Novel Molecular Clusters Having Aluminum – Phosphorus, Aluminum – Arsenic, and Gallium – Arsenic Skeletons, and Synthesis of an $Al_4As_6Li_4$ Rhombododecahedron

Matthias Driess,* Stephan Kuntz, Klaus Merz, and Hans Pritzkow

Abstract: The cyclocondensation reaction of the primary silylarsanes **4a**, **b** with the trimethylamine adducts of alane (**5a**) leads, under liberation of H_2, to the four-membered 1,3-diarsa-2,4-dialuminetane heterocycles **2a**, **b**. The latter derivatives were characterized by NMR spectroscopy and a single-crystal X-ray diffraction analysis. Compound **2a** consists of a puckered four-membered Al_2As_2 ring, which contains three-coordinate As and four-coordinate Al centers and, surprisingly, the NMe_3 groups are *cis* oriented. Upon heating of **2a**, **b** in toluene, the NMe_3 groups at the Al centers are readily cleaved and the resulting unsolvated Al_2As_2 rings trimerize, affording the novel hexagonal prismatic Al_6As_6 cluster compounds **1a**, **b**. The latter were characterized by (^1H, ^{27}Al) NMR and IR spectroscopy, and the structure of **1a** was established by a X-ray diffraction analysis. The conversion of the silylarsane **4a** with the amine – gallane **5b** and of the silylphosphane **4c** with the amine – alane **5a**, respectively, gives directly, that is, without NMR-spectroscopically detectable intermediates, the hexameric arsagallane and phosphaalane clusters **1c** and **1d**, respectively. They are isostructural with **1a**. Interestingly, the δ (^{27}Al) values of **1a** (48), **1b** (40), and **1d** (46) are relatively small compared to that of **2a** (127) and **2b** (140), although the Al centers are in all cases four-coordinate, due to the ring strain in **1a**, **b**, and **1d**. The reaction of the silylarsane **4a** with $[LiAlH_4]$ in the molar ratio of 1:1 in Et_2O as solvent gives, under elimination of H_2, access to the unusual novel heteroaggregate **3**, which has a rhombododecahedral $Al_4As_6Li_6$ skeleton. The structure of **3** was established by X-ray diffraction. Surprisingly, the same reaction of the starting materials in 1,2-dimethoxyethane instead of Et_2O as solvent leads to an unusual triple ion pair compound.

Keywords: aluminum · arsenic · clusters · gallium · lithium

Introduction

There is currently considerable interest in volatile low-molecular-weight single-source precursors for the synthesis of binary and multinary III/V semiconductors with remarkable optoelectronic properties, such as GaN, InGaAs, and InGaAlP, by MOVPE (*m*etal*o*rganic *v*apor *p*hase *e*pitaxy) and CBE (*c*hemical *b*eam *e*pitaxy) techniques.[1] However, higher molecular-weight aluminum und gallium chalcogenides and pnictides, respectively, are potentially useful cocatalysts for the polymerization reactions of unsaturated organic substrates. For instance, the alumoxanes $[tBuAl(\mu_3\text{-}O)]_n$ ($n = 6, 7, 9$) can act as cocatalysts in the Pd-catalyzed conversion of CO and ethene to furnish polyketone polymers [2] and are functional models of MAO (*m*ethyl*a*lum*o*xane) which is a cocatalyst in the Ziegler – Natta polmerization process.[3] However, structure – reactivity relationships concerning aluminum and gallium pnictide cage compounds have been investigated far less than the chalcogenides of type **A**[4] and the imino derivatives **B**.[5, 6] Hitherto phosphaimino derivatives of gallane were known, which are tetrameric and adopt the cubane-like structure **C**.[7]

$[R\text{—}MX]_n$	$[R\text{—}MNR']_m$	$[R\text{—}GaPR']_4$
A: M = Al, Ga	**B**: M = Al, Ga	**C**: R = Alkyl, C_5Me_5, PR_2
X = O, S, Se, Te	X = O, S, Se, Te	R' = Alkyl, Aryl
R = Alkyl, C_5Me_5	R = H, Alkyl, Aryl, Cl	
n = 4-9	R' = Alkyl, Aryl	
	m = 4, 6	

We report here on the first hexameric arsinoalanes and -gallanes **1a – c**, and on the phosphorus homologue **1d**, in which the Al and Ga centers are each bonded to one H atom (Scheme 1). These compounds are formed by trimerization of the corresponding M_2E_2 ring dimers **2** (M = Al, Ga; E = As, P). Furthermore we describe the new heteroaggregate **3**, which has a rhombododecahedral $Al_4As_6Li_4$ skeleton.

