corresponding gallium trihalides in toluene [14] and were recrystallized from toluene prior to use. ^1H (299.943 MHz) and ^{13}C (75.429 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer. A Normag No. 2029 apparatus was used to determine molecular weights cryoscopically in cyclohexane. Analysis of the volatile reaction products for Me_3SiX ($X = Cl$, Br) was accomplished by hydrolysis followed by titration of the resulting HX with standard NaOH to the phenolphthalein endpoint. Melting points were obtained in sealed tubes on a Buchi 510 Melting Point apparatus and were uncorrected. Elemental analyses were carried out at E + R Microanalytical Laboratory, Corona, NY.

Preparation of $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (1)

Diphenylgallium chloride (0.517 g, 2.00 mmol) in 50 ml of C_6H_6 and **3** (0.298 g, 1.01 mmol) in 10 ml of C_6H_6 were combined in a 100 ml bulb equipped with a Teflon valve and a magnetic stir bar. Stirring the solution for 48 h at room temperature, followed by removal of the solvent and Me_3SiCl (0.838 mmol, 84% yield) in vacuo afforded a white solid. Extraction of the solid with five 10 ml portions of ligroin, followed by cooling of the combined extracts to −17 °C for 11

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* Reference number with asterisk indicates a note in the list of references.

days gave **1** as colorless crystals (0.390 g, 55.3% yield) m.p. 143–144 °C dec. (Found: C, 51.31; H, 5.67; mol wt, 642 ± 36 (cryoscopic, 0.206 g in 14.8 g cyclohexane). $C_{30}H_{38}AsClGa_2Si_2$ calcd.: C, 51.10; H, 5.44%; mol wt 705); ^1H NMR (C_6D_6): δ 0.01 (s, Me_3Si), 7.21–7.31 (m, Ph), 7.91–7.95 (m, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.14 (s, Me_3Si), 128.30, 128.72, 135.81, 146.57 (m, Ph).

Reaction of Ph_2GaCl and $(Me_3Si)_3As$ (3) (3/1 mol ratio) at room temperature

Diphenylgallium chloride (0.475 g, 1.83 mmol) in 40 ml of C_6H_6 and **3** (0.182 g, 0.618 mmol) in 10 ml of C_6H_6 were combined in a 100 ml bulb equipped with a Teflon valve and a magnetic stir bar. Stirring the solution for 72 h at room temperature followed by removal of the solvent and Me_3SiCl (0.562 mmol) in vacuo afforded a white solid. ^1H and ^{13}C NMR spectra of the solid in C_6D_6 showed it to be a mixture of products, the predominant being **1**. No peaks corresponding to free Ph_2GaCl were observed. Extraction of the solid with three 10 ml portions of ligroin followed by cooling of the combined extracts to −17 °C for 11 days gave **1** as colorless crystals (0.233 g, 53.5% yield). The m.p., ^1H and ^{13}C NMR spectra of the crystals were identical to those of an authentic sample of **1**.

Reaction of Ph_2GaCl and $(Me_3Si)_3As$ (3) (3/1 mole ratio) at 80 °C

Diphenylgallium chloride (0.374 g, 1.44 mmol) in 40 ml of C_6H_6 and **3** (0.138 g, 0.469 mmol) in 10 ml of C_6H_6 were combined in a 100 ml bulb equipped with a Teflon valve and a magnetic stir bar. The bulb was attached to a vacuum line, cooled to −196 °C, and degassed. Stirring the solution for 16 days at 80 °C, followed by removal of the solvent and Me_3SiCl (1.15 mmol) in vacuo, gave a yellow solid. ^1H and ^{13}C NMR spectra of the solid in C_6D_6 both showed only peaks corresponding to Ph_3Ga. Extraction of the solid with 40 ml of hot ligroin left a bright yellow solid. Addition of 5 ml of C_7H_8 to the hot, light yellow extract, followed by cooling to −17 °C for 3 days afforded Ph_3Ga as colorless crystals (0.036 g, 12% yield). The m.p., ^1H and ^{13}C NMR spectra of the crystals were identical to those of an authentic sample of Ph_3Ga. A ^1H NMR spectrum of the bright yellow, ligroin insoluble solid in C_6D_6 showed only very broad peaks in the phenyl region, characteristic of a polymer.

Preparation of $[Ph_2GaAs(SiMe_3)_2]_2$ (4)

Diphenylgallium chloride (0.273 g, 1.05 mmol) in 30 ml of C_6H_6 and lithium bis(trimethylsilyl)arsenide (0.238 g, 1.04 mmol) in 60 ml of C_6H_6 were combined in a 100 ml bulb equipped with a ground glass stopper and a magnetic stir bar. Stirring the mixture for 21 h at room temperature followed by filtration of the solid LiCl and removal of the solvent from the filtrate in vacuo gave a brown solid. Washing the solid with 20 ml of ligroin removed the brown impurity, leaving a white solid which was recrystallized from hot ligroin to give colorless crystals (0.148 g, 32.0% yield) m.p. 229–230 °C dec. (Found: C, 48.73; H, 6.40; mol wt, 801 ± 68 (cryoscopic, 0.062 g in 14.35 g cyclohexane). $C_{36}H_{56}As_2Ga_2Si_4$ calcd.: C, 48.56; H, 6.34%; mol wt 890; ^1H NMR (C_6D_6): δ 0.31 (s, Me_3Si), 7.22–7.34 (m, Ph), 7.88–7.91 (m, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 4.82 (s, Me_3Si), 127.75, 128.02, 137.62, 149.55 (m, Ph).

