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Phosphide coupling in the reaction of $Sn(NMe_2)_2$ with MesPHLi; synthesis and structure of the Sn(II) phosphide dianion $[\{Sn(\mu\text{-}PMes)\}_2(MesP)_2]^{2-}$ (Mes = 2,4,6-$Me_3C_6H_2$)

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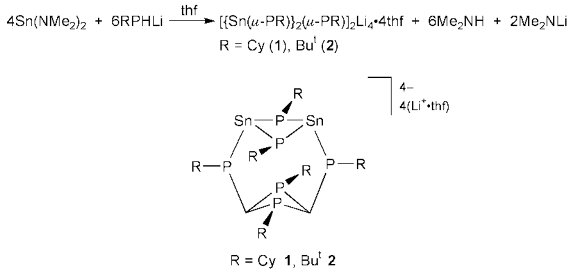
In contrast to the reactions of other primary phosphides with $Sn(NMe_2)_2$, the reaction of MesPHLi with $Sn(NMe_2)_2$ results in partial coupling of MesP groups in the product (which contains the novel Sn(II) dianion $[\{(Sn(\mu\text{-}PMes)\}_2(MesP)_2]^{2-}$).

We recently showed that the heterometallic Sb(III) cage $[\{Sb(PCy)_3\}_3Li_6]$ (Cy = C_6H_{11}) decomposes at relatively low temperature (30–40 °C) into Zintl compounds containing the Sb_7^{3-} anion.[1] The isolation of $[CyP]_4$ from this 'cage-to-alloy' reaction suggests that the formation of P–P bonds (the strongest homonuclear Group 15 bond) provides the thermodynamic driving force.[1] In related studies it was shown that probable intermediates in the formation of E_7^{3-} Zintl ions (E = As, Sb) are cyclic anions of the type $[(RP)_nE]^-$.[2,3] A key observation was that the ease of formation of the Zintl compounds is dependent (among other factors) on the nature of the R substituent of the RP^{2-} groups.[3] Thus, reaction of MesPHLi with $As(NMe_2)_3$ at room temperature in the presence of TMEDA [= $(Me_2NCH_2)_2$] leads to rapid (1 h) formation of $As_7Li_3\cdot 3TMEDA$, whereas prolonged reaction (12 h) of a range of aliphatic primary phosphides with $As(NMe_2)_3$ under similar conditions gives complexes containing $[(RP)_nAs]^-$ anions (n = 3 or 4), it being necessary to reflux these reactions in order to effect formation of Zintl compounds.[3] The synthesis and structure of $[\{(Sn(\mu\text{-}PMes)\}_2(MesP)_2]Li_2\cdot 2TMEDA$ **2** reported here provides the first evidence that the reactivity pattern established for Group 15 phosphides has broader implications to other p block elements.

In earlier studies we had observed that the reaction of $[SnNBu^t]_4$ with CyPHLi (1:6 equiv.) in thf gives the heterometallic complex $[\{Sn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2Li_4\cdot 4thf$ **1**, containing the metallacylic tetraanion $[\{Sn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2^{2-}$.[4] The impetus for further studies came with the surprising finding that the same complex is also produced by the reaction of $Sn(NMe_2)_2$ with CyPHLi in thf using a range of stoichiometries (from 1:1.5 to 1:3 equiv., respectively) (Scheme 1).[5] In fact other aliphatic primary phosphides react similarly with $Sn(NMe_2)_2$ in thf. For example, reaction of Bu^tPHLi with $Sn(NMe_2)_2$ gives $[\{Sn(\mu\text{-}PBu^t)_2\}_2(\mu\text{-}PBu^t)]_2Li_4\cdot 4thf$ **2** (in *ca.* 60% yield), whose structure is essentially identical to **1**.[5] However, the analogous reaction of MesPHLi (Mes = 2,4,6-$Me_3C_6H_2$) with $Sn(NMe_2)_2$ gives a radically different result. The product isolated in the presence of the bidentate donor TMEDA (addition of which was necessary to facilitate crystallisation) is $[\{(Sn(\mu\text{-}PMes)\}_2(PMes)_2]Li_2\cdot 2TMEDA$ **3** (in 96% yield).† Some indication of the different outcome of the reaction with MesPHLi is provided by room-temperature NMR studies. In contrast to **1** and **2** where the two ^{31}P NMR environments are markedly different (*e.g.* δ −180 and −249 in **1**), the P environments of **3** occur at very similar chemical shifts (δ −156.7 and −157.5). In addition, the electronic environment of the Sn centres in **3** (δ −154.6) is clearly vastly different from that found in **1** and **2** (*ca.* δ +690).[4] However, the Sn–P coupling was poorly resolved in the spectra of **3** so that no information concerning the connectivities of either nucleus within the core of the complex could be gleaned.



