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Synthesis and Metallation of the Diphosphanylsilane *i*$Pr_2Si(PHMe)_2$

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The reaction of $[LiAl(PHMe)_4]$ with *i*Pr_2SiCl_2 yields the dialkyldiphosphanylsilane *i*$Pr_2Si(PHMe)_2$ (**1**). This compound is formed as a diastereomeric mixture and was identified by NMR spectroscopy and mass spectrometry. Silane **1** reacts with $[Sn\{N(SiMe_3)_2\}_2]$ and $[Zn\{N(SiMe_3)_2\}_2]$ to form the polycyclic compounds $[Sn\{SnN(SiMe_3)_2\}_2\{iPr_2Si(PMe)_2\}_2]$ (**2**) and $[\{ZnN(SiMe_3)_2\}_3\{iPr_2Si(PMe)_2\}_2H]$ (**3**), respectively. The tricyclic compound **2** possesses one Sn–Sn bond and contains tin atoms in the formal oxidation states +1, +2 and +3. The central structural motif of the zinc–phosphorus cluster **3** is a $Zn_3P_4Si_2$ cage. The compounds $[iPr_2Si\{P(Me)MEt_2\}_2]_2$ (**4**: M = Al; **5**: M = Ga), which feature an adamantane-like cage formed by four metal, four phosphorus and two silicon atoms can be obtained by the reaction of **1** with MEt_3 (M = Al, Ga). (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

In the last few years reactions of primary silylphosphanes or -arsanes (R_3SiEH_2; E = P, As) with amide or alkyl compounds of different main- and subgroup metals have been applied several times to synthesise metal–phosphorus and metal–arsenic compounds.[1–3] Cyclic and cage-like species were obtained by these reactions. The molecular structures of the reaction products can be influenced by the silyl groups attached to the P or As atom. The reactions of $[Sn\{N(SiMe_3)_2\}_2]$ with R_3SiEH_2 (E = P, As) serve as an example. Thus, the hexagonal-prismatic compounds $[SnESiiPr_3]_6$ (E = P, As) are formed starting from *i*Pr_3SiEH_2, whereas the reaction of *t*Bu_3SiPH_2 with $[Sn\{N(SiMe_3)_2\}_2]$ yields the heterocubane $[SnPSitBu_3]_4$.[2] Recently, it was shown that the diisopropyldiphosphanylsilane *i*$Pr_2Si(PH_2)_2$ is a very promising starting compound for the formation of novel ternary clusters. For example, it reacts with MEt_3 (M = Al, Ga, In) to form the ternary compounds $[iPr_2Si\{P(H)MEt_2\}_2]_2$ (M = Al, Ga, In), which exhibit an $M_4P_4Si_2$ adamantane cage as the central structural motif.[3] In this paper, the synthesis of the new diphosphanylsilane *i*$Pr_2Si(PHMe)_2$ and its reactions with the metal amides $[Sn\{N(SiMe_3)_2\}_2]$ and $[Zn\{N(SiMe_3)_2\}_2]$, as well as with the alkyl compounds $AlEt_3$ and $GaEt_3$, are described.

Results and Discussion

A solution of $[LiAl(PHMe)_4]$ in DME was treated with *i*Pr_2SiCl_2 and furnished the dialkyldiphosphanylsilane *i*$Pr_2Si(PHMe)_2$ (**1**) in about 30% yield. Because of the high inversion barrier of the phosphorus atoms, compound **1** forms as a diastereomeric mixture. Therefore, the $^{31}P\{^1H\}$ NMR spectrum of **1** shows two singlet signals at $\delta = -190.2$ and -193.1 ppm. Two triplets at δ = 19.3 and 21.3 ppm, with $^1J_{Si,P}$ coupling constants of 44 and 45 Hz, can be observed in the $^{29}Si\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum, the signals of the diastereomers are superposed. One can observe a multiplet for the methyl groups at δ = 0.93 ppm, a multiplet for the isopropyl groups at δ = 1.06 ppm, and a quadruplet of doublets for the PH protons at δ = 2.20 ppm. The phosphorus-decoupled ^1H NMR spectrum shows two doublets at δ = 0.94 and 0.93 ppm for the methyl groups, with $^3J_{H,H}$ coupling constants of 7.4 Hz. The mass spectrum of **1** shows the molecular peak at *m*/*z* = 208, as well as peaks for the fragments $[M^+ - Me]$, $[M^+ - PHMe]$ and $[M^+ - C_3H_6]$.