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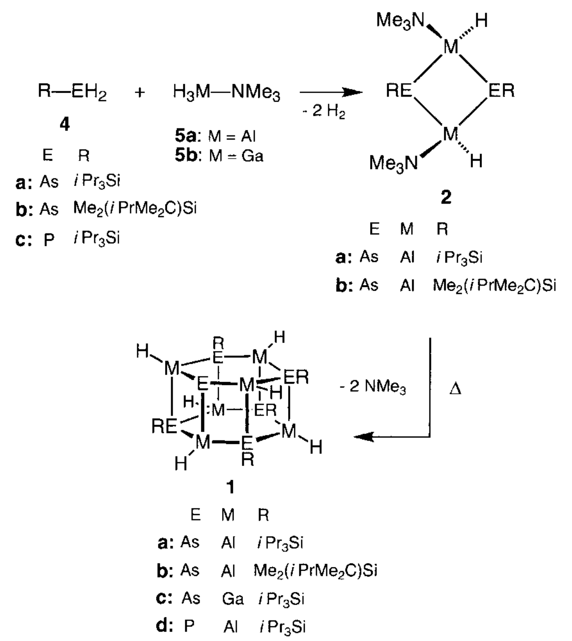


Scheme 1. Synthesis of **2a**, **b** and **1a**–**d**.

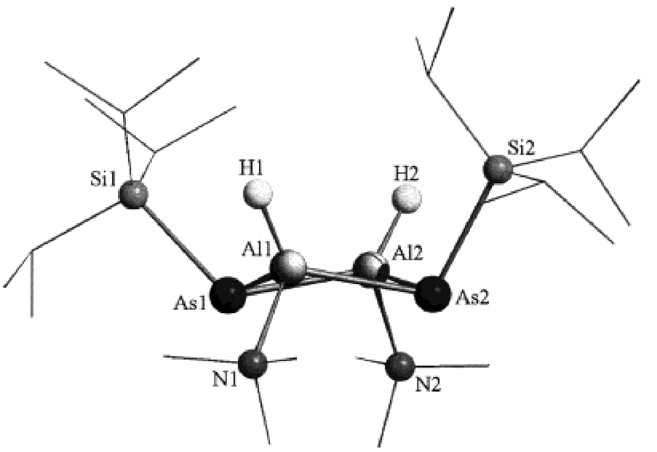


Figure 1. Molecular structure of **2a**. Selected distances [Å] and angles [°]: Al1–As1 2.439(2), Al1–As2 2.460(2), Al1–N1 2.044(3), Al1–H1 1.56(4), Al2–As1 2.439(2), Al2–As2 2.444(2), Al2–N2 2.036(3), Al2–H2 1.59(4); As1-Al1-As2 100.19(7), As1-Al2-As2 100.64(6), Al1-As1-Al2 76.38(6), Al2-As2-Al2 75.91(6).

Results and Discussion

A facile method to form M–P and M–As bonds (M = Al, Ga) is represented by the reaction of primary phosphanes and arsanes (protic E–H bonds) with H_3M–base adducts (M = Al, Ga; hydridic M–H bonds), which takes place under elimination of H_2. Thus, the reaction of the silylarsanes **4a** and **b** with **5a** furnishes, under evolution of H_2, the heterocycles **2a** and **b**, respectively. These heterocycles are the first compounds of this type. Their composition is proven by correct elemental analyses and the constitution is established by NMR spectroscopy (^1H, ^{27}Al) and X-ray diffraction. According to a single-crystal X-ray structure determination, **2a** consists of a puckered four-membered Al_2As_2 ring with pyramidally λ^3, σ^3-coordinated As atoms and tetrahedrally surrounded aluminum centers (Figure 1). The Me_3N groups at the Al centers are surprisingly *cis*-oriented to each other, which is probably due to the steric demand of the silyl group at arsenic.