Scheme 1

The low-temperature X-ray structure of **3**‡ shows that the complex is an ion-paired species, arising from the association of a $[\{(Sn(\mu\text{-}PMes)\}_2(PMes)_2]^{2-}$ dianion with two TMEDA solvated Li^+ cations (Fig. 1). In addition, there are two molecules of toluene in the lattice for each molecule of **3**. Although only a few Sn(II) and Pb(II) complexes containing RP^{2-} ligands have been structurally characterised,[4,6] (like **3**) the majority of these are ion-paired molecular species contain-

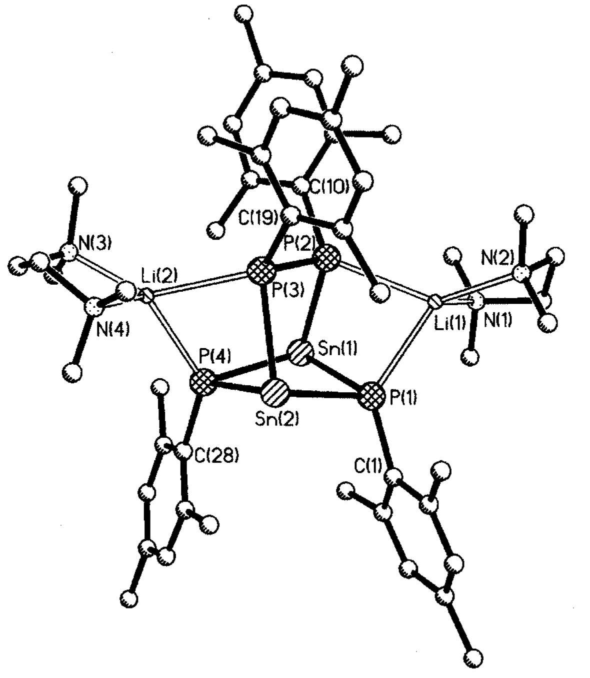


Fig. 1 The heterometallic cage structure of **3**. H atoms, lattice-bound toluene molecules and the disorder about the $-CH_2CH_2-$ groups of the TMEDA ligands have been omitted for clarity. Key bond lengths (Å) and angles (°); Sn(1)–P(1) 2.635(1), Sn(1)–P(2) 2.636(1), Sn(1)–P(4) 2.627(1), Sn(2)–P(1) 2.615(1), Sn(2)–P(3) 2.648(1), Sn(2)–P(4) 2.646(1), Li(1)–P(1) 2.518(8), Li(1)–P(2) 2.596(7), Li(2)–P(3) 2.609(7), Li(2)–P(4) 2.533(7), P(2)–P(3) 2.186(2), Li(1,2)–N(1,2,3,4) range 2.090(8)–2.118(8); Sn(1)–P(1,2)–Sn(2) mean 86.8, P(1)–Sn(1,2)–P(4) mean 90.6, P(1)–Sn(1)–P(2)/P(3)–Sn(2)–P(4) mean 75.8, P(4)–Sn(1)–P(2)/P(4)–Sn(2)–P(3) mean 93.7, Sn–{P(2)–P(3)} mean 99.8.

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ing Sn(II) phosphide anions coordinated to alkali or alkaline earth metal cations. However, in none of these previous examples has the formation of a P–P bond (*via* coupling of RP^{2-} anions) been observed. Of particular note in comparison with **3**, is the formation of $[(\mathrm{Me_3Si})\mathrm{PSn}(\mu\text{-}\mathrm{PSiMe_3})]_2(\mathrm{Ca}\cdot2\mathrm{thf})_2$ in the reaction of $[\mathrm{Ca}\{\mathrm{PSiMe_3}\}_2]$ with $\mathrm{SnCl_2}$.[6b] The latter complex contains a $[(\mathrm{Me_3Si})\mathrm{PSn}(\mu\text{-}\mathrm{PSiMe_3})]_2{}^{4-}$ tetraanion whose framework can be regarded as related to the $[\{(\mathrm{Sn}(\mu\text{-}\mathrm{PMes})\}_2(\mathrm{PMes})_2]^{2-}$ dianion of **3** by 2e reduction and cleavage of the P–P bond.

Examination of the bond lengths and angles found in the bicyclic $\mathrm{Sn_2P_4}$ core of **3** indicates that there is a considerable amount of strain in this arrangement. Thus, although the Sn–P bond lengths are similar to those found in the few structurally characterised Sn(II) complexes containing RP^{2-} ligands,[6] these bonds fall over a wide range of values [2.615(1)–2.648(1) Å]. In addition, the Sn(II) centres adopt highly irregular pyramidal geometries, with the P–Sn–P angles involved being in the range 75.75(3)–94.71(3)°. Clearly, the distortions found in the $\mathrm{Sn_2P_4}$ core can be partly attributed to the geometric constraints involved in the coordination of the MesPPMes ligand to the two Sn centres of the $\mathrm{Sn_2(PMes)_2}$ dimer unit. Some evidence for this view is seen in the compression of the P–P bond of the MesPPMes ligand [P(2)–P(3) 2.186(2) Å]; a value which is significantly shorter than that observed for the $\mathrm{Bu^tPPBu^t}$ groups in the Sn(IV) complex $[\mathrm{ClSn}\{\mathrm{Bu^tPPBu^t}\}_3\mathrm{SnCl}]$[7]) (2.237 Å). However, the highly distorted geometry of the Sn(II) centres in **3** is primarily the result of the chelation of each of the pseudo-tetrahedral $\mathrm{Li^+}$ cations by a P centre of the MesPPMes group [Li(1,2)–P(2,3) mean 2.60 Å[7]] and by a MesP ligand [Li(1,2)–P(1,4) mean 2.53 Å[7]] of the $[\{(\mathrm{Sn}(\mu\text{-}\mathrm{PMes})\}_2(\mathrm{MesP})_2]^{2-}$ dianion. This coordination to the $\mathrm{Li^+}$ ions results in the compression of the associated P–Sn–P angles [P(1)–Sn(1)–P(2) and P(3)–Sn(2)–P(4) mean 75.8°; *cf.* 90.59(3)–94.71(3)° for the remaining P–Sn–P angles].

