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Synthesis and Characterization of $(Me_3Si)_2AsCH_2RCH_2As(SiMe_3)_2$ (R = CH_2, $SiMe_2$) and $Ph_2GaCl(Ph)_2Ga(Me_3Si)As$—$(CH_2)_3As(SiMe_3)Ga(Ph)_2ClGaPh_2$

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ABSTRACT

The synthesis and characterization of

$$(Me_3Si)_2AsCH_2RCH_2As(SiMe_3)_2$$
$$[R = CH_2\ (\mathbf{1}),\ SiMe_2\ (\mathbf{2})]$$

is described. Compound **1** *reacts with four equivalents of* Ph_2GaCl *to produce*

$$Ph_2GaCl(Ph)_2Ga(Me_3Si)As—(CH_2)_3As(SiMe_3)Ga(Ph)_2ClGaPh_2\ (\mathbf{3}),$$

whose structure was deduced by use of ^1H *and* $^{13}C\{^1H\}$ *NMR spectroscopy.*

INTRODUCTION

For the past several years our group has been exploring ways of forming the Ga–As bond. Methods of doing this pioneered by us include the reaction between a silylarsine and a halogallane to eliminate a halosilane [1, 2], and coupling between a lithium arsenide and halogallane to eliminate lithium halide [3, 4]. Along with the alkane elimination routes employing primary or secondary arsines and tertiary alkyl gallium compounds first utilized by Coates [5, 6], these methods have provided the primary routes toward forming Ga–As bonds. In all of this work to date, the arsenic-containing reactants have all been monoarsine type compounds. It occurred to us that suitable bisarsines could be used as precursors to gallium-arsenic-containing monomers which could then be polymerized perhaps forming the linear chains of gallium- and arsenic-containing macromolecules which, upon subsequent chemical or physical processing, could be transformed into micro-structural GaAs wires for possible use in microelectronic devices [7]. Since the halosilane elimination route to Ga–As bond formation yields a volatile byproduct, we decided that specific silylated bisarsines would be desirable target molecules. We describe herein our initial efforts in this vein, and the use of one of the resulting bisarsine compounds to prepare a novel organogallium–arsenic compound.

EXPERIMENTAL

General Comments

All reactions and manipulations were performed under vacuum or under dry, oxygen-free N_2 or Ar atmospheres using standard Schlenk techniques or in a Vacuum/Atmospheres HE-43 Dri-Lab. All solvents were drived by refluxing over and distilling from sodium benzophenone under N_2, then degassed by several freeze-pump-thaw cycles. The pentane and ligroin (bp 95–110°C) stills included several milliliters of tetraglyme to solubilize the sodium benzophenone. $LiAs(SiMe_3)_2 \cdot 2THF$ was prepared by the method of Becker [8]. 1,3-Dichloropropane and bis(chloromethyl)dimethylsilane (Aldrich) were dried by refluxing over and distilling from P_2O_5, then degassed by several freeze-pump-thaw cycles. Diphenylgallium chloride was prepared by heating gallium trichloride (Strem) and triphenylgallium [9] in a 1:2 mole ratio in toluene,

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then recrystallizing from toluene. ^1H NMR spectra were run at 299.943 MHz on a Varian XL-300 spectrometer; chemical shifts are in ppm versus C_6D_5H δ = 7.15 ppm. $^{13}C\{^1H\}$ NMR spectra were run at 75.429 MHz on the Varian instrument or at 22.50 MHz on a JEOL FX-90Q spectrometer; chemical shifts are in ppm versus C_6D_6 δ = 128.00 ppm. Analysis of the volatile reaction products for Me_3SiCl was performed by hydrolysis followed by NaOH titration of the resulting HCl solution to the phenolphthalein endpoint. Elemental analyses were performed by E + R Microanalytical Laboratory, Corona, NY. Melting points were obtained in sealed tubes on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin Elmer 297 infrared spectrometer. Raman spectra were obtained in the range 50–1200 cm^{-1} on neat samples using the Ar 514.5 nm line for excitation with the image focused into a double monochromator and measured with a photomultiplier tube. Mass spectra were obtained on a Perkin Elmer 5988A GC/MS in the DIP/EIMS mode at 20 eV.