The average Al–As distance is 2.447(2) Å and thus is only slightly little longer than the value in the borazine analogue $(Mes^*AlAsPh)_3$ (2.430 Å, Mes* = 2,4,6-tBu$_3C_6H_2$) which, however, has only three-coordinate Al centers.[8] The average endocyclic angle at arsenic is much smaller (76.14(6)°) than the respective angle at the Al atom (100.41(7)°). The Al–N distances of 2.044(3) and 2.036(3) in **2a** are significantly shorter than that in $[\mathbf{5a}]_2$ (2.063(8) Å).[9] The compounds **2a** and **2b** are thermally sensitive and rearrange to the corresponding clusters **1a**, **b**, a process which may be easily monitored by ^{27}Al NMR spectroscopy. Apparently, the ^{27}Al nuclei in **2a**, **b** are relatively deshielded at $\delta = 127$ and 140, respectively, compared to those in **1a** ($\delta = 48$) and **1b** ($\delta = 40$), respectively. Notably the δ values of **2a**, **b** are in the characteristic region of four-coordinate Al compounds, whereas the chemical shifts of **1a** and **1b** indicate an unusual shielding, and the δ values are between those expected for four- and five-coordinate Al compounds.[10] This difference is probably due to ring strain in the prismatic skeleton of **1a**, **b**. The Me_3N donor molecules are easily cleaved off upon heating of **2a** in toluene, and the donor-free Al_2As_2 cycles trimerize to form the hexameric arsinoalane **1a**, which possesses a hexagonal prismatic Al_6As_6 skeleton, as shown by an X-ray crystal structure determination (Figure 2). Crystals of **1b**, prepared in similar way to those of **1a**, were not suitable for an X-ray crystal structure determination.

Compound **1a** has a center of symmetry and consists of two puckered six-membered Al_3As_3 rings that are linked together through six transversal Al–As bonds, thus implying six four-

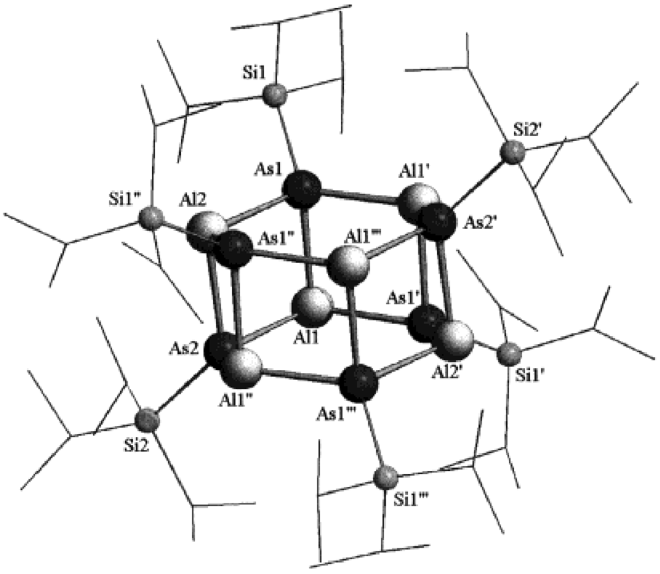
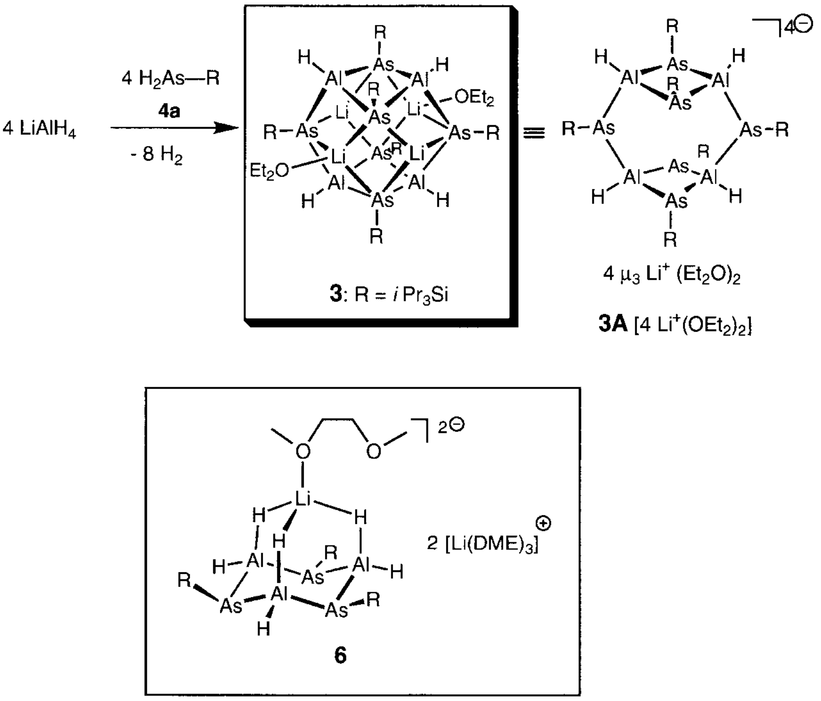