Compound **1** reacts with $[Sn\{N(SiMe_3)_2\}_2]$ in heptane to give a red solution from which orange crystals can be obtained at –35 °C. An X-ray crystal structure determination revealed that $[Sn\{SnN(SiMe_3)_2\}_2\{iPr_2Si(PMe)_2\}_2]$ (**2**) (Figure 1) has been formed.[4] This compound shows a polycyclic $Sn_3P_4Si_2$ core structure, which is formed by two Sn_2P_2Si rings and one Sn_2P_2 ring. Two of the tin atoms bear one $N(SiMe_3)_2$ substituent each, whereas the central tin atom has no exocyclic ligands. Remarkably, a tin–tin bond [Sn(1)–Sn(3)] appears in the molecular structure of **2**, hence compound **2** contains three electronically different tin atoms.[5] The ^{119}Sn Mössbauer spectrum (recorded at 77 K with a $BaSnO_3$ source) could be fitted with six Lorentzian lineshape components at 4.0, 3.3, 2.5, 2.1, 1.6, and

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1.3 mm s^{-1} with approximately equal intensities. The linewidths of these components (0.8 mm s^{-1}) are close to the expected natural linewidth. These six Lorentzians most likely comprise three spectral components that are split into doublets by nuclear electronic quadrupolar interactions with the spin 3/2 nuclear excited state of ^{119}Sn, consistent with the expectation of three distinct crystallographic sites. As there is currently no body of suitable reference data, we cannot identify the specific sets of lines making up these three quadrupolar doublets with certainty. In view of the crystallographic information, it appears plausible, however, to group these six lines into one doublet centred near 1.5 mm s^{-1}, characterised by a rather small quadrupolar splitting [this doublet is most likely assignable to the four-coordinate Sn(3) site], and two doublets having relatively large quadrupolar splittings, which are assigned to the three-coordinate Sn(1) and Sn(2) sites. While we cannot specify isomeric shifts and quadrupolar splitting parameters of Sn(1), Sn(2) and Sn(3) beyond doubt at the present time, we can nevertheless conclude that the Mössbauer spectrum is consistent with the proposed structure.

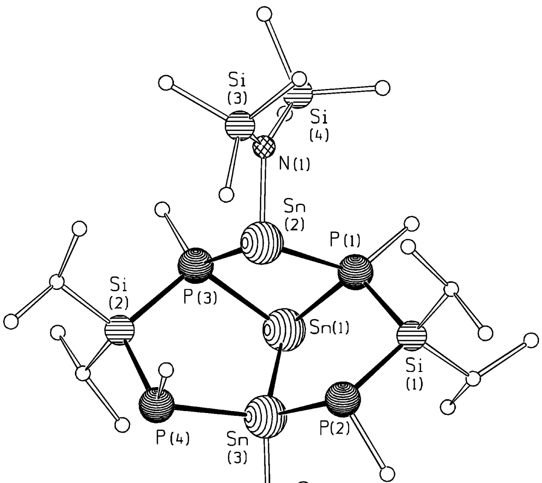

Figure 1. Molecular structure of **2**. Selected bond lengths [pm] and angles [°]: Sn(1)–Sn(3) 288.1(1), Sn(1)–P(1) 263.2(1), Sn(1)–P(3) 261.5(1), Sn(2)–N(1) 210.6(4), Sn(2)–P(1) 266.9(1), Sn(2)–P(3) 270.1(1), Sn(3)–N(2) 210.4(3), Sn(3)–P(2) 256.1(1), Sn(3)–P(4) 256.9(1), Si(1)–P(1) 226.4(1), Si(1)–P(2) 226.8(1), Si(2)–P(3) 226.8(2), Si(2)–P(4) 224.8(2); P(1)–Sn(1)–Sn(3) 84.66(3), P(3)–Sn(1)–Sn(3) 86.03(3), P(1)–Sn(1)–P(3) 84.47(3), P(2)–Sn(3)–P(4) 107.93(4), P(2)–Sn(3)–Sn(1) 111.26(3), P(4)–Sn(3)–Sn(1) 110.33(3), P(1)–Sn(2)–P(3) 82.12(4), P(1)–Si(1)–P(2) 105.73(5), P(3)–Si(2)–P(4) 111.33(3), Sn(1)–P(1)–Sn(2) 93.46(4), Si(1)–P(2)–Sn(3) 101.16(5), Sn(1)–P(3)–Sn(2) 93.09(3), Si(2)–P(4)–Sn(3) 100.13(5).

