Synthesis and Characterisation of Novel Main Group Element Clusters with Tin-Phosphorus, Tin-Arsenic, and Germanium-Phosphorus Skeletons

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The reaction of $i\mathrm{Pr_3SiPLi_2}$ with $\mathrm{SnCl_2}$ in the mol ratio 1:1 leads to the formation of $[\mathrm{Sn_7(PSi}i\mathrm{Pr_3)_7}]$ (**1**). The cluster $[\mathrm{Sn_8(PSi}i\mathrm{Pr_3)_6Cl_2}]$ (**3**) is obtained, if the same reaction is carried out with a slight excess of the metal salt. Similar lithium chloride elimination reactions between $\mathrm{SnCl_2}$ and $i\mathrm{Pr_3SiAsLi_2}$ in the mol ratio 1:1 and 2:3, however, yield $[\mathrm{Sn_7(AsSi}i\mathrm{Pr_3)_7}]$ (**2**) and $[\mathrm{Sn_4(AsSi}i\mathrm{Pr_3)_6Li_4(Et_2O)_2}]$ (**4**), respectively. The metal salt $\mathrm{GeCl_2(diox)_2}$ (diox = 1,4-dioxane) reacts with $i\mathrm{Pr_3SiPLi_2}$ to give $[\mathrm{Ge_6(PSi}i\mathrm{Pr_3)_6}]$ (**5**). Compounds **1**–**5** were characterised by NMR and IR spectroscopic techniques as well as elemental analysis. The crystal structures were identified by X-ray diffraction analysis, which confirmed that the heptameric skeletons of **1** and **2** are structurally analogous. The Sn/P cluster **3** contains subvalent tin atoms, while **4** forms a $\mathrm{Sn_4As_6Li_4}$ rhombododecahedron and **5** a slightly distorted hexagonal prism.

Introduction

A survey of coordination chemistry literature reveals that besides investigations into the formation of polynuclear complexes with the participation of transition metals,[1−3] an increasing number of studies are currently devoted to problems of synthesis and characterisation of cluster compounds containing elements from the main groups.[4] For a better understanding of the correlation between size, structure and properties of binary semiconductor compounds, the availability of clusters of different size and structure is of considerable interest. However, the knowledge on 14/15 cluster compounds is still relatively scarce. For the systems Sn/P and Sn/As there are only a few cyclic and cage compounds reported to date.[5,6] Even fewer examples are known for Ge/P compounds.[7]

Different types of starting materials and synthetic methods have been described for the synthesis of tin phosphorus and germanium phosphorus compounds. A convenient method for the formation of Sn−P bonds is the metalation of primary phosphanes $\mathrm{RPH_2}$ (R = $i\mathrm{Pr_3Si}$, $t\mathrm{Bu_3Si}$) with $\mathrm{Sn[N(SiMe_3)_2]_2}$, leading to $[\mathrm{Sn_4(PSi}t\mathrm{Bu_3)_4}]$ and $[\mathrm{Sn_6(PSi}i\mathrm{Pr_3)_6}]$ species.[5b,5c] Salt elimination reactions between $\mathrm{NaAsH_2}$ and $\mathrm{Sn^{IV}}$ compounds such as $t\mathrm{Bu_2SnCl_2}$ have been used for the synthesis of Sn/As compounds.[6a][6c] Recently Fenske and co-workers reported the catalytic transformation of $\mathrm{P(SnMe_3)_3}$ into the Sn/P-cage compound $[\mathrm{P_4(SnMe_2)_6}]$.[5a]

Herein we report on the successful synthesis of new 14/15 compounds with unknown structural motifs. Simple lithium chloride elimination reaction of $i\mathrm{Pr_3SiELi_2}$ (E = P, As) with the metal salts $\mathrm{SnCl_2}$ and $\mathrm{GeCl_2(diox)_2}$ (diox = 1,4-dioxane) was used in these reactions.[8]

Results and Discussion

The reaction of $i\mathrm{Pr_3SiPLi_2}$ with $\mathrm{SnCl_2}$ in the mol ratio 1:1 in $\mathrm{Et_2O}$ yields $[\mathrm{Sn_7(PSi}i\mathrm{Pr_3)_7}]$ (**1**) which can be obtained as red crystals by cooling the reaction mixture to 0 °C. The X-ray analysis revealed that the compound consists of seven Sn atoms and seven $\mathrm{PSi}i\mathrm{Pr_3}$ fragments. **1** crystallises in the trigonal space group $R\bar{3}$.

