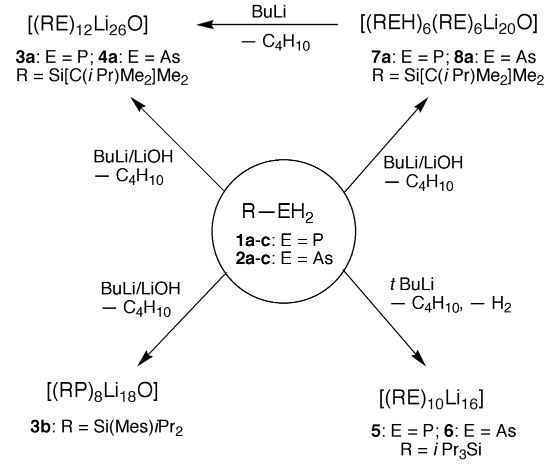
Lithiated Clusters from Primary Silylphosphanes and Silylarsanes: Spherical Bodies with and without Li_2O Filling**

Matthias Driess,* Ulrich Hoffmanns, Stefan Martin, Klaus Merz, and Hans Pritzkow

Dedicated to Professor Dirk Walther
on the occasion of his 60th birthday

Dilithiated primary phosphanes and arsanes are among the most important nucleophilic transfer reagents in the organoelement chemistry of phosphorus and arsenic; however, their structural chemistry (structure–reactivity relationship) has not been studied in detail.[1] We recently showed that *soluble* molecular derivatives such as **3b** and **4a**, in which Li_2O or another coligand are encapsulated or associated, are surprisingly readily accessible by lithiation of triorganosilyl-substituted primary phosphanes **1** and arsanes **2** (Scheme 1).[2, 3] The inclusion of Li_2O in ionic aggregates has also been observed for other systems,[4] which raised the question of whether Li_2O displayed a structure-directing effect. Furthermore, clusters of this kind are potential model compounds for the dissolution and nucleation of ionic crystals.[5]



Scheme 1. Synthesis of the clusters **3**–**6** from **1** and **2**. Mes = 2,4,6-trimethylphenyl.

In order to clarify how the encapulated aggregates **3** and **4** are formed and whether the Li_2O molecule acts as a template ("aggregation nucleus"), further studies were necessary. We report here on the lithiation of the primary silylphosphane RPH_2 **1c** as well of the homologous arsane $RAsH_2$ **2c** (R = iPr$_3$Si) with two molar equivalents of tBuLi in toluene, which were carried out under strict exclusion of Li_2O; these reactions led to the novel decameric clusters **5** and **6**, which are remarkable in two respects: they are not only the first Li_2O-free, closed aggregates of this type, but also unprecedented mixed-valent lithium pnictides. In addition we describe the partially lithiathed dodecameric clusters **7a** and **8a**, which are formed by the partial lithiation of **1a** and **2a** with BuLi in the presence of LiOH. They display a dumbbell-shaped Li_2O core and are isolable intermediates in the formation of the fully lithiated multishell clusters **3a** and **4a**, which have a $[Li_6O]^{4+}$ core.

The reaction of **1a** and **2a** with freshly sublimed tBuLi in the molar ratio 1:2 in toluene as solvent at −80 °C led to the decameric lithium pnictides **5** and **6**, respectively, as yellow octahedrally shaped crystals in 75 and 68 % yield, respectively. Compounds **5** and **6** are also formed when LiOH-free (freshly prepared) BuLi in Et_2O is used instead of tBuLi as the lithiating agent. Their single-crystal X-ray structure analyses[6] revealed the surprising result that although decameric Li_2O-free clusters are present in both cases, these do not display a Li/E ratio of 2:1 expected for a dilithium silylphosphanediide or -arsanediide, respectively. Instead a mixed-valent, lithium-poor phosphanediyl-dilithium phosphanediide and the corresponding Li–As cluster with a Li/E ratio 1.6:1 are obtained (Figure 1). This implies, however, that the clusters are formed by a redox reaction, which is supported by evolution of H_2 during the lithiation reaction in amounts ranging between 85 and 89 % of those expected. The induced H_2 elimination appears plausible for thermodynamic reasons, since the formation of the E–H bonds in phosphanes and arsanes is endothermic,[7] and moreover a closed cluster framework is more favorable. Remarkably the clusters are formed with H_2 evolution also if tBuLi is present in toluene at −80 °C and less than one molar equivalent of **1c** and **2c**, respectively, are added. That no "residual" E–H bonds are present in **5** and **6**, is also confirmed by ^{1}H NMR and IR spectra.