In the ^{31}P{^{1}H} NMR spectrum of **2** one signal with one pair of Sn satellites at δ = –181.5 ppm ($^1J_{P,Sn}$ = 948 Hz), which corresponds to P(2) and P(4), and another signal with two pairs of Sn satellites at δ = –176.6 ppm ($^1J_{P,Sn}$ = 1105 and 935 Hz), which corresponds to P(1) and P(3), can be observed. The ^{117}Sn NMR spectrum shows three broad signals with a triplet structure at δ = 39, 172 and 290 ppm.

The Sn(1)–Sn(3) bond length of 288.1 pm is within the usual range for Sn–Sn single bonds; the Sn–P bonds in compound **2** are between 256.1 and 266.9 pm. In the mixed-valence Sn/P cluster [$Sn_8(PSi$*i*$Pr_3)_6Cl_2$] described recently, the Sn–Sn bonds are in the range 283.4–288.8 pm and the Sn–P bonds are in the range 253.8–272.8 pm.[6]

The reaction of **1** with the zinc amide [$Zn\{N(SiMe_3)_2\}_2$] in heptane yields a colourless solution from which crystals of [$\{ZnN(SiMe_3)_2\}_3\{$*i*$Pr_2Si(PMe)_2\}_2H$] (**3**) can be obtained. Compound **3** crystallises in the orthorhombic space group $Pna2_1$ and was refined as an inversion twin (Figure 2). The molecular structure contains a heavily folded six-membered Zn_3P_3 ring. Each zinc atom binds to one exocyclic $N(SiMe_3)_2$ substituent, and each phosphorus atom bears one methyl group. Two of the phosphorus atoms [P(1) and P(2)] of this ring are further connected by an Si*i*Pr_2 group to form a four-membered ZnP_2Si ring. The third phosphorus atom [P(3)] binds to an Si*i*Pr_2PHMe fragment. The phosphorus atom of this PHMe group [P(4)] coordinates the opposite zinc atom of the ring [Zn(1)]. Therefore, Zn(1) has a coordination number of four, whereas Zn(2) and Zn(3) have a trigonal-planar coordination. Due to the lower coordination, the Zn–P and Zn–N bonds at Zn(2) and Zn(3) are significantly shorter than to Zn(1) [Zn(1)–P = 246.6–250.1 ppm, Zn(1)–N = 192.3 pm, Zn(2,3)–P = 234.9–241.2 ppm, Zn(2,3)–N = 189.8 and 189.2 pm]. In the zinc–phosphorus ring compound [$MeZn\{\mu\text{-}P(SiMe_3)_2\}]_3$, in which the coordination of all Zn atoms is trigonal-planar, the Zn–P bonds are, on average, 238 pm long.[7] The ring compound [$Zn_2Cl_2\{\mu\text{-}P(SiMe_3)_2\}_2(P$*n*$Pr_3)_2$] shows Zn atoms with coordination number four due to the coordination of additional phosphane ligands. In this compound, the Zn–P(μ_2) bonds are 242.6 to 244.7 pm long, whereas the terminal Zn–P bonds amount to 240.8–243.0 pm.[8] The hydrogen atom at P(4) could not be satisfactorily fitted in the difference map; however, the ^{1}H and ^{31}P NMR spectra of **3** give clear evidence for the presence of a hydrogen atom. Beside the signals of the PMe, $SiMe_3$ and Si*i*Pr_2 groups, the ^{1}H NMR spectrum shows a weak doublet of multiplets with a $^1J_{P,H}$ coupling constant of 270 Hz; in the ^{1}H{^{31}P} NMR spectrum this signal appears as a quadruplet with a $^3J_{H,H}$ coupling constant of 7.5 Hz. In the ^{31}P{^{1}H} NMR spectrum four multiplets for the four different phosphorus atoms in **3** can be observed in the range from δ = –150 to –200 ppm (ABCD spin system). In the ^{31}P NMR spectrum the signal at δ = –155 ppm is further split by a $^1J_{P,H}$ coupling (see Figure 3a,b), therefore this signal can be assigned to P(4). Quantum chemical calculations with the Turbomole program package were applied to allocate the three remaining multiplets to specific P atoms. The method applied was DFT with the BP86 functional and a TZVPP basis set for all atoms;[9,10] for performance reasons the resolution-of-identity (RI) approximation was used.[11] The reference for the chemical shifts was H_3PO_4, computed with the same parameters as were used for the cluster. Those calculations that gave chemical shifts closest to the experimental values were performed as single-point calculations with the geometry obtained from the X-ray structure analysis. As the position of the hydrogen atom at P(4) could not be determined by the experiment, its distance to the phosphorus atom was varied systematically. Geometry optimisations with different basis sets led to deviations from the experimental values of about δ = 15–30 ppm, although the order of peaks for P(1), P(2) and P(3) was always retained. For a given geometry of the cluster, the shift of P(4) is extremely sensitive to the P–H distance and the H–P–C bond angle. Thus, the correct combination of distance and angle could not definitely be fixed. The best agreements were achieved for a distance of about 150 pm at an angle of 100°. The resulting chemical shifts are given in Table 1.

