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Summary: The reactions of trimethylaluminum with diphenylarsine, Ph_2AsH, and phenyl(trimethylsilylmethyl)arsine, Ph(Me_3SiCH_2)AsH, in 1:1 mole ratios afford the trimeric compounds $[Me_2AlAsPh_2]_3 \cdot (C_7H_8)_2$ (**1**) and $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (**2**), respectively. Compounds **1** and **2** are the first Al-As six-membered ring compounds to be structurally characterized by single-crystal X-ray crystallography, as well as ^1H and ^{13}C solution NMR spectroscopy. X-ray crystallographic analysis revealed that trimer **1** is a toluate which crystallizes in the monoclinic space group $P\,2_1/n$, with $a = 14.549(6)$ Å, $b = 22.838(7)$ Å, $c = 16.891(4)$ Å, and $\beta = 105.12(5)°$ for $Z = 4$. Trimer **2**

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crystallizes in the triclinic system, space group $P\bar{1}$, and has two unique molecules in a unit cell with dimensions of a = 15.619(7) Å, b = 17.487(6) Å, c = 19.863(6) Å, $\alpha = 94.86(3)°$, $\beta = 101.41(3)°$, and $\gamma = 113.34(3)°$ for $Z = 4$. The six-membered Al-As rings in both **1** and **2** occupy chair conformations, furnishing both trimers with structural characteristics similar to cyclohexane. The Al and As centers of both **1** and **2** reside in pseudotetrahedral environments, with the Al—As bond lengths ranging from 2.512(3)Å to 2.542(3) Å in **1**, and from 2.504(5) Å to 2.526(5) Å in **2**.

Introduction

Two previous reports from our laboratory focused on efforts to use dehalosilylation and salt-elimination reactions between alkylaluminum halides and silyl arsenic reagents to prepare aluminum-arsenic compounds which might serve as single-source molecular precursors to the semiconductor material AlAs.[1,2] Although these synthetic routes led to the isolation and characterization of some novel compounds, the number of Al—As bonds formed in the products was limited. Attempted dehalosilylation reactions between R_2AlCl (R = Me, Et, ^{i}Bu) and $As(SiMe_3)_3$ in 1:1 molar ratios afforded Lewis acid-base adduct compounds with the formula $R_2(Cl)Al{\bullet}As(SiMe_3)_3$, while lithium coupling reactions between R_2AlCl (R = Me, Et, ^{i}Bu) and $LiAs(SiMe_3)_2$ produced solely dimeric compounds of the type $[R_2AlAs(SiMe_3)_2]_2$. In an effort to synthesize Al-As compounds with a higher degree of association, we have begun to investigate alternative reaction pathways.

Traditionally, alkane-elimination reactions involving trialkylaluminum species and primary or secondary arsines (eqs 1 and 2) have been shown to be quite useful in the synthesis of compounds containing a large number of Al—As bonds, beginning with the definitive work reported by Coates and co-workers in the mid-1960's.[3,4] Therein, they reported the condensation reaction between Me_3Al and Me_2AsH to yield an oligomeric product, $[Me_2AlAsMe_2]_n$ (**3**) which was determined to be polymeric in the solid state and trimeric in solution,[4] and the reaction of Me_3Al and Ph_2AsH to

$$(CH_3)_3Al + R_2AsH \longrightarrow [(CH_3)_2AlAsR_2]_n + CH_4\uparrow \tag{1}$$

$$(CH_3)_3Al + RAsH_2 \longrightarrow [(CH_3)_2AlAsR(H)]_n + CH_4\uparrow \tag{2}$$

R = alkyl or phenyl $\qquad$ $n = 2, 3$

generate a dimeric compound, $[Me_2AlAsPh_2]_2$ (**4**).[3] An analogous dimer, $[Me_2Al(\mu\text{-}{}^t Bu_2As)]_2$ was prepared by Cowley and Jones and co-workers from the reaction of trimethylaluminum and dibutylarsine,[5] and more recently, they synthesized the Al-As trimers, $[{}^t Bu_2Al(\mu\text{-}AsH_2)]_3$ (**6**)[6] and $[{}^t Bu_2AlAs({}^t Bu)H]_3$, (**7**)[7] from the reaction of tri-*tert*-butylaluminum with AsH_3 and ${}^t BuAsH_2$, respectively. The functionality of the alkane-elimination reaction in Al-As systems, as demonstrated by the aforementioned compounds **3**-**7**, led us to further investigate the chemistry of Me_3Al and various bulky secondary arsines in an effort to synthesize compounds which might be trimeric or tetrameric in nature. Herein, we report the preparation of the di-substituted arsine, $Ph(Me_3SiCH_2)AsH$, and the synthesis and structural characterization of $[Me_2AlAsPh_2]_3{\cdot}(C_7H_8)_2$ (**1**) and $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (**2**), which are the first aluminum-arsenic trimers to be characterized by X-ray crystallographic techniques.

Experimental Section

General Considerations. All reactions and manipulations were carried out under vacuum, in a Vacuum Atmospheres HE-493 Dri-Lab under an argon atmosphere, or under N_2 using standard Schlenk apparatus. Pentane was dried over $LiAlH_4$, while all other solvents were distilled from sodium/benzophenone ketyl under dry nitrogen. NMR solvents were vacuum-distilled prior to use. Me_3Al was purchased from Aldrich Chemical Company, Inc. and used without further purification. Ph_2AsH[8] and $PhAsH_2$[9] were prepared by literature methods. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (300.0 and 75.4 MHz, respectively) in 5 mm-tubes. Low-temperature ^1H NMR spectra were recorded on a Varian

Unity-500 spectrometer (500.1 MHz) in sealed 5-mm tubes. ^{1}H NMR spectra were referenced to TMS using the residual protons of benzene-d_6 at δ 7.15 ppm or toluene-d_8 at δ 2.09 ppm, while ^{13}C NMR spectra were referenced to TMS using the residual carbons of benzene-d_6 at δ 128.0 ppm. IR spectra were recorded on a Perkin-Elmer 297 spectrometer. Melting point (uncorrected) were obtained on a Thomas-Hoover Uni-melt apparatus in flame-sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York. X-ray crystallographic data were collected on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at the Single Crystal X-Ray Facility at the University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Synthesis of Ph(Me$_3$SiCH$_2$)AsH. Liquid ammonia (100 mL) was condensed into a 500 mL flask equipped with a septum cap, a glass-encased stir-bar, and an N$_2$ inlet that was connected to a manifold with a bubbler. Sodium metal (0.8 g, 35 mmol) was added to the liquid NH$_3$, then PhAsH$_2$ (4.0 g, 30 mmol) was added *via* syringe. The mixture slowly turned from blue to green and finally to a clear bright yellow solution. The septum cap was replaced with a dropping funnel containing Me$_3$SiCH$_2$Cl (4.8 g, 39 mmol) dissolved in ether (40 mL), which was added dropwise to the reaction mixture. The ammonia was allowed to evaporate, and the mixture warmed to room temperature, where the yellow color persisted for several hours. After 24 h, the mixture was filtered through a frit to give a yellow liquid. The filtrate was concentrated *in vacuo* then distilled (0.1 mm Hg, 52-54 °C) to give a clear, colorless liquid, which was shown to have PhAsH$_2$ contamination by proton NMR. The liquid was redistilled *via* Vigareaux column (0.07 mm Hg, 54 °C) and 6.3 g (75% yield) of pure Ph(Me$_3$SiCH$_2$)AsH were obtained. Anal. Calcd. (Found) for C$_{10}$H$_{17}$AsSi: C, 49.99 (50.00); H, 7.13 (7.13). ^{1}H NMR: δ 0.06 [s, Si(C*H*$_3$)$_3$, 9H], 0.76 and 1.05, 3.77 (m, C*H*$_2$, As*H*, 3H, ABX pattern, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 10.4 Hz), 7.08 and 7.45 (m, C$_6$*H*$_5$, 5H). ^{13}C NMR: δ -0.49 [s,Si(*C*H$_3$)$_3$], 7.1 (s, *C*H$_2$), 127.9, 128.7, 134.1, 138.9 (s, *C*$_6$H$_5$). IR: 2950 (m), 2875 (w), 2050 (As—H) (m), 1430 (w), 1260 (w), 1250 (w), 1060 (br), 850 (s, br), 720 (m), 710 (m), 690 (m).