*Reaction of **4** with Ph_2GaCl*

Diphenylgallium chloride (0.0070 g, 0.027 mmol) and **4** (0.0116 g, 0.013 mmol) were combined with 1.5 ml of C_6D_6 in an NMR tube. The tube was sealed under vacuum with a flame. ^1H and ^{13}C NMR spectra recorded on the solution after 21 h at room temperature showed only peaks corresponding to **1**.

Preparation of $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Br}$ (2)

Diphenylgallium bromide (0.602 g, 1.98 mmol) in 50 ml of C_6H_6 and **3** (0.298 g, 1.01 mmol) in 10 ml of C_6H_6 were combined in a 250 ml bulb equipped with a Teflon valve and a magnetic stir bar. Stirring the solution for 65 h at room temperature followed by removal of the solvent and Me_3SiBr (0.886 mmol, 89% yield) in vacuo afforded a light yellow solid. Extraction of the solid with five 10 ml portions of ligroin followed by cooling of the combined extracts to $-17\,^\circ C$ for 44 h gave **2** as colorless crystals (0.394 g, 53.1% yield) m.p. 151–152°C dec. (Found: C, 48.37; H, 5.38, mol wt, 826 ± 53 (cryoscopic, 0.146 g in 12.93 g cyclohexane). $C_{30}H_{38}AsGa_2Si_2Br$ calcd.: C, 48.10; H, 5.11%; mol wt 749); ^1H NMR (C_6D_6): δ 0.01 (s, Me_3Si), 7.21–7.30 (m, Ph), 7.92–7.95 (m, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.09 (s, Me_3Si), 128.27, 128.72, 135.99, 145.98 (m, Ph).

*X-ray crystal structure analyses of **1** and **2***

Crystal data. $C_{30}H_{38}AsClGa_2Si_2$ (**1**), M 704.62, monoclinic, a 10.560(3), b 15.797(3), c 20.591(4) Å, β 92.17(2)° (from 25 orientation reflections, $30° < \theta < 38°$), V 3433(2) Å^3, $Z = 4$, D_c 1.363 g cm^{-3}, μ(Cu-K_α) radiation (λ 1.5418 Å) 45.3 cm^{-1}; space group $P2_1/c$ (C_{2h}^5) uniquely from the systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$; crystal dimensions: $0.10 \times 0.20 \times 0.22$ mm.

$C_{30}H_{38}AsBrGa_2Si_2$ (**2**), M 749.08, monoclinic, a 10.653(1), b 15.777(2), c 20.517(2) Å, β 91.97(1)° (from 25 orientation reflections, $36° < \theta < 45°$), V 3446(1) Å^3, $Z = 4$, D_c 1.444 g cm^{-3}, μ(Cu-K_α) 51.6 cm^{-1}; space group $P2_1/c$ (C_{2h}^5) as for **1**; crystal dimensions: $0.20 \times 0.34 \times 0.40$ mm.

Crystallographic measurements. For X-ray data collection, crystals of **1** and **2** were sealed inside thin-walled capillaries. Intensity data ($+h$, $+k$, $\pm l$; θ_{max} 55°, 4583 reflections for **1**; θ_{max} 67°, 6485 reflections for **2**) were recorded on an Enraf Nonius CAD-4 diffractometer (Cu-K_α radiation, incident-beam graphite monochromator, ω–2θ scans; scan width: $(1.1 + 0.14 \tan \theta)°$ for **1**, $(1.0 + 0.14 \tan \theta)°$ for **2**). Equivalent reflections were averaged (R merge on I; 0.025 for **1**, 0.019 for **2**) to yield 4303 and 6133 reflections for **1** and **2**, respectively, from which those 1562 (**1**) and 3093 (**2**) with $I > 3.0\sigma(I)$ were retained for the analyses. The data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections (T_{max}/T_{min} 1.00/0.62 for **1**; 1.00/0.52 for **2**) were also applied.

