Synthesis and Characterisation of Ternary Cage Compounds with Adamantane-Like $M_4P_4Si_2$ (M = Al, Ga, In) Core Structures

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The reactions of $[LiAl(PH_2)_4]$ or $[NaAl(PH_2)_4]$ with Et_2SiCl_2 or iPr$_2$SiCl$_2$ yield the dialkyldiphosphanylsilanes $Et_2Si(PH_2)_2$ (**1**) and iPr$_2$Si(PH$_2$)$_2$ (**2**), respectively. Both compounds were identified by NMR spectroscopy as well as mass spectrometry. Compound **2** reacts with MEt_3 (M = Al, Ga, In) to form the cage compounds $[i\text{Pr}_2\text{Si}\{\text{P(H)ME}t_2\}_2]_2$ (**3**: M = Al, **4**: M = Ga, **5**: M = In). These three clusters were fully characterised by NMR and IR spectroscopy as well as by single-crystal X-ray diffraction. The central structural motif of **3**–**5** is an adamantane-like cage composed of four metal, four phosphorus and two silicon atoms. They are the first ternary clusters with these combinations of elements and crystallise isotypical in the triclinic space group $P\bar{1}$; the lattice constants are: **3**: a = 1129.0(6), b = 1164.8(8), c = 1750.6(8) pm; α = 83.63(5), β = 81.53(4), γ = 73.39(5)°; **4**: a = 1125.9(7), b = 1159.0(7), c = 1744.7(7) pm; α = 83.71(4), β = 81.89(4), γ = 73.05(5)°; **5**: a = 1147.4(2), b = 1174.7(2), c = 1753.3(4) pm; α = 85.32(3), β = 82.03(3), γ = 73.40(3)°.

Introduction

In the last few years reactions of primary silylphosphanes or -arsanes (R_3SiEH_2, E = P, As) with hydrido- or alkylaluminium, -gallium or -indium compounds have been applied several times to synthesise molecular compounds of these element combinations.[1−3] Cyclic and also cage-like 13/15 compounds were obtained from these reactions. The molecular structures of the reaction products can be influenced by the silyl group attached to the P or As atom. The reactions of $InEt_3$ with R_3SiPH_2 may serve as an example. Starting from iPr$_3$SiPH$_2$, the heterocubane-like compound $[EtInPSi\textit{i}Pr_3]_4$ is formed whereas the reaction of ThexMe$_2$SiPH$_2$ (Thex = CMe$_2$$i$Pr) with $InEt_3$ yields the hexagonal prismatic molecule $[EtInPSiThexMe_2]_6$.[2] By using the sterically less demanding $SiMe_3$ group a $SiMe_3$/H substituent exchange occurs and results in the formation of the cyclic compound $[Et_2InP(SiMe_3)_2]_2$.[3]

Whereas the dimethyldiphosphanylsilane $Me_2Si(PH_2)_2$ has been known in the literature for several years, dialkyldiphosphanylsilanes with sterically demanding alkyl groups such as ethyl or isopropyl are as yet unknown.[4] Reaction of these compounds with alkylaluminium, -gallium or -indium species will result in the formation of novel ternary group13/Si/P compounds. The first species of this class of compounds $[i\text{Pr}_2\text{Si}\{\text{P(H)ME}t_2\}_2]_2$ (**3**: M = Al, **4**: M = Ga, **5**: M = In), which could be obtained by the reactions of iPr$_2$Si(PH$_2$)$_2$ (**2**) with MEt_3, are described herein.