The compounds crystallize isotypically in the tetragonal space group $P4/nnc$. The topology of the oval $E_{10}Li_{16}$ cluster framework (E = P, As) can be described in a simplified way as a doubly capped archimedean antiprism comprising 10 E centers, and a Li center is located on each of the 16 deltahedral faces of this body (Figure 2). Thereby, two E atoms are five-coordinate, whereas the rest are six-coordinate. However, the corresponding Li–E, Si–E, and Li–Li distances show no special features in comparison to those of related lithium pnictides such as **3b** and **4a**,[2] and the Li–E distances of the differently coordinated E centers are almost the same. The electrostatically favorable arrangement of the cation (Li) and anion building blocks (iPr$_3$SiE) implies, however, not only two chemically different E and Si centers in the ratio of 4:1 in each case, but also two different Li centers in the ratio 1:1. This is confirmed by cross-polarization magic-angle-spinning (CP/MAS) solid-state NMR spectra of **5**; the $^{29}Si\{^{31}P\}$ NMR spectrum shows two singlets at $\delta = 29.0$ and 27.9 in the ratio 1:4 and the $^7Li\{^{31}P\}$ NMR spectrum two singlets at $\delta = 1.65$ and 1.42 (1:1).[8] The composition of the lithium-poor aggregates is also substantiated by correct elemental analyses (C,

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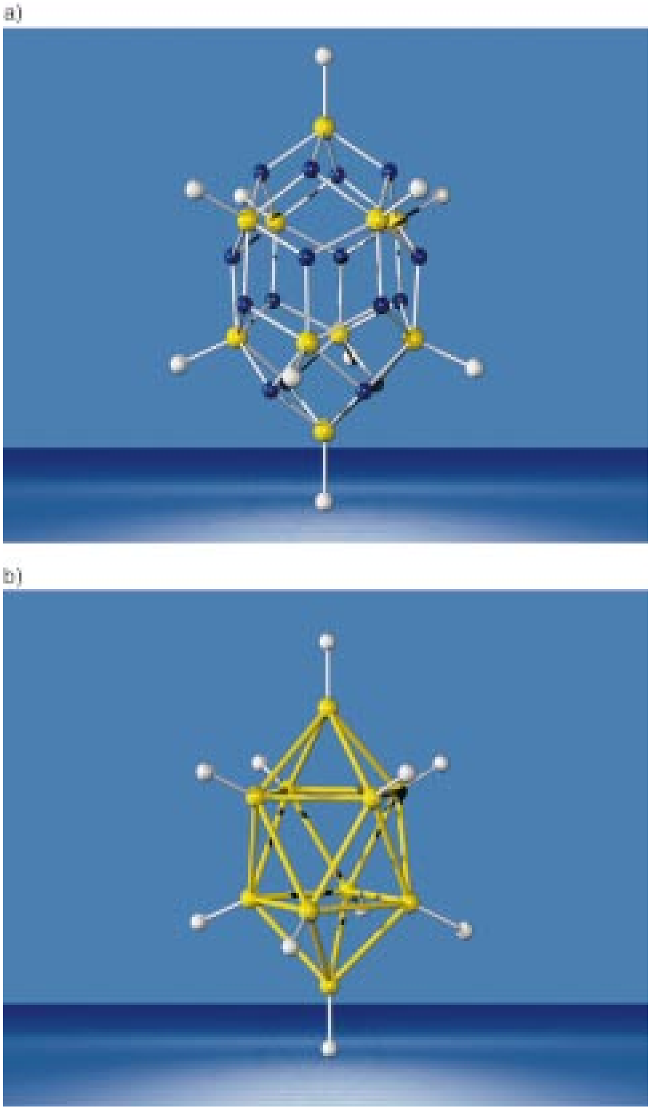

Figure 1. a) Structures of the frameworks of the isotypic compounds **5** and **6** in the crystal (without *i*Pr groups). Si = gray, Li = blue, E(P,As) = yellow. Selected distances [Å] in **5**: P–Si 2.208(3), P–Li 2.56(1), Li–Li 2.77(2)–3.05(2). b) Topology of the anionic E_{10} framework in **5** and **6**.

