Bis(t-butyl)phosphido Complexes of Tin(II) and Lead(II); Analogues of Lithium-complexed Carbanions

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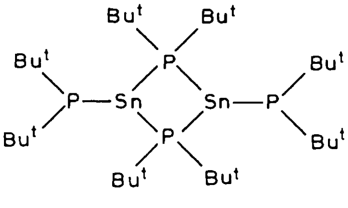
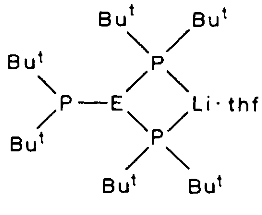
The reaction of $\mathrm{Li[PBu^t_2]}$ with $\mathrm{SnCl_2}$ or $\mathrm{PbCl_2}$ in tetrahydrofuran (thf) solution affords the isostructural 'ate' complexes, $\mathrm{[Li(thf)\{E(PBu^t_2)_3\}]}$ (E = Sn or Pb), both of which have been characterised by *X*-ray crystallography.

Compared with the transition metals, there are relatively few phosphido derivatives of the heavier main-group elements. We have therefore initiated a survey of the reactions of the $\mathrm{[PBu^t_2]^-}$ anion with, *e.g.*, the halides of these elements. duMont and co-workers[1] have previously reported that the reaction of $\mathrm{K[PBu^t_2]}$ with $\mathrm{SnCl_2}$ (or $\mathrm{Et_3PSnCl_2}$) in toluene in 2:1 stoicheiometry results in the dimer, $\mathrm{[Sn(PBu^t_2)_2]_2}$, for which they proposed structure (**1**). It was also noted that, under comparable conditions, the reaction of tin dihalides with $\mathrm{Li[PBu^t_2]}$ affords $\mathrm{Bu^t_2PSnX}$. We have now found that in tetrahydrofuran (thf) solution, $\mathrm{Li[PBu^t_2]}$ reacts with $\mathrm{SnCl_2}$ or $\mathrm{PbCl_2}$ in 3:1 stoicheiometry to afford the novel 'ate' complexes, (**2**) and (**3**), respectively. *X*-Ray-quality air-sensitive crystals of orange-yellow (**2**) and red (**3**) were grown from n-hexane solutions at −20 °C.†



(**1**)



(**2**); E = Sn
(**3**); E = Pb

Compounds (**2**) and (**3**) can be regarded as tin and lead analogues of heteroatom-substituted carbanions. There is, in fact, considerable interest in such species, particularly in regard to the geometry at the anionic centre. For example, $\mathrm{\{Li[C(SiMe_3)_3]\cdot 2thf\}_2}$ and $\mathrm{\{Li[C(SiMe_2Ph)_3]\cdot thf\}}$ assume pyramidal carbanionic geometries[2,3] whilst in $\mathrm{\{Li[C(PMe_2)_3]\cdot thf\}_2}$ the $\mathrm{CP_3}$ moiety is almost planar.[4] As anticipated on the basis of the usual group trends, the tin and lead anions are distinctly more pyramidal (Figure 1) than the corresponding carbanions (sum of angles at Sn and Pb = 308.5

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† *Crystal data for* (**2**): $\mathrm{C_{28}H_{62}LiOP_3Sn}$, $M = 633.36$, monoclinic, $P2_1/c$ (No. 14), $a = 11.590(2)$, $b = 20.366(3)$, $c = 15.836(2)$ Å, $\beta = 104.51(1)^\circ$, $U = 3618.6$ Å, $Z = 4$, $D_c = 1.163$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.5$ cm^{-1}.

Crystal data for (**3**): $\mathrm{C_{28}H_{62}LiOP_3Pb}$, $M = 721.86$, monoclinic, $P2_1/c$ (No. 14), $a = 11.707(3)$, $b = 20.401(4)$, $c = 15.847(3)$ Å, $\beta = 104.40(2)^\circ$, $U = 3665.4$ Å^3, $Z = 4$, $D_c = 1.308$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 48.1$ cm^{-1}. Totals of 5665 and 5563 unique reflections were measured on an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leqslant 2\theta \leqslant 48.0^\circ$ ($\theta/2\theta$ scan mode) for (**2**) and (**3**), respectively. The data were corrected for Lorentz, polarisation, and decay effects. An empirical absorption correction was applied in the case of (**3**). The structures were solved (direct methods) and refined (difference Fourier, full-matrix, least-squares) using 2938 and 1803 reflections for (**2**) and (**3**) respectively $[I > 3.0\sigma(I)]$. The final residuals were $R = 0.0744$ and $R_w = 0.0810$ for (**2**) and $R = 0.0667$ and $R_w = 0.064$ for (**3**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