The cluster can be described as follows: The tin and phosphorus atoms Sn1, Sn1′, Sn1′′ and P1, P2, P2′, P2′′ form a heterocubane, however, the fourth Sn atom is missing. Instead of it the three P atoms P2, P2′, P2′′ are connected to the corresponding Sn atoms (Sn2, Sn2′, Sn2") which also form an incomplete heterocubane together with P3, P3′, P3′′ and Sn3. The Sn−P bonds in **1** are 264.5 pm on average. This value is within the range of lengths typically observed for most of the already known $\mathrm{Sn^{II}}$/P compounds.[5] All of the P centres are coordinated to three tin atoms and one triisopropylsilyl group, forming a very distorted tetrahedral environment. The tin atoms possess no exocyclic ligands and consequently only have a coordination number of three.

The compound $[\mathrm{Sn_7(AsSi}i\mathrm{Pr_3)_7}]$ (**2**) is formed by the reaction of $i\mathrm{Pr_3SiAsLi_2}$ with $\mathrm{SnCl_2}$ (1:1) in diethyl ether as a solvent. The compound crystallises isotypically into **1** (see Figure 1). Therefore its structure will not be discussed in

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detail. The average Sn−As bond lengths are 272.8 pm. The As−Si bond lengths are in the range of 234.5 to 238.7 pm. All values are in the usual range for single bonds between these elements.[6,10]

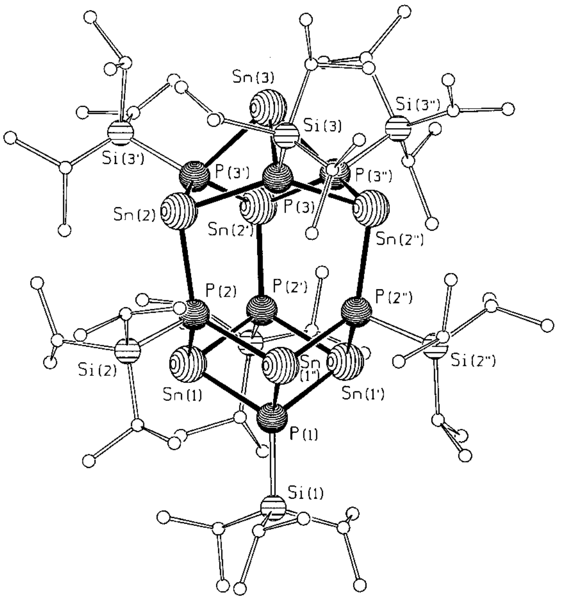

Figure 1. Molecular structure of **1**, selected bond lengths (pm) and angles (°): Sn−P 262.3(3)−265.8(3), Si−P 225.2(6)−228.1(4); Sn−P(1)−Sn 96.2(1), Sn(1)−P(2)−Sn(1′) 96.3(1), Sn(1)/Sn(1′)−P(2)−Sn(2) 123.3(1)−223.9(1), Sn(2)−P(3)−Sn(2′) 133.5(1), Sn(2)/Sn(2′)−P(3)−Sn(3) 90.4(1)−90.6(1), P(1)−Sn(1)−P(2)/P(2′) 83.6(1)−83.8(1), P(2)−Sn(1)−P(2′) 100.6(1), P(2)−Sn(2)−P(3)/P(3′) 101.0(1)−101.3(1), P(3)−Sn(2)−P(3′) 84.5(1), P−Sn(3)−P 83.4(1)

Similar heptameric structures have been found for the related imidoalanes, imidogallanes and phosphinidene-alanes [RMER′]$_7$ (M = Al: E = N, P; M = Ga: E = N).[9]

Surprisingly, when the corresponding reaction between Li$_2$PSi*i*Pr$_3$ and SnCl$_2$ is carried out with a slight excess of the metal salt, the compound [Sn$_8$(PSi*i*Pr$_3$)$_6$Cl$_2$] (**3**) is obtained.