Preparation of [Me$_2$AlAsPh$_2$]$_3$•(C$_7$H$_8$)$_2$ (1) A 250-mL round-bottomed reaction flask was charged with a toluene (30 mL) solution of Ph$_2$AsH (0.365 g, 1.59 mmol) and a stir-bar.

While the arsine solution was stirring, Me_3Al (0.114 g, 1.58 mmol) dissolved in toluene (30 mL) was slowly added to give a clear, colorless reaction solution. During the addition of the Me_3Al solution, the evolution of bubbles was observed. The reaction flask was immersed in an oil bath, and the solution heated to 110 °C for 2 d with no change in appearance. The volatiles were removed *in vacuo* to give a white crystalline solid, which was recrystallized from toluene at -15 °C. After 24 h, colorless X-ray quality single crystals grew out of the solution and were found to be the toluate trimer **1** (0.275 g, 50.1% yield), mp 170-172 °C, becomes yellowish brown upon melting . Anal. Calcd. (Found) for the desolvated trimer, $C_{42}H_{48}Al_3As_3$: C 58.76 (53.47, 53.99, 54.10); H 5.64 (4.71, 4.75, 4.37) (see Results and Discussion). ^1H NMR: δ 0.148 [s, $Al(CH_3)_2$, 6H], 0.189 [s, $Al(CH_3)_2$, 9H], 0.283 [s, $Al(CH_3)_2$, 3H], 2.109 (s, C_6H_5-CH_3-toluene of solvation, 6H), 6.978 and 7.486 (m, C_6H_5-CH_3-toluene of solvation, 10H), 7.062 and 7.560 [m, $(C_6H_5)_2As$, 30H]. ^{13}C NMR: δ -0.042 [s, $Al(CH_3)_2$], 129.4, 131.4, 132.8, and 139.2 (s, C_6H_5).

Preparation of $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (2). Me_3Al (0.075g, 1.04 mmol) was dissolved in 30 mL of toluene, and the solution was transferred to a 250-mL round-bottomed, screw-top reaction flask equipped with a stir-bar. $Ph(Me_3SiCH_2)AsH$ (0.250 g, 1.04 mmol) was dissolved in toluene (30 mL), and the resulting solution was slowly added to the Me_3Al solution to give a clear, colorless reaction mixture. During the addition of the arsine solution, the evolution of bubbles was observed. The reaction solution was heated to 110 °C for 2d while stirring with no change in appearance. Volatiles were removed *in vacuo*, leaving a light yellow, viscous, oily liquid. The reaction oil was extracted with 20 mL of pentane, and this solution was refrigerated at -15 °C. After 2d, colorless, football-shaped, X-ray quality single crystals of **1** grew out of the pentane solution (0.166 g, 53.9% yield), mp turns glassy (73-77 °C) before melting at 78 °C. Anal. Calcd. (Found) for $C_{36}H_{66}Al_3As_3Si_3$: C 48.64 (39.52, 38.61); H 7.48 (6.12, 5.52) (see Results and Discussion). ^1H NMR: δ -0.122 [s, $Al(CH_3)_2$, 18H], 0.019 [s, $Si(CH_3)_3$, 27H], 0.067 (s, CH_2, 6H), 7.174 and 7.640 (m, C_6H_5, 15H). ^{13}C NMR: δ -0.637 [s, $Al(CH_3)_2$], -0.119 [s, $Si(CH_3)_3$], 0.247 (s, CH_2), 129.2, 133.2, 134.2, 139.4, and 140.4 (s, C_6H_5).

Low-Temperature ^{1}H NMR Studies of 1 and 2. Reasonable low-temperature ^{1}H NMR spectra of **1** could not be obtained due to the insolubility of this compound at temperatures below 0 °C. However, low-temperature ^{1}H NMR spectra of a **2** were successfully acquired. In a dry box, solid **2** (20.5 mg, 0.0236 mmol) was added to an NMR tube, then dissolved in 0.7 mL of toluene-d_8. The tube was sealed and then placed in the 500 MHz NMR probe. ^{1}H NMR spectra were recorded at increments of 10 °C between 25 °C and -45 °C. ^{1}H NMR (-45 °C): δ -0.140 [s, Al(CH_3)$_2$, 18H], 0.025 [s, Si(CH_3)$_3$, 27H], 0.088 (s, CH_2, 6H), 7.392 and 7.639 (m, C_6H_5, 15H).

X-Ray Structural Analysis of 1 and 2. Crystallographic data and measurements for **1** and **2** and summarized in Table 1. Single colorless crystals of **1** and **2** were individually affixed to the end of a glass fiber using a viscous oil under an inert nitrogen atmosphere, then transferred to a goniometer head and cooled to -130 °C under a nitrogen flow. X-ray intensity data were recorded using the ω–2θ scan mode. The structures of **1** and **2** were solved by direct methods and the refined unit-cell parameters were derived from the diffractometer setting angles ($30° < 2\theta < 40°$) for 24 reflections for **1**, and 44 reflections for **2**. Intensity data were corrected for absorption using ψ-scans; positional and thermal parameters were refined using least-squares adjustment techniques. In the final iterations, hydrogen atoms were incorporated at their calculated positions using a riding model. Two unique molecules of **2** were found to occupy the unit cell. ORTEP[10] diagrams showing the solid-state structures and the atom labeling schemes of **1** and **2** are shown in Figures 1-3. Neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 11.

Results and Discussion

Synthesis and Structure of [$Me_2AlAsPh_2$]$_3$•(C_7H_8)$_2$ (1). For some time now, our laboratory has been interested in the preparation of ring compounds containing aluminum-arsenic bonds, which may act as single-source precursors to the electronic material AlAs. Previously, alkane-elimination reactions between group 13 trialkyls and various pnicogen hydride species have been used by others to prepare trimeric compounds in several group 13-15 systems.[6-7,12-15] Thus, we have turned to the alkane-elimination reaction as a possible route to novel Al-As compounds. The reaction of trimethylaluminum and diphenylarsine, Ph_2AsH, in a 1:1 molar ratio in refluxing toluene eliminates methane to afford the solvated trimer, $[Me_2AlAsPh_2]_3{\cdot}(C_7H_8)_2$ (**1**) (eq 3). Compound **1** is an air-sensitive colorless solid which can be recrystallized from toluene at

$$Me_3Al + Ph_2AsH \xrightarrow[110\ ^\circ C]{toluene} \underset{(\mathbf{1})}{1/3[Me_2AlAsPh_2]_3.(C_7H_8)_2} + CH_4\uparrow \qquad (3)$$

-15 °C . Although Coates and Graham published the reaction of 1:1 molar reaction of Me_3Al with Ph_2AsH in benzene in 1963, they reported the product as being the dimeric compound, $(Me_2AlAsPh_2)_2$ (**4**), based on the results of metal-analysis and cryoscopic molecular weight determination; however, no x-ray crystal structure of **4** was obtained.[3] Thus, the reaction was repeated in our laboratory in an effort to isolate X-ray-quality single crystals of the Al-As product, which could be used to confirm the degree of association in the solid state structure of the oligomeric species.