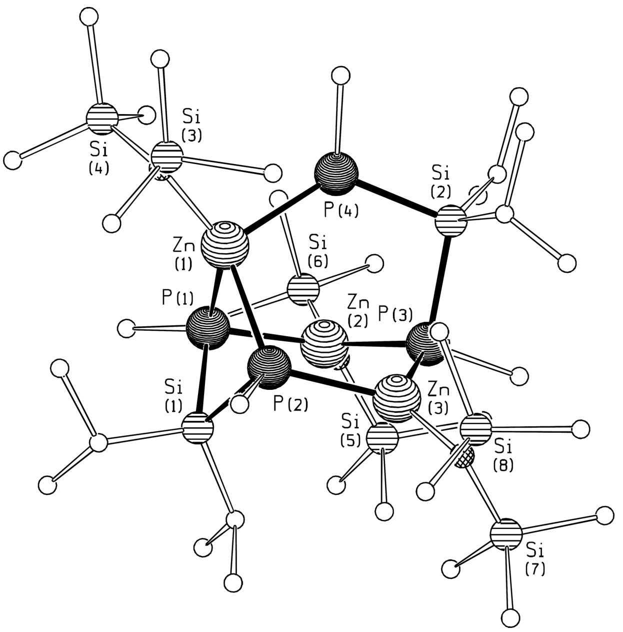

Figure 2. Molecular structure of **3**. Selected bond lengths [pm] and angles [°]: Zn(1)–P(1) 250.1(2), Zn(1)–P(2) 246.6(3), Zn(1)–P(4) 249.5(4), Zn(1)–N(1) 192.3(7), Zn(2)–P(1) 236.7(2), Zn(2)–P(2) 241.2(2), Zn(2)–N(2) 189.8(6), Zn(3)–P(2) 234.9(3), Zn(3)–P(3) 238.8(2), Zn(3)–N(3) 189.2(6), P(1)–Si(1) 224.6(4), P(2)–Si(1) 227.4(4), P(3)–Si(2) 224.2(3), P(4)–Si(2) 219.5(5); P(1)–Zn(1)–P(2) 81.13(8), P(1)–Zn(1)–P(4) 95.47(13), P(2)–Zn(1)–P(4) 109.15(12), P(1)–Zn(2)–P(3) 109.66(8), P(2)–Zn(3)–P(3) 106.56(8), Si(1)–P(1)–Zn(2) 106.42(12), Si(1)–P(1)–Zn(1) 87.65(10), Si(1)–P(2)–Zn(3) 107.44(12), Si(1)–P(2)–Zn(1) 87.88(11), Si(2)–P(3)–Zn(3) 103.96(11), Si(2)–P(4)–Zn(1) 124.61(18), P(1)–Si(1)–P(2) 91.21(12), P(3)–Si(2)–P(4) 102.54(14).