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Results and Discussion

A solution of $[LiAl(PH_2)_4]$ in tetraglyme reacts with Et_2SiCl_2 to form the dialkyldiphosphanylsilane $Et_2Si(PH_2)_2$ (**1**). This compound can be isolated from the reaction mixture by vacuum condensation in about 50% yield. The less volatile compound iPr$_2$Si(PH$_2$)$_2$ (**2**) can be obtained in about 70% yield from the reaction of $[NaAl(PH_2)_4]$ with iPr$_2$SiCl$_2$ in DME. The ^{31}P NMR spectra of both molecules show a triplet of higher order at δ = −242.7 (**1**) and −254.2 ppm (**2**). The high resolution spectrum of **1** (see Figure 1) allows the complete analysis of all coupling constants by an iterative process;[5] the fine structure of the

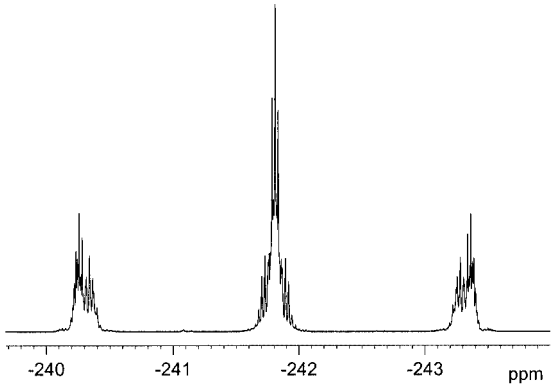

Figure 1. ^{31}P NMR Spectrum of **1** in C_6D_6

triplet of **2** cannot be fully resolved. Therefore only the $^1J_{P,H}$ coupling constants were determined. The mass spectra of both compounds show the molecule peaks at m/z = 152 (**1**) and 180 (**2**) as well as peaks for the fragments $R_2SiPH_2^+$, $RSi(H)PH_2^+$ and $H_2SiPH_2^+$.

Reaction of **1** with triethylgallium or triethylindium results in the formation of oily precipitates, which have not been characterised so far. $^{31}P\{^1H\}$ NMR investigations of the reaction mixtures showed several broad signals, which indicate that polymeric compounds have been formed. In contrast to the latter, the sterically more demanding compound **2** reacts with MEt_3 (M = Al, Ga, In) in heptane at ambient temperature with elimination of ethane and the formation of a white, crystalline precipitate. These products can be dissolved by warming the reaction mixtures slightly. Subsequent cooling of the solutions to 6 °C yields colourless crystals.[6] X-ray analysis (Table 1) confirmed that the compounds $[i\mathrm{Pr}_2\mathrm{Si}\{\mathrm{P(H)MEt}_2\}_2]_2$ (**3**: M = Al, **4**: M = Ga, **5**: M = In) had formed as described in Equation (1). Recently, Kaskel and co-workers reported reactions of $Si(NHEt)_4$ with AlR_3, which result in the formation of the ternary Al/Si/N compounds $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)_2]_2$ (R = Me, Et).[7] Whereas compounds **3** and **4** are stable in solution, too, a benzene solution of the indium compound **5** decomposes after several days with further elimination of ethane. At the same time a yellow, oily, precipitate appears.

$$2\ i\mathrm{Pr}_2\mathrm{Si(PH_2)_2} + 4\ \mathrm{MEt_3} \rightarrow [i\mathrm{Pr}_2\mathrm{Si}\{\mathrm{P(H)MEt}_2\}_2]_2\ (\mathrm{M = Al, Ga, In}) + 4\ \mathrm{C_2H_6} \quad (1)$$

Compounds **3**, **4** and **5** crystallise isotypical in the triclinic space group $P\bar{1}$ (the structure of **3** is shown in Figure 2 as an example). The central structural motif is an adamantane-like cage composed of four aluminium, gallium or indium atoms, four phosphorus and two silicon atoms. Cage compounds of these element combinations have not been reported so far. In these moieties, the phosphorus atoms are in the bridgehead positions and the metal and silicon atoms are in the secondary positions. This results in an eight-membered M_4P_4 (M = Al, Ga, In) ring, where the opposite phosphorus atoms [P(1), P(3) and P(2), P(4)] are bridged by $i\mathrm{Pr}_2\mathrm{Si}$ groups on different sides of the ring. The M_4P_4 ring is therefore strongly distorted and shows a boat-like conformation.

