Stoichiometric assembly of $[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me$; a highly fluxional antimony(III) phosphinidine complex containing Me_2NH ligation of lithium†

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All of the Me_2NH produced by the reaction of $[Sb(NMe_2)_3]$ with $CyP(H)Li$ ($Cy = C_6H_{11}$) coordinates the Li^+ cations of the product $[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me$ 1; the complex contains the first example of a group 15 metal phosphinidine anion $\{[Sb(PR)_3]^{3-}\}$.

Although group 13 metal imido (RN^{2-}) and phosphinidine (RP^{2-}) compounds are now comparatively common,[1] far fewer imido complexes are known for the heaviest (most metallic) group 14 (Sn, Pb) and 15 (Sb, Bi) elements. We have recently investigated the use of the stepwise metallation of primary amines with organolithiums and $[Sb(NMe_2)_3]$ as a general strategy to a range of polyimido antimony anions, *e.g.* the $[Sb(NR)_3]^{3-}$ trianion of the cage complex $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2thf]$.[2,3] These species have an extensive coordination chemistry towards alkali, transition and p-block metals, where they act as surprisingly robust multidentate ligands.[4] A related methodology, involving the transmetallation reactions of lithiated primary amines and phosphines with imido tin(II) cubanes,[5] provides an approach to the metallacyclic phosphinidine complex $[Sn(\mu\text{-}PCy)_2(\mu\text{-}PCy)]_2(Li\cdot thf)_4$.[6]

We report here the stoichiometric assembly of the complex $[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me$ **1** from the reaction of $[Sb(NMe_2)_3]$ with $CyP(H)Li$ (Scheme 1).‡ The cage arrangement of **1** is similar to that occurring in the imido antimony(III) complex $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2thf]$[3] and in a few unsolvated group 14 cages of Si^{IV} and Ge^{IV}.[7] However, this complex contains the first phosphinidine anion of a group 15 element (As–Bi). Although solvation of alkali-metal cations by NH_3 has been well documented for solutions of the metals in liquid ammonia,[8] the incorporation of a small protic ligand such as Me_2NH (a gas above 7 °C) in a reaction involving conventional organic solvents is a surprising structural feature of **1**.

$$2[Sb(NMe_2)_3] + 6CyP(H)Li \xrightarrow{\text{thf–toluene}} \underset{\mathbf{1}}{[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me}$$

Scheme 1

A low-temperature X-ray crystallographic study of **1**§ shows it to be a mixed-metal cage complex, $[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me$, consisting of a 14-membered $\{Sb_2P_6Li_6\}$ core (Fig. 1). In addition there are two lattice-bound toluene molecules per molecule of **1**. The structure, which arises from the association of two $[Sb(PCy)_3]^{3-}$ trianions by six Li^+ cations, can be described as a hexameric phosphido-lithium 'stack' capped at the open Li_3P_3 faces by two Sb atoms. However, direct evidence of the integrity of the $[Sb(PCy)_3]^{3-}$ trianions of **1**, and the fact that these units dominate the bonding pattern of the core,[9] is given in the ^7Li NMR spectrum in which a binomial septet ($^1J_{^{31}P^7Li}$ 14 Hz) occurs as a result of the coupling of all the Li^+ cations to the P atoms of two intact trianions (203–298 K) (Fig. 2). Preliminary semi-empirical PM3 calculations¶ indicate that interchange of the six Li^+ cations occurs by a

