Modular Chemistry with Aluminum Phosphanides: Cluster Formation of $(AlP)_n$ ($n = 3,6,7$), Al_4P_3, and $Al_4Li_4P_6$ Frameworks

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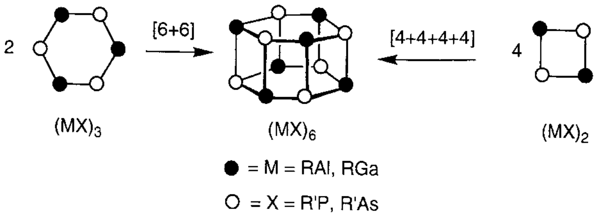
Abstract: The Al_3P_3 heterocycle **1** is formed in 94% yield by the reaction of the primary silylphosphane **6a** with Me_3Al in toluene at 70°C. While **1** crystallizes in an isomerically pure form, in which the six-membered Al_3P_3 ring prefers the chair conformation and the P-H hydrogen atoms adopt *exo* positions, it isomerizes in solution to give different diastereomers as shown by ^1H and ^{31}P NMR spectroscopy. Intermolecular cyclocondensation of **1** at 110°C in toluene leads, under liberation of methane, to the distorted hexameric-prismatic $(AlP)_6$ cluster **2** in 98% yield. The capability of **1** to function as a building block was further used for the synthesis of the solvent-separated ion pair $[Li(thf)_2]^+$ $[(Me_2Al)_4(PR)_3]^-$ (**3**) which was prepared by a one-pot reaction of **1** with *n*BuLi and Me_2AlCl in 15% yield. The structure of **3** was established by an X-ray diffraction analysis. Double deprotonation at phosphorus in **1** with $RPLi_2$ ($R = i{\rm Pr}_3Si$) (molar ratio 1:2), and subsequent transformation of the reaction mixture with Me_3Al afforded the novel donor-solvent-free cluster **4** in 62% yield. The latter consists of a rhombododecahedral $Al_4Li_4P_6$ framework, in which the Li centers are three-coordinate. The reaction of the silylphosphane **6b** with the trimethylamine adduct of alane furnishes not only the hexamer $(RPAlH)_6$ ($R = (i{\rm PrMe_2C})$-Me_2Si) but also the corresponding heptamer **5**, which has a nonregular polyhedral $(AlP)_7$ framework and represents the first cluster of this type.

Keywords: aggregation · aluminum · cluster compounds · phosphorus · pnictides

Introduction

The availability of molecular cluster compounds of different sizes, such as metal clusters[1] and II/VI colloids,[2] is of considerable interest for the development of the chemistry and physics of nanoparticles.[3] Therefore a great deal of research activity is currently devoted to the development of novel methods for the synthesis of tailored and functional clusters starting from simple molecular building blocks. One of the important optoelectronic materials are binary and multinary III/V semiconductors (e.g., GaN, InGaAs, InGaAlP; triel/pentel phases), which are accessible by thermal decomposition of molecular single-source precursors in the gas phase (chemical vapor deposition, CVD) or in solution.[4] However, the mechanism of the cluster formation and reasons behind the different dispersions are as yet hardly understood. A useful model system for cluster formation is provided by the intermolecular conversion of small, molecular III (triel)/V (pentel) aggregates into larger ones. This modular construction principle is based on the aggregation of the building blocks through the formation of additional donor–acceptor bonds (Scheme 1).



Scheme 1. Formation of hexagonal-prismatic $(MX)_6$ frameworks from MX dimers and trimers.

Molecular triel phosphanide and arsanide aggregates with different $(MX)_n$ frameworks ($M = Al$,[5] Ga;[6] $X = P$, As; $n = 2,3,4,6$) appear to be particularly suitable for this process, since dimeric, trimeric, and other oligomeric building blocks are readily available. On the other hand, triel phosphanides and arsanides have been investigated far less than related aluminum– and gallium–nitrogen analogues (triel-imino aggregates)[7] and therefore deserve special attention. Correspondingly, the formation of aluminum arsanides with a higher degree of aggregation ($n > 2$) has been demonstrated so far only in the case of dimeric, NMe_3-stabilized aluminum arsanides which, under elimination of NMe_3, easily undergo