In contrast to **1**, **3** contains an excess of Sn relative to PSi*i*Pr$_3$ groups and possesses two chloride ligands. **3** crystallizes in the monoclinic space group $P2_1/c$. A formal charge of −2 can be assigned to each of the six PSi*i*Pr$_3$ fragments, the two Cl ions contribute one negative charge each. Therefore the total formal negative charge to be compensated amounts to −14. Consequently, the molecule must consist of two types of Sn atoms due to the neutrality of the molecule. The outer Sn atoms (Sn1, Sn2, Sn3, Sn4) are in the +2 oxidation state and account for +8 of the total formal positive charge. The remaining four tin centres (Sn5, Sn6, Sn7, Sn8) compensate with a formal charge of +6, indicating that a reduction process must have taken place. These tin atoms form the structural core and exhibit three Sn−Sn bonds. The middle bond between Sn5 and Sn6 (283.4 pm) is slightly shorter than the adjacent two Sn−Sn bonds (Sn5−Sn7 288.8 pm, Sn6−Sn8 288.0 pm). However they are still in the range of normal tin-tin bonds as found in grey tin (280 pm) or in the tin-phosphorus compound [P$_2$(Sn$_2$Me$_4$)$_3$] (279 pm).[5g] Two of the tin atoms (Sn5 and Sn6) of this four-membered tin fragment are tetrahedrally surrounded by two P and two Sn atoms. Two phosphorus and one tin atom coordinate the other two Sn atoms (Sn7 and Sn8). The outer Sn centres (Sn1, Sn2, Sn3, Sn4) are also three-coordinate due to the coordination of either three phosphorus atoms (Sn3 and Sn4) or two phosphorus atoms and one chloride ligand (Sn1 and Sn2). These Cl ligands are most likely oriented in this asymmetric manner as a result of the sterically demanding *i*Pr$_3$Si moieties and weak bonding interactions between Cl1 and Sn2 (Cl1···Sn2 distance: 303.0 pm). Assuming that the tetrahedrally surrounded Sn atoms (Sn5 and Sn6) contribute four electrons to the cluster framework, the core structure possesses 42 valence electrons for 21 bonds (dark lines in Figure 2) and therefore the cluster is electron precise.

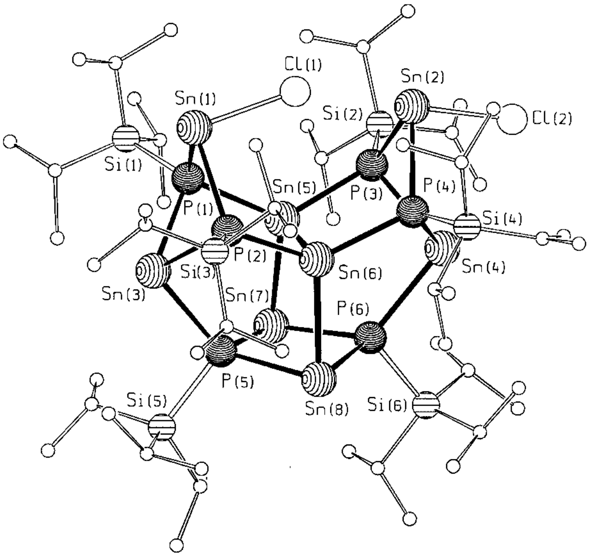

Figure 2. Molecular structure of **3**, selected bond lengths (pm) and angles (°): Sn(5)−Sn(6) 283.4(1), Sn(5)−Sn(7) 288.8(2), Sn(6)−Sn(8) 288.0(2), Sn(1)−Cl(1) 257.2(6), Sn(2)−Cl(2) 255.3(6), Sn−P 253.8(5)−272.8(5), Si−P 226.7(5)−228.3(5); Sn(5)−Sn(6)−Sn(8) 100.10(4), Sn(6)−Sn(5)−Sn(7) 99.05(4)