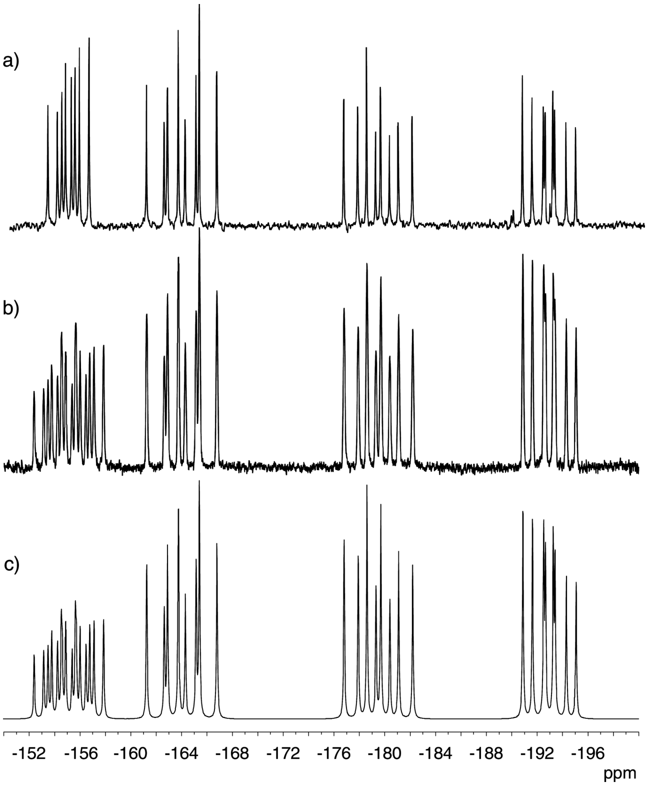

Figure 3. ^{31}P NMR spectra of **3** (C_6D_6): a) experimental ^{31}P{^{1}H} NMR spectrum; b) experimental ^{31}P NMR spectrum; c) simulated ^{31}P NMR spectrum.

Table 1. Calculated and experimental ^{31}P chemical shifts for compound **3**.

	P(1)	P(2)	P(3)	P(4)
Calculated	–157	–171	–190	–151
Experimental	–164	–179	–193	–155

A complete analysis of the ^{31}P NMR spectrum by an iterative optimisation of the coupling constants yielded the values $J_{P1,P2}$ = 302.4, $J_{P1,P3}$ = 202.4, $J_{P1,P4}$ = 168.8, $J_{P2,P3}$ = 217.3, $J_{P2,P4}$ = 134.1, $J_{P3,P4}$ = 93.2 Hz and $^1J_{P4,H}$ = 272.7 Hz; the simulated spectrum is shown in Figure 3c.[12]

Compound **1** reacts with MEt$_3$ (M = Al, Ga) in heptane at ambient temperature with elimination of ethane. Recrystallisation from benzene yielded colourless crystals of the composition [*i*Pr$_2$Si{P(Me)MEt$_2$}$_2$]$_2$·2C$_6$H$_6$ (**4**: M = Al; **5**: M = Ga). The molecular structures of **4** and **5** (Figure 4) are almost identical to the compounds [*i*Pr$_2$Si{P(H)-MEt$_2$}$_2$]$_2$ (M = Al, Ga, In), described recently, but with methyl groups bound to the phosphorus atoms instead of hydrogen atoms.[3] The central structural motif is an adamantane-like cage of four aluminium or gallium atoms, four phosphorus and two silicon atoms. 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$_4$P$_4$ (M = Al, Ga) ring where the opposite phosphorus atoms [P(1), P(3) and P(2), P(4)] are bridged by *i*Pr$_2$Si groups on different sides of the ring. The M$_4$P$_4$ ring is therefore strongly distorted and shows a boat-like conformation. The observed P–M and P–Si bond lengths are in the typical range for single bonds between these elements [**4**: Al–P = 242.8(1)–244.3(1), P–Si = 228.5(1)–228.8(1) pm; **5**: Ga–P = 241.5(1)–243.5(1), P–Si = 228.2(2)–229.3(2) pm]. Each of the metal atoms is bound to two exocyclic ethyl groups, and the silicon atoms possess two isopropyl groups each.