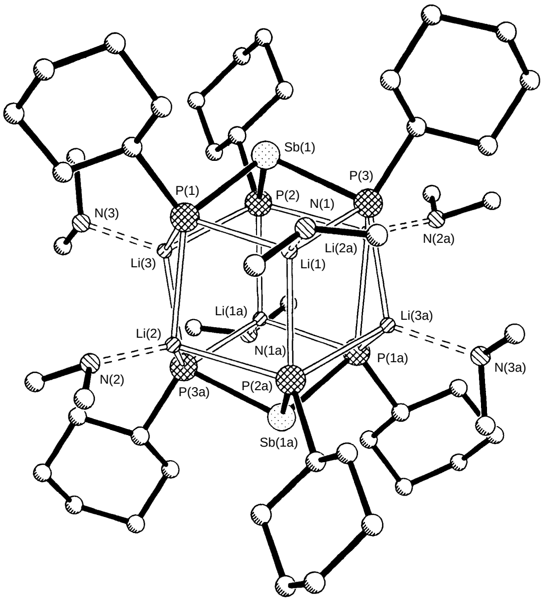

Fig. 1 The molecular structure of $[Sb(PCy)_3]_2Li_6\cdot 6HNMe_2\cdot 2C_6H_5Me$ **1** showing the atom numbering scheme. The $C_6H_5Me_3$ lattice solvation and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–P(1) 2.519(6), Sb(1)–P(2) 2.517(5), Sb(1)–P(3) 2.516(5), Li(1)–P(3) 2.59(3), P(1)–Li(3) 2.56(3), Li(1)–P(1) 2.55(3), Li(3)–P(2) 2.62(3), P(1)–Li(2) 2.62(3), N(3)–Li(3) 2.08(3), N(2)–Li(2) 1.96(4), N(1)–Li(1) 2.10(4); P(3)–Sb(1)–P(2) 101.3(2), P(2)–Sb(1)–P(1) 103.4(2), P(3)–Sb(1)–P(1) 100.3(2).

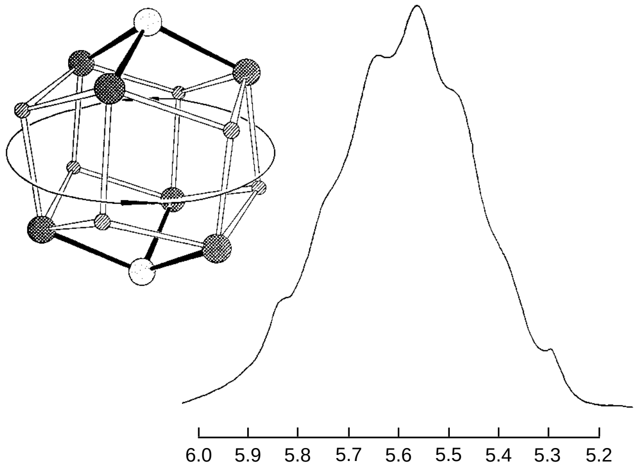

Fig. 2 Dynamic 'carousel' process and the ^7Li NMR spectrum of **1**

dynamic ('carousel') process, analogous to that observed for $[Me_2Si(NSiMe_3)_2]_2InLi$ in solution,[10] in which the Sb^{III} centres are not involved. The ^{31}P NMR chemical shift (δ −263.5) is vastly different to that observed for $[(2,4,6\text{-}Bu^t{}_3C_6H_2)P{=}Sb\{CH(SiMe_3)_2\}]$ (δ 600),[11] reflecting the development of negative charge on the P centres of **1**.

In the polymeric ladder structure of the monolithiated cyclohexyl phosphine precursor to **1** $(CyPHLi{\cdot}thf)_\infty$,[12] the P–Li bonds (av. 2.61 Å) are similar to those found in **1** [range 2.55(3)–2.66(3) Å]. The Sb–P bonds in **1** (av. 2.52 Å) are close to those observed in $[SbP(2,4,6\text{-}Bu^t{}_3C_6H_2)]_2$ [range 2.561(2)–2.583(1) Å] (the only other Sb or Bi phosphinidine complex to be structurally characterised).[13] An interesting structural feature of complex **1** is that the P–Sb–P angles (av. 101.6°) are significantly larger than the N–Sb–N angles (av. 94.5°) found in the related imido complex $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6{\cdot}2thf]$.[3] Although the flattening of the $[Sb(PCy)_3]^{3-}$ trianion may partially reflect the differences in the extents of Lewis-base solvation of the cores {two thf in $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6{\cdot}2thf]$ and six Me_2NH in **1**}, it is likely that the major reason for this is the lower electronegativity difference between Sb and P (*ca.* 0.2 on the Pauling scale; *cf.* 1.1 between Sb and N).

A particularly novel structural feature of **1** is the complexation of the six Li^+ cations of the core by Me_2NH. This is a gas above 7 °C and its formation can be envisaged as normally providing the thermodynamic driving force in the reactions of $[Sb(NMe_2)_3]$ with organic acids. However, the stoichiometric inclusion into **1** of all the Me_2NH formed in this reaction is surprising since it not only competes for Li^+ coordination with thf but exists as a gas under normal conditions. ^1H NMR spectroscopic studies and elemental analysis of **1** illustrate that, although the Me_2NH ligation is almost completely removed by placing the complex under vacuum (0.1 atm, 15 min), this solvation is comparatively robust and is largely retained in fresh samples not subjected to reduced pressure. Recent *ab initio* calculations[14] on the deprotonation of organic acids (RH) with lithium amides (R'_2NLi)[15] suggest that complexation of the amine produced (R'_2NH) to the Li^+ cation {in $[(R'_2NH)LiR]$} may contribute significantly to the thermodynamics of these reactions. The formation of **1** provides the first direct evidence in favour of this proposition and that even for gaseous amines Li^+ ligation is likely to play a role.