X-ray crystallographic analysis of a single crystal of **1** reveals that it is a toluene-solvated trimeric compound that crystallizes in the monoclinic system, space group $P2_1/n$. The unit cell of **1** contains four molecules of the trimer, each associated with two molecules of toluene. An ORTEP[10] diagram showing the solid state conformation and atom numbering scheme of **1** is provided in Figure 1. Tables 1, 2, and 4 list the crystallographic data, non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, and selected bond lengths and bond angles for **1**, respectively .

The six-membered ring in **1** is comprised of alternating Me_2Al and $AsPh_2$ units and is non-planar in the solid state, instead occupying a chair conformation analogous to that of cyclohexane (Figure 2). This deviation from planarity is reflected in the endo- and exocyclic bond angles of **1**. The As-Al-As ring angles in **1** range from 99.1(1)° to 101.1(1)°, while the Al-As-Al angles lie between 118.1(1)° and 122.7(1)°. The values for the endocyclic angles in **1** correspond to those of the Al-N-Al and N-Al-N angles in the trimeric compound $[Me_2AlNH_2]_3$ (**8**),which was reported by Interrante and co-workers and was shown to reside in a skew-boat conformation.[13] The Al and As centers in **1** all reside in distorted tetrahedral environments, with the greatest degree of distortion occurring in the exocyclic C-Al-C and C-As-C angles, which average to 120.3° and 100.4°, respectively. As is the case in other group 13-15 trimers including **8**, $[{}^{t}Bu_2GaNH_2]_3$,[6] $[Me_2InAsMe_2]_3$,[12] $[Me_2GaP{}^{i}Pr_2]_3$,[14] $[{}^{t}Bu_2GaPH_2]_3$,[15] $[Me_2AlPMe_2]_3$,[16] $[Me_2InPPh_2]_3$,[17] and $[(Me_3Si)_2AlP(H)Ph]_3$,[18] the endocyclic angles at the pnicogen sites of **1** are significantly greater than tetrahedral, whereas the angles at the metal centers are less than tetrahedral. This observation is in agreement with the Valence Shell Electron Pair Repulsion (VSEPR) Model for this class of compounds.[19] The Al—As bond lengths in trimer **1** range from 2.512(3) Å to 2.542(3) Å, and are well-within the limits observed in other reported aluminum-arsenic oligomers.[1-2, 20]

The ^{1}H and ^{13}C solution NMR spectra for **1** are consistent with the presence of the trimeric structure, as shown in Figures 1 and 2, in solution. The Me_2Al protons give rise to three singlets in the methyl region of the ^{1}H NMR spectra at δ 0.148, 0.189, and 0.283 ppm, respectively. These signals have an integrated peak-ratio of 6H:9H:3H, and exhibit a downfield shift from the Me_2Al peaks of **2**, an effect attributable to the presence of the phenyl rings bonded to the As atoms. As can be seen in Figure 2, the axial CH_3 group bound to the Al(4) center is somewhat "sandwiched" between the axial phenyl rings of As(1) and As(2), subjecting its protons to the electron-withdrawing character of the two aromatic rings and shifting the ^{1}H NMR signal to δ 0.283 ppm. The ^{1}H NMR spectrum for **1** also contains multiplets at δ 7.062 and 7.560 ppm, corresponding to the phenyl protons of the trimeric structure. The toluene of solvation also gives rise to peaks in the phenyl region of the ^{1}H NMR spectrum of **1** at δ 2.109, 6.978 and 7.486 ppm. The ^{13}C solution NMR spectrum of **1** also contains peaks that are consistent with the trimeric solid-state structure shown in Figure 1.

The elemental analyses of $[Me_2AlAsPh_2]_3{\bullet}(C_7H_8)_2$ (**1**) (desolvated) for carbon and hydrogen were performed; however, results for multiple samples of **1** were found to be consistently low. The observed percentages of carbon were outside of the acceptable range (58.76, calcd.; 53.47, 53.99 and 54.10, found), as were the those of hydrogen (5.64, calcd.; 4.71, 4.75, and 4.37, found). Elemental analyses of [$Me_2AlAs(CH_2SiMe_3)Ph]_3$ (**2**) for carbon and hydrogen were also observed to be quite low [(C: 48.64, calcd.; 39.52 and 38.61, found) (H: 7.48, calcd.; 6.12 and 5.52, found]. These results may presumably be due to circumstances of analysis, which include: (1) failure of the samples to quantitatively decompose, (2) elimination of an alkane, and/or (3) elimination of a volatile component, such as Ph_2AsH from **1** or $Ph(Me_3SiCH_2)AsH$ from **2**. The X-ray crystallographic structural solutions, solution NMR data, and the isolation of crystalline solids of **1** and **2** at room temperature with sharp melting points (170-172 °C and 177-178 °C, respectively) support the existence of pure compounds. Low elemental analyses for carbon and hydrogen have previously been reported for several other group 13-15 oligomeric compounds.[13, 17, 21, 22]

Synthesis of Phenyl(trimethylsilylmethyl)arsine, $Ph(Me_3SiCH_2)AsH$. In an effort to further investigate the alkane-elimination reactions between trimethylaluminum and bulky arsines, we utilized the alkyl/aryl secondary arsine, $Ph(Me_3SiCH_2)AsH$ (**9**). The disubstituted nature of $Ph(Me_3SiCH_2)AsH$ (**9**) not only alters the steric demands of the arsenic center, but also changes the acidity of this ligand, as compared to that of Ph_2AsH. It has been demonstrated by Issleib and Kümmel that the As—H bonds in diaryl arsines tend to be more acidic than the As—H bonds of both aryl/alkyl-disubstituted and dialkyl arsines in elimination reactions.[23] This difference in the acidities of the As—H bonds in **9** and Ph_2AsH was evident in previous reactions with Me_3Ga, in which the alkane-eliminations reactions with phenyl arsines proceeded in a slightly more facile fashion than analogous reactions with $Ph(CH_2SiMe_3)AsH$.[24] Compound **9** was synthesized *via* a reaction route[25] in which $PhAsH_2$ was metallated with sodium in liquid NH_3, followed by a coupling reaction with Me_3SiCH_2Cl to afford the desired arsine (eqs 4 and 5). Upon distillation, the pure product is obtained in approximately 75% yield. Compound **9** is a pyrophoric, colorless liquid and is stable at room temperature for an indefinite period of time when stored under argon or in a sealed tube. The purity of $Ph(Me_3SiCH_2)AsH$ was verified by ^1H and ^{13}C NMR and partial elemental analysis before the compound was used in reactions.

$$\mathrm{PhAsH_2 + Na^\circ \xrightarrow{NH_3} PhAsNaH + 1/2H_2\uparrow} \qquad (4)$$

$$\mathrm{PhAsNaH + Me_3SiCH_2Cl \xrightarrow[NH_3]{Et_2O} \underset{\substack{(\mathbf{9})\\ 75\%\ Yield}}{Ph(Me_3SiCH_2)AsH} + NaCl} \qquad (5)$$