Figure 2. Solid-state structure of **1a** (**1c** and **1d** are isotypic). Selected distances [Å] and angles [°]: As1–Al1 2.511(3), As1–Al2 2.470(2), As2–Al1 2.468(3), As2–Al2 2.504(4), As1–Al1′ 2.464(3); Al1-As1-Al2 84.9(1), Al1-As2-Al2 85.05(9), Al1′-As1-Al2 122.5(1), Al1′-As1-Al1 84.5(1), As2-Al1-As1 94.8(1), As1-Al2-As2 94.9(1), As1′-Al1-As1 95.3(1), As1″-Al2-As1 115.4(2), Al1″-As2-Al1 123.7(1).

membered Al_2As_2 ring increments in the skeleton. The average Al–As distance is 2.488(3) Å and thus only marginally longer than the value in **2a**. The average endocyclic angle at arsenic in the Al_3As_3 ring (123.3(1)°) is significantly larger than that at aluminum (114.6(2)°), whereas the reverse is true in the Al_2As_2 ring increments (Al-As-Al 84.9(1), As-Al-As 94.8(1)°). Apparently, the bulky iPr$_3$Si groups at arsenic shield the Al–H bonds sterically, resulting in a almost spherical molecule shape. The topography of the molecule is practically identical with that of the nitrogen analogue (HAlN*i*Pr)$_6$.[5] Vibrational spectroscopic data of such complex aggregates are relatively rare. IR-(Infrared) and Raman-spectroscopic investigations of **1a** revealed the mode of the total symmetric stretching vibration of the Al_6As_6 cage at 299 cm^{-1} (Raman active) and the asymmetric cage vibration lies at 340 cm^{-1}. Because of the proximity of the latter vibrations to the As–Si stretching mode (ca. 380 cm^{-1}) one expects a significant vibration coupling. However, the Al–H vibration can be identified as the only pure stretching vibration modes which appear at $\nu = 1814$, 1790 (sh) (IR active) and 1824, 1819 (sh) cm^{-1} (Raman active), respectively. Whereas the reaction of **4a**, **b** with **5a** furnishes the compounds **1a**, **b** via **2a**, **b** as isolable intermediates, the conversion of iPr$_3$SiAsH$_2$ (**4a**) with H_3GaNMe_3 (**5b**) and of iPr$_3$SiPH$_2$ (**4c**) with H_3AlNMe_3 (**5a**), respectively, takes place under similarly mild reaction conditions (room temperatur, Et_2O as solvent) but an intermediate of the type **2** could not be detected. The hexameric arsinogallane **1c** and the phosphinoalane **1d** were isolated in 71 and 92% yield, respectively, and have been characterized by NMR spectroscopy and elemental analyses. Their molecular structures are isotypic with **1a** but the quality of the crystals is moderate, that is, a discussion of their geometry is meaningless. The ^{31}P NMR chemical shift of **1d** at $\delta = -277$ indicates a strong σ-donor effect from aluminum to the P centers, and the ^{27}Al NMR chemical shift at $\delta = 46$ is identical to the values obtained for the arsenic homologues **1a**, **b**. It is instructive to compare the stretching vibration spectra of **1c** (Ga_6As_6 skeleton) and **1a** (Al_6As_6 skeleton): The total symmetric stretching vibration of the Ga_6As_6 skeleton in **1c** appears in the Raman spectrum at $\nu = 175$ cm^{-1} [**1a** (Al–As): 299 cm^{-1}]; this frequency coincides with the deformation mode of the iPr$_3$Si group, which is a very weak asymmetric mode that lies at $\nu =$ 235 cm^{-1} (IR-active). The ν(GaH) mode (2087 cm^{-1}, IR; 2019, 2091 cm^{-1}, Raman) is blue-shifted by more than 200 cm^{-1}(!) compared to the ν(AlH) bands in **1a** (1814, 1790 cm^{-1}, IR) and this clearly demonstrates the special position of gallium in Group 13, since it is more electronegative than aluminum in its compounds (1.756 vs. 1.613 according to Allen)[11] and has a relatively small covalent radius.