Structural analysis. The crystal structure of **1** was solved by direct methods (MULTAN11/82) and that of **2** followed from its isomorphous nature. Approximate non-hydrogen atom positions for **1** were derived in part from a E-map and from a series of difference Fourier syntheses. Full-matrix least-squares adjustment of positional and anisotropic temperature factor parameters for these atoms, with hydrogen atoms included at their calculated positions in the later iterations, converged at $R = 0.040$ ($R_w = 0.051$, GOF 1.1) [15*]. Final non-hydrogen atom coordinates for **1** were used as initial input for isomorphous **2**, and corresponding full-matrix least-squares parameter refinement converged at $R = 0.042$ ($R_w = 0.053$,

Table 1

Non-hydrogen atom fractional coordinates ($\times 10^4$) for $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2X}$ (X = Cl (**1**), X = Br (**2**)), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Compound **1**			
As	2801.1(11)	958.3(10)	2090.1(6)
Ga	1902.5(13)	2399.2(11)	2135.5(7)
Ga′	4855.8(14)	1542.6(12)	2478.2(8)
Cl	3991(3)	2951(2)	2394(2)
Si	2818(3)	381(3)	1034(2)
Si′	1869(3)	7(3)	2821(2)
C(1)	1130(11)	252(11)	766(6)
C(2)	3691(14)	−620(10)	1047(7)
C(3)	3605(15)	1108(11)	477(6)
C(1′)	2802(13)	−984(10)	2823(7)
C(2′)	190(11)	−161(10)	2563(7)
C(3′)	1965(13)	516(10)	3635(6)
C(11)	877(11)	2546(8)	2900(5)
C(12)	1347(12)	2917(9)	3455(6)
C(13)	591(14)	3016(10)	4011(7)
C(14)	−651(14)	2702(11)	3975(6)
C(15)	−1127(12)	2358(10)	3421(6)
C(16)	−368(11)	2272(9)	2878(6)
C(17)	1397(11)	2939(8)	1322(5)
C(18)	2228(13)	3291(11)	895(7)
C(19)	1828(14)	3694(13)	316(7)
C(20)	601(14)	3776(12)	172(7)
C(21)	−253(12)	3458(11)	564(7)
C(22)	154(12)	3032(10)	1150(6)
C(11′)	6105(9)	1431(10)	1821(6)
C(12′)	6286(12)	2027(10)	1336(7)
C(13′)	7136(13)	1906(11)	833(7)
C(14′)	7754(13)	1161(12)	804(7)
C(15′)	7661(12)	550(11)	1263(7)
C(16′)	6786(11)	713(10)	1764(7)
C(17′)	5265(11)	1381(9)	3400(6)
C(18′)	4968(13)	1950(10)	3868(7)
C(19′)	5224(15)	1799(14)	4523(7)
C(20′)	5898(19)	1155(13)	4736(8)
C(21′)	6108(24)	573(13)	4290(9)
C(22′)	5906(18)	688(11)	3615(8)
Compound **2**			
As	2759.3(7)	1002.8(5)	2099.0(4)
Ga	1805.9(8)	2423.8(6)	2141.7(4)
Ga′	4812.5(8)	1556.0(7)	2494.7(5)
Br	3962.9(8)	3076.9(6)	2417.4(5)
Si	2776.4(19)	419.9(16)	1037.7(10)
Si′	1833.5(19)	39.0(14)	2824.0(10)
C(1)	1123(7)	262(7)	768(4)
C(2)	3658(9)	−579(7)	1048(5)
C(3)	3505(10)	1204(8)	485(4)
C(1′)	2754(8)	−962(6)	2820(5)
C(2′)	178(7)	−142(6)	2545(5)
C(3′)	1916(9)	505(6)	3649(4)
C(11)	778(6)	2562(5)	2911(4)

Table 1 (continued)

Atom	*x*	*y*	*z*
C(12)	1209(8)	2933(5)	3490(4)
C(13)	431(10)	2998(6)	4021(4)
C(14)	−763(10)	2708(7)	3978(5)
C(15)	−1222(8)	2333(7)	3417(5)
C(16)	−444(7)	2279(6)	2879(4)
C(17)	1285(7)	2979(5)	1319(4)
C(18)	2106(8)	3320(7)	891(5)
C(19)	1675(10)	3707(8)	327(5)
C(20)	447(9)	3751(7)	177(4)
C(21)	−378(8)	3411(7)	576(4)
C(22)	56(7)	3012(6)	1139(4)
C(11′)	6049(6)	1423(5)	1825(4)
C(12′)	6272(7)	1998(6)	1347(5)
C(13′)	7090(8)	1850(7)	850(5)
C(14′)	7714(8)	1147(8)	813(5)
C(15′)	7531(8)	513(8)	1276(5)
C(16′)	6713(8)	676(7)	1785(4)
C(17′)	5206(7)	1404(6)	3419(4)
C(18′)	4901(9)	1923(7)	3902(5)
C(19′)	5192(10)	1784(8)	4559(5)
C(20′)	5809(12)	1113(8)	4730(5)
C(21′)	6117(15)	518(8)	4284(6)
C(22′)	5797(12)	677(8)	3623(5)

GOF 1.4). Final non-hydrogen atom positional parameters for **1** and **2** are listed in Table 1. ORTEP diagrams of the molecules are in Fig. 1 and 2. Corresponding bond lengths and angles are listed alongside each other for comparison in Table 2;