Preparation of $(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2$ (**1**)

A combination of 2.40 g (6.44 mmol) of $LiAs(SiMe_3)_2 \cdot 2THF$ and 0.370 g (3.27 mmol) of 1,3-dichloropropane in 40 mL of pentane was placed into a 50-mL round-bottom flask. The mixture was stirred for 24 h at RT under dry Ar, forming a white solid that was presumed to be LiCl. The mixture was then filtered and the solvent was stripped from the filtrate, leaving behind a light yellow oily liquid. The liquid was fractionally distilled in vacuo (0.01 torr). The fraction distilling at 125°C was saved and weighed 0.73 g (47% yield). Analysis found for $C_{15}H_{42}Si_4As_2$ (calc): %C, 37.13 (37.17); %H, 8.79 (8.73). ^1H NMR (C_6D_6, 20°C): δ = 0.29 (s, $SiMe_3$, 36H), 1.83–1.88 (m, CH_2, 4H), 1.91–2.04 (m, CH_2, 2H). $^{13}C\{^1H\}$ NMR (22.50 MHz, C_6D_6, 20°C): δ = 1.78 ($SiMe_3$), 15.23 (CH_2), 34.68 (CH_2). IR data (neat film, KBr plates, cm^{-1}): 3785 w, 3730 w, 3635 w, 2960 vs, 2905 vs, 2855 ssh, 2790 msh, 2640 w, 2470 w, 2330 w, 2080 w, 1992 w, 1934 m, 1866 m, 1443 s, 1418 ssh, 1400 s, 1370 msh, 1337 msh, 1330 msh, 1312 s, 1288 s, 1260 vssh, 1249 vs, 1219 s, 1198 s, 1140 m, 1025 m, 915 msh, 860 vssh, 830 vs, 778 ssh, 748 vs, 738 vssh, 690 vs, 672 msh, 621 vs, 600 s. Raman data (cm^{-1}): 1196 m, 862 m, 840 m, 750 m, 690 s, 676 s, 630 vs, 554 m, 538 s, 522 w, 348 vs, 246 msh, 205 s, 178 s, 108 m. The mass spectrum showed a molecular ion at m/e = 484, as well as lower mass ions including those corresponding to $(M - H)^+$, $(M - Me)^+$, and $(M - SiMe_3)^+$ at m/e = 483, 469, and 411, respectively.

Preparation of $(Me_3Si)_2AsCH_2Si(Me)_2CH_2As(SiMe_3)_2$ (**2**)

A combination of 2.371 g (6.366 mmol) of $LiAs(SiMe_3)_2 \cdot 2THF$ and 0.501 g (3.19 mmol) of bis(chloromethyl)dimethylsilane in 5 mL of THF and 40 mL of pentane was placed in a 50-mL round-bottom flask. The mixture was stirred for 24 h at RT under N_2, forming a white solid that was presumed to be LiCl. The mixture was filtered and the solvent was stripped, leaving behind a yellow liquid. The liquid was fractionally distilled in vacuo (0.01 torr) and the fraction distilling at 120°C was saved. Yield: 1.21 g, 72%. Analysis found for $C_{16}H_{46}Si_5As_2$ (calc): %C, 36.34 (36.34); %H, 8.62 (8.77). ^1H NMR (C_6D_6, 20°C): δ = 0.29 (s, $SiMe_3$, 36H), 0.37 (s, $SiMe_2$, 6H), 0.76 (s, CH_2, 4H). $^{13}C\{^1H\}$ NMR (22.50 MHz, C_6D_6, 20°C): δ = −5.80 ($SiMe_2$), −1.04 (CH_2), 1.51 ($SiMe_3$). The ^{13}C methylene resonance was identified through an INEPT sequence.