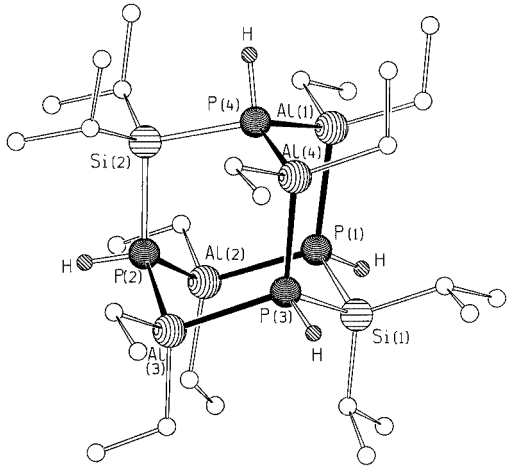

Figure 2. Molecular structure of **3**

The observed P−M and P−Si bond lengths are in the typical range for single bonds between these elements (seen Table 2).[1−3,8] The very similar Al−P and Ga−P bond

Table 1. Crystallographic data of **3**, **4** and **5** [STOE-IPDS2 (Mo-K_α radiation, λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 (In, Ga, Al, P, Si, C refined anisotropically, H atoms at the phosphorus atoms refined isotropically, all other H atoms were calculated at ideal positions)][6]

Compound	**3**	**4**	**5**
Formula	$C_{28}H_{72}P_4Al_4Si_2$	$C_{28}H_{72}P_4Ga_4Si_2$	$C_{28}H_{72}P_4In_4Si_2$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Formula units	2	2	2
Temperature	200 K	200 K	200 K
Lattice constants	a = 1129.0(6) pm	a = 1125.9(7) pm	a = 1147.4(2) pm
	b = 1164.8(8) pm	b = 1159.0(7) pm	b = 1174.7(2) pm
	c = 1750.6(8) pm	c = 1744.7(7) pm	c = 1753.3(4) pm
	α = 83.63(5)°	α = 83.71(4)°	α = 85.32(3)°
	β = 81.53(4)°	β = 81.89(4)°	β = 82.03(3)°
	γ = 73.39(5)°	γ = 73.05(5)°	γ = 73.40(3)°
Volume	2176(2) Å^3	2150(2) Å^3	2240.8(8) Å^3
density	1.063 g/cm^3	1.340 g/cm^3	1.553 g/cm^3
2Θ range	3−50°	4−50°	4−54°
Reflections measured	13966	12583	17889
Independent reflections	7084 (R_{int} = 0.0563)	7104 (R_{int} = 0.0603)	9101 (R_{int} = 0.0535)
Ind. reflections with $F_0 > 4\sigma(F_0)$	5860	5611	7614
Parameter	359	359	362
μ(Mo-K_α)	0.326 mm^{-1}	1.340 mm^{-1}	2.244 mm^{-1}
R1	0.0627	0.0657	0.0382
wR2 (all data)	0.1863	0.1919	0.1088
Residual electron density	0.463 e/Å^3	0.827 e/Å^3	0.620 e/Å^3

Table 2. Selected bond lengths (pm) and bond angles (°) for **3**−**5**

	3 [M = Al]	**4** [M = Ga]	**5** [M = In]
P−M	244.7(2) − 246.3(2)	243.0(2) − 245.4(2)	261.6(1) − 262.8(1)
P−Si	226.9(2) − 228.0(2)	227.6(2) − 229.7(2)	226.1(1) − 226.8(1)
P−M−P	94.63(7) − 95.68(7)	94.71(7) − 96.01(7)	92.12(4) − 93.08(4)
P−Si−P	103.27(7) − 103.70(7)	102.33(9) − 102.87(9)	105.18(5) − 105.41(5)
M−P−M	113.65(6) − 116.00(6)	114.01(7) − 115.98(7)	111.41(4) − 113.42(4)