Scheme 2. Formation of **3** and structure of **6**.

A remarkably facile way to cluster compounds with Al, As, and Li centers as skeleton atoms is provided by the reaction of the primary silylarsane **4a** with [LiAlH$_4$] in the molar ratio of 1:1 in Et_2O as solvent (Scheme 2). This leads, under evolution of H_2, to the heteroaggregate **3**, which can be isolated in the form of sparingly soluble, pale yellow crystals. Its structure was established by an X-ray crystal structure determination (Figure 3).

The generation of **3** may be simply described by a stepwise cyclocondensation reaction of four molar equivalents of [LiAlH$_4$] with six arsane molecules. This initially gives rise to the tetraionic Al_4As_6 skeleton **3A**, which bears four Li counterions (two of which are each coordinated by one Et_2O molecule) for neutralization. Further cyclocondensation of this intermediate with two equivalents of arsane finally affords **3**. The formation of **3** is very surprising since the same reaction of the starting materials in 1,2-dimethoxyethane (DME) instead of Et_2O as solvent leads to the unusual triple ion pair **6** as the sole product.[12] Apparently, the drastic solvent-dependence suggests that the coordination of the Li ions and the strength of the interaction of the solvated Li centers with the anionic Al, As backbone mainly determines the reaction site, but the mechanism is still unknown. Furthermore, it is remarkable that the reaction of primary amines with [LiAlH$_4$] does not lead to nitrogen-analogous cage compounds.[13]

The ^{1}H NMR spectrum of **3** reveals the presence of two solvent molecules Et_2O, and the ^{27}Al NMR spectrum shows a broad signal at $\delta = 51$. The latter value is identical with the respective values in **1a**, **1b**, and **1d**, and seems typical for λ^4, σ^3-coordinate Al centers in the environment of three pnictogen and one H centers. The centrosymmetric structure of the rhombododecahedral $Al_4As_6Li_4$ skeleton in **3** may be viewed as close packing of the anionic RAs^{2-} particles (arsanediides) with Li$^+$ and HAl^{2+} ions. The topography of the cluster skeleton is identical with that of the donor-solvent-free dimeric triarsanide aggregate [(iPr$_3$Si–AsLi)$_3$GetBu]$_2$,[14]