The rhombododecahedron [Sn$_4$(AsSi*i*Pr$_3$)$_6$Li$_4$(Et$_2$O)$_2$] (**4**, Figure 3) can be isolated if the reaction of SnCl$_2$ with *i*Pr$_3$SiAsLi$_2$ is carried out in the ratio 2:3.

Two four-membered Sn$_2$As$_2$ rings are observed in the molecule. The Sn atoms are three-coordinate. The As atoms reveal a coordination number of five. These rings are bridged by the As centres As3 and As3′. The resulting Sn$_4$As$_6$ skeleton carries a formal charge of −4, which is compensated by four Li counterions. Each Li ion binds to one As atom of the two Sn$_2$As$_2$ rings and to one of the bridging As centres. Li1 and Li1′ are further coordinated by one diethyl ether molecule each. The Sn^{II}−As bonds in **4** are 274.1 pm on average and are therefore longer than the representative Sn^{IV}−As bonds (263.1−261.5 pm) in the ring compounds (*t*Bu$_2$SnAsH)$_2$ and (*t*Bu$_2$SnAsSiMe$_3$)$_2$.[6a,6c] A Sn−As bond length of 270−277 pm, how-

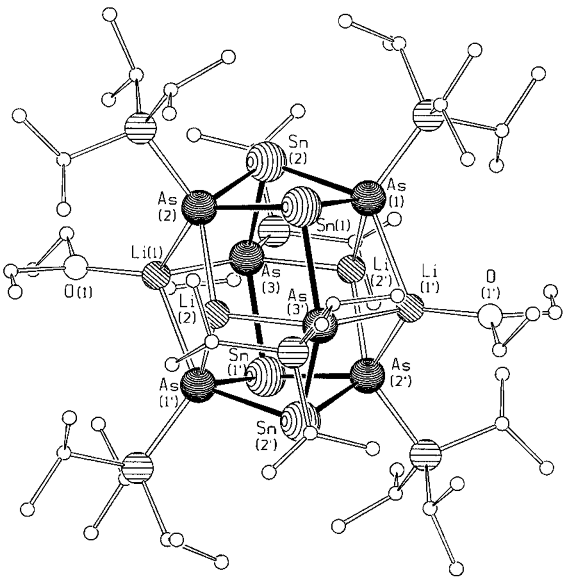

Figure 3. Molecular structure of **4**, selected bond lengths (pm) and angles (°): Sn−As 272.0(4)−278.8(2), As−Si 234.6(3)−236.7(4), As−Li 257(2)−279(2); Sn(1)−As(1)−Sn(2) 85.37(4), Sn(1)−As(2)−Sn(2) 85.44(4) Sn(1′)−As(3)−Sn(2) 137.49(4), As(1)−Sn(1)−As(2) 91.34(4), As(1)−Sn(1)−As(3′) 90.64(5), As(2)−Sn(1)−As(3′) 98.25(4), As(1)−Sn(2)−As(2) 91.86(4), As(1)−Sn(2)−As(3) 99.41(4), As(2)−Sn(2)−As(3) 91.87(4)

ever, can be observed in the cyclic arsanylstannylene [Sn{As(SiMe$_3$)$_2$}$_2$]$_2$ and [Sn(As*t*Bu$_2$)Cl]$_2$ [6d,6e] as well as in **2**. A similar rhombododecahedral structure is observed for the related tin-phosphorus compound [Sn$_4$(PCy)$_6$-{Li(THF)}$_4$] and the aluminium-arsenic compound [(HAl)$_4$-(AsSi*i*Pr$_3$)$_6$Li$_4$(Et$_2$O)$_2$].[11]