Synthesis and Structure of $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (2). An alkane-elimination reaction between the disubstitued arsine, **9**, and Me_3Al was attempted in an effort to prepare additional oligomeric compounds containing more than one Al—As bond. To this end, trimethylaluminum was combined with $Ph(Me_3SiCH_2)AsH$ in a 1:1 molar ratio in toluene at 110 °C to give a yellow viscous oil (eq 6). Pentane extraction of the reaction solution, followed by cooling to -15 °C afforded colorless crystals of **2** suitable for X-ray crystallographic analysis. Trimer **2** crystallizes in the triclinic space group $P\bar{1}$, with two unique molecules present in the unit cell. Figure 3 shows an ORTEP[10] diagram of the solid state conformation and atom numbering scheme of **2**. Crystallographic data are listed in Table 1, while non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, and selected bond lengths and bond angles for **2** are given in Tables 3 and 5, respectively .

$$\mathrm{Me_3Al + Ph(Me_3SiCH_2)AsH \xrightarrow[110\ ^\circ C]{toluene} \underset{(\mathbf{2})}{1/3[Me_2AlAs(CH_2SiMe_3)Ph]_3} + CH_4\uparrow} \qquad (6)$$

As in compound **1**, both molecules of **2** have six-membered rings which adopt chair conformations analogous to cyclohexane. In trimer **2**, the phenyl groups reside in the axial positions, and the trimethylsilylmethyl groups are located in the equatorial positions (Figure 3). However, in the CH_2SiMe_3 groups bound to the As centers of **2**, there is a small, but significant difference in the rotation of the CH_3 groups about the Si atoms in each of the crystallographically independent molecules. Two unique molecules were also present in the asymmetric unit of the In-As trimer, $[Me_2InAsMe_2]_3$, which was initially prepared by Beachley and Coates in 1965,[4] and recently characterized by X-ray crystallography by Cowley and Jones *et al.*[12] However, in the solid state of this trimeric compound, one molecule contained an approximately planar six-membered ring, while the other molecule possessed a puckered In_3As_3 ring, which had neither a classic chair nor boat conformation.[12]

The Al and As centers in both molecules **2a** and **2b** all reside in pseudotetrahedral environments, with distortions following the trends of those in compound **1**. The As-Al-As bond angles range from 102.6(2)° to 105.5(2)° in **2a**, and 119.0(2)° to 124.2(2)° in **2b**. Likewise, the Al-As-Al angles have ranges of 102.6(2)°-104.8(2)° and 118.2(2)°-122.2(2)° for **2a** and **2b**, respectively. The exocyclic C-Al-C angles in molecule **2a** average to 120.8°, while those of **2b** have an average value of 121.5°. The C-As-C angles are also slightly different in molecules **2a** and **2b** (104.5° and 102.6°, respectively). The difference in the positioning of the As-(CH_2SiMe_3) groups in **2a** versus **2b** is evident in the Al-As-C bond angles at those sites (Table 5). For example, the Al(11)-As(11)-C(111) angle in **2a** is 95.3(4)°, while the corresponding angle of Al(21)-As(21)-C(211) in **2b** has a value of 112.0(4)°.

The Al—As bond lengths in compound **2** are comparable to those in trimer **1**. In molecule **2a**, the Al—As bond lengths range from 2.504(5) Å to 2.526(5) Å, while the corresponding bond lengths in **2b** are between 2.514(5) Å and 2.524(5) Å. Though nearly equivalent, the Al—As bonds in **2a** are notably unique from their counterparts in **2b**. For example, the As(11)—Al(13) bond in **2a** is 2.513(5) Å in length, while As(21)—Al(23) has a length of 2.521(5) Å. Similarly, the As(12)—Al(11) bond length is 2.504(5) Å, and the analogous As(22)—Al(21) bond is 2.522(5) Å long. The exocyclic Al—C bond lengths also vary slightly between molecules **2a** and **2b**. Whereas the Al(11)—C(116) bond length is 1.99(2) Å, the corresponding bond, Al(21)—C(216) is 1.96(2) Å in length. Therefore, as is reflected in the deviations of the bond angles and lengths described above, the two unique chair-conformations of $[Me_2AlAs(CH_2SiMe_3)(Ph)]_3$ do have significant differences in the geometries of their Al_3As_3 six-membered rings.

The ^1H and ^{13}C solution NMR spectra for **2** are in agreement with a trimeric solid-state structure as shown in Figures 3. However, the unique molecules of **2** are not distinguishable by means of solution NMR experiments; but rather, the ^{1}H NMR spectra obtained at between 25 °C and -45 °C indicate equivalent $AlMe_2$, AsPh, and $As(CH_2SiMe_3)$ proton environments, with no observable dynamic behavior at low temperatures. The observed NMR data (*vide supra*) suggest the possibility of the presence of a planar form of the molecule in solution, or perhaps, a rapid inversion between the two potential chair conformations of the trimer by way of an intermediate boat conformer, giving rise to magnetically-equivalent Al methyl groups, as suggested by Beachley and Coates.[4]

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and thermal paramterers (22 pages). Ordering information is given on any current masthead page.

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Table 1. Crystallographic Data and Measurements[a] for $[Me_2AlAsPh_2]_3 \cdot (C_7H_8)_2$ (1) and $[Me_2AlAs(CH_2SiMe_3)(Ph)]_3$ (2)

	1	2
Molecular formula	$C_{56}H_{64}Al_3As_3$	$C_{36}H_{66}Al_3As_3Si_3$
Formula weight	1042.12	888.88
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	14.549(6)	15.619(7)
b, Å	22.838(7)	17.487(6)
c, Å	16.891(4)	19.863(6)
α, deg	-	94.86(3)
β, deg	105.12(5)	101.41(3)
γ, deg	-	113.34(4)
V, Å^3	5418(3)	4802(3)
Z	4	4
D_{calcd}, Mgm^{-3}	1.278	1.230
$F(000)$	2154	1850
μ (mm^{-1})	1.91	2.22
λ, Å	0.71073	0.71073
temp. °C	-130	-130
crystal dimens, mm	0.30 x 0.25 x 0.25	0.40x 0.30 x 0.20
T_{max}:T_{min}	0.702:0.700	0.614:0.611
scan type	ω-2θ	ω-2θ
$2\theta_{max}$, deg	45	45
total no of refls recorded	6413	12591

Table 1. Continued

	1	**2**
no of non-equiv refls	6409	12591
R_{merge}, on I	1.000	0.000
no of refls retained	3326 [$I > 2.5\sigma(I)$]	6318 [$I > 2.0\sigma(I)$]
no of parameters refined	559	812
R, R_w[b]	0.045 (0.045)	0.057 (0.085)
goodness-of-fit[c]	1.19	0.99
max shift/σ ratio; esd in final least-squares cycle	0.010	0.017
final $\Delta\rho$(e/Å^3) max;min	0.480;-0.410	0.870;-1.070

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[a] Crystallographic calculations were performed on a DEC 3000/400 computer using the NRCVAX suite of structure determination programs.[26] [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized. [c] Goodness-of-fit = $[\Sigma w\Delta^2/(N_{obs} - N_{para})]^{1/2}$