lengths reflect the fact that the covalent radii of Al and Ga are almost identical due to d-block contraction. Each of the metal atoms is bound to two exocyclic ethyl groups and the silicon atoms possess two isopropyl groups each. The phosphorus atoms bind to one hydrogen atom, which was localised during the refinement of the crystal structures. Moreover, the IR spectra of **3**, **4** and **5** show strong peaks at 2306 cm^{-1} (**3**), 2305 cm^{-1} (**4**), 2303 cm^{-1} (**5**) which can be assigned to the P−H stretching vibrations. The ^{31}P NMR spectra reveal multiplets of higher order for all three compounds ([AX]$_4$ spin system). Figure 3 displays the ^{31}P NMR spectrum of **5**. Unfortunately, the comparatively broad signals in the ^{31}P NMR spectra of **3**−**5** (see Figure 3 inset) do not allow an iterative determination of the coupling constants with satisfactory accuracy. As expected, the $^{31}P\{^1H\}$ NMR spectra only show singlets at δ = −250.0 (**3**), 244.2 (**4**) and −273.5 ppm (**5**).

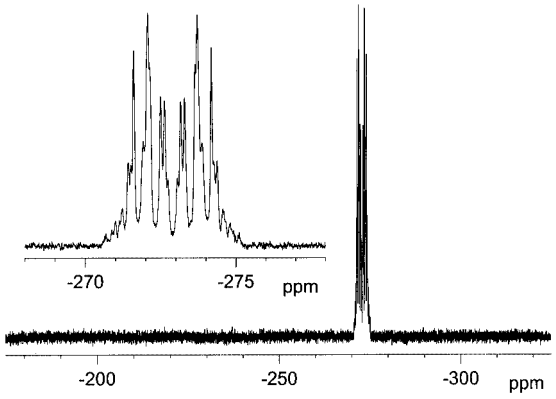

Figure 3. ^{31}P NMR Spectrum of **5** in C_6D_6

Experimental Section

All manipulations were performed with rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded on a Bruker DPX Avance 300 or on a Bruker AC 250 instrument. $[NaAl(PH_2)_4]$, $[LiAl(PH_2)_4]$, $GaEt_3$ and $InEt_3$ were prepared according to the literature.[9−11] $AlEt_3$ was purchased from Aldrich and used as received.

1: Et_2SiCl_2 (4.0 g, 0.025 mol) was added to 100 mL of a 0.13 M solution of $[LiAl(PH_2)_4]$ in tetraglyme at −40 °C. The colour of the solution changed from slightly yellow to colourless. During this time a white precipitate also formed. After agitation for ten minutes the product was condensed into a cold trap at −196 °C under oil pump vacuum. During the condensation the reaction mixture was warmed up to room temperature. After five hours the condensation was complete. Trace amounts of solvent were removed from the product by a second condensation under a stationary vacuum of $5{\cdot}10^{-3}$ mbar. Compound **1** was obtained as a colourless, pyrophoric liquid. Yield: 2.0 g (52%). $^1H\{^{31}P\}$ NMR (C_6D_6): δ = 0.670 (q, $^3J_{H,H}$ = 7.9 Hz, 4 H, CH_2), 0.909 (t, $^3J_{H,H}$ = 7.9 Hz, 6 H, CH_3), 1.350 (m, 4 H, PH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 8.4 (t $^2J_{C,P}$ = 2.6 Hz, CH_3), 10.3 (t $^3J_{C,P}$ = 7.3 Hz, CH_2) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 12.8 (t $^1J_{Si,P}$ = 33 Hz) ppm. ^{31}P NMR (C_6D_6): δ = −242.7 [m/t, coupling constants from iterative optimisation: $^1J_{PH}$ = −184.1, $^2J_{P,P}$ = 11.9, $^3J_{PH(PH2)}$ = −4.4, $^4J_{H,H(PH2/PH2)}$ = 0.4, $^3J_{PH(CH2)}$ = 3.0 Hz (corresponds with $AA'X_2X'_2Y_2Y'_2$ spin system)].[5] MS (EI, 70 eV): *m*/*z* (%) = 152 (8.6) [M^+], 119 (56) [M^+ − PH_2], 95 (10) [$HSi(PH_2)_2^+$] 91 (100) [$EtSi(H)PH_2^+$], 63 (42) [$H_2Si(PH_2)_2^+$].