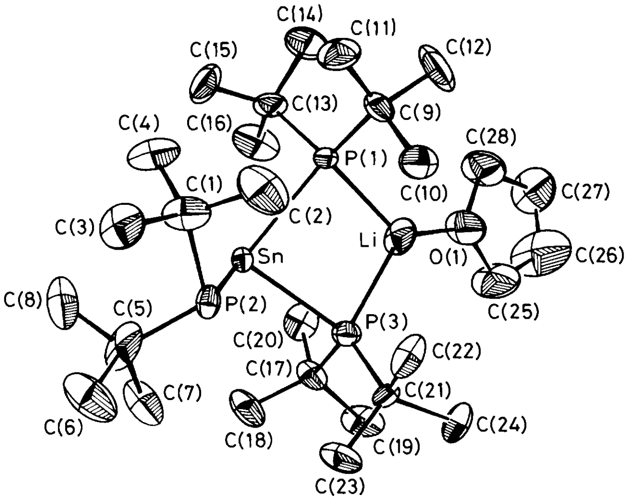

Figure 1. View (ORTEP) of [Li(thf){Sn(PBu$^t_2$)$_3$}] (**2**), showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows [the corresponding values for (**3**) are given in brackets]: Sn(Pb)–P(1) 2.702(3) [2.814(6)], Sn(Pb)–P(2) 2.684(4) [2.766(7)], Sn(Pb)–P(3) 2.671(4) [2.758(9)], P(1)–Li 2.49(3) [2.57(6)], P(3)–Li 2.48(3) [2.46(4)]; Sn(Pb)–P(1)–Li 89.0(6) [89.0(1)], Sn(Pb)–P(3)–Li 90.0(7) [92.0(1)], P(1)–Sn(Pb)–P(3) 84.1(1) [82.2(3)], P(1)–Sn(Pb)–P(2) 120.2(1) [118.4(2)], P(2)–Sn(Pb)–P(3) 104.2(11) [103.7(3)].

and 304.4° respectively). Phosphorus–lithium distances in diorganophosphides[5] have been found to depend on co-ordination number, being 2.49 and 2.63 Å for three- and four-co-ordinate lithium, respectively. The P–Li distances in (**2**) [av. 2.48(3) Å] and (**3**) [av. 2.51(6) Å] are thus consistent with the chelate interaction of P(1) and P(3) with a Li(thf) unit. The co-ordination of one rather than two thf molecules is presumably a consequence of steric constraints. The average Sn–P distance in (**2**) (2.686 Å) is comparable to that in [Sn{C(PMe$_2$)$_3$}] (2.707 Å),[6] the only other structurally characterised Sn^{II}–P compound. To the best of our knowledge no structural data are available for Pb^{II}–P bonds.

The ^{119}Sn n.m.r. chemical shift of (**2**) (δ − 1310 p.p.m.) is a further indication of the negative charge at Sn. Interestingly, the ^{119}Sn resonance of (**2**) is a quartet [$^1J(^{119}Sn–^{31}P)$ 1360 Hz] and the ^{31}P resonances of both (**2**) (δ 47.2) and (**3**) (δ 71.5) are singlets (with ^{117}Sn, ^{119}Sn, and ^{207}Pb satellites)‡ at ambient temperature, thus implying a fluxional process in which P–Sn or P–Pb bonding is maintained. No significant changes were apparent in the ^{119}Sn or ^{31}P spectra at −80 °C. A reasonable transition state for the migratory process is one in which the Li(thf) moiety is bonded equally to all three phosphorus atoms. Interestingly, this transition state-geometry corresponds to that of the ground state of Tl(OBu^t)$_3$Sn.[7] However, we cannot rule out more complex mechanisms on the basis of the present evidence.

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‡ $^1J(^{117}Sn–P)$ 1300, $^1J(^{119}Sn–P)$ 1360, $^1J(^{207}Pb–P)$ 1770 Hz.