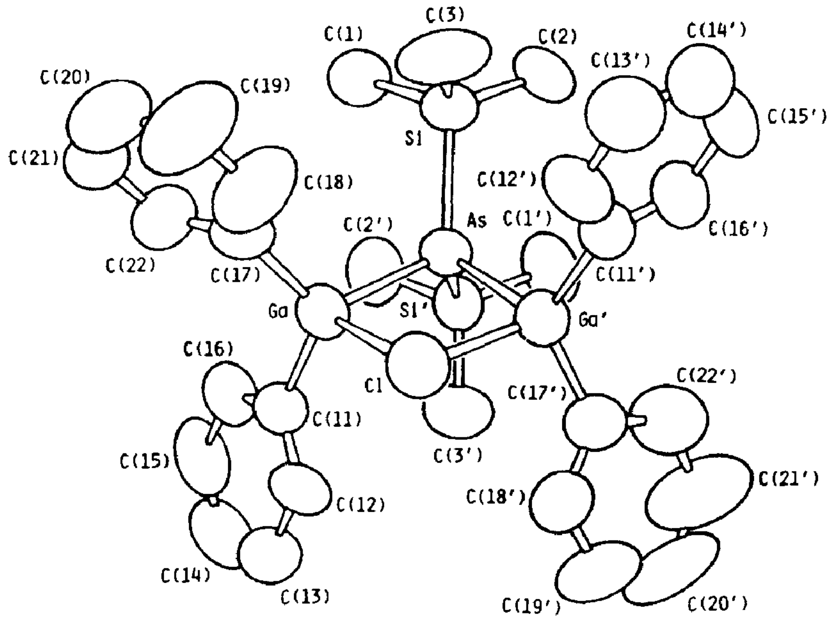

Fig. 1. ORTEP diagram of $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ (**1**) (hydrogen atoms omitted for clarity).

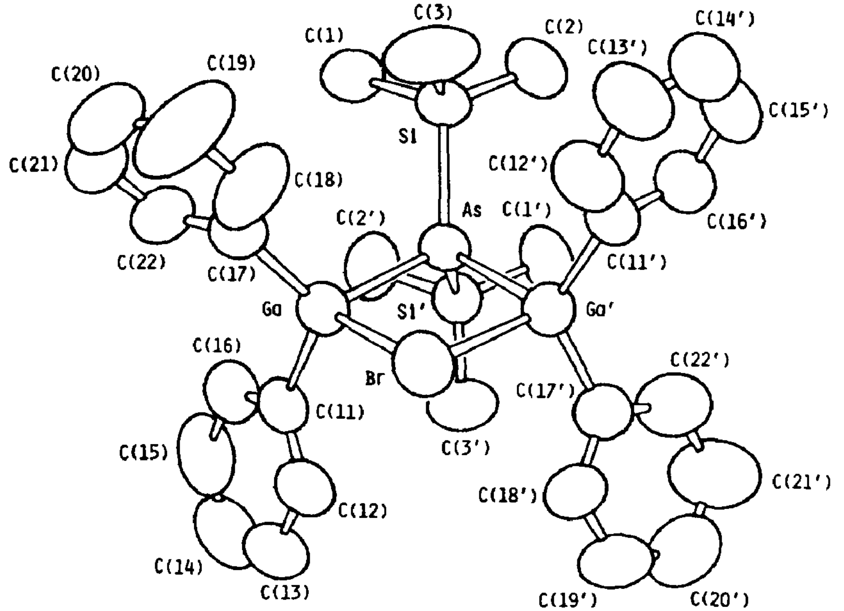

Fig. 2. ORTEP diagram of $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Br}$ (2) (hydrogen atoms omitted for clarity).

selected torsion angles are in Table 3. Displacements of atoms from least-squares planes are provided in Table 4. Tables of thermal parameters, hydrogen atom parameters, torsion angles, and observed and calculated amplitudes for **1** and **2** are available from the authors (RLW).

Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf Nonius Structure Determination Package incorporating the direct methods program MULTAN11/82. Neutral atom scattering factors used in all structure-factor calculations were taken from reference 16. In the least-squares iterations, $\Sigma w\, \Delta^2$ $[w = 1/\sigma^2(|F_o|),\ \Delta = (|F_o| - |F_c|)]$ was minimized.

Discussion

When **3** reacts with either Ph_2GaCl or Ph_2GaBr in a 1/2 mole ratio at room temperature, the predominant product is **1** or **2**, respectively, both corresponding to elimination of only one equivalent of Me_3SiX. Even when the reaction of **3** with Ph_2GaCl is performed in a 1/3 mole ratio at room temperature, the predominant product is **1**. This behavior is interesting since it contrasts with that involved in formation of the product $[(THF)Br_2Ga]_3As$ (**5**) [7] isolated from the reaction of **3** with $GaBr_3$ (1/3 mole ratio), which corresponds to elimination of three equivalents of Me_3SiBr. That **1** and **2** do not eliminate a second equivalent of Me_3SiX at room temperature to produce $(Ph_2Ga)_2AsSiMe_3$ can be understood by assigning formal charges to the ring atoms. A positive formal charge on the As atom is expected to increase the reactivity of the attached Si atoms toward negatively charged species. A halogen atom bridging two gallium centers is assigned a positive formal charge and therefore would not be expected to react with the Si. This reasoning must rule out the possible ionic solution species, $(Ph_2Ga)_2As(SiMe_3)_2{}^+X^-$, since the X^- ion