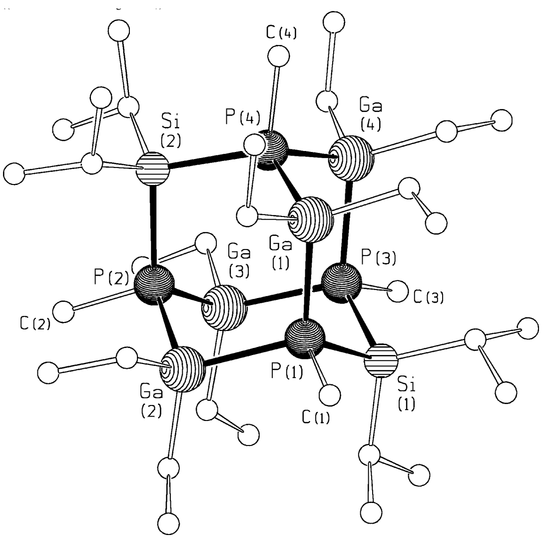

Figure 4. Molecular structure of **5**. Selected bond lengths [pm] and angles [°]: Ga(1)–P(1) 243.5(1), Ga(1)–P(4) 241.5(1), Ga(2)–P(1) 242.1(1), Ga(2)–P(2) 242.2(1), Ga(3)–P(2) 242.0(1), Ga(3)–P(1) 241.5(1), Ga(4)–P(3) 242.4(1), Ga(4)–P(4) 241.5(1), P(1)–Si(1) 228.7, P(3)–Si(1) 228.9(2), P(2)–Si(2) 229.3(2), P(4)–Si(2) 228.2(2); Si–P–Ga 114.23(6)–115.63(6), Ga–P–Ga 109.32(5)–110.28(5), P–Ga–P 110.47(5)–101.24(4).

Experimental Section

General: All manipulations were performed under nitrogen, with rigorous exclusion of oxygen and moisture, using a Schlenk line. Solvents were dried and freshly distilled before use. NMR spectra were recorded with a Bruker DPX Avance 300 or with a Bruker AC 250 instrument. [LiAl(PHMe)$_4$] and GaEt$_3$ were prepared according to the literature.[13] AlEt$_3$, [Sn{N(SiMe$_3$)$_2$}$_2$] and [Zn{N(SiMe$_3$)$_2$}$_2$] were obtained from Aldrich and used as received. Crystallographic data of **2**–**5** are shown in Table 2.[4]

1: *i*Pr$_2$SiCl$_2$ (3.0 g, 0.016 mol) was added to 50 mL of a 0.16 M solution of [LiAl(PHMe)$_4$] in DME at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. Subsequently, pentane (50 mL) was added and the yellow precipitate was removed by filtration. Finally, the solvent was distilled off under reduced pressure at room temperature and the residue was distilled under vacuum. Compound **1** was obtained as a colourless liquid at 40 °C (10^{-3} mbar). Yield: 1.0 g (32%). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ = 0.93 (d, $^3J_{H,H}$ = 7.4 Hz, 6 H, P–Me), 0.94 (d, $^3J_{H,H}$ = 7.4 Hz, 6 H, P–Me), 1.15 (m, 14 H, *i*Pr), 2.20 (qd, $^3J_{H,H}$ = 7.4, $^1J_{P,H}$ ≈ 194 Hz, 2 H, P–H) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = –3.2 (m, P–Me), 14.0 [m, *C*H(CH$_3$)$_2$], 19.4 [s, CH(*C*H$_3$)$_2$] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = 19.3 (t, $^1J_{P,Si}$ = 44 Hz), 21.3 (t, $^1J_{P,Si}$ = 45 Hz) ppm. ^{31}P NMR (C$_6$D$_6$): δ = –190.2 (d, $^1J_{P,H}$ = 194 Hz), –193.1 (d, $^1J_{P,H}$ = 195 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 208 (90) [M$^+$], 193 (10) [M$^+$ – Me], 161 (80) [M$^+$ – PHMe], 119 (100) [M$^+$ – C$_3$H$_6$], 43 (60) [*i*Pr$^+$].