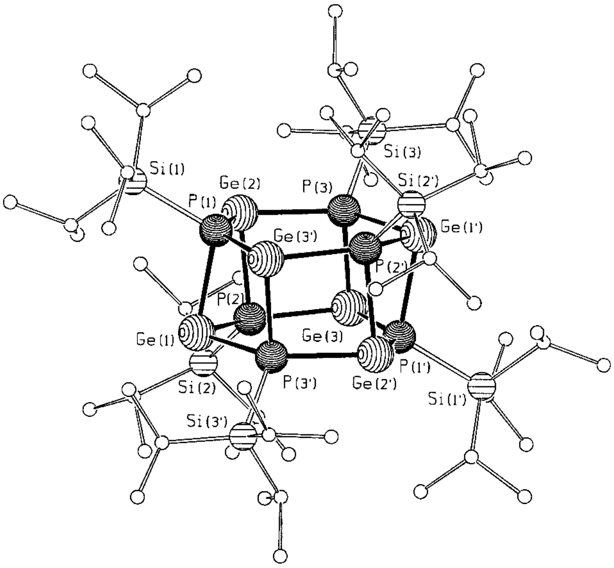

Figure 4. Molecular structure of **5**, selected bond lengths (pm) and angles (°): Ge−P 241.6(2)−248.7(2), P−Si 226.6(3)−227.9(2); Ge−P−Ge(four-membered ring): 90.78(5)−92.69(4), Ge−P−Ge(six-membered ring): 135.14(7)−137.67(9), P−Ge−P(four-membered ring): 85.84(6)−88.83(7), P−Ge−P(six-membered ring): 10071(6)−103.48(6)

[Ge$_6$(PSi*i*Pr$_3$)$_6$] (**5**, Figure 4) is obtained from the reaction of *i*Pr$_3$SiPLi$_2$ with GeCl$_2$(diox)$_2$. The compound crystallises in the triclinic space group $P\bar{1}$ with two independent inversion symmetric molecules in the elementary cell. They differ insignificantly; therefore only one of them will be discussed.

The Ge and P atoms form a distorted hexagonal prism, in which all of the Ge centres are coordinated trigonal-pyramidally by three P atoms. The P atoms are surrounded by one triisopropylsilyl group and three Ge atoms. The average Ge−P distances within each Ge$_3$P$_3$ plane (242.5 pm) are slightly shorter than the corresponding Ge−P distances between the Ge$_3$P$_3$ rings (247.7 pm). These values are larger than the corresponding Ge^{IV}−P distances in [*t*BuMes-GePH]$_2$ (234.6 pm) but shorter than the Ge^{II}−P bonds in [Ge(P*t*Bu$_2$)Cl]$_2$ (248.8−249.3 pm).[7] The molecular structure of **5** is analogous to the tin compounds [Sn$_6$(ESi*i*Pr$_3$)$_6$] (E = P, As) and the lead arsenic compound [Pb$_6$(AsSi-*i*Pr$_3$)$_6$].[5c,6b,12]

Experimental Section

All manipulations were carried out under rigorous exclusion of oxygen and moisture, using a Schlenk line and nitrogen atmosphere. All solvents were dried and freshly distilled before usage. The starting materials *i*Pr$_3$SiPH$_2$, *i*Pr$_3$SiAsH$_2$, GeCl$_2$(diox)$_2$ were prepared according to the relevant instructions found in the literature.[13] SnCl$_2$ was obtained from Aldrich and used as received. The ^{1}H and ^{31}P NMR spectra were recorded with a Bruker AC 250 spectrometer. All isolated compounds gave C,H analyses consistent with their formulas. In the IR spectra the typical peaks of the *i*Pr$_3$Si groups are observed.