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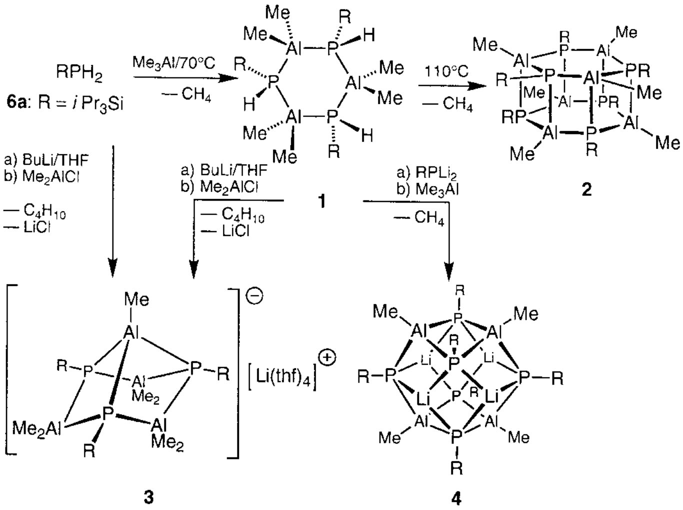
trimerization to give clusters with a hexameric $(AlAs)_6$ skeleton (Scheme 1).[8] We report here on the first modular aluminum phosphanide trimer **1**, which easily dimerizes to the hexamer **2** and forms the anionic Al_4P_3 cage in **3**, and the $Al_4Li_4P_6$ cluster **4** (see Scheme 2). Furthermore, we describe the first aluminum phosphanide heptamer **5** which formally consits of two complementary anionic Al_4P_3 and cationic Al_3P_4 cluster halves.

Results and Discussion

The heterocycle **1** is accessible by the reaction of the primary silylphosphane **6a** with $AlMe_3$ at 70 °C in the molar ratio of 1:1 in 94 % yield (Scheme 2). While solutions of **1** as expected show a diastereomeric mixture (^1H and ^{31}P NMR spectra),[5b, 6e] it crystallizes in an isomerically pure form with a chairlike Al_3P_3 framework and the P-H hydrogen atoms in axial positions, owing to the steric demand of the silyl groups (Figure 1). This is proven by an X-ray structure analysis which revealed Al–P (2.453(2) Å) and Si–P distances (2.281(3) Å) similar to those observed in related dimers and trimers.[5]



Scheme 2. Synthesis of **1**–**4**.

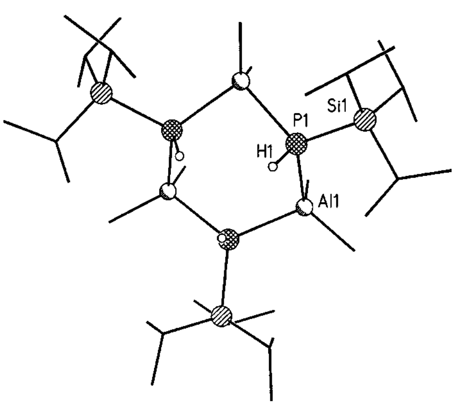


Figure 1. Solid-state structure of **1**. Selected distances [Å] and angles [°]: Al1–P1 2.453(2), P1–Si1 2.281(3), P1–H1 1.36(7); Si1-P1-Al1 117.22(6), Al1-P1-Al1 116.12(11), Si1-P1-H1 98(3), Al1-P1-H1 101(1).