The incorporation of a phosphorus donor functionality in the $[Sb(PCy)_3]^{3-}$ trianion creates a softer ligand set and a greater ligand bite than the imido congeners and may allow the stabilisation of low oxidation state transition-metal centres.

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Footnotes and References

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† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/cccenha.htm

‡ *Synthesis of* **1**: to a stirred and chilled suspension of $[LiP(H)Cy]_n$ (7.53 mmol of monomer) in toluene (5 ml) was added a solution of $[Sb(NMe_2)_3]$ (2.51 mmol, 1.36 cm^3, 1.84 mol dm^{-3} in toluene). The suspension was stirred and gradually allowed to warm towards 0 °C at which stage a yellow precipitate was observed. This was dissolved by the addition of chilled toluene (8 cm^3) and thf (1 cm^3). The red solution produced was stored at −35 °C for 48 h over which period crystals suitable for X-ray diffraction studies grew. The complex loses Me_2NH of solvation gradually at 25 °C and this is almost completely removed by placing **1** under vacuum (15 min, 0.1 atm). However, if isolated without exposure to vacuum the Me_2NH is largely retained. The following data refer to this material: yield 1.02 g (57%); decomp. 170 °C; IR (Nujol), major bands at 1257m, 1178s, 1051s, 992.5m, 897s, 846s, 730m, 694w cm^{-1}; ^1H NMR (400.16 MHz, +25 °C, $C_6D_5CD_3$), δ 7.0 (5 H, m, aryl C–H, $C_6\mathit{H}_5CH_3$), 3.94 (13 H, s, Me, Me_2NH), 2.5–1.2 [33 H, overlapping m, Cy and $C_6H_5C\mathit{H}_3$ (2.10)]; ^7Li NMR (1.55.513 MHz, +25 °C, $C_6D_5CD_3$), δ 5.57 (binomial spt, $^1J_{^{31}P^7Li}$ 14 Hz) (rel. to LiCl–D_2O) (δ 7.14 rel. to PhLi–$C_6D_5CD_3$); ^{31}P NMR (162.000 MHz, +25 °C, $C_6D_5CD_3$), δ −263.5 [rel. to neat $(MeO)_3P$; br s, width at half-height 1130 Hz]; Analysis Calc. C, 52.3; H, 8.7; N, 5.6. Found: C, 52.0; H, 8.4; N, 4.4 (no N remains after 15 min at 0.1 atm).

§ *Crystal data* for **1**; $C_{31}H_{62}Li_3N_3P_3Sb$, M = 712.32, monoclinic, space group $P2_1/c$, a = 13.460(3), b = 18.123(3), c = 16.589(4) Å, β = 99.83(2)°, U = 3987(2) $Å^3$, Z = 4, D_c = 1.187 Mg m^{-3}, T = 150(2) K, μ(Mo-Kα) = 0.834 mm^{-1}, $F(000)$ = 1496. Yellow cubes, crystal dimensions 0.30 × 0.25 × 0.20 mm. 3717 reflections ($2\theta < 45.0°$) were collected on a Siemens R3mV diffractometer using Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator and ω–2θ scans ($2.57 \leqslant \theta \leqslant 19.99°$). 3717 independent reflections (R_{int} = 0.021) after a semiempirical absorption correction was applied. The structure was solved using direct methods and refined by full-matrix least squares based on F^2 (SHELXL93),[16] with all non-hydrogen atoms assigned anisotropic displacement parameters; cyclohexyl, toluene and amine H atoms were fixed in idealised positions and allowed to ride on the relevant C or N atoms. The refinement converged to R_1 = 0.0748 for data $I > 2\sigma(I)$ and wR_2 = 0.2722 for all data, goodness of fit = 1.013, and weighting scheme $w = 1/[\sigma^2(F_o{}^2) + (0.0597P)^2 + 18.32P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$. Largest peak and hole in the final difference map; 0.913, −0.689 e $Å^{-3}$. Crystals of **1** were weakly diffracting. Restraints were applied for the lattice-bound toluene which is disordered over two (50 : 50) sites about a twofold axis. CCDC 182/564.

¶ Calculations were carried out using VAMP 5.6 (Oxford Molecular) (J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209) on a Silicon Graphics R4400 workstation.

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