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_{eq}(Å^2)
As1	0.10902(7)	0.15148(4)	0.18003(6)	1.99(5)
As2	0.33284(7)	0.05756(4)	0.18636(6)	1.86(5)
As3	0.31053(7)	0.13661(4)	0.38148(6)	1.93(5)
Al4	0.1584(2)	0.0623(1)	0.1119(2)	2.2(1)
Al5	0.3914(2)	0.0485(1)	0.3414(2)	2.3(2)
Al6	0.1327(2)	0.1494(1)	0.3328(2)	2.2(1)
C11	0.1497(6)	0.2232(4)	0.1364(6)	2.1(5)
C12	0.2060(6)	0.2646(4)	0.1861(5)	2.4(5)
C13	0.2361(7)	0.3141(4)	0.1535(6)	2.8(5)
C14	0.2102(7)	0.3240(4)	0.0697(7)	3.2(6)
C15	0.1534(7)	0.2828(4)	0.0194(6)	2.8(5)
C16	0.1223(6)	0.2321(4)	0.0514(6)	2.4(5)
C21	-0.0291(6)	0.1596(4)	0.1397(5)	2.1(5)
C22	-0.0710(7)	0.2128(5)	0.1479(6)	3.1(5)
C23	-0.1685(7)	0.2209(5)	0.1182(6)	3.2(5)
C24	-0.2231(7)	0.1745(5)	0.0789(6)	3.4(6)
C25	-0.1834(7)	0.1213(5)	0.0722(6)	3.5(6)
C26	-0.0872(7)	0.1132(4)	0.1028(6)	3.1(5)
C31	0.3716(7)	-0.0126(4)	0.1401(6)	2.2(5)
C32	0.3971(7)	-0.0143(4)	0.0673(6)	2.5(5)
C33	0.4248(7)	-0.0659(5)	0.0368(6)	3.3(6)
C34	0.4241(7)	-0.1174(5)	0.0781(7)	3.6(6)
C35	0.3964(9)	-0.1176(5)	0.1495(7)	4.5(7)

Table 2. Continued

C36	0.3711(7)	-0.0661(5)	0.1792(5)	3.3(6)
C41	0.4087(7)	0.1160(4)	0.1474(5)	1.8(5)
C42	0.3662(7)	0.1645(5)	0.1047(6)	3.2(6)
C43	0.4224(9)	0.2083(4)	0.0825(7)	4.0(7)
C44	0.5197(9)	0.2040(5)	0.1058(7)	3.8(7)
C45	0.5628(7)	0.1559(5)	0.1494(6)	3.3(6)
C46	0.5076(7)	0.1117(4)	0.1702(5)	2.5(5)
C51	0.3441(7)	0.1288(4)	0.5002(5)	1.6(4)
C52	0.4354(6)	0.1388(4)	0.5461(5)	2.3(5)
C53	0.4607(7)	0.1302(4)	0.6288(6)	3.0(5)
C54	0.3951(9)	0.1111(4)	0.6685(6)	3.3(6)
C55	0.3039(7)	0.0995(4)	0.6241(6)	3.3(6)
C56	0.2769(7)	0.1086(4)	0.5394(6)	2.8(5)
C61	0.3735(6)	0.2101(4)	0.3693(5)	1.7(5)
C62	0.4349(7)	0.2145(4)	0.3189(6)	2.3(5)
C63	0.4728(7)	0.2688(5)	0.3068(6)	3.4(6)
C64	0.4498(8)	0.3183(5)	0.3442(6)	3.5(6)
C65	0.3910(8)	0.3141(4)	0.3948(6)	2.9(6)
C66	0.3511(7)	0.2601(4)	0.4077(5)	2.7(5)
C71	0.1402(7)	0.0749(5)	-0.0054(6)	4.2(6)
C72	0.1087(7)	-0.0091(4)	0.1505(6)	3.6(6)
C73	0.3251(7)	-0.0170(4)	0.3758(6)	3.1(5)
C74	0.5305(7)	0.0550(5)	0.3798(6)	4.2(6)
C75	0.0978(7)	0.2227(4)	0.3765(6)	3.6(6)
C76	0.0680(7)	0.0761(4)	0.3460(6)	2.8(5)

Table 2. Continued

C81	0.7808(16)	0.3192(7)	0.3407(10)	14.2(16)
C82	0.7491(12)	0.3811(6)	0.3222(8)	5.1(8)
C83	0.8095(9)	0.4289(11)	0.3477(8)	6.9(10)
C84	0.7768(15)	0.4864(9)	0.3277(11)	8.1(12)
C85	0.6875(17)	0.4945(8)	0.2863(12)	8.1(13)
C86	0.6276(11)	0.4502(10)	0.2613(8)	6.9(11)
C87	0.6563(11)	0.3949(7)	0.2785(8)	5.3(8)
C91	0.7210(16)	0.6474(10)	0.1688(12)	13.9(16)
C92	0.6702(13)	0.6245(9)	0.1019(10)	7.9(12)
C93	0.5948(10)	0.6552(5)	0.0488(10)	5.2(8)
C94	0.5424(17)	0.6272(7)	-0.0227(15)	12.0(17)
C95	0.5555(16)	0.5761(11)	-0.0411(12)	12.6(16)
C96	0.6339(12)	0.5483(7)	0.0125(10)	8.2(10)
C97	0.6913(11)	0.5656(6)	0.0815(10)	6.4(9)

Table 3. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 2, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}(Å^2)
Molecule 1				
As11	0.6986(1)	0.6889(1)	0.2132(1)	1.77(8)
As12	0.8639(1)	0.7384(1)	0.4075(1)	2.19(8)
As13	0.6068(1)	0.7415(1)	0.3740(1)	2.16(8)
Al11	0.8716(3)	0.7450(2)	0.2834(2)	1.7(2)
Al12	0.7697(3)	0.8055(3)	0.4590(3)	3.0(2)
Al13	0.5796(3)	0.7400(3)	0.2443(2)	2.1(2)
Si11	0.6370(3)	0.6883(3)	0.0397(2)	2.6(2)
Si12	1.1001(3)	0.7926(3)	0.4590(2)	3.1(2)
Si13	0.5140(4)	0.8262(4)	0.4825(3)	4.5(3)
C111	0.7304(10)	0.7262(9)	0.1265(8)	2.5(8)
C112	0.6449(15)	0.5960(11)	-0.0097(8)	4.8(12)
C113	0.6730(14)	0.7782(12)	-0.0086(10)	4.9(12)
C114	0.5152(11)	0.6622(10)	0.0488(7)	3.2(9)
C115	0.9235(11)	0.8673(9)	0.2813(8)	3.1(8)
C116	0.9265(13)	0.6714(10)	0.2448(8)	3.5(10)
C121	0.6404(10)	0.5651(8)	0.1936(7)	1.9(8)
C122	0.5721(12)	0.5207(8)	0.2229(8)	2.8(9)
C123	0.5330(13)	0.4328(10)	0.2140(9)	3.6(10)
C124	0.5704(13)	0.3916(10)	0.1731(9)	3.5(9)
C125	0.6418(13)	0.4368(10)	0.1428(8)	3.5(10)
C126	0.6803(11)	0.5231(9)	0.1532(7)	2.4(8)
C131	0.9908(11)	0.8063(10)	0.4723(7)	3.1(8)