The correspondingly reactive PH and AlMe functions in **1** facilitate the intermolecular condensation reaction to **2** at 110 °C in toluene; that is, two six-membered Al_3P_3 rings are linked together under liberation of CH_4. An X-ray structure elucidation of **2** proves the presence of a distorted hexagonal-prismatic $(AlP)_6$ skeleton (Figure 2). The Al–P distances in the Al_3P_3 base (2.379(2), 2.387(2) Å are only marginally shorter than those in the four-membered Al_2P_2 ring moieties (2.430(2) Å), thus implying a strong flattening out with respect to the original Al_3P_3 chair conformation in **1**. The cluster topology of **2** is identical with that in AlH-analogous $(AlAs)_6$ aggregates, which, however, were obtained through trimerization of the respective $(AlAs)_2$ building blocks according to Scheme 1.[8] The comparatively high P–H bond acidity of **1** also opens up other modular reaction pathways. Thus, reaction of **1** with *n*BuLi and Me_2AlCl (molar ratio of 1:2:1) in THF affords the solvent-separated ion pair **3**, which contains a Al_4P_3 aggregate anion. Remarkably, **3** is more efficiently accessible by a one-pot reaction of **6a** with *n*BuLi and Me_2AlCl in the molar ratio of 5:5:4 as outlined in Scheme 2. The multinuclear NMR spectra of **3** do not display any unexpected features, and the ^{27}Al NMR spectrum shows expectedly only one very broad signal at $\delta = 49$ ($h_{1/2} = 3200$ Hz).[8] The constitution of **3** has been corroborated by an X-ray structure analysis which revealed that the Al–P distances in the separated Al_4P_3 anion are only a little shorter than that observed in **1** (Figure 3).

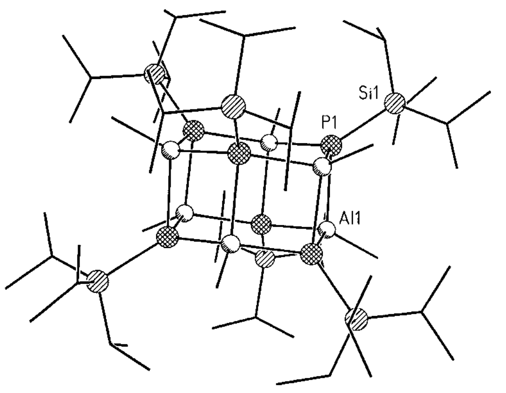


Figure 2. Molecular structure of **2**. Selected distances [Å] and angles [°]: Al1–P1 2.379(2), P1–Si1 2.262(2), Al1–C 1.861(3); Si1-P1-Al1 116.00(7), Al1-P1-Al (Al_3P_3 moieties) 122.44(6), Al1-P1-Al (Al_2P_2 moieties) 84.17(6).

Double deprotonation at phosphorus in **1** with $RPLi_2$ as a base ($R = SiiPr_3$) in the molar ratio 1:2 in toluene leads to a phosphanide mixture that also contains RPHLi. Its reaction with one molar equivalent of $AlMe_3$ furnishes the neutral rhombododecahedral $Al_4Li_4P_4$ cluster **4** in 62 % yield; **4** represents the first lithium aluminum phosphanediide of this type. It crystallizes in the monoclinic space group $P2_1/n$, and the bonding and topology of the centrosymmetric $Al_4Li_4P_4$ framework is identical with that of the currently described arsenic homologues.[8] However, all Li centers (λ^3 coordination) in **4** are coordinatively unsaturated (Figure 4). The Al–P and Li–P distances are identical with those in related phosphanediides[9] and **1**–**3**. Furthermore, in experiments

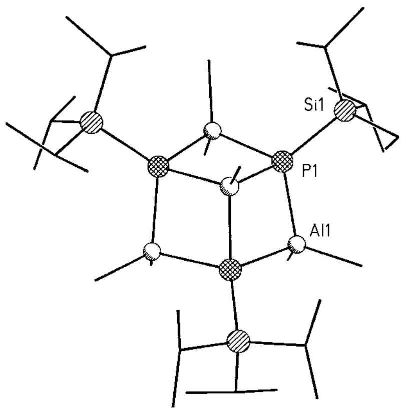


Figure 3. Molecular structure of the Al_4P_3 anion in the $[Li(thf)_4]$ salt **3**. Selected distances [Å] and angles [°]: Al1–P1 2.422(3), P1–Si1 2.250(3), Al1–C 2.010(6); Al1-P1-Al (Al_3P_3 moiety) 112.16(10), P1-Al1-P (Al_2P_2 moieties) 92.47(11).