1: A butyllithium solution (1.25 mL, 1.6 M; 2 mmol) was added to a solution of *i*Pr$_3$SiPH$_2$ (0.19 g, 1 mmol) in Et$_2$O (10 mL) at 0 °C. After stirring for 10 min, this solution was added to a suspension of SnCl$_2$ (0.19 g, 1 mmol) in Et$_2$O (15 mL) at 0 °C. The reaction mixture was allowed to warm up to ambient temperature and then stirred for an additional 16 hours. The resulting red solution was filtered to remove the precipitated LiCl and cooled to 0 °C. Red crystals of **1** formed over a period of 5 days. Yield: 0.1 g (32%). C$_{63}$H$_{147}$P$_7$Si$_7$Sn$_7$ (2149.11): calcd. C 35.21, H 6.89; found C 34.63, H 6.60. ^{1}H NMR ([D$_8$]toluene): δ = 1.0−1.5 (m, *i*Pr) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene): δ = −243.9 (s), −294.9 (s), −373.0 (s) ppm.

2: BuLi (1.63 mL, 1.6) was added at 0 °C to a solution of *i*Pr$_3$Si-AsH$_2$ (0.31 g, 1.3 mmol) in Et$_2$O (10 mL). This solution was added at 0 °C to a suspension of SnCl$_2$ (0.25 g, 1.3 mmol) in Et$_2$O (10 mL). The purple red mixture was stirred for an additional 18 . The resulting red solution was filtered to remove the precipitated LiCl and cooled to 0 °C. Red crystals of **2** formed over a period of 5 days. Yield: 0.13 g (28.5%). C$_{63}$H$_{147}$As$_7$Si$_7$Sn$_7$ (2457.74): calcd. C 30.80, H 6.03; found C 30.11, H 5.99. ^{1}H NMR (C$_6$D$_6$): δ = 1.0−1.5 (m, *i*Pr) ppm.

3: A butyllithium solution (1.19 mL, 1.6 M) was added to a solution of *i*Pr$_3$SiPH$_2$ (0.18 g, 0.95 mmol) in Et$_2$O (5 mL) at 0 °C. After warming to room temperature, the solution of *i*Pr$_3$SiPLi$_2$ was added to a suspension of SnCl$_2$ (0.22 g, 1.16 mmol) in Et$_2$O (20 mL) at 0 °C. Subsequently, the red mixture was warmed to ambient temperature while stirring and then agitated overnight. The resulting red solution was filtered to remove the precipitated LiCl and cooled to 0 °C. Red crystals of **3** formed over a period of 5

Table 1. Crystallographic data of **1**−**5**[8]

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{63}H_{147}P_7Si_7Sn_7$	$C_{63}H_{147}As_7Si_7Sn_7$	$C_{54}H_{126}Cl_2P_6Si_6Sn_8$	$C_{62}H_{146}As_6Li_4O_2Si_6Sn_4$	$C_{54}H_{126}Ge_6P_6Si_6$
Space group	$R\bar{3}$	$R\bar{3}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	6	6	4	2	2
Temperature	200 K	200 K	200 K	200 K	200 K
Lattice constants	a = 2058.3(3) pm	a = 2068.9(3) pm	a = 2258.9(5) pm	a = 1440.9(3) pm	a = 1402.8(3) pm
	b = 2058.3(3) pm	b = 2068.9(3) pm	b = 1376.4(3) pm	b = 2296.7(5) pm	b = 1497.1(3) pm
	c = 4000.0(8) pm	c = 4067.6(8) pm	c = 2782.4(6) pm	c = 1453.0(3) pm	c = 1927.9(4) pm
	α = 90°	α = 90°	α = 90°	α = 90°	α = 80.02(3)°
	β = 90°	β = 90°	β = 100.56(3)°	β = 109.53(3)°	β = 80.74(3)°
	γ = 120°	γ = 120°	γ = 90°	γ = 90°	γ = 76.80(3)°
Volume	14676(4) Å^3	15078(4) Å^3	8504(3) Å^3	4532(2) Å^3	3851(1) Å^3
Density	1.459 g/cm^3	1.623 g/cm^3	1.679 g/cm^3	1.498 g/cm^3	1.350 g/cm^3
2Θ range	2.5−50°	2.5−44°	3−48°	3.5−45°	3−48°
Reflections measured	13564	15285	23804	16732	17306
Independent reflections	5676 (R_{int} = 0.0423)	4082 (R_{int} = 0.0313)	12372 (R_{int} = 0.0695)	5743 (R_{int} = 0.1451)	11709 (R_{int} = 0.0551)
Ind. reflections with $F_o > 4\sigma(F_o)$	3993	3490	6210	4176	7019
Parameter	253	244	685	354	649
μ(Mo-K_α)	1.988 mm^{-1}	4.107 mm^{-1}	2.599 mm^{-1}	3.375 mm^{-1}	2.560 mm^{-1}
$R1$	0.0593	0.0460	0.0556	0.0630	0.0458
$wR2$ (all data)	0.1975	0.1557	0.1349	0.1699	0.1081
Residual electron density	2.164 e/Å^3	1.357 e/Å^3	2.201 e/Å^3	0.952 e/Å^3	0.953 e/Å^3