Table 3. Continued

C132	1.1956(12)	0.8418(12)	0.5430(9)	4.5(11)
C133	1.0758(13)	0.6792(12)	0.4363(10)	5.1(12)
C134	1.1456(12)	0.8492(11)	0.3898(8)	3.7(10)
C135	0.8305(14)	0.9252(10)	0.4512(12)	5.9(12)
C136	0.7616(12)	0.7706(12)	0.5507(8)	4.5(11)
C141	0.8313(13)	0.6247(10)	0.4289(9)	3.8(10)
C142	0.8559(15)	0.6156(12)	0.4963(10)	5.0(12)
C143	0.8274(19)	0 .5347(20)	0.5134(14)	7.9(19)
C144	0.7744(19)	0.4624(16)	0.4611(16)	7.4(20)
C145	0.7504(14)	0.4719(11)	0.3927(12)	5.3(14)
C146	0.7814(12)	0.5564(9)	0.3783(8)	3.1(9)
C151	0.5304(12)	0.8033(11)	0.3931(9)	3.8(11)
C152	0.6236(15)	0.9179(12)	0.5368(11)	6.0(13)
C153	0.4845(15)	0.7341(13)	0.5275(10)	6.2(13)
C154	0.4136(17)	0.8603(19)	0.4668(10)	9.3(22)
C155	0.6285(10)	0.8588(9)	0.2324(9)	3.0(9)
C156	0.4404(11)	0.6643(10)	0.2039(8)	3.3(9)
C161	0.5318(10)	0.6279(9)	0.3871(7)	2.3(8)
C162	0.4308(11)	0.5888(11)	0.3660(9)	4.0(10)
C163	0.3814(15)	0.5050(14)	0.3739(10)	6.3(13)
C164	0.4298(16)	0.4581(11)	0.3969(9)	4.5(12)
C165	0.5274(15)	0.4950(11)	0.4189(9)	4.1(12)
C166	0.5782(12)	0.5799(10)	0.4130(8)	3.0(9)

Table 3. Continued

Molecule 2				
As21	1.2150(1)	0.8346(1)	0.8116(1)	1.55(7)
As22	1.1920(1)	0.7923(1)	1.0002(1)	1.57(8)
As23	0.9725(1)	0.8007(1)	0.8636(1)	1.74(7)
Al21	1.3165(3)	0.8612(3)	0.9343(2)	1.9(2)
Al22	1.0453(3)	0.8221(3)	0.9924(2)	2.0(2)
Al23	1.0787(3)	0.8796(3)	0.7895(2)	2.0(2)
Si21	1.4060(3)	0.8982(3)	0.7443(2)	2.3(2)
Si22	1.2272(3)	0.8018(3)	1.1726(2)	2.3(2)
Si23	0.7876(3)	0.8414(3)	0.7883(2)	2.9(2)
C211	1.2907(10)	0.9022(8)	0.7506(7)	1.9(7)
C212	1.4441(11)	0.9516(10)	0.6698(8)	3.6(9)
C213	1.3930(13)	0.7866(10)	0.7280(10)	4.6(11)
C214	1.5023(10)	0.9613(9)	0.8248(8)	2.9(8)
C215	1.4030(10)	0.8047(9)	0.9452(7)	2.6(8)
C216	1.3650(10)	0.9837(9)	0.9652(7)	2.4(8)
C221	1.1683(10)	0.7179(8)	0.7634(7)	2.4(8)
C222	1.1687(11)	0.6552(9)	0.8013(8)	2.7(9)
C223	1.1261(12)	0.5700(9)	0.7661(9)	3.7(10)
C224	1.0870(12)	0.5511(10)	0.6949(9)	3.5(10)
C225	1.0874(12)	0.6128(10)	0.6570(8)	3.5(9)
C226	1.1267(12)	0.6976(9)	0.6919(7)	2.8(9)
C231	1.2789(11)	0.8326(9)	1.0951(7)	2.5(8)
C232	1.1475(12)	0.6874(9)	1.1568(8)	3.2(9)
C233	1.3312(13)	0.8258(11)	1.2487(9)	4.1(10)

Table 3. Continued

C234	1.1640(12)	0.8672(9)	1.1932(8)	3.0(9)
C235	1.0999(12)	0.9459(8)	1.0259(8)	3.0(9)
C236	0.9840(11)	0.7433(9)	1.0327(8)	3.0(9)
C241	1.1586(11)	0.6706(8)	0.9856(6)	1.6(8)
C242	1.2287(11)	0.6412(8)	1.0080(7)	2.2(8)
C243	1.2085(14)	0.5558(10)	0.9925(9)	3.5(10)
C244	1.1150(15)	0.5007(10)	0.9528(9)	3.8(11)
C245	1.0490(12)	0.5305(10)	0.9279(8)	3.4(9)
C246	1.0711(10)	0.6169(8)	0.9448(7)	2.3(7)
C251	0.8734(10)	0.8418(9)	0.8688(8)	2.8(9)
C252	0.7344(14)	0.7382(11)	0.7286(10)	5.2(12)
C253	0.8503(12)	0.9283(10)	0.7453(9)	3.8(10)
C254	0.6894(13)	0.8615(13)	0.8153(10)	5.0(12)
C255	1.1351(11)	0.9965(9)	0.8392(8)	3.2(9)
C256	1.0218(15)	0.8480(13)	0.6891(9)	5.6(13)
C261	0.8959(10)	0.6805(8)	0.8283(7)	1.7(7)
C262	0.8245(12)	0.6337(10)	0.8559(8)	3.6(10)
C263	0.7731(13)	0.5471(11)	0.8345(10)	4.5(10)
C264	0.8019(14)	0.5061(10)	0.7839(11)	4.7(10)
C265	0.8739(13)	0.5519(10)	0.7565(10)	4.4(11)
C266	0.9241(11)	0.6395(8)	0.7780(9)	3.3(9)

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[Me_2AlAsPh_2]_3\cdot(C_7H_8)_2$ (1) with Estimated Standard Deviations in Parentheses.

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a). Bond Lengths

As(1)—Al(4)	2.534(3)	As(1)—C(11)	1.951(9)
As(1)—Al(6)	2.513(3)	As(2)—C(31)	1.931(9)
As(2)—Al(4)	2.524(3)	As(3)—C(51)	1.945(8)
As(2)—Al(5)	2.542(3)	Al(4)—C(71)	1.95(1)
As(3)—Al(5)	2.512(3)	Al(5)—C(73)	1.95(1)
As(3)—Al(6)	2.519(3)	Al(6)—C(75)	1.95(1)

b). Bond Angles

Al(4)-As(1)-Al(6)	118.1(1)	As(1)-Al(4)-C(71)	111.2(3)
Al(4)-As(2)-Al(5)	122.7(1)	As(2)-Al(4)-C(72)	102.1(3)
Al(5)-As(3)-Al(6)	121.2(1)	C(71)-Al(4)-C(72)	119.8(5)
As(1)-Al(4)-As(2)	100.1(1)	Al(5)-As(3)-C(51)	101.2(3)
As(2)-Al(5)-As(3)	99.1(1)	Al(6)-As(3)-C(61)	109.7(3)
As(1)-Al(6)-As(3)	101.1(1)	C(51)-As(3)-C(61)	100.9(4)
Al(4)-As(1)-C(11)	110.8(3)	As(2)-Al(5)-C(73)	108.1(3)
Al(6)-As(1)-C(21)	102.3(3)	As(3)-Al(5)-C(74)	111.4(3)
C(11)-As(1)-C(21)	100.0(4)	C(73)-Al(5)-C(74)	120.5(4)

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $[Me_2AlAs(CH_2SiMe_3)(Ph)]_3$ (2), with Estimated Standard Deviations in Parentheses.