2: iPr_2SiCl_2 (7.4 g, 0.04 mol) was added to 100 mL of a 0.25 M solution of $[NaAl(PH_2)_4]$ in DME at −50 °C. The reaction mixture was then warmed up to room temperature over a period of 16 hours. Subsequently 100 mL pentane was added and the yellow precipitate removed by filtration. Finally, the solvent was distilled off under reduced pressure at room temperature and the residue was distilled under vacuum to give **2** as a colourless, pyrophoric liquid at 90−100 °C (25 Torr). Yield: 5.0 g (70%). ^1H NMR (C_6D_6): δ = 1.050 (s, 14 H, *i*Pr), 1.367 (m/d, $^1J_{P,H} \approx$ 190 Hz, 4 H, PH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.2 [t $^2J_{C,P}$ = 6.3 Hz, $CH(CH_3)_2$], 18.6 (t $^3J_{C,P}$ = 2.2 Hz, CH_3) ppm. ^{31}P NMR (C_6D_6): δ = −254.2 (t, $^1J_{PH} \approx$ −190 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 180 (24) [M^+], 147 (100) [M^+ − PH_2], 105 (65 [$iPrSi(H)PH_2^+$], 43 (12.5) [iPr^+].

3: $AlEt_3$ (0.62 g, 5.4 mmol) was added to a stirred solution of $iPr_2Si(PH_2)_2$ (0.5 g, 2.78 mmol) in 20 mL of heptane. After 20 minutes a white precipitate formed. The latter was dissolved by warming the reaction mixture slightly. Compound **3** formed as large colourless crystals within three days at 6 °C. Yield: 0.9 g (96%); $C_{28}H_{72}Al_4P_4Si_2$ (696.9): calcd. C 48.26, H 10.41; found C 48.13, H 10.20. ^1H NMR (C_6D_6): δ = 0.58 (q, $^3J_{H,H}$ = 8.0 Hz, 16 H, CH_2CH_3), 1.14 [d, $^3J_{H,H}$ = 7.5 Hz, 24 H, $CH(CH_3)_2$], 1.46 (t, $^3J_{H,H}$ = 8.0 Hz, 24 H, CH_2CH_3), 1.70 [hep, $^3J_{H,H}$ = 7.5 Hz, 4 H, $CH(CH_3)_2$] ppm; P*H* not observed. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.1 (br. s, CH_2), 10.0 (s, CH_2CH_3), 19.4 [s, $CH(CH_3)_2$], 21.7 [s, $CH(CH_3)_2$] ppm. ^{31}P NMR (C_6D_6): δ = −250.0 (m) ppm. IR (KBr): 2945(vs) cm^{-1}, 2864(vs), 2719(w), 2306(s), 1463(vs), 1411(m), 1388(m), 1366(m), 1221(m), 1070(m), 1020(m), 976(m), 948(m), 918(m), 876(s), 822(w), 667(m), 625(s), 572(m), 537(m), 495(s), 405(s). MS (EI, 70 eV, 190 °C): *m*/*z* (%) = 695 (4) [M^+ − H], 667 (74) [M^+ − Et], 581 (13) [M^+ − iPr_2Si − H], 553 (95) [M^+ − iPr_2Si − Et], 467 (6) [M^+ − $2iPr_2Si$ − H], 523 (33) [M^+ − iPr_2Si − H − 2Et], 319 (44) [$M/2^+$ − Et], 114 (61) [iPr_2Si^+], 85 (100) [Et_2Al^+].