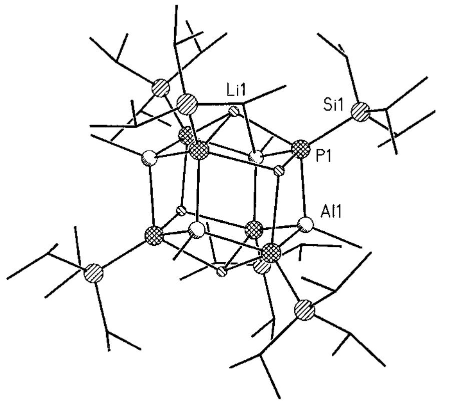


Figure 4. Solid-state structure of **4**. Selected distances [Å] and angles [°]: Al1–P1 2.425(2), Li1–P1 2.495(6), Li1–Li 2.864(8), P1–Si1 2.235(2).

toward the synthesis of higher $(AlP)_n$ clusters ($n > 6$) starting from simple building blocks, we demonstrated that the reaction of the silylphosphane **6b** with $H_3Al(NMe_3)$ furnishes not only predominantly the respective hexagonal-prismatic $(AlP)_6$ derivative **2′** but also the heptamer **5**, which, however crystallizes very slowley from the reaction mixture [Eq. (1)].

$$\underset{\textbf{6b}:\ R = (iPrMe_2C)Me_2Si}{RPH_2} \xrightarrow[-\,H_2,\ -\,NMe_3]{H_3Al(NMe_3)} \underset{\textbf{2'}}{(RP{-}AlH)_6} + \underset{\textbf{5}}{(RP{-}AlH)_7} \qquad (1)$$

Since **5** cannot be dissolved in common organic solvents without decomposition, its structure could only be established by single-crystal X-ray diffraction analysis. The oval Al_7P_7 framework with its four-coordinate Al and P atoms can be simply described as an adduct composed of two complementary (ionic) Al_3P_4 and Al_4P_3 cluster halves that are linked together through three P (donor)–Al (acceptor) bonds, in which the Al–P distances of the "anchor bonds" are similar with those in the cluster halves (Figure 5).

Furthermore, it is remarkable that the identical "free" anionic Al_4P_3 cluster half is in fact present in **3** (see Figure 3). Similar heptameric structures have also been observed for related iminoalanes $[RAlNR']_7$ ($R = R' = Me$, Et).[7g] Octameric clusters $[RAlNR']_8$ are also accessible by variation of the synthetic conditions and the steric requirements of the substituents at aluminum and nitrogen, but they also have a nonregular polyhedral framework.[7h] The latter oligomeric iminoalanes provide support for the existence of higher phosphorus analogues. We are currently investigating whether larger $(AlP)_n$ and $(AlAs)_n$ clusters are accessible by similar synthetic methods.

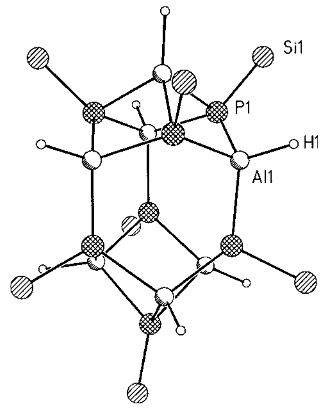


Figure 5. Molecular structure of **5**. For clarity the organic groups at silicon are omitted. Selected distances [Å]: Al1–P1 2.395(6), P1–Si1 2.265(6).

Experimental Section

All experiments were routinely carried out under anerobic and anhydrous conditions by using Schlenk techniques. Solvents were appropriately dried, destilled, and saturated with Ar prior to use. NMR spectra were recorded on a Bruker DPX250 spectrometer using dry degassed $[D_8]$toluene: ^{1}H NMR (250 MHz), ^{31}P NMR (101 MHz), ^{27}Al NMR (65 MHz); chemical shifts (δ) are given relative to external standards (^{1}H, TMS; ^{31}P, 85% H_3PO_4; ^{27}Al, 30% $AlCl_3$). All isolated compounds gave C, H analyses consistent with their formulas.