In summary, the reactions of $\mathrm{Sn(NMe_2)_2}$ with RPHLi (R = Cy, $\mathrm{Bu^t}$) and MesPHLi parallel those with Group 15 reagents $\mathrm{E(NMe_2)_3}$ (E = As, Sb, Bi) and a range of lithium primary phosphides (RPHLi). In this context, the $[\{(\mathrm{Sn}(\mu\text{-}\mathrm{PMes})\}_2(\mathrm{PMes})_2]^{2-}$ dianion core of **3** can be regarded as the Group 14 counterpart of the previously studied Group 15 $[(\mathrm{RP})_n\mathrm{E}]^-$ anions. The $[\{(\mathrm{Sn}(\mu\text{-}\mathrm{PMes})\}_2(\mathrm{MesP})_2]^{2-}$ anion of **3** has the potential to act as a multi-electron donor to a range of main group and transition metal complexes, yielding a variety of mixed-metal complexes. Furthermore, the thermolysis of **3** and similar complexes may lead to further P–P bond formation, providing a route to Sn Zintl phases.

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Notes and references

† *Synthesis of* **3**: to a solution of $\mathrm{MesPH_2}$ (0.94 ml, 6.0 mmol) in toluene (20 ml) at −78 °C was added $\mathrm{Bu^nLi}$ (4.0 ml, 6.0 mmol, 1.6 mol $\mathrm{dm^{-3}}$ in hexanes). Stirring at room temperature (1 h) produced a yellow precipitate of the monolithiate. To this suspension at −78 °C was added a solution of $\mathrm{Sn(NMe_2)_2}$ (0.42 g, 2.0 mmol) in toluene (10 ml). Warming to room temperature led to the formation of a red–orange precipitate which was dissolved by the addition of TMEDA (1 ml, excess). Storage at 5 °C for 24 h gave orange crystalline blocks of **3**. Spectroscopic and analytical studies of **3** show that the toluene solvation found in the lattice is removed by placing crystalline samples under vacuum (*ca.* 15 min, 10^{-1} atm) during isolation. Yield 1.04 g (96%). ^{1}H NMR (400.16 MHz, $\mathrm{d_8}$-toluene, +25 °C), δ 6.92 (S, 8H, aryl C–H), 2.90 (s, 12H, 4-Me of Mes), 2.65 (s, 24H, 2,6-Me of Mes), 1.97 (s, 24H, $\mathrm{Me_2N}$ of TMEDA), 1.83 (br s, 8H, $-\mathrm{CH_2CH_2}-$ of TMEDA). ^{31}P NMR (161.98 MHz, $\mathrm{d_8}$-toluene, +25 °C, rel. 80% $\mathrm{H_3PO_4}$–$\mathrm{D_2O}$), δ −156.7 (s), −157.5 (s). ^{7}Li NMR (155.55 MHz, $\mathrm{d_8}$-toluene, +25 °C), δ 0.20 (s). ^{119}Sn NMR (141.21 MHz, $\mathrm{d_8}$-toluene, +25 °C, rel. sat. $\mathrm{SnCl_2}$–$\mathrm{D_2O}$), δ −154.6 (br s). Satisfactory (C,H,N) analysis was obtained for **3**(−2toluene).

‡ *Crystal data* for **3**: $\mathrm{C_{62}H_{92}Li_2N_4P_4Sn_2}$, M = 1268.54, monoclinic, space group $P2_1/c$, Z = 4, a = 21.4284(3), b = 13.5986(2), c = 22.9153(2) Å, β = 94.644(9)°, V = 6655.51(15) Å^3, μ(Mo-Kα) = 0.884 $\mathrm{mm^{-1}}$, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 60891 reflections collected, 15148 were independent (R_{int} = 0.059). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.053 [$I > 2\sigma(I)$] and $wR2$ = 0.174 (all data).[8] The $-\mathrm{CH_2CH_2}-$ groups of one of the TMEDA ligands are disordered over two sites. This was modelled with 50% occupancy in each. CCDC 156336. See http://www.rsc.org.suppdata/cc/b0/b010201f/ for crystallographic data in .cif or other electronic format.

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