H, Li, P, As), and cryoscopic investigations in benzene gave a degree of aggregation of $n \approx 8$, that is, the molecules show almost no tendency for dissociation, which appears understandable in view of the electron deficiency of the cluster. Correspondingly, the multinuclear NMR spectra of **5** and **6** in solution and in the solid state are almost identical. Thus, the ^{31}P NMR spectrum of **5** in solution displays two broad singlets at $\delta = -366$ and -371 in the ratio 1:4, and in the ^{29}Si{^{31}P} NMR spectrum, as in the CP/MAS solid-state NMR spectrum, two singlets occur at almost identical δ values. How can the electronic structure of these evidently mixed-valent pnictides be described simply? Formally the clusters consist of two units of the low-valent “anediyls” [RE:] and eight units of the “anediide” $RELi_2$ (E = P, As). Since the large E–E distances (>4 Å) rule out localized E–E bonds, a delocalization of the framework valence electrons in the cluster is evidently achieved through multicenter bonds, which are mediated through the Li centers, and in fact without the occurrence of Li–Li bonds; this is in agreement with the inconspicuous ^{7}Li NMR shifts of **5** and **6**, which correspond to those of low-coordinate Li ions such as in **3b** and **4a**.[2] As expected the addition of a small amount of LiOH or Li_2O to solutions of **5** and **6** did not lead to a cluster rearrangement to an aggregate such as **3b** or **4a**. Fascinatingly, the lithiation of **1c** and **2c** with BuLi in the presence of LiOH proceeds differently. In this reaction dodecameric Li_2ER aggregates with a $[Li_6O]^{4+}$ core analogous to **4a** are formed, whose framework topology has been characterized by X-ray crystallography.[9] The results confirm the structure-determining influence of LiOH and Li_2O on the formation of the cluster. Partial lithiation of **1a** and **2a** with BuLi in the ratio 2:3 in the presence of LiOH in toluene has led to the isolation of the intermediates **7a** and **8a** in the construction of the closed clusters **3a** and **4a**, respectively. These intermediates form colorless crystals, which are sparingly soluble in toluene, but dissolve well in THF. Their constitution was determined on the basis of a crystal structure analysis.[6] The “open” clusters have a three-dimensional, wheel-like $E_{12}Li_{18}$ ladder structure (E = P, As), in which the 12 E centers form an icosahedral framework, as in the completely lithiated aggregate **3a** (see below) and in **4a**;[2] the Li_2O guest sits inside and acts as the “stabilizing axis of the wheel” (Figure 2). The E–H hydrogen atoms, which were detected in the ^{1}H NMR and IR spectra, are very probably localized on the E atoms of the hexagonal E_3Li_3 “openings”. The “inner” Li atoms of Li_2O are each coordinated to four E centers, in contrast the “outer” Li atoms are only three-coordinate. This results in differently coordinated E atoms with the coordination numbers 5, 6, and 7.

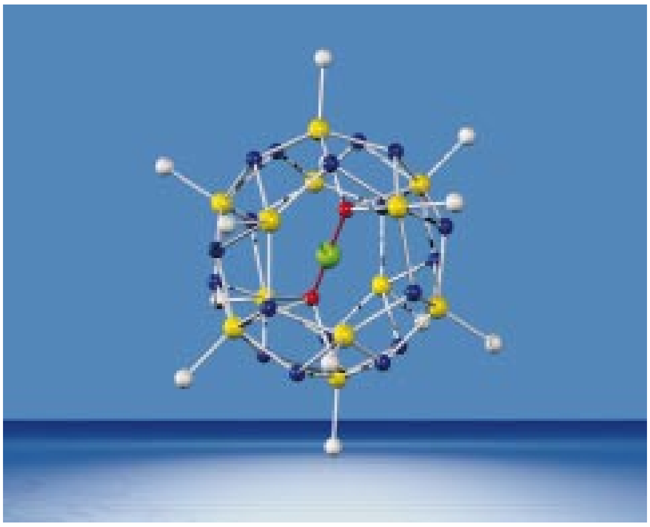

Figure 2. Structure of the cluster in the isotypic compounds **7a** and **8a** in the crystal. Selected average distances [Å] in **8a**: As–Si 2.32(2), Li–As 2.47–2.78(4), Li–O 2.14(10).