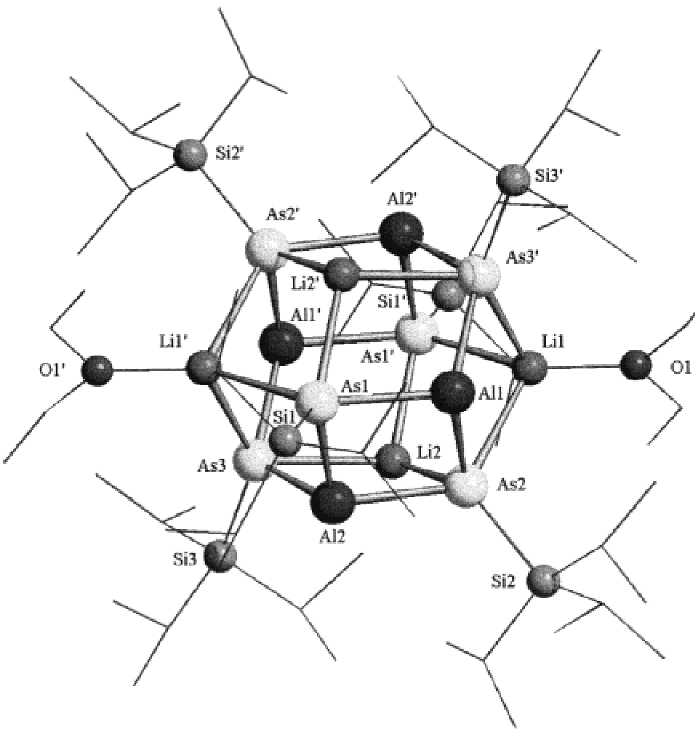


Figure 3. Solid-state structure of **3**. Selected distances [Å] and angles [°]: As1–Al2 2.486(6), As1–Al1 2.515(5), As1–Li2′ 2.56(3), As1–Li1′ 2.80(3), Al1–As3′ 2.482(5), Al1–As2 2.491(6), As2–Li2 2.46(2), As2–Al2 2.516(5), As2–Li1 2.78(3), Al2–As3 2.510(5), As3–Al1′ 2.482(5), As3–Li2 2.65(3), As3–Li1′ 2.66(3), O1–Li1 1.91(3); As2-Al1-As3′ 102.5(2), As1-Al1-As2 100.5(2), As1-Al1-As3′ 109.2(2), As2-Li1-As3′ 91.0(7), As1′-Li1-O1 120.7(11), As2-Li2-As3 106.6(9), As2-Li2-As1′ 113.0(11), As1′-Li2-As3 102.7(9), Al1-As1-Al2 79.3(2), Al1-As1-Li2′ 74.1(6), Al1-As2-Li1 80.3(6), Li1-As2-Li2 73.3(8), Al1′-As3-Li1′ 82.8(6), Al2-As3-Li2 69.9(5).

with related triamides,[15] and with a recently described lithium aluminum phosphanide.[16] Extra electronic stabilization of each arsenic μ_3-coordinate Li center is achieved by solvation with one Et_2O molecule for Li1 or in the case of the Li2 center by Li-H-C interactions with *i*Pr groups close by. The average Al–As distance of 2.494(6) Å is longer than that in **1a** due to the (higher) fivefold coordination of the As centers. The Li–As distances (2.48(3)–2.85(3) Å) are quite different for steric and electronic reasons. We are presently investigating whether **1a**–**1d** are potentially cocatalysts for ethene polymerization and for the co-oligomerization of ethene and CO to give polyketones. Furthermore, experiments to develop a method for stibinoalanes and related gallanes are in progress.

Experimental Section

All experiments were routinely carried out under anerobic and anhydrous conditions by using Schlenk techniques. Solvents were appropriately dried, distilled, and saturated with argon prior to use. The starting compounds **4a**–**c**[17] and **5a**, **b**[18]were prepared according to the literature. NMR spectra were recorded on a Bruker DPX 250 spectrometer using dry degassed C_7D_8: ^1H NMR (250 MHz), ^{31}P NMR (101 MHz), ^{27}Al NMR (65 MHz); chemical shifts (δ) are given relative to external standards (^1H, $SiMe_4$; ^{31}P, 85% H_3PO_4; ^{27}Al, 30% $AlCl_3$). All isolated compounds gave C, H analyses consistent with their formulas.

Synthesis of 1,3-Bis(triisopropylsilyl)-2,4-bis(trimethylamine)-1,3-diarsa-2,4-dialuminetane (2a) and 1,3-Bis(dimethylthexylsilyl)-2,4-bis(trimethylamine)-1,3-diarsa-2,4-dialuminetane (2b)

2a: A solution of **5a** (0.48 g, 5.38 mmol) in Et_2O (50 mL) was allowed to react at 35 °C with **4a** (1.26 g, 5.38 mmol). After the evolution of H_2 was complete, the clear solution was concentrated to about 5 mL and stored at −25 °C, whereby the product crystallized. Yield: 1.61 g (2.52 mmol), 94%; m.p. 135 °C (decomp). ^1H NMR: $\delta = 2.11$ (s, 42H; *i*PrSi), 2.21 (s, 18H; NMe_3), Al–H not observed; ^{27}Al NMR: $\delta = 127$ (br); selected IR spectral data (KBr pellet): ν(Al–H) = 1772 cm^{-1} (sh); $C_{24}H_{62}Al_2As_2N_2Si_2$ (638.7): calcd C 45.13, H 9.78, N 4.39; found C 44.98, H 9.76, N 4.27.

2b: A similar procedure was used to that for the synthesis of **2a**, starting from **5a** (0.36 g, 4.03 mmol) and **4b** (0.88 g, 4.03 mmol) **4b**. Yield of the colorless solid: 1.09 g (1.78 mmol), 89%; m.p. 109 °C (decomp). ^1H NMR: $\delta = 0.79$ (s, 12H; MeSi), 1.16 (br d, 26H; Me_2(*i*Pr)C), 2.23 (s, 18H; NMe_3), Al-H not observed; ^{27}Al NMR: $\delta = 140$ (br); selected IR spectral data (KBr pellet): ν (Al–H) = 1781 cm^{-1} (sh); $C_{22}H_{58}Al_2As_2N_2Si_2$ (610.7): calcd C 43.27 , H 9.57 , N 4.59; found C 43.55, H 9.55, N 4.44.