Preparation of $Ph_2\overline{GaCl(Ph)_2Ga(Me_3Si)As}$—$(CH_2)_3\overline{As(SiMe_3)Ga(Ph)_2ClGa}Ph_2$ (**3**)

A solution of 0.259 g (1.00 mmol) of Ph_2GaCl in 30 mL of benzene and a solution of 0.124 g (0.250 mmol) of **1** in 10 mL of benzene were combined in a 50-mL one-necked round-bottom flask equipped with a Teflon Kontes valve. The stopcock was closed, and the solution was stirred for 6 days at RT. The volatiles were then vacuum-transferred into another flask, hydrolyzed, and titrated to reveal that 0.519 mmol of Me_3SiCl have been produced in the reaction. The solid residue was extracted with eight 10-mL portions of ligroin that were then combined and filtered. Cooling the filtrate to −17°C for 10 days produced 0.047 g (14.4% yield) of tiny white fibrous crystals, which were dried in vacuo: mp 181–182°C (dec.). Analysis found for $C_{57}H_{64}Cl_2Si_2Ga_4As_2$ (calc): %C, 52.25 (52.47), %H, 5.24 (4.94). ^1H NMR (C_6D_6, 20°C): δ = −0.06 (s, $SiMe_3$, 18H), 1.37–2.32 (m, CH_2, 6H), 7.17–7.42, 7.60–7.63, 7.77–7.86, 8.09–8.12 (m, Ph, 40H). $^{13}C\{^1H\}$ NMR (75.429 MHz, C_6D_6, 20°C): δ = 0.62 ($SiMe_3$), 15.69 (CH_2), 28.27 (CH_2), 128.16 (Ph), 128.43 (Ph), 136.64 (Ph), 136.79 (Ph), 137.65 (Ph), 138.50 (Ph), 145.44 (Ph), 146.37 (Ph). IR data (Nujol mull, KBr plates, cm^{-1}): 3065 ssh, 3045 s, 2730 w, 2670 wbr, 1952 wbr, 1879 wbr, 1840 wbr, 1612 w, 1580 w, 1425 vs, 1410 msh, 1341 m, 1333 m, 1301 m, 1280 m, 1258 s, 1231 m, 1219 m, 1190 m, 1170 w, 1158 m, 1150 msh, 1141 wsh, 1080 s, 1070 msh, 1060 msh, 1048 wsh, 1025 s, 1000 s, 958 m, 919 w, 886 msh, 841 vssh, 831 vs, 806 ssh, 750 ssh, 730 vs, 700 vs, 667 s, 650 wsh, 645 m, 620 s. Raman data [10] (cm^{-1}): 1122 vs, 1024 m, 998 s, 694 w, 660 m, 622 w, 356 m, 226 w, 180 w, 146 m, 92 m, 70 m.

RESULTS AND DISCUSSION

The synthesis of $(Me_3Si)_2AsCH_2RCH_2As(SiMe_3)_2$ (R = CH_2 (**1**), $SiMe_2$ (**2**)) proceeds in organic solvents according to Equation 1.

$$2LiAs(SiMe_3)_2\cdot 2THF + ClCH_2RCH_2Cl \longrightarrow (Me_3Si)_2AsCH_2RCH_2As(SiMe_3)_2 + 2LiCl + 4THF \quad (1)$$

R = CH_2 (**1**), $SiMe_2$ (**2**)