Synthesis of the $(AlP)_3$ heterocycle 1: A solution of $AlMe_3$ (0.72 g, 10 mmol) in toluene (25 mL) and Et_2O (15 mL) was allowed to react with **6a** (1.90 g, 10 mmol). After the mixture had been heated at 70 °C for 12 h, the volatile components were removed in vacuum at 50 °C. The solid residue was recrystallized from a little hexane, affording colorless needles. Yield: 2.31 g (3.14 mmol), 94%. ^{1}H NMR: $\delta = -0.12$ (t, 9H; AlMe), 1.10 (m, 63H; *i*Pr), 1.15 (br, 3H; PH); ^{27}Al NMR: $\delta = 43$ (br); ^{31}P NMR: $\delta = -241.0$ (m), -244.1 (br.m), -249.3 (br.t), -251.7 (br.t); elemental analysis calcd (%) for $C_{33}H_{84}Al_3P_3Si_3$ (739.1): C 53.62, H 11.45; found: C 53.29, H 11.40.

Synthesis of the $(AlP)_6$ cluster 2: A solution of **1** (0.74 g, 1.00 mmol) in toluene (20 mL) was refluxed for 12 h. After the evolution of CH_4 was complete, the solution was cooled to room temperature, whereby the product crystallized. Yield: 0.68 g (0.49 mmol), 98%. ^{1}H NMR: $\delta = 0.25$ (s, 18H; AlMe); 1.21 (d, 126H; *i*Pr); ^{27}Al NMR: $\delta = 46$ (br); ^{31}P NMR: $\delta = -235$ (br); elemental analysis calcd (%) for $C_{66}H_{150}Al_6P_6Si_6$ (1460.1): C 54.29, H 10.35; found: C 54.41, H 10.33

Formation of the Li salt 3: A solution of **6a** (6.40 g, 33.67 mmol) in THF (20 mL) was treated at −70 °C with BuLi (21.0 mL, 33.6 mmol of a 1.6 M solution in hexane), whereby a clear, pale-yellow solution was formed. After removal of all volatiles in vacuum, the lithium phosphanide was dissolved in hexane (ca. 50 mL) and allowed to react at −70 °C with Me_2AlCl (33.7 mL, 33.7 mmol of a 1 M solution in hexane). The resulting slurry was stirred for 8 h and subsequently filtered. The ion pair crystallized from the clear solution at 4 °C within a few days in the form of colorless needles. Yield: 5.30 g (4.94 mmol), 15%. M. p. 80 °C (decomp); ^{1}H NMR ($[D_8]$THF): $\delta = 3.66$ (m, 16H; THF), 1.80 (m, 16H; THF), 1.47 (sept, ^3J(H,H) = 7.5 Hz, 3H, Me_2CH), 1.16 (d, ^3J(H,H) = 5.6 Hz, 54H, Me_2CH),

Table 1. Crystal data and structure refinement for compounds **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
formula	$C_{33}H_{84}Al_3P_3Si_3$	$C_{66}H_{150}Al_6P_6Si_6$	$C_{50}H_{116}Al_4LiO_4P_3Si_3$	$C_{58}H_{138}Al_4Li_4P_6Si_6$	$C_{56}H_{140}Al_7P_7Si_7$
formula weight	739.12	1460.10	1073.47	1325.72	1415.96
temperature [K]	203	203	203	203	203
crystal system.	trigonal	tetragonal	monoclinic	monoclinic	triclinic
space group	*R3m*	$P4_2/m$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [Å]	22.311(4)	13.955(8)	17.48(2)	13.089(6)	12.79(4)
b [Å]	22.311(4)	13.955(8)	20.59(3)	23.12(2)	13.83(4)
c [Å]	8.521(5)	21.99(2)	19.48(2)	15.021(9)	25.37(7)
α [°]	90	90	90	90	94.6(1)
β [°]	90	90	94.82(4)	115.83(3)	103.96(6)
γ [°]	120	90	90	90	95.46(7)
volume [Å^3]	3674(2)	4282(5)	6983(14)	4091(4)	4308(22)
Z	3	2	4	2	2
ρ [g m^{-3}]	1.002	1.133	1.021	1.076	1.092
F(000)	1224	1596	2360	724	770
crystal size [mm]	0.2 × 0.3 × 0.2	0.2 × 0.1 × 0.3	0.2 × 0.2 × 0.2	0.1 × 0.2 × 0.1	0.2 × 0.1 × 0.3
θ_{max}[^{0}]	25.00	25.12	25.08	25.14	25.78
hkl range	−1/17, −26/1, −1/10	−16/5, −13/8, −26/25	−18/20, −16/24, −22/15	−14/15, −27/27, −17/10	−15/12, −16/15, −29/29
reflections collected	1534	10300	16616	20837	22632
independent reflections	901	3746	10058	7232	15238
μ [cm^{-1}]	2.68	3.06	2.21	1.47	1.71
transmission	1.000 0.472	1.000 0.538	1.000 0.318	0.980 0.670	1.000 0.508
parameters	76	200	592	352	722
goodness-of-fit on F^2	0.886	0.992	0.939	1.147	1.020
*R*1 [$I > 2\sigma(I)$]	0.0427	0.0652	0.0942	0.0605	0.0874
w*R*2 (all data)	0.0890	0.2036	0.2861	0.1836	0.2359
residual electron density [e Å^{-3}]	0.172/−0.243	0.469/−0.497	0.878/−1.204	0.953/−0.475	0.720/−0.783