(continued on p. 24)

Table 2

Interatomic distances (Å) and angles (deg.) for $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2X}$ (X = Cl (**1**), X = Br (**2**)), with estimated standard deviations in parentheses

	Compound 1	Compound 2
(a) Bond lengths		
As–Ga	2.469(2)	2.464(1)
As–Ga′	2.463(2)	2.466(1)
As–Si	2.359(4)	2.364(2)
As–Si′	2.367(4)	2.366(2)
Ga–X	2.412(3)	2.564(1)
Ga′–X	2.409(4)	2.568(1)
Ga–C(11)	1.96(1)	1.964(8)
Ga′–C(11′)	1.93(1)	1.947(8)
Ga–C(17)	1.94(1)	1.965(8)
Ga′–C(17′)	1.95(1)	1.943(8)
Si–C(1)	1.86(1)	1.845(8)
Si′–C(1′)	1.85(2)	1.859(9)
Si–C(2)	1.83(2)	1.834(11)
Si′–C(2′)	1.85(1)	1.857(8)
Si–C(3)	1.84(2)	1.865(11)
Si′–C(3′)	1.86(1)	1.845(9)
C(11)–C(12)	1.36(2)	1.39(1)
C(11′)–C(12′)	1.39(2)	1.36(1)
C(11)–C(16)	1.38(2)	1.38(1)
C(11′)–C(16′)	1.35(2)	1.38(1)
C(12)–C(13)	1.43(2)	1.40(1)
C(12′)–C(13′)	1.41(2)	1.38(1)
C(13)–C(14)	1.40(2)	1.35(1)
C(13′)–C(14′)	1.35(2)	1.30(2)
C(14)–C(15)	1.34(2)	1.37(1)
C(14′)–C(15′)	1.36(2)	1.40(2)
C(15)–C(16)	1.41(2)	1.41(1)
C(15′)–C(16′)	1.43(2)	1.41(1)
C(17)–C(18)	1.38(2)	1.37(1)
C(17′)–C(18′)	1.36(2)	1.33(1)
C(17)–C(22)	1.35(2)	1.35(1)
C(17′)–C(22′)	1.35(2)	1.37(2)
C(18)–C(19)	1.40(2)	1.37(1)
C(18′)–C(19′)	1.39(2)	1.39(1)
C(19)–C(20)	1.32(2)	1.34(1)
C(19′)–C(20′)	1.31(3)	1.29(2)
C(20)–C(21)	1.33(2)	1.33(1)
C(20′)–C(21′)	1.32(3)	1.36(2)
C(21)–C(22)	1.43(2)	1.38(1)
C(21′)–C(22′)	1.41(2)	1.41(2)
(b) Bond angles		
Ga–As–Ga′	88.70(7)	91.62(4)
Si–As–Si′	111.0(2)	110.22(8)
Ga–As–Si	114.1(1)	113.76(7)
Ga′–As–Si	114.0(1)	113.95(6)
Ga–As–Si′	113.0(1)	112.40(6)
Ga′–As–Si′	114.5(1)	113.87(6)
As–Ga–X	89.5(1)	90.35(4)
As–Ga′–X	89.8(1)	90.21(4)
As–Ga–C(11)	111.4(4)	111.8(2)
As–Ga′–C(11′)	110.8(4)	110.1(2)

Table 2 (continued)

