Fragmentation of an imido tin(II) cubane; syntheses and structures of heterobimetallic complexes containing tin(II) imido and phosphinidine anions

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The reactions of the imido tin(II) cubane $[SnNBu^t]_4$ with 3 equiv. of $[C_{10}H_7NHLi]$ ($C_{10}H_7$ = 1-naphthyl) and 6 equiv. of $[C_6H_{11}PHLi]$ (C_6H_{11} = cyclohexyl) produce $[Li(thf)_4]^+[(Bu^tN)(C_{10}H_7N)_3Sn_3Li{\cdot}thf]^-{\cdot}thf{\cdot}PhMe$ 1 and $[\{Sn_2(PC_6H_{11})_3\}_2Li_4{\cdot}4thf]{\cdot}2thf$ 2, respectively, containing the first structurally characterised polyimido and polyphosphinidine anions of a divalent group 14 metal.

Recently we have investigated the use of group 15 metal dimethylamido complexes $[ECl_{3-x}(NMe_2)_x]$ (E = Sb, Bi; x = 2, 3) as precursors in the synthesis of a range of metallo-organic compounds.[1] We found that these species are particularly potent bases and doubly deprotonate primary amines (RNH_2) at low temperatures, producing dimeric imido complexes containing $[E(\mu\text{-}NR)]_2$ cores.[1a,b] The reactions of these dimethylamido metal complexes with metallated primary amines $[(RNHLi)_n]$ result in a range of mixed-metal cage compounds containing novel polyimido–group 15 metal anions.[1c,d] Lately we have extended this work to group 14 by investigating the synthetic utility of $[Sn(NMe_2)_x]$ (x = 2, 4)[2] with primary and metallated primary amines. The reagent $[Sn(NMe_2)_2]$ reacts with a variety of primary amines, furnishing a general and facile synthesis to the imido tin(II) cubanes $[SnNR]_4$.[3] We here report that acid/base fragmentation reactions of $[SnNBu^t]_4$[4] with monolithiated primary amines and phosphines ($[REHLi]_n$; E = N, P) provide a new route to tin(II) polyimido and polyphosphinidine anions.

The reactions of $[SnNBu^t]_4$ with $[C_{10}H_7NHLi]$ (1 : 3 equiv.) or with $[C_6H_{11}PHLi]$ (1 : 6 equiv.), respectively, give $[Li(thf)_4]^+[(Bu^tN)(C_{10}H_7N)_3Sn_3Li{\cdot}thf]^-{\cdot}thf{\cdot}PhMe$ 1 ($C_{10}H_7$ = 1-imidonaphthyl) and $[\{Sn_2(PC_6H_{11})_3\}_2Li_4{\cdot}4thf]{\cdot}2thf$ 2 (C_6H_{11} = cyclohexyl). Although the mechanisms of these reactions are not clear, 1 results from the formal extrusion of a tris(amido)stannate unit, $[Sn(\mu\text{-}HNBu^t)_3Li]$, and 2 is formed by formal acid/base exchange of the NBu^t groups for PC_6H_{11}.†

A low-temperature X-ray crystallographic study of 1‡ shows it to be an ion-separated species $[Li(thf)_4]^+[(Bu^tN)(C_{10}H_7N)_3Sn_3Li{\cdot}thf]^-{\cdot}thf{\cdot}PhMe$ (Fig. 1). In addition, there is one molecule of thf and one toluene molecule per formula unit in the lattice. The heterometallic $[(Bu^tN)(C_{10}H_7N)_3Sn_3Li{\cdot}thf]^-$ anion has a cubane structure (which can be regarded as a Li-substituted Sn_4N_4 unit) in which the three $C_{10}H_7N^{2-}$ imido ligands have similar environments, each bridging the Li centre and two Sn centres within the cubane. The Bu^tN^{2-} group bridges all three Sn atoms and is located at the opposite corner to the Li^+ cation. The coordination of the Li^+ cation by a thf ligand ensures that it adopts a typical pseudo-tetrahedral geometry [Li–O 1.94(2) Å, av. angle about Li 107.6°].[8] Overall, the anion of 1 can be regarded as arising from the association of the tripodal polyimido tin(II) dianion $[(Bu^tN)(C_{10}H_7N)_3Sn_3]^{2-}$ with a thf solvated Li^+ cation.

Within the Sn_2N_2 faces of the anion of 1, the Sn–N bond lengths (av. 2.18 Å) and the angles about the Sn (av. N–Sn–N 80.4°) and N (av. Sn–N–Sn 99.3°) centres are all uniform and similar to those previously observed in imido $[SnNR]_4$ cubanes.[3,4] However, the accommodation of the Li^+ cation into the cubane framework results in wider angles at the Sn centres within the SnN_2Li faces [av. N–Sn–N 87.1°] than those found in the Sn_2N_2 rings. Further distortion of the cubane arises from the inherent shortness of the Li–N bonds (av. 2.10 Å) compared to the Sn–N (av. 2.18 Å) bonds. As a result, the Li^+ cation is displaced towards the centroid of the Sn_3LiN_4 cubane (av. Sn–N–Li 90.6°).