−0.45 (br, 21 H, $AlCH_3$); ^{31}P NMR ([D$_8$]THF): $\delta = -280.9$ (s); ^{27}Al NMR ([D$_8$]THF): $\delta = 48$ (br., $w_{1/2} = 3200$ Hz); ^7Li NMR ([D$_8$]THF): $\delta = -4.91$ (s); elemental analysis calcd (%) for $C_{50}H_{116}Al_4LiO_4P_3Si_3$ (1073.5): C 55.94, H 10.89; found: C 55.65, H 10.85.

Synthesis of the $Al_4Li_4P_6$ cluster 4: A solution of $AlMe_3$ (0.36 g, 5 mmol) in a solvent mixture of toluene (5 mL) and Et_2O (15 mL) was treated with iPr$_3$SiPH$_2$ (1.43 g, 7.5 mmol). The mixture was heated at 70 °C for 12 h and subsequently allowed to react at −78 °C with *n*BuLi (3.2 mL of a 1.6 M solution in hexane). The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. After the gas evolution was complete, the clear yellow solution was concentrated to about 10 mL, whereby the product crystallized in the form of colorless crystals. Yield: 1.37 g (0.78 mmol), 62 %; ^7Li NMR: $\delta = -2.68$ (br); ^{27}Al NMR: $\delta = 36$ (br); ^{31}P NMR: $\delta = -319$ (br); elemental analysis calcd for $C_{58}H_{138}Al_4Li_4P_6Si_6$ (1325.7): C 52.54, H 10.49; found C 52.21, H 10.45.

Synthesis of the $(AlP)_7$ cluster 5: A solution of $H_3Al(NMe_3)$ (0.89 g, 10 mmol) in Et_2O (25 mL) was allowed to react at −78 °C with **6b** (2.08 g, 10 mmol). The reaction mixture was cooled to room temperature within 12 h, concentrated in vacuum to about 5 mL and stored at −25 °C. Crystallization from the solution, which contained mainly **2′**,[7] afforded colorless crystals of **5** after several months. Yield: 20 mg (0.01 mmol), 1 %; elemental analysis calcd (%) for $C_{56}H_{140}Al_7P_7Si_7$ (1416.0): C 47.50, H 9.96; found: C 47.11, H 9.92.

X-ray structural analysis: Experimental details on the X-ray crystal structure determinations of **1**–**5** are listed in Table 1. Intensity data were collected on a Bruker-AXS-SMART diffractometer at −70 °C by using $Mo_{K\alpha}$ radiation in ω scans. The structures were solved by direct methods (SHELXS97) and refined by full-matrix least-square methods based on F^2 using all measured reflections (SHELXL97) with anisotropic temperature factors for all non-hydrogen atoms except for Li; the hydrogen atoms were isotropically considered. 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-141775 (**1**), CCDC-141771 (**2**), CCDC-141774 (**3**), CCDC-141772 (**4**), and CCDC-141773 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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