Compound **7a** presumably dissociates only slightly in donor solvents such as [D$_8$]THF, since the ^{31}P NMR spectrum shows two broad signals at $\delta = -365$ and -362 for the ^{31}P cores of the different PLi_2 groups, whereas the P atoms of the PHLi groups display a doublet at $\delta = -301$ (^1J(P,H) = 152 Hz). Three broad signals at $\delta = 1.10$, 1.40, and 5.56 in the ratio of about 1:2:4 were observed in the ^{7}Li NMR spectrum; the low-field signal at $\delta = 5.56$ is unprecedented for lithium phosphanides. The addition of six molar equivalents of BuLi to such solutions leads exclusively to the cluster **3a** which is analogous to **4a**. Compound **3a** exists almost in tact in solution and its ^{7}Li NMR spectrum shows three signals at $\delta = -1.70$, -0.80, and 2.10 (ratio 1:2:10); the latter is almost identical with that of **4a**.[2] The analogous transformation was also observed in the lithiation of **8a**, which leads smoothly to **4a**. As expected, compound **3a** [6] is isotypic to **4a** and its geometric parameters do not show any special features in comparison to those of **3b**[2] (Figure 3).

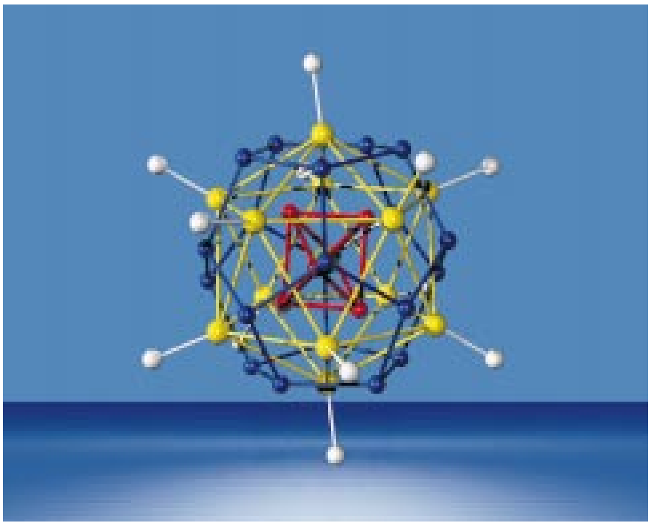

Figure 3. Shell-like structure of **3a** in the crystal. The organic groups are omitted for clarity. Si = gray, P_{12} shell = yellow, OLi_6 shell = red, green. Selected average distances [Å]: P–Si 2.205(1), Li–P 2.466(8)–2.644(7), Li–Li 2.50(1)–3.48(2), Li–O 1.863(8).

It should be possible to observe the stepwise generation of molecular dilithium pnictide clusters also in the formation of other mixed clusters of this type. Investigations are in progress on the inclusion of Li_2S and other guests instead of Li_2O.

Experimental Section

5: Compound **1c** (1.22 g, 6.42 mmol) in toluene (20 mL) was treated at −80 °C with *t*BuLi (6.6 mL of a 1.6 M solution in pentane, Aldrich), and a yellow suspension was formed with H_2 evolution. After the suspension was allowed to warm to room temperature (5 h), it was heated to about 50 °C. This led to the formation of a clear yellow solution, from which yellow octahedrally shaped crystals were obtained on slow cooling. Yield: 1.00 g (0.48 mmol, 75%); ^{1}H NMR (200 MHz, [D$_8$]toluene): $\delta = 1.0-1.2$ (m, 210H, *i*Pr); ^{31}P NMR (81 MHz, [D$_8$]toluene): $\delta = -366$ (br., 2P), −371 (br., 8P); ^{29}Si NMR (39 MHz, [D$_8$]toluene): $\delta = 27.6$ (m, 2Si), 28.8 (m, 8Si); ^{7}Li NMR (97 MHz, [D$_8$]toluene): $\delta = 1.45$ (br., 8Li), 1.66 (br., 8Li); correct C,H,Li,P analysis.