Many other bisarsines have been synthesized by this alkali metal arsenide route, including Ph_2As—$(CH_2)_nAsPh_2$ (n = 1–6) [11–15], $Cy_2As(CH_2)_4AsCy_2$ (Cy = cyclohexyl) [11], $Me_2As(CH_2)_nAsMe_2$ (n = 1, 5), $Me(Cl)As(CH_2)_nAs(Cl)Me$ (n = 2, 3) [14], and $(Me_3Si)_2AsCH_2As(SiMe_3)_2$ [8]. Other methods of making bisarsines have included the reaction of acetyl chloride, As_2O_3, and $AlCl_3$ to make $Cl_2AsCH_2AsCl_2$ [16, 17], the synthesis of $(HO)(O)(Ph)AsCH_2CH_2$—$As(Ph)(O)(OH)$ from ethylene bromide and phenyldichloroarsine in aqueous NaOH [18, 19], and interestingly the insertion of vinyl fluoride into the As–As bond of tetramethyldiarsine to make $Me_2AsCH_2CHFAsMe_2$ [20]. Curiously, though, the attempted preparation of $(Me_3Si)_2AsCH_2CH_2As$—$(SiMe_3)_2$ and Ph_2As—$CH_2CH_2AsPh_2$ using ethylene bromide and $LiAs(SiMe_3)_2\cdot 2THF$ or $KAsPh_2$, respectively, yielded ethylene deinsertion products of the type R_2As—AsR_2 [8, 15], even though formal ethylene deinsertion probably did not occur since it is believed that the desired products were not obtained even transiently. Since these desired products can be obtained in a different manner [12–14, 19], the problem may likely be caused by the use of the bromide, though this issue is far from settled. However, this synthetic route was recently taken advantage of in the synthesis of $Mes_2AsAsMes_2$ (Mes = mesityl) from $LiAsMes_2$ and ethylene bromide [21].

The new compounds **1** and **2** are both colorless, air- and water-sensitive, vacuum-distillable oils. Their sharp boiling points, elemental analyses, and ^1H and ^{13}C NMR spectra, and for **1** its mass spectrum, are all consistent with the proposed formulations. It should also be noted that several of the IR and Raman bands of **1** correspond to those found in $(Me_3Si)_nAsH_{3-n}$ (n = 1–3) [22, 23], particularly for n = 2, as may be expected for C_s local symmetry about the arsenic atoms.

In analogy to our syntheses of the mono-mixed-bridge compounds $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2X$ (X = Cl, Br) [24, 25], reaction of **1** with 4 equivalents of Ph_2GaCl in benzene yields a compound formulated as the bis-mixed-bridge $Ph_2GaCl(Ph)_2Ga(Me_3Si)As$—$(CH_2)_3As(SiMe_3)Ga(Ph)_2ClGaPh_2$ (**3**) (Equation 2). The stoichiometry of the chlorotrimethylsilane byproduct was confirmed by hydrolysis and titration of the reaction volatiles for HCl. Compound **3** was obtained as very fine, whisker-like colorless crystals from ligroin and as a solvate from toluene, neither of which has as yet proved suitable for characterization by X-ray crystallography.

A number of pieces of evidence lead us to believe that we have the correct formulation for **3**. The fact that the material was obtained as crystals with a definite melting point, indicates that it is a single compound, as is supported also by its clean ^1H and $^{13}C\{^1H\}$ NMR spectra. The production of one equivalent of Me_3SiCl per arsenic atom corresponds to what is found in the synthesis of the mono-mixed-bridge compounds [24, 25]. The positions and correct integrations of the ^1H NMR signals argues for a proton stoichiometry as formulated, and the $^{13}C\{^1H\}$ NMR spectrum, particularly the fact that eight phenyl carbon signals are observed, is consistent with the proposed idealized C_{2v} symmetry structure shown in Figure 1. In this structure there are two types of phenyl groups, those proximal and those distal to the trimethylsilyl groups, each of which has four different types of carbons, assuming that there is free rotation about the Ga–C_{ipso} bonds. This gives eight different types of phenyl carbons, as is observed in the $^{13}C\{^1H\}$ NMR spectrum. Any sort of conformational flexibility about the trimethylene backbone must be rapid on the NMR time scale, since the time-averaged ^1H and $^{13}C\{^1H\}$ NMR spectra of the flexible species would be similar to those of the rigid structure as drawn. However, because there are two different types of phenyl groups, any sort of fluxionality consisting of Ga–Cl bond cleavage followed by rotation about the corresponding Ga–As bond, with subsequent reformation of the Ga–Cl bond, cannot be rapid on the NMR time scale, as this would make the phenyl groups that are proximal and distal to the trimethylsilyl group chemically equivalent. Likewise, fluxional processes involving Ga–As bond cleavage accompanied by conformational changes about the dangling arm with subsequent Ga–As bond reformation are ruled out.