Synthesis of the Al_6As_6 clusters 1a and 1b

1a: A solution of **5a** (0.25 g, 2.81 mmol) in toluene (25 mL) was allowed to react with **4a** (0.66 g, 2.81 mmol) at 110 °C. After 3 h the solution was concentrated at room temperature in vacuum (10^{-2} Torr) to about 5 mL. Fractional crystallization at −25 °C afforded colorless crystals of **1a**. The crystals contain one formula unit toluene. Yield: 0.66 g (0.42 mmol), 90%; m.p. 198 °C (decomp); alternatively when a solution of **2a** (1.61 g, 2.52 mmol) in toluene (50 mL) was heated at 110 °C and subsequently the solution was concentrated to about 5 mL in vacuum, **1a** (1.2 g, 0.77 mmol) was obtained in 89% yield after crystallization at −25 °C; ^1H NMR: $\delta = 1.38$ (d, *J*(H, H) = 6.9 Hz, 108H; *Me*$_2$CH-Si), 1.60 (sept, *J*(H, H) = 6.9 Hz, 18H; Me_2C*H*Si), Al–H not observed; ^{27}Al NMR: $\delta = 48$ (br); selected IR spectral data (KBr pellet): ν (Al–H) = 1814, 1790 cm^{-1} (sh); $C_{61}H_{140}Al_6As_6Si_6$ (1653.7): calcd C 44.30 , H 8.53; found C 44.10, H 8.55.

1b: A similar procedure was used to that for the synthesis of **1a**, starting from **5a** (0.25 g, 2.81 mmol) and **4b** (0.62 g, 2.81 mmol) in toluene (25 mL) at 110 °C and subsequent crystallization. The crystals contain one formula unit toluene. Yield: 0.69 g (0.47 mmol), 90%; m.p. 109 °C (decomp); ^1H NMR: $\delta = 0.84$ (s, 36H; MeSi), 1.21 (br.m, 78H; Me_2(*i*Pr)C), Al–H not observed; ^{27}Al NMR: $\delta = 40$ (br.); selected IR spectral data(KBr pellet): ν(Al–H) = 1778 cm^{-1} (s); $C_{55}H_{128}Al_6As_6Si_6$ (1569.6): calcd C 42.09 , H 8.22; found C 41.78, H 8.19.

Synthesis of the Ga_6As_6 cluster 1c: A similar procedure was used to that for the synthesis of **1a**, starting from **5b** (0.20 g, 1.59 mmol) and **4a** (0.37 g, 1.59 mmol) in toluene (25 mL) at 110 °C. Concentration of the solution to about 5 mL and crystallization at −25 °C afforded **1c**. The crystals contain one formula unit toluene. Yield: 0.35 g (0.19 mmol), 71%; m.p. 98 °C (decomp); ^1H NMR: $\delta = 1.32$ (d, *J*(H, H) = 6.8 Hz, 108H; *Me*$_2$CHSi), 1.55 (sept, *J*(H, H) = 6.8 Hz, 18H; Me_2C*H*Si), 5.95 (br, 6H, GaH); selected IR spectral data (KBr pellet): $\nu = 2087$ cm^{-1} (s); $C_{61}H_{140}As_6Ga_6Si_6$ (1910.1): calcd C 38.36 , H 7.39; found C 38.02, H 7.21.

Synthesis of the Al_6P_6 cluster 1d: A similar procedure was used to that for the synthesis of **1a**, starting from **5a** (o.20 g, 2.24 mmol) and **4c** (0.43 g, 2.24 mmol) in toluene at 110 °C. Concentration of the solution to about 5 mL and crystallization at −25 °C afforded colorless crystals. Yield: 0.44 g (0.34 mmol), 92%; m.p. 105 °C (decomp); ^1H NMR: $\delta = 1.32$ (d, *J*(H, H) = 6.9 Hz, 108H; *Me*$_2$CHSi), 1.58 (sept, *J*(H, H) = 6.9 Hz, 18H; Me_2C*H*Si), 5.39 (br, 6H; AlH); ^{27}Al NMR: $\delta = 46$ (br); ^{31}P NMR: $\delta = -277$ (br); selected IR spectral data (KBr pellet): $\nu = 1828$ cm^{-1} (s); $C_{61}H_{140}Al_6P_6Si_6$ (1390.0): calcd C 52.71, H 10.15; found C 52.44, H 10.02.