	Compound **1**	Compound **2**
As–Ga–C(17)	117.8(4)	118.7(2)
As–Ga′–C(17′)	115.3(3)	115.9(2)
X–Ga–C(11)	108.0(3)	107.4(2)
X–Ga′–C(11′)	107.5(5)	107.6(2)
X–Ga–C(17)	104.6(4)	103.6(2)
X–Ga′–C(17′)	105.1(4)	103.9(3)
C(11)–Ga–C(17)	120.0(5)	119.5(3)
C(11′)–Ga′–C(17′)	122.6(5)	123.2(3)
Ga–X–Ga′	91.3(1)	87.10(4)
As–Si–C(1)	106.0(4)	106.9(2)
As–Si′–C(1′)	107.7(5)	108.2(3)
As–Si–C(2)	110.0(5)	110.1(3)
As–Si′–C(2′)	109.0(5)	108.5(3)
As–Si–C(3)	110.6(5)	108.6(3)
As–Si′–C(3′)	106.8(5)	108.2(3)
C(1)–Si–C(2)	112.8(7)	111.8(5)
C(1′)–Si′–C(2′)	112.6(7)	111.3(4)
C(1)–Si–C(3)	109.5(6)	108.7(4)
C(1′)–Si′–C(3′)	110.7(7)	109.5(4)
C(2)–Si–C(3)	108.0(8)	110.7(5)
C(2′)–Si′–C(3′)	109.9(6)	111.0(4)
Ga–C(11)–C(12)	122(1)	123.9(5)
Ga′–C(11′)–C(12′)	124(1)	125.1(6)
Ga–C(11)–C(16)	119(1)	118.6(6)
Ga′–C(11′)–C(16′)	121(1)	119.7(6)
C(12)–C(11)–C(16)	119(1)	117.5(7)
C(12′)–C(11′)–C(16′)	115(1)	115.1(7)
C(11)–C(12)–C(13)	122(1)	120.8(8)
C(11′)–C(12′)–C(13′)	123(1)	123.2(9)
C(12)–C(13)–C(14)	118(1)	120.5(8)
C(12′)–C(13′)–C(14′)	118(1)	121.6(10)
C(13)–C(14)–C(15)	120(1)	120.6(9)
C(13′)–C(14′)–C(15′)	123(1)	119.3(10)
C(14)–C(15)–C(16)	121(1)	118.9(8)
C(14′)–C(15′)–C(16′)	116(1)	118.6(10)
C(11)–C(16)–C(15)	121(1)	121.7(8)
C(11′)–C(16′)–C(15′)	125(1)	122.2(9)
Ga–C(17)–C(18)	125(1)	123.9(6)
Ga′–C(17′)–C(18′)	124(1)	126.8(8)
Ga–C(17)–C(22)	120(1)	119.7(6)
Ga′–C(17′)–C(22′)	121(1)	118.9(7)
C(18)–C(17)–C(22)	115(1)	116.4(8)
C(18′)–C(17′)–C(22′)	115(1)	114.1(9)
C(17)–C(18)–C(19)	123(1)	120.8(8)
C(17′)–C(18′)–C(19′)	122(2)	124.9(10)
C(18)–C(19)–C(20)	120(1)	120.9(10)
C(18′)–C(19′)–C(20′)	123(2)	119.2(11)
C(19)–C(20)–C(21)	120(1)	119.9(9)
C(19′)–C(20′)–C(21′)	114(2)	121.1(11)
C(20)–C(21)–C(22)	120(1)	119.2(8)
C(20′)–C(21′)–C(22′)	125(2)	118.0(12)
C(17)–C(22)–C(21)	122(1)	122.7(8)
C(17′)–C(22′)–C(21′)	119(2)	122.5(11)

Table 3

Selected torsion angles [a] (deg.) for $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2X}$ (X = Cl (**1**), X = Br (**2**)), with estimated standard deviations in parentheses

	Compound **1**	Compound **2**		Compound **1**	Compound **2**
Ga′–As–Ga–X	6.1(1)	6.55(4)	Ga–As–Ga′–X	−6.1(1)	−6.54(4)
Ga′–As–Ga–C(11)	−103.1(4)	−102.3(2)	Ga–As–Ga′–C(11′)	−114.8(5)	−115.4(3)
Ga′–As–Ga–C(17)	112.4(4)	112.3(3)	Ga–As–Ga′–C(17′)	100.5(5)	99.0(3)
Si–As–Ga–X	−109.7(1)	−110.59(7)	Si′–As–Ga′–X	−121.0(2)	−121.98(7)
Si–As–Ga–C(11)	141.1(4)	140.5(2)	Si′–As–Ga′–C(11′)	130.4(5)	129.1(3)
Si–As–Ga–C(17)	−3.4(4)	−4.9(3)	Si′–As–Ga′–C(17′)	−14.3(5)	−16.4(3)
Si′–As–Ga–X	122.2(2)	123.26(7)	Si–As–Ga′–X	109.7(2)	110.43(8)
Si′–As–Ga–C(11)	13.1(4)	14.4(2)	Si–As–Ga′–C(11′)	1.1(5)	1.6(3)
Si′–As–Ga–C(17)	−131.5(4)	−131.0(3)	Si–As–Ga′–C(17′)	−143.6(5)	−144.0(5)
As–Ga–X–Ga′	−6.3(1)	−6.30(4)	As–Ga′–X–Ga	6.3(1)	6.29(4)
C(11)–Ga–X–Ga′	106.1(4)	106.7(2)	C(11′)–Ga′–X–Ga	118.0(4)	117.5(2)
C(17)–Ga–X–Ga′	−125.0(4)	−126.0(2)	C(17′)–Ga′–X–Ga	−109.9(4)	110.5(2)

[a] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D.

would be expected to attack the Si atoms easily through its unoccupied 3*d* orbitals. An intermediate in the formation of **5** with a structure analogous to **1** and **2** but having phenyl groups replaced by Br atoms, appears reasonable. This intermediate would contain singly coordinate Br atoms activated for attack on the Si atoms by the negative formal charges on the Ga atoms, leading to formation of $(Br_2Ga)_2As\text{-}SiMe_3$ (**6**). Attack of **6** by another mole of $GaBr_3$ to create another mixed bridge intermediate, followed by elimination of the last equivalent of Me_3SiBr, could give **5**. In order to produce singly coordinate halogen atoms out of **1** and **2**, breaking of the bridging Ga–X–Ga′ bonds must occur, an event which would be endoenergic. Alternatively, dissociation of **1** and **2** to give Ph_2GaX and $Ph_2GaAs(SiMe_3)_2$, followed by formation of Me_3SiX, may require an activation energy which is not overcome at room temperature.