It should be noted here that in the X-ray crystal structures of the mono-mixed bridge compounds, the halogen atoms are out of the Ga–As–Ga′ planes, which should render both the phenyl and trimethylsilyl groups inequivalent on the NMR time scale; this is not observed [24, 25]. In the solution NMR studies of those compounds, however, it is impossible to distinguish whether an envelope-flapping

$$\underset{(1)}{(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2} + 4Ph_2GaCl \longrightarrow \underset{(3)}{Ph_2GaCl(Ph)_2Ga(Me_3Si)As(CH_2)_3As(SiMe_3)Ga(Ph)_2ClGaPh_2} + 2Me_3SiCl \quad (2)$$

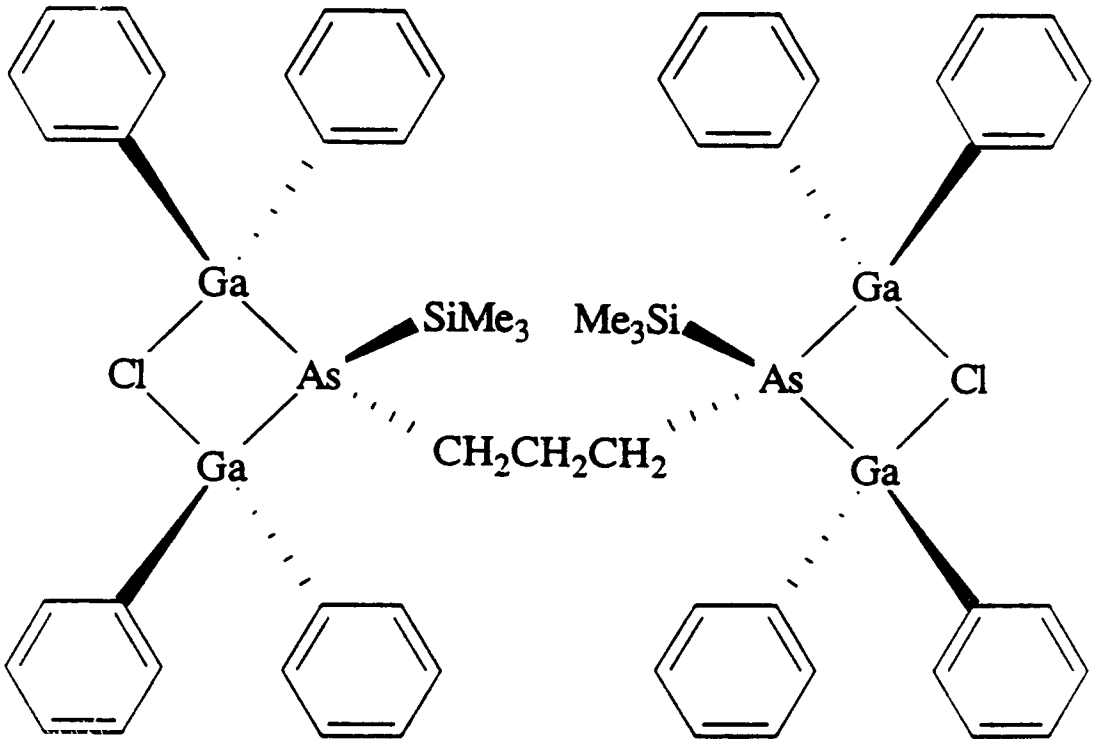

FIGURE 1 Proposed structure for **3**.

or an arm-off mechanism as described above is operating. Regardless, in **3** an envelope-flapping motion would be NMR invisible because the two different groups on the arsenic atoms render the two phenyl groups on each gallium atom chemically inequivalent.

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