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a). Bond Lengths

Molecule 1		Molecule 2	
As(11)—Al(11)	2.526(5)	As(21)—Al(21)	2.524(5)
As(11)—Al(13)	2.513(5)	As(21)—Al(23)	2.521(5)
As(12)—Al(11)	2.504(5)	As(22)—Al(21)	2.522(5)
As(12)—Al(12)	2.519(5)	As(22)—Al(22)	2.523(5)
As(13)—Al(12)	2.510(5)	As(23)—Al(22)	2.514(5)
As(13)—Al(13)	2.523(5)	As(23)—Al(23)	2.515(5)
As(11)—C(111)	1.98(2)	As(21)—C(211)	1.99(1)
As(11)—C(121)	1.96(1)	As(21)—C(221)	1.96(1)
Al(11)—C(115)	1.97(2)	Al(21)—C(215)	1.96(2)
Al(11)—C(116)	1.99(2)	Al(21)—C(216)	1.96(1)

b). Bond Angles

Molecule 1		Molecule 2	
Al(11)-As(11)-Al(13)	123.4(2)	Al(21)-As(21)-Al(23)	119.8(2)
Al(11)-As(12)-Al(12)	119.0(2)	Al(21)-As(22)-Al(22)	122.2(2)
Al(12)-As(13)-As(13)	124.2(2)	Al(22)-As(23)-As(23)	118.2(2)
As(11)-Al(11)-As(12)	105.5(2)	As(21)-Al(21)-As(22)	102.6(2)
As(12)-Al(12)-As(13)	103.9(2)	As(22)-Al(22)-As(23)	104.8(2)
As(11)-Al(13)-Al(13)	102.6(2)	As(21)-Al(23)-Al(23)	103.5(2)
Al(11)-As(11)-C(111)	95.3(4)	Al(21)-As(21)-C(211)	112.0(4)

Table 5. Continued

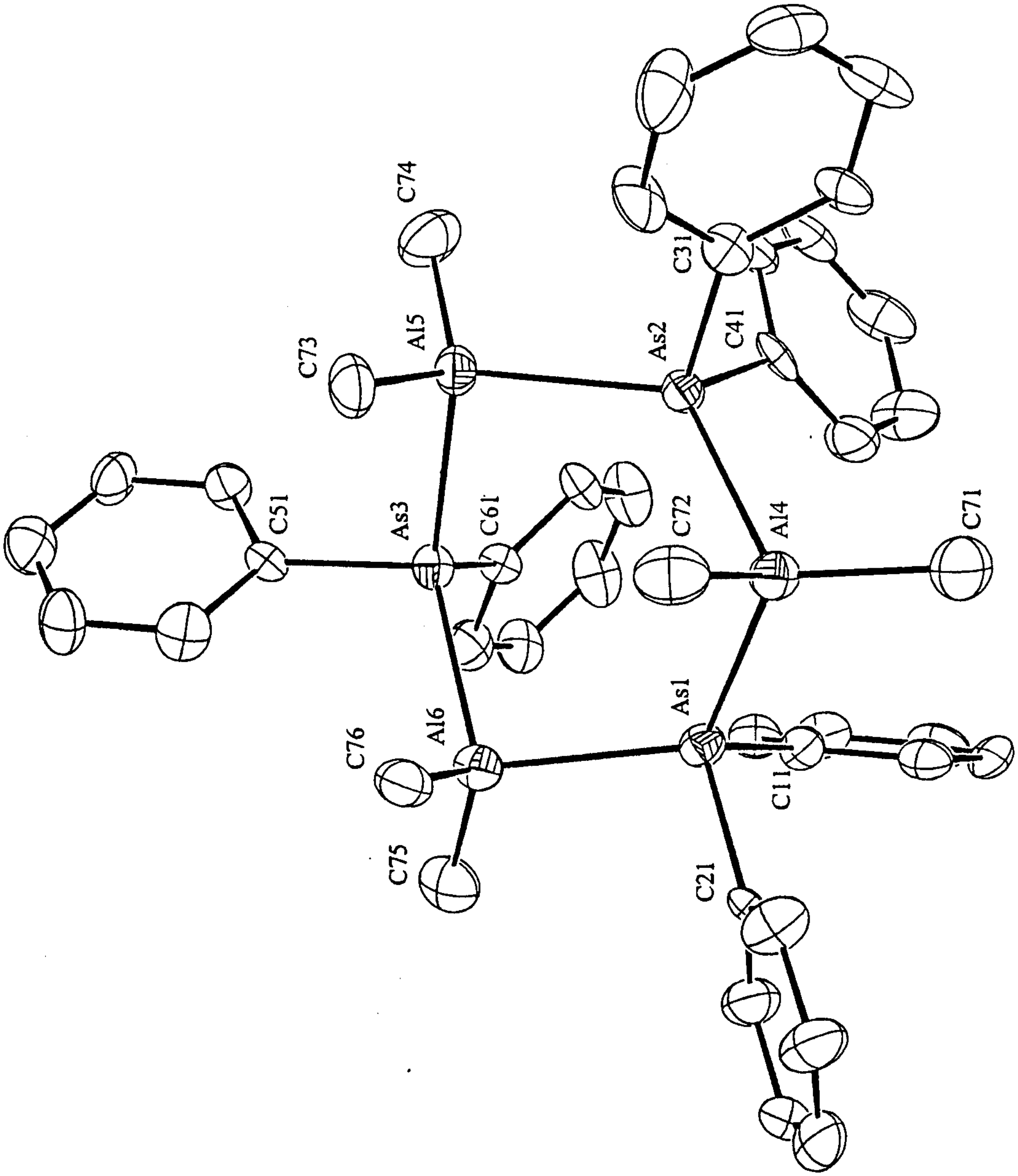
C(111)-As(11)-C(121)	106.5(6)	C(211)-As(21)-C(221)	103.0(6)
As(11)-Al(11)-C(115)	103.6(5)	As(21)-Al(21)-C(215)	114.6(5)
C(115)-Al(11)-C(116)	122.0(7)	C(215)-Al(21)-C(216)	121.3(6)
Al(12)-As(12)-C(131)	98.1(5)	Al(22)-As(22)-C(231)	111.9(4)
C(131)-As(12)-C(141)	103.3(7)	C(231)-As(22)-C(241)	102.5(6)
As(12)-Al(12)-C(135)	105.0(6)	As(22)-Al(22)-C(235)	103.7(5)
C(135)-Al(12)-C(136)	121.4(9)	C(235)-Al(22)-C(236)	120.6(7)

Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid state structure of $[Me_2AlAsPh_2]_3 \cdot (C_7H_8)_2$ (1). Hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid state structure of $[Me_2AlAsPh_2]_3 \cdot (C_7H_8)_2$ (1), viewed parallel to the plane of the six-membered ring and shows the chair-conformation of compound 1. Hydrogen atoms have been omitted for clarity.

Figure 3. ORTEP diagram (30% probability ellipsoids) showing the solid state structure of Molecule 1 of $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (2), viewed parallel to the plane of the six-membered ring. Hydrogen atoms have been omitted for clarity.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Al5
As2
C31
C41
C51
As3
C61
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Al4
C71
C76
Al6
As1
C11
C75
C21

Figure 1.