days. Yield: 0.1 g (30%). $C_{54}H_{126}Cl_2P_6Si_6Sn_8$ (2150.4): calcd. C 30.16, H 5.92; found C 30.89, H 6.43. ^{1}H NMR ([D$_8$]toluene): δ = 1.2−1.4 (m, *i*Pr) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene): δ = −372.3 (s) ppm.

4: BuLi (1.23 mL, 1.6 M) was added dropwise to a solution of *i*Pr$_3$SiAsH$_2$ (0.23 g, 0.98 mmol) in Et$_2$O (10 mL) at 0 °C. The resulting yellow solution was added at 0 °C to a suspension of SnCl$_2$ (0.12 g, 0.65 mmol) in Et$_2$O (15 mL).The purple red mixture was stirred for an additional 16 h and then filtered. After cooling of the solution to 0 °C **4** was obtained as violet crystals. Yield: 0.09 g (27%). Elemental analysis after drying in vacuo. $C_{54}H_{126}As_6Li_4Si_6Sn_4$ (1896.16): calcd. C 34.21, H 6.70; found C 34.17, H 6.853. ^{1}H NMR (C$_6$D$_6$): δ = 0.8−1.4 (m, *i*Pr) ppm.

5: BuLi (0.99 mL 1.6 M) was added at 0 °C to a solution of *i*Pr$_3$SiPH$_2$ (0.15 g, 0.79 mmol)in Et$_2$O (5 mL). This solution was added at 0 °C to a suspension of GeCl$_2$(diox)$_2$ (0.25 g, 0.79 mmol) in Et$_2$O (20 mL). The orange mixture was stirred overnight and than filtered. After cooling of the solution to 0 °C **5** was obtained as orange crystals. Yield: 0.05 g (24%). $C_{54}H_{126}Ge_6P_6Si_6$ (1565.49): calcd. C 41.43, H 8.11; found C 40.56, H 7.81. ^{31}P(^{1}H) (C$_6$D$_6$): δ = −323.3 (s) ppm. ^{1}H(C$_6$D$_6$): δ = 1.42 [d, $^3J_{H,H}$ = 7.5 Hz, CH(C*H*$_3$)$_2$], 1.82 [sept, $^3J_{H,H}$ = 7.5 Hz, C*H*(CH$_3$)$_2$] ppm.

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[8] STOE-IPDS2 (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 (Sn, Ge, As, P, Si, C refined anisotropically, H atoms were calculated at ideal positions). For compound **2** the C atoms of one *i*Pr$_3$Si group were refined isotropically, no H atoms were calculated. The solvent molecules of compound **4** were refined isotropically, no H atoms were calculated at these C atoms. CCDC-219412 (for **1**),

-219414 (for **2**), -219413 (for **3**), -219415 (for **4**) and -219416 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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