2: [Sn{N(SiMe$_3$)$_2$}$_2$] (0.51 g, 1.15 mmol) was added to a solution of *i*Pr$_2$Si(PHMe)$_2$ (0.12 g, 0.58 mmol) in heptane (5 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. During this time the colour of the solution changed from orange to red, and small amounts of a precipitate appeared. After filtration, the solution was cooled to –35 °C. Orange crystals of compound **2** appeared within 2 d. Yield: 0.25 g (79%). C$_{28}$H$_{76}$N$_2$P$_4$Si$_6$Sn$_3$ (1089.4): calcd. C 30.87, H 7.03, N 2.57; found C 30.91, H 7.05, N 2.44. ^{1}H NMR (C$_6$D$_6$): δ = 0.51 [s, 18 H, N(SiMe$_3$)$_2$], 0.58 (s, 9 H, SiMe$_3$), 0.80 (s, 9 H, SiMe$_3$), 1.07–1.33 (m, 28 H, *i*Pr), 1.83 (d, $^2J_{P,H}$ = 5.0 Hz, 6 H, PMe), 1.96 (d, $^2J_{P,H}$ = 8.1 Hz, 6 H, PMe) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene, 50 °C): δ = –176.6 (br.), –181.5 (br.) ppm. ^{117}Sn{^{1}H} NMR (C$_6$D$_6$): δ = 39 (t, $^1J_{Sn,P}$ ≈ 1000 Hz), 172 (t, $^1J_{Sn,P}$ ≈ 935 Hz), 290 (t, $^1J_{Sn,P}$ ≈ 1340 Hz) ppm.

3: [Zn{N(SiMe$_3$)$_2$}$_2$] (0.22 g, 0.57 mmol) was added to a solution of *i*Pr$_2$Si(PHMe)$_2$ (0.06 g, 0.29 mmol) in 5 mL of heptane at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The solution was then cooled to 6 °C. Colourless crystals of **3** appeared after 2 d. Yield: 0.13 g (62%). C$_{34}$H$_{95}$N$_3$P$_4$Si$_8$Zn$_3$ (1090.9): calcd. C 37.44, H 8.78, N 3.85; found C 37.10, H 8.51, N 3.69. ^{1}H{^{31}P} NMR ([D$_8$]toluene): δ = 0.27 [s, 18 H, Si(C*H*$_3$)$_3$],

Table 2. Crystallographic data of **2**–**5**.[4]

Compound	**2**	**3**	**4**	**5**
Empirical formula	C$_{28}$H$_{76}$N$_2$P$_4$Si$_6$Sn$_3$	C$_{34}$H$_{94}$N$_3$P$_4$Si$_2$Zn$_3$	C$_{32}$H$_{80}$P$_4$Al$_4$Si$_2$·2C$_6$H$_6$	C$_{32}$H$_{80}$P$_4$Ga$_4$Si$_2$·2C$_6$H$_6$
Space group	$P2_1/n$	$Pna2$	$P\bar{1}$	$P\bar{1}$
Formula units	4	4	2	2
Temperature [K]	200	200	200	200
a [pm]	1259.4(3)	2861.1(6)	1119.1(2)	1120.1(2)
b [pm]	1591.0(3)	1584.0(3)	1354.3(3)	1357.2(3)
c [pm]	2529.3(5)	1335.2(3)	1864.5(4)	1868.3(4)
α [°]	90	90	81.83(2)	81.86(3)
β [°]	98.28(3)	90	86.41(3)	86.28(3)
γ [°]	90	90	86.52(4)	86.79(3)
Volume [10^6 pm^3]	5015.1(7)	6051(2)	2787.9(10)	2802.5(10)
Density [gcm^{-3}]	1.443	1.196	1.083	1.280
2Θ range [°]	3–52	4–45	3–50	3–54
Reflections measured	22665	24840	11927	14814
Independent reflections	9721 (R_{int} = 0.0422)	7875 (R_{int} = 0.0362)	8231 (R_{int} = 0.0545)	10439 (R_{int} = 0.0708)
Independent reflections with $F_o > 4\sigma(F_o)$	8409	7166	5835	7432
Parameters	388	470	487	487
μ(Mo-K_α) [mm^{-1}]	1.774	1.468	0.268	2.086
Flack parameter	–	0.514	–	–
R_1	0.0373	0.0574	0.0555	0.0657
wR_2 (all data)	0.1073	0.1603	0.1601	0.1792
Residual electron density [e/Å^3]	2.170	1.446	0.378	0.647