6: In a reaction analogous to that for the synthesis of **5, 6** was obtained in the form of yellow crystals from **2c** (1.22 g, 5.2 mmol) by metalation with *t*BuLi in toluene. Yield: 0.9 g (0.36 mmol, 68%); ^{1}H NMR (200 MHz, [D$_8$]toluene): $\delta = 1.0$ (s, 36H), 1.1–1.3 (m, 174H); ^{29}Si NMR (39 MHz, [D$_8$]toluene): $\delta = 16.7$ (s, 2Si), 17.5 (s, 8Si); ^{7}Li NMR (97 MHz, [D$_8$]toluene): $\delta = 1.40$ (s, 8Li), 1.68 (s, 8Li); correct C,H,Li,As analysis.

7a: BuLi (3.6 mL, 1.6 M solution in hexane, Aldrich) was added dropwise to a solution of **1a** (0.5 g, 2.83 mmol) and LiOH (ca. 1 mg) in toluene (60 mL) at −80 °C. The reaction mixture was allowed to warm to room temperature within 5 h and then the solvent was removed in vacuo. The yellow, solid residue was dissolved at 40 °C in a little toluene, separated from a small amount of insoluble material by filtration and subsequently fractionally crystallized in the temperature range from 40–20 °C. Yield: 0.32 g (0.14 mmol, 60%) colorless crystals; ^{1}H NMR (250 MHz, [D$_8$]THF): $\delta = -1.78$ (d, 6H, PH, ^1J(H,P) = 152 Hz), 0.26–0.33 (m, 72H, MeSi), 0.56–0.61 (m, 72H, MeC), 1.08–1.16 (m, 72H, *Me*$_2$CH), 2.22–2.51 (m, 12H, Me$_2$C*H*); ^{31}P NMR (101 MHz, [D$_8$]THF): $\delta = -301$ (br. d, 6P, ^1J(P,H) = 152 Hz), −362 (br., 3P), −365 (br., 3P); ^{7}Li NMR (97 MHz, [D$_8$]THF): $\delta = 1.10$ (br.), 1.40 (br.), 5.56 (br.); IR (KBr): $\tilde{\nu} = 1930$ cm^{-1} (P–H); correct C,H,Li analysis.

8a: In a reaction analogous to that for the synthesis of **7a, 8a** was obtained in the form of colorless crystals from **2a** (0.45 g, 2 mmol) by lithiation with BuLi/LiOH in toluene. Yield: 0.29 g (0.1 mmol, 47%); ^{1}H NMR (250 MHz, [D$_8$]THF): $\delta = -1.63$ (s, 6H, AsH), 0.24–0.33 (m, 72H, MeSi), 0.56–0.60 (m, 72H, MeC), 1.07–1.14 (m, 72H, *Me*$_2$CH), 2.20–2.50 (m, 12H, Me$_2$C*H*); ^{7}Li NMR (97 MHz, [D$_8$]THF): $\delta = 1.05$ (s), 1.61 (s), 5.21 (s); IR (KBr): $\tilde{\nu} = 1897$ cm^{-1} (As–H); correct C,H,Li analysis.

3a, 4a: Compound **7a** (0.16 g, 0.07 mmol) or **8a** (0.145 g, 0.05 mmol), respectively, were dissolved in THF (ca. 40 mL) and treated at −40 °C with six equivalents of BuLi in hexane. The mixture was allowed to warm to room temperature, and all volatile components were removed in vacuo (10^{-2} Torr). The pale yellow residue was dissolved in toluene (ca. 3 mL) at 40 °C, and crystallized on cooling to 20 °C. Yield: 0.14 g (0.061 mmol, 86%) and 0.12 g (0.043 mmol, 82%), respectively. **3a**: ^{1}H NMR (250 MHz, C$_6$D$_6$): $\delta = 1.18-1.37$ (br. m, 112H, *i*Pr), 2.06 (s, 12H, *p*-Me), 2.15 (s, 12H, *p*-Me), 2.79 (br., 48H, *o*-Me), 6.74 (s, 16H, arom. H); correct C,H,Li analysis. **4a**: see ref. [2].