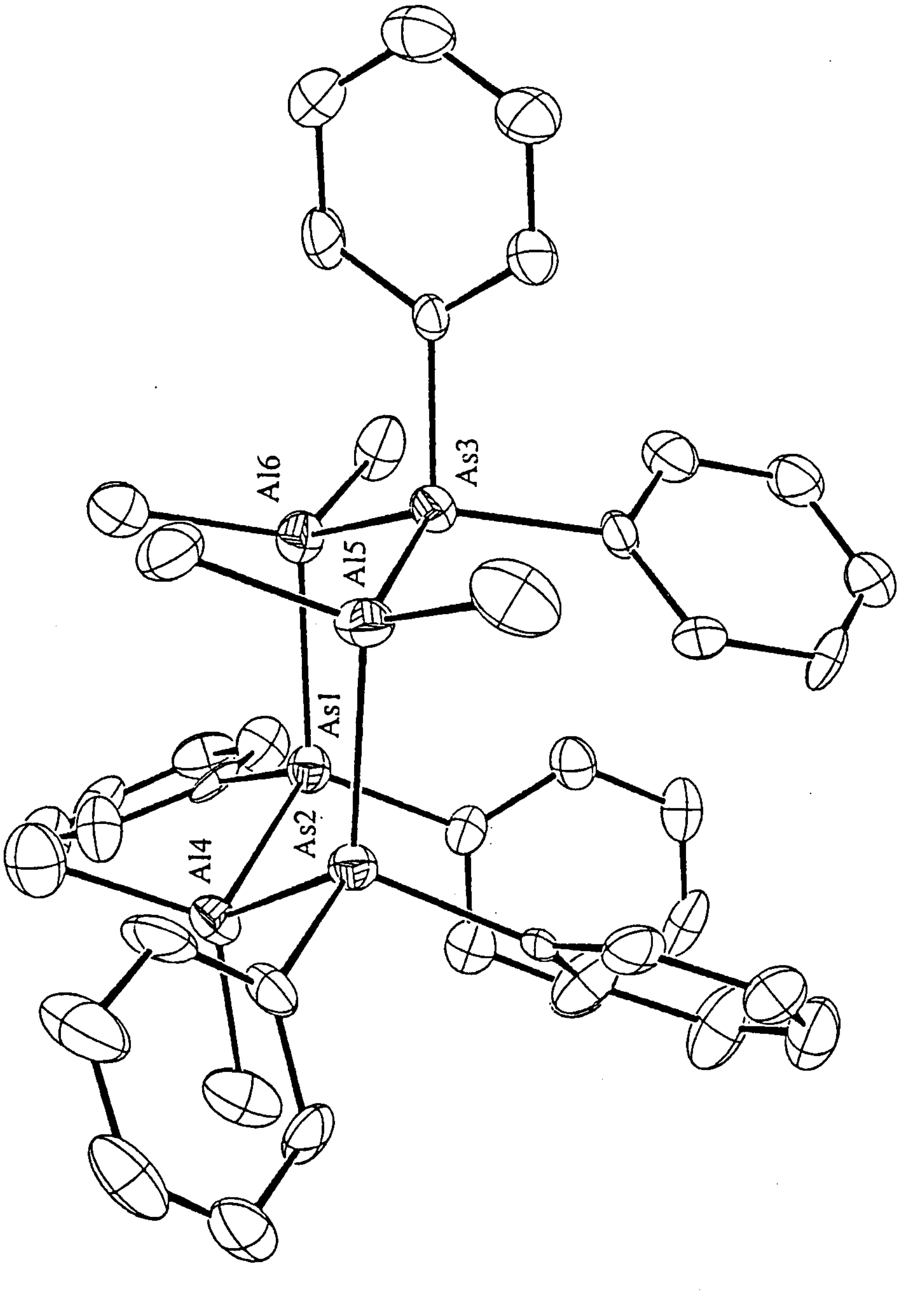

Figure 2.

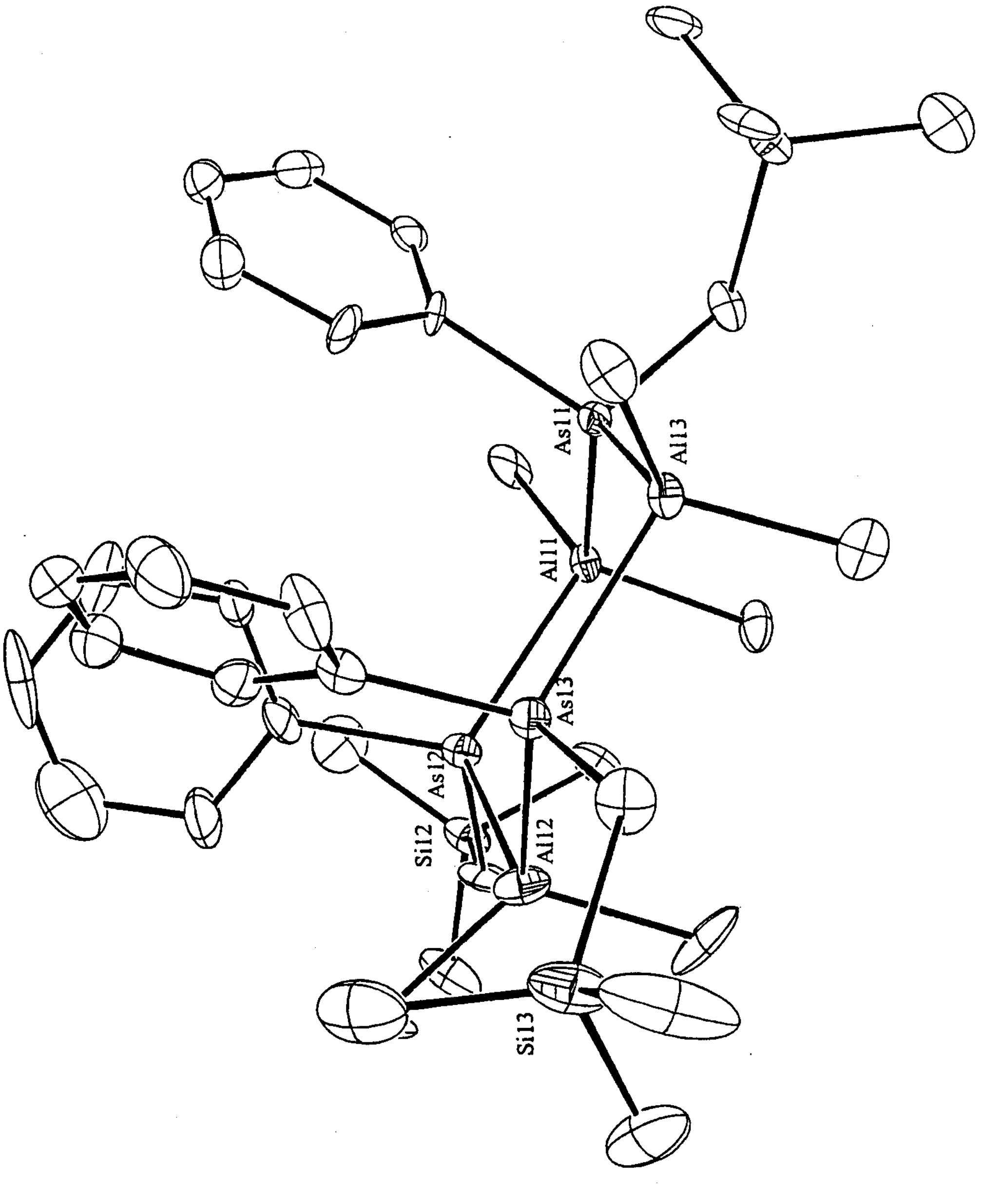

Figure 3.

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