The low-temperature X-ray structure of 2 shows it to be a mixed-metal cage complex $[\{Sn_2(PC_6H_{11})_3\}_2Li_4{\cdot}4thf]{\cdot}2thf$, containing a fourteen-membered $[Sn_4P_6Li_4]$ core (Fig. 2).‡ In addition, there are two lattice-bound molecules of thf per molecule of 2. Similar core geometries to 2 have been observed in the antimony(III) complex $[(PhCH_2CH_2NLi)_3Sb{\cdot}thf]_2$[1d] and in the germanium(IV) and silicon(IV) complexes $[\{(Pr^i_3Si)$-

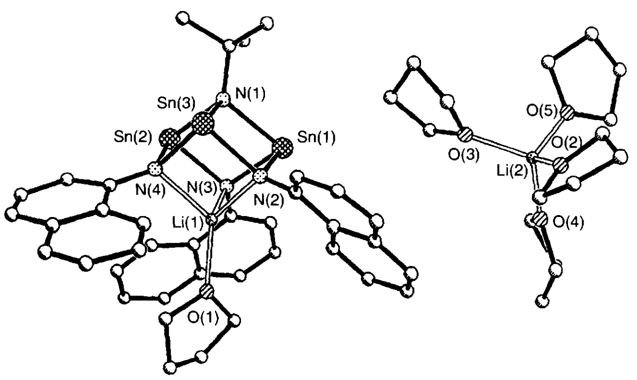

Fig. 1 Molecular structure of 1. Hydrogen atoms and lattice-bound thf solvation have been omitted for clarity.

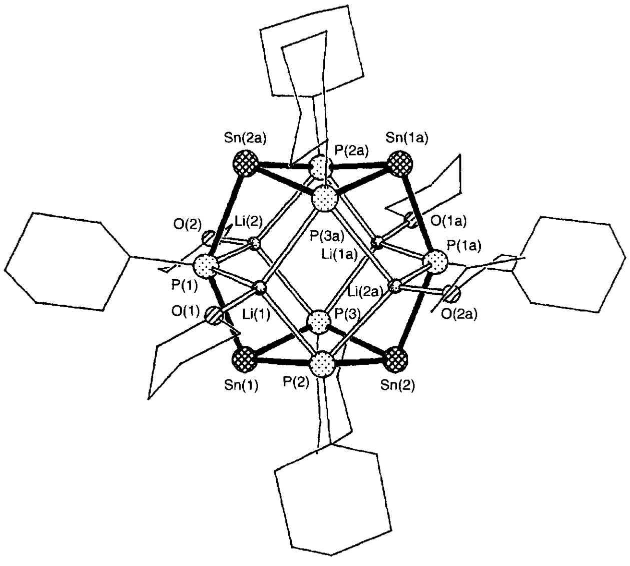

Fig. 2 Molecular structure of 2. Hydrogen atoms and lattice-bound thf solvation have been omitted for clarity.

$ELi\}_3E'Bu^t]_2$ (E = As, E′ = Ge;[8a] E = P, E′ = Si[8b]) and $[(RNLi)_3SiR']_2$ (R = Me_3Si, R′ = Me, Bu^t, Ph;[8c] R = Bu^t, R′ = Ph;[8d] R = Me, R′ = Bu^t[8e]).[9]

Molecules of **2** are constructed from the association of the tin(II) phosphinidine tetraanion $[\{Sn_2(PC_6H_{11})_3\}_2]^{4-}$ with four thf solvated Li^+ cations. This tetraanion unit can be visualised as being constructed from two puckered $Sn_2(\mu\text{-}PC_6H_{11})_2$ dimer rings linked together by two dimer-bridging PC_6H_{11} groups or, alternatively, as four tris(phosphido)stannate (SnP_3) moieties interlinked into a metallocyclic structure. The Sn–P bonds within **2** are all of similar lengths {2.606(4)–2.628(3) Å; *cf.* av. 2.68 Å in $[Bu^t{}_2PSn(\mu\text{-}PBu^t{}_2)_2Li\cdot thf]$}[10] and the SnP_3 units assume similar distorted pyramidal geometries [P–Sn–P 88.4(1)–100.1(1)°]. The four Li^+ cations are bound to the P centres of the $Sn_2(\mu\text{-}PC_6H_{11})_2$ dimer units and to the P centres of the dimer-bridging PC_6H_{11} groups in the equator of the $[\{Sn_2(PC_6H_{11})_3\}_2]^{4-}$ anion [P–Li 2.51(2)–2.64(2) Å]. These distances are similar to those observed in a number of lithium phosphide complexes.[7d,10] Further thf solvation of the Li^+ cations completes their coordination spheres and gives a similar pseudo-tetrahedral geometry for each (Li–O 1.92 Å, sum of angles about Li 108.6°). As a result of the complexation of the Li^+ cations, all the P atoms of the cage have similar square-based pyramidal geometries (each PC_6H_{11} group being bonded to two Li and two Sn centres).