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[6] Crystal structure analyses: **5**: tetragonal, space group *P*4/*nnc*, $a = 16.397(7)$, $c = 25.24(1)$ Å, $Z = 2$, $V = 6785(6)$ Å^3, 2981 independent reflections ($I > 2\sigma(I)$), one *i*Pr group is disordered, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms included in calculated positions. $R1 = 0.0812$ (observed reflections), $wR2 = 0.2382$ (all data). Compound **6** is isotypic with **5**, $a = 16.496(9)$, $c = 25.629(13)$ Å, $Z = 2$, $V = 6971(6)$ Å^3, 1645 independent reflections ($I > 2\sigma(I)$). $R1 = 0.0956$ (observed reflections), $wR2 = 0.2671$ (all data). Compound **3a** is isotypic with **4a**:[5] monoclinic, space group $P2_1/n$, $a = 19.337(3)$, $b = 19.116(3)$, $c = 19.357(3)$ Å, $\beta = 92.00(1)°$, $Z = 4$, $V = 7151(2)$ Å^3, 12784 independent reflections ($I > 2\sigma(I)$), all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions. $R1 = 0.0545$ (observed reflections), $wR2 = 0.1370$ (all data). **8a**: triclinic, space group $P\bar{1}$, $a = 17.148(3)$, $b = 17.317(4)$, $c = 17.565(4)$ Å, $\alpha = 65.24(3)$, $\beta = 67.00(3)$, $\gamma = 65.13(3)°$, $Z = 1$, $V = 4149(1)$ Å^3, 7878 independent reflections ($I > 2\sigma(I)$). $R1 = 0.1252$ (observed reflections), $wR2 = 0.3544$ (all data). The silyl groups are disordered, As and Si atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. The cell contains several other atoms (5–6 in the asymmetric unit), which probably belong to

disordered solvent molecules (Et_2O), but which cannot be unambiguously assigned. Compound **7a** is isotypic with **8a**, but the quality of the crystals was very low. The intensities were measured with a Bruker-axs-SMART diffractometer (**5**, **3a**, **7a**) and with a Siemens-P4 diffractometer (**6**, **8a**) ($Mo_{K\alpha}$ radiation, $\lambda = 0.71707$ Å, ω scan, $T = 203$ K). The structures were solved by direct methods (SHELXS97), and refined against F^2 with all measured reflections (SHELXL97). 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-119661 (**3a**), CCDC-119662 (**5**), and CCDC-119663 (**8a**). 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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$[In_3(In_2)_3(PhP)_4(Ph_2P_2)_3Cl_7(PEt_3)_3]$–A New Molecular III/V Compound Featuring an Unusual 19-Atom Cage

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In the last few years, enormous interest has been generated in the synthesis of molecular III/V cages owing to the diverse optical and electronic properties of binary III/V materials. For the In/P system, several compounds containing In_2P_2 four-membered rings,[1] In_3P_3 six-membered rings,[2] or In_4P_4 heterocubanes[3] as central structural units have been synthesized and characterized by X-ray structure analysis. Furthermore, the generation of nanometer-sized particles of the binary InP phase was investigated intensively, for example, by reaction of $InCl_3$ or $InCl(C_2O_4)$ and $P(SiMe_3)_3$ at high temperatures[4] or by thermolysis of molecular InP compounds.[5] The resulting products were characterized by X-ray powder diffraction and by transmission electron microscopy (TEM) experiments. It was possible to synthesize InP nanoparticles in a size range of 2 to 10 nm.[6]

We report here the synthesis and structure determination[7] of the InP cluster compound **1** (Figure 1), which consists of a 19-atom cage with a diameter of about 0.7 nm.[8] Compound **1** was obtained from the reaction of $InCl_3$ with PEt_3 and $PhP(SiMe_3)_2$ [Eq. (1)]. Besides the loss of Me_3SiCl and the formation of In–P bonds, redox processes occur during the reaction which lead to the formation of additional P–P and In–In bonds.