4: $GaEt_3$ (0.85 g, 5.4 mmol) was added to a stirred solution of $iPr_2Si(PH_2)_2$ (0.5 g, 2.78 mmol) in 20 mL of heptane. After 20 mi-

nutes a white precipitate formed. The latter was dissolved by warming the reaction mixture slightly. Compound **4** formed as large colourless crystals within three days at 6 °C. Yield: 1.1 g (94%); $C_{28}H_{72}Ga_4P_4Si_2$ (867.8): calcd. C 38.75, H 8.36; found C 38.45, H 8.40. ^{1}H NMR (C_6D_6): δ = 1.03 (q, $^3J_{H,H}$ = 8.0 Hz, 16 H, CH_2CH$_3$), 1.19 [d, $^3J_{H,H}$ = 7.5 Hz, 24 H, CH(CH_3)$_2$], 1.47 (t, $^3J_{H,H}$ = 8.0 Hz, 24 H, CH$_2$CH_3), 1.72 [hep, $^3J_{H,H}$ = 7.5 Hz, 4 H, CH(CH$_3$)$_2$] ppm; PH not observed. ^{13}C{^{1}H} NMR (C_6D_6): δ = 8.3 (br. s, CH$_2$), 11.4 (s, CH$_2$$CH_3$), 19.4 [s, CH($CH_3$)$_2$], 21.6 [s, CH(CH$_3$)$_2$] ppm. ^{31}P NMR (C_6D_6): δ = −244.2 (m) ppm. IR (KBr): 2945(vs) cm^{-1}, 2894(s), 2861(vs), 2813(w), 2721(w), 2305(s), 1459(s), 1421(m), 1388(m), 1365(m), 1286(vw), 1227(vw), 1183(w), 1070(m), 1019(s), 999(vs), 955(m), 931(vw), 917(w), 875(s), 816(w), 665(s), 631(m), 564(m), 544(m), 496(vs). MS (EI, 70 eV, 170 °C): m/z (%) = 837 (1) [M$^+$ − Et], 681 (2) [(Et$_2$Ga)$_4$(PH)$_4$$iPr^+$], 292 (100) [($iPr_2$SiPH)$_2^+$].

5: InEt$_3$ (1.1 g, 5.4 mmol) was added to a stirred solution of iPr$_2$Si(PH$_2$)$_2$ (0.5 g, 2.78 mmol) in 20 mL of heptane. After 20 minutes a white precipitate formed. The latter was dissolved by warming the reaction mixture slightly. Compound **3** formed as large colourless crystals within three days at 6 °C. Yield: 0.8 g (55%); $C_{28}H_{72}In_4P_4Si_2$ (1048.2): calcd. C 32.08, H 6.92; found C 31.15, H 6.83. ^{1}H NMR (C_6D_6): δ = 1.215 (m, overlap of iP, 44 Hr, CH_2CH$_3$), 1.656 (t, $^3J_{H,H}$ = 8.1 Hz, 24 H, CH$_2$CH_3) ppm; PH not observed. ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.2 (br. s, CH$_2$), 13.7 (s, CH$_2$$CH_3$), 19.5 [s, CH($CH_3$)$_2$], 23.3 [s, CH(CH$_3$)$_2$] ppm. ^{31}P NMR (C_6D_6): δ = −273.5 (m) ppm. IR (KBr): 2944(vs) cm^{-1}, 2862(vs), 2817(w), 2722(w), 2303(s), 1462(vs), 1420(w), 1386(w), 1373(m), 1246(vw), 1225(m), 1158(s), 1070(m), 1019(w), 996(m), 956(m), 918(m), 877(s), 660(w), 634(vs), 560(w), 506(s), 492(s), 396(m).

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[6] CCDC-210253 (**3**), -210254 (**4**) and -201083 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

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