Although Veith and Frank have shown that the *intact* Sn_4N_4 units of imido tin(II) cubanes form Lewis-base adducts with Lewis acids [*e.g.* the reaction of $[SnNBu^t]_4$ with $AlCl_3$ producing $[SnNBu^t]_4\cdot 2AlCl_3$],[11] the potential of imido tin(II) cubanes as precursors in the synthesis of other main group metal cages has not been reported. Clearly the extent of the reactions of $[SnNR]_4$ with organic acids, as illustrated by the structures of **1** and **2**, largely depend on the acidities of the reactants. Thus, whereas the reaction of $[SnNBu^t]_4$ with $[C_{10}H_7NHLi]$ results in partial fragmentation of the original cubane motif (with the retention of an NBu^t group) in **1**, the reaction with $[C_6H_{11}PHLi]$ results in substitution of all the NBu^t groups and in the formation of an expanded cage arrangement in **2**. Although a number of higher oxidation state (IV) group 14 anions are known,[8,9] **1** and **2** are representatives of a new class of low oxidation state (II) anion compounds. They are the first examples of compounds containing tin(II) polyimido (RN^{2-}) and polyphosphinidine (RP^{2-}) anions to be characterised in the solid state.

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Footnotes

† *Syntheses*: **1**; $[SnNBu^t]_4$ (0.5 mmol) was prepared by the *in situ* reaction of $[Bu^tNH_2]$ (0.210 cm³, 2.0 mmol) with $[Sn(NMe_2)_2]$ (0.414 g, 2.0 mmol) in toluene (20 cm³). On heating to reflux a yellow solution of the cubane was produced. This was added to a suspension of $[C_{10}H_7NHLi]$, prepared by the reaction of 1-aminonaphthalene (0.215 g, 1.5 mmol) in toluene (5 cm³) and thf (5 cm³) at 25 °C with Bu^nLi in hexanes (1.0 cm³, 1.5 mmol, 1.5 mol dm⁻³). The mixture was brought to reflux (20 min) after which all the yellow $[C_{10}H_7NHLi]$ had dissolved and a red–orange solution was formed. This solution was filtered (Celite) and addition of hexane (5 cm³) gave a yellow solid which was then heated gently back into solution. Storage (5 °C, 48 h) gave yellow crystalline blocks of **1**; yield = 0.25 g (41%); mp darkens at 140 °C, melts at 188–191 °C; IR (Nujol), ν_{max}/cm^{-1} *ca.* 3080 (aryl C–H stretch), other major bands at 1547, 1500, 1275, 1223, 1043, 884; ^1H NMR (250 MHz, +25 °C, C_6D_6), δ 8.89–8.85 (3 H, m, $C_{10}H_7$), 8.14–8.11 (3 H, m, $C_{10}H_7$), 7.92–6.88 (15 H, m, $C_{10}H_7$), 3.45 (20 H, s, thf), 1.65 (9 H, s, Bu^t), 1.40–1.31 (20 H, m, thf). Satisfactory elemental analyses (C, H, N) were obtained.

2; A solution of $[SnNBu^t]_4$ (0.5 mmol) in toluene (20 cm³) (as prepared in the synthesis of **1**) was added to a solution of $[C_6H_{11}PHLi]$, prepared by the reaction of Bu^nLi (2.0 cm³, 3.0 mmol, 1.5 mol dm⁻³) with $[C_6H_{11}PH_2]$ (0.39 cm³, 3.0 mmol) in toluene (5 cm³) and thf (5 cm³). An instantaneous red colour was observed. The reaction mixture was brought to reflux (5 min) before being filtered (Celite). The solvent was reduced to half volume under vacuum and a red–orange solid precipitated. This was heated gently back into solution and storage (−15 °C, 24 h) gave red crystalline blocks of **2**; yield 0.37 g (55%); decomp. 200 °C to a black solid; ν_{max}/cm^{-1} no diagnostic bands (major bands at 1043, 800 cm⁻¹); ^1H NMR (250 MHz, +25 °C, C_6D_6), δ 1.13–2.90 (66 H, overlapping m, C_6H_{11}) 3.80 (10 H, m, thf), 1.45 (10 H, m, thf); ^{31}P NMR (101.3 MHz, +25 °C, C_6D_6, relative to PMe_3), −184.2 [m (^7Li–^{31}P coupling), $^1J_{Sn-P}$ 1070 Hz], −249.5 [m (^7Li–^{31}P coupling), $^1J_{Sn-P}$ *ca.* 550 Hz]; ^{119}Sn NMR (125 MHz, +25 °C, C_6D_6, relative to $SnCl_2/D_2O$), δ −139.5 [dt, $^1J_{P-Sn}$ 1070, 550 Hz]. Satisfactory elemental analyses (C, H, P) were obtained.

‡ *Crystal data*: **1**; $C_{65}H_{91}Li_2N_4O_6Sn_3$, M_w = 1394.37, triclinic, space group $P\bar{1}$, a = 13.740(3), b = 14.516(3), c = 17.472(3) Å, α = 73.97(3), β = 78.97(3), γ = 77.99(3)°, U = 3243(1) Å³, Z = 2, λ = 0.71073