0.31 [s, 36 H, Si(CH_3)$_3$], 1.19 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3PH), 1.20–1.35 (m, 28 H, Si*iPr*$_2$), 1.46 (s, 3 H, CH_3P), 1.50 (s, 3 H, CH_3P), 151 (s, 3 H, CH_3P), 3.03 (q, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH$_3$P*H*) ppm. ^{29}Si{^{1}H} NMR ([D$_8$]toluene): δ = –4.9 (s, SiMe$_3$), –4.5 (s, SiMe$_3$), –3.9 (s, SiMe$_3$), 2.1 (s, Si*i*Pr$_2$) ppm. ^{31}P{^{1}H} NMR ([D$_8$]-toluene): δ = –154 (m), –164 (m), –179 (m), –193 (m) ppm. Raman: $\tilde{\nu}$ = 2950 (s), 2918 (s), 2899 (vs), 2342 (w), 1461 (w), 1230 (w), 879 (w), 681 (m), 627 (m), 467 (w), 397 (m), 180 (m), 114 (m) cm^{-1}.

4: A solution of AlEt$_3$ (1.2 mL, 1.0 M) in hexane (1.2 mmol) was added, with stirring, to a solution of *i*Pr$_2$Si(PHMe)$_2$ (0.13 g, 0.60 mmol) in heptane (5 mL). After 16 h, all volatile compounds were removed under vacuum. Recrystallisation of the residue from 2 mL of benzene yielded **4**·2C$_6$H$_6$ as large, colourless crystals within 3 d. Yield: 0.18 g (66%). C$_{32}$H$_{80}$Al$_4$P$_4$Si$_2$ (909.16): calcd. C 51.04, H 10.71; found C 50.03, H 10.58. ^{1}H NMR (C$_6$D$_6$): δ = 0.73 (q, $^3J_{H,H}$ = 7.8 Hz, 16 H, CH_2CH$_3$), 1.33 [d, $^3J_{H,H}$ = 7.5 Hz, 24 H, CH(CH_3)$_2$], 1.56 (m, 36 H, CH$_2$CH_3, PCH_3), 1.70 [sept, $^3J_{H,H}$ = 7.5 Hz, 4 H, C*H*(CH$_3$)$_2$] ppm. ^{31}P NMR (C$_6$D$_6$): δ = –181.3 (s) ppm.

5: GaEt$_3$ (0.18 g, 1.16 mmol) was added, with stirring, to a solution of *i*Pr$_2$Si(PHMe)$_2$ (0.123 g, 0.58 mmol) in heptane (5 mL). After 16 h, all volatile compounds were removed under vacuum. Recrystallisation of the residue from 2 mL of benzene yielded **5**·2C$_6$H$_6$ as large, colourless crystals within 3 d. Yield: 0.20 g (64%). C$_{32}$H$_{80}$Ga$_4$P$_4$Si$_2$ (1080.1): calcd. C 41.60, H 8.73; found C 42.67, H 8.92. ^{1}H NMR (C$_6$D$_6$): δ = 1.15 (q, $^3J_{H,H}$ = 7.2 Hz, 16 H, CH_2CH$_3$), 1.36 [d, $^3J_{H,H}$ = 7.5 Hz, 24 H, CH(CH_3)$_2$], 1.60 (m, 36 H, CH$_2$CH_3, PCH_3), 2.20 [sept, $^3J_{H,H}$ = 7.5 Hz, 4 H, C*H*(CH$_3$)$_2$] ppm. ^{31}P NMR (C$_6$D$_6$): δ = –167.2 (s) ppm.

Supporting Information (see footnote on the first page of this article): Details about the ^{119}Sn Mössbauer spectrum of compound **2**.

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