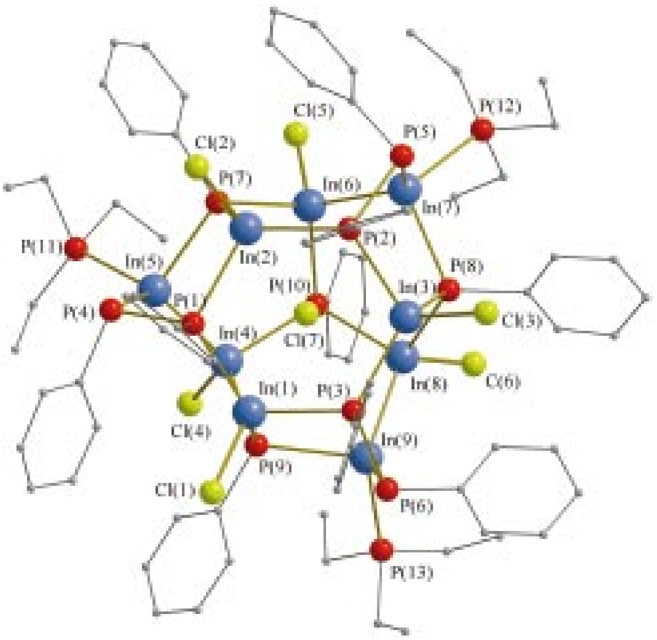

Figure 1. Molecular structure of **1** in the crystal. Selected bond lengths [pm] and angles [°]: In–Cl 241.2–245.0, In–P 253.3–261.6, In–In 273.5–275.1, P–P 220.1–223.1; P-P-In 99.2–116.3 (P(1), P(2), and P(3)), P-P-In 96.0–96.3 (P(4), P(5), and P(6)), P-In-P 101.1–126.1, In-P-In 97.3–113.1, In-In-P 102.1–126.3.

$$9\,InCl_3 + 3\,PEt_3 + 10\,PhP(SiMe_3)_2 \rightarrow \underset{\mathbf{1}}{[In_3(In_2)_3(PhP)_4(Ph_2P_2)_3Cl_7(PEt_3)_3]} + 20\,Me_3SiCl \qquad (1)$$

Compound **1** crystallizes in the space group $P\bar{1}$ as a racemate with both enantiomers appearing in the unit cell. The 19-atom polyhedron is built up by nine In and ten P atoms. If the ligands are considered as four PPh^{2-} groups (P(7) to P(10)), three $P_2Ph_2^{2-}$ groups (P(1)–P(4), P(2)–P(5), P(3)–P(6)), and seven Cl^- ligands, a total charge of 21+ can be calculated for the nine In atoms of the cluster. In(1), In(2), and In(3) show no In–In bonds and can be assigned the formal oxidation state 3+, whereas atoms In(4) to In(9) have the formal charge 2+ and correspondingly form In_2 pairs (In(4)–In(5), In(6)–In(7), In(8)–In(9)). Assuming that lone pairs are present at P atoms P(4), P(5), and P(6), the polyhedron possesses 54 valence electrons for 27 bonds and features exclusively two-electron, two-center bonds. All interatomic distances lie in the usual range for single bonds. The In–P distances range between 253.3 and 261.6 pm, the In–In bonds are 274.1 pm on average. These values correspond well to analogous bonds occurring in other In/P compounds; for example, in $[\{(tBu_2P)_2InCl\}_2]$ or $[MesInPMes]_4$ (Mes = 2,4,6-$Me_3C_6H_2$) the In–P bonds range between 258.2 and 266.0 pm[1–3] and in $[Trip_4In_2]$ (Trip = 2,4,6-$i Pr_3C_6H_2$)[9] or $[In_2I_4(nPr_3P)_2]$[10] the In–In single bonds are 277.5 and 274.5 pm, respectively. In contrast, longer In–In distances of

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