Formation of the $Al_4As_6Li_4$ cluster 3: A solution of [$LiAlH_4$] (0.11 g, 3 mmol) in Et_2O (50 mL) was allowed to react with an equimolar amount of **4a** (0.69 g) at room temperature until the evolution of H_2 was complete (ca. 6 h). The pale yellow solution was concentrated to about 5 mL. Fractional crystallization at −25 °C afforded **3**. Yield: 0.39 g (0.33 mmol), 44%; m.p. 78 °C (decomp); ^1H NMR: $\delta = 1.16$ (t, 12H; (CH_3CH$_2$)$_2$O), 1.35 (m, 126H; *Me*$_2$*CH*Si), 3.35 (q, 8H; (CH$_3$*CH*$_2$)$_2$O), Al–H not observed; ^{27}Al NMR:

Table 1. Crystal data and structure refinement for compounds **1a**, **2a**, and **3**.

	1a	**2a**	**3**
formula	$C_{54}H_{132}Al_6As_6Si_6$	$C_{24}H_{62}Al_2As_2N_2Si_2$	$C_{62}H_{146}Al_4As_6Li_4O_2Si_6$
formula weight	1561.54	638.74	1677.52
temperature [K]	203(2)	203(2)	203(2)
crystal system	tetragonal	triclinic	monoclinic
space group	$P4(2)/m$	$P\bar{1}$	$P2(1)/n$
a [Å]	13.926(4)	11.782(8)	14.391(6)
b [Å]	13.926(4)	12.351(8)	22.55(2)
c [Å]	22.403(8)	13.182(8)	14.654(6)
α [°]	90	96.92(5)	90.00
β [°]	90	93.89(5)	109.68(3)
γ [°]	90	110.22(5)	90.00
volume [$Å^3$]	4345(2)	1774.5(20)	4477.8(40)
Z	2	2	2
ρ [g cm^{-3}]	1.194	1.195	1.244
$F(000)$	1632	680	1760
crystal size [mm]	0.3 × 0.3 × 0.2	0.7 × 0.3 × 0.25	0.2 × 0.2 × 0.1
$\Theta_{\text{max.}}$[°]	27.50	28	22.5
hkl range	0/18, 0/18, 0/29	−15/15, −16/16, 0/17	0/9, 0/24, −15/14
reflections collected	5446	8578	4883
independent reflections	5046	6085	4613
abs. coeff. [cm^{-1}]	2.452	2.014	2.366
transmission	0.485 1.000	0.777 0.999	
parameters	178	341	370
goodness-of-fit on F^2	0.876	1.027	0.613
$R1$ [$I > 2\sigma(I)$]	0.0588	0.0418	0.0541
$wR2$ (all data)	0.2231	0.0899	0.1239
residual electron density [e $Å^{-3}$]	1.633/−0.474	0.381/−0.525	0.510/−0.337

$\delta = 51$ (br); selected IR spectral data (KBr pellet): $\nu(Al-H) = 1812\ cm^{-1}$ (sh); $C_{61}H_{140}Al_6P_6Si_6$ (1390.0): calcd C 52.71, H 10.15; found C 52.44, H 10.02.

X-Ray structural analyses: Experimental details on the X-ray crystal structure determinations of **1a**, **2a**, and **3** are listed in Table 1. Intensity data were collected on a Siemens-Stoe AED2 (**2a**) and on a Siemens P4 diffractometer (**1a** and **3**) at −70 °C with absorption corrections, using $Mo_{K\alpha}$ radiation in ω scans. The structures were solved by direct methods (SHELXS86)[19a] and refined by full-matrix least-square methods based on F^2 using all measured reflections (SHELXL93)[19b] with anisotropic temperature factors for all non-hydrogen atoms except for Li. The positions of the H atoms, with exception of the Al−H hydrogen atoms in **1a**, were calculated. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100720. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments: We thank the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm Polyedermoleküle), the University of Bochum, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen for financial support. We are also indebted to Prof. Dr. J. Weidlein for measuring IR and Raman spectra.

Received: March 13, 1998 [F 1051]

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