In our previous communication on **1** [10], we reported that heating a sample of **1** in C_6D_6 at 80 °C for one month produced Me_3SiCl, **4**, and other unidentified products, indicating that other reaction pathways are also possible at elevated temperatures. Indeed, when **3** and Ph_2GaCl, 1/3 mole ratio, were heated to 80 °C, 80% of the Me_3SiCl possible was produced along with Ph_3Ga and a small amount of an unidentified polymer. No evidence for formation of $(Ph_2Ga)_3As$ was observed. Assuming that **1** is an intermediate in the reaction, intramolecular rearrangement of **1** at high temperature could produce an As, phenyl mixed bridge structure having a singly coordinate Cl atom. Subsequent loss of Ph_3Ga would yield $Ph(Cl)GaAs(SiMe_3)_2$ which could polymerize or react with the third mole of Ph_2GaCl to generate more Ph_3Ga in a similar way. This pathway is not unreasonable, since evidence for bridging of two gallium centers by unsaturated hydrocarbon groups has been reported [17*]. An alternate pathway to the generation of Ph_3Ga can occur via loss of Ph_2GaCl from **1** to give **4**. Reaction of Ph_2GaCl to form Ph_3Ga and $GaCl_3$ in an equilibrium step, followed by reaction of $GaCl_3$ with **1** or **4** could lead to a polymer and a build-up of Ph_3Ga.

Table 4

Equations of least-squares planes through groups of atoms in $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2X}$ (X = Cl (**1**), X = Br (**2**)) in the form: $pX + qY + rZ - S = 0$ [a], with, in parentheses, displacements (Å) of selected atoms from these planes

Compound **1**
Plane A: As, Ga, Ga′
$0.2848X + 0.1579Y - 0.9455Z + 3.0314 = 0$
(As 0.000, Ga 0.000, Ga′ 0.000, Cl 0.256, Si 1.939, Si′ −1.956, C(11) −1.78, C(17) 1.58, C(11′) 1.64, C(17′) −1.73)
Plane B: C(11)–C(16)
$-0.2972X + 0.8955Y - 0.3313Z - 1.4273 = 0$
(Ga −0.037, Cl −0.082, C(11) −0.01, C(12) 0.00, C(13) 0.01, C(14) −0.02, C(15) 0.01, C(16) 0.01)
Plane C: C(17)–C(22)
$0.0376X - 0.8686Y - 0.4940Z + 5.3285 = 0$
(Ga −0.065, Cl −1.004, C(17) 0.00, C(18) −0.01, C(19) 0.01, C(20) 0.00, C(21) 0.00, C(22) 0.00)
Plane B′: C(11′)–C(16′)
$-0.7238X - 0.4075Y - 0.5569Z + 7.5710 = 0$
(Ga′ 0.167, Cl 0.012, C(11′) 0.00, C(12′) 0.01, C(13′) −0.02, C(14′) 0.02, C(15′) −0.01, C(16′) 0.00)
Plane C′: C(17′)–C(22′)
$0.8802X + 0.4646Y - 0.0973Z - 4.9973 = 0$
(Ga′ −0.018, Cl 0.234, C(17′) 0.00, C(18′) 0.01, C(19′) −0.04, C(20′) 0.06, C(21′) −0.05, C(22′) 0.03)

Compound **2**
Plane A: As, Ga, Ga′
$0.2869X + 0.1672Y - 0.9433Z + 2.9946 = 0$
(As 0.000, Ga 0.000, Ga′ 0.000, Br 0.293, Si 1.926, Si′ −1.954, C(11) −1.78, C(17) 1.60, C(11′) 1.65, C(17′) −1.73)
Plane B: C(11)–C(16)
$-0.3042X + 0.8945Y - 0.3276Z - 1.4767 = 0$
(Ga −0.034, Br 0.009, C(11) −0.01, C(12) 0.00, C(13) 0.00, C(14) 0.01, C(15) −0.01, C(16) 0.01)
Plane C: C(17)–C(22)
$0.0763X - 0.8713Y - 0.4847Z + 5.2909 = 0$
(Ga −0.035, Br −1.033, C(17) −0.02, C(18) 0.01, C(19) 0.00, C(20) −0.01, C(21) 0.00, C(22) 0.02)
Plane B′: C(11′)–C(16′)
$-0.7301X - 0.3898Y - 0.5613Z - 7.5890 = 0$
(Ga′ 0.146, Br −0.43, C(11′) 0.00, C(12′) 0.00, C(13′) 0.00, C(14′) −0.01, C(15′) 0.01, C(16′) −0.01)
Plane C′: C(17′)–C(22′)
$0.8786X + 0.4670Y - 0.0997Z - 4.9738 = 0$
(Ga′ 0.012, Br 0.358, C(17′) 0.02, C(18′) −0.01, C(19′) −0.01, C(20′) 0.02, C(21′) −0.01, C(22′) −0.01)

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[a] Cartesian coordinates (X, Y, Z) are related to the fractional atomic coordinates (x, y, z) in Table 1 by the transformations: $X = xa + zc\cos\beta$, $Y = yb$, $Z = zc\sin\beta$.

In the coupling reaction between $LiAs(SiMe_3)_2$ and Ph_2GaCl, analogous to that used to prepare the first monomeric mono(arsino)gallane $(C_5Me_5)_2GaAs(SiMe_3)_2$ [6], the dimer, **4**, was formed. Cryoscopic molecular weight data confirm that **4** is a dimer in solution and thus is the first reported dimeric arsinogallane having bridging $As(SiMe_3)_2$ groups. Presumably, the steric interactions of the phenyl groups with the bulky Me_3Si groups are not large enough to stabilize a monomeric form. The reaction of **4** with Ph_2GaCl in a 1/2 mole ratio at room temperature produced **1** quantitatively, implying that **4** undergoes monomer–dimer equilibrium. Assuming a bimolecular reaction between Ph_2GaCl and the monomer of **4**, the formation of **1** must have a lower activation energy than elimination of Me_3SiCl, since the latter involves bond breaking.

X-ray crystal structure analyses of **1** and **2** revealed that the asymmetric units comprise discrete isostructural molecules (Fig. 1 and 2) containing the aforementioned As- and halogen-bridged Ga–As–Ga′–Cl and Ga–As–Ga′–Br rings, respectively [10]. Selected structural details are presented in Table 2–4. Outward rotation of the Ga–C(17) and Ga–C(11′) bond vectors to relieve substituent steric overcrowding which would be present with a planar four-membered ring and overall C_{2v} molecular symmetry results in a mean dihedral angle about ring bonds of 6.2° in **1** and 6.6° in **2**, and thus the rings are not strictly planar (ΔCl 0.256 Å in **1**, Δ**Br** 0.293 Å in **2** from the respective Ga–As–Ga′ planes). The degree of ring puckering found here is somewhat less than in the $(Ga–As)_2$ ring of $\{Ga[As(CH_2SiMe_3)_2]_3\}_2$ [4] where the mean corresponding dihedral angle at 10.2° reflects the more severe steric overcrowding associated with the bulkier ring substituents. In contrast to the situation in $(Ga–As)_2$ rings where endocyclic bond angles subtended at As and Ga differ significantly (range: 94.57(4)–96.02(4)° and 83.58(4)–85.02(2)°, respectively) [2], those in **1** (88.70(7)° at As; 89.5(1) and 89.8(1)° at Ga) and **2** (91.62(4)° at As; 90.35(4) and 90.21(4)° at Ga) are almost equal within each ring. Enlarged values in **2** vs. **1** are not unexpected since Br is larger than Cl. At the bridging Cl atom, the bond angle (91.3(1)°) is nearly the same as that of 91.4(1)° in $[Ga(C_5H_5)Cl_2]_2$ (**7**) [18] and it is intermediate between that of 86(2)° in $[GaCl_3]_2$ (**8**) [19] and the mean of 97.4(2)° in $[Ga(C_5Me_5)_2Cl]_2$ (**9**) [18]. The mean C–Ga–C angles in **1** (121.3(5)°) and **2** (121.4(3)°) are close to the corresponding value of 120.8(2)° in $[Ph_2GaAs(CH_2SiMe_3)]_2$ [20]. Significantly larger Si–As–Si′ angles (111.0(2)° in **1** and 110.22(8)° in **2**) are present than in $[(Me_3Si)_2AsLi \cdot DME]_2$ (DME = 1,2-dimethoxyethane) (**10**) (103.2(4)°) [21]. Mean Ga–As bond lengths in **1** [2.466(2) Å) and **2** (2.465(1) Å) are equal and are shorter than any found within $(Ga–As)_2$ rings (range: 2.513(1)–2.581(1) Å) [2]. The mean Ga–Cl distance at 2.411(4) Å is longer than the corresponding length in **8** [2.29(9) Å] as well as the mean of those in **7** (2.363(3) Å) and the mean of those in the ion $Ga_2Cl_7^-$ (2.304 Å) [22], but it is shorter than the mean in **9** (2.448(7) Å). Mean Si–As distances in **1** (2.363(4) Å) and **2** (2.365(2) Å) are equal and are significantly longer than in **10** (2.307(7) Å). The Ga–Br–Ga′ bond angle (87.10(4)°) and the mean Ga–Br bond distance (2.566(1) Å) are the first reported values obtained by X-ray crystallography on a compound having a Ga–Br–Ga′ moiety, and the latter is substantially greater than the non-bridging Ga–Br length at 2.378(1) Å in $\{BrGa[As(CH_2SiMe_3)_2]_2\}_2$ [2] as well as the corresponding means in **5** (2.331(6) Å) and $[Br_2GaAs(CH_2SiMe_3)_2]_3$ (2.327(2) Å) [23]. Finally, the ^{13}C NMR spectra and the experimentally determined molecular weights of **1** and **2** indicate they both have the same molecular structure in solution as in the solid state.

Acknowledgement

We thank the Office of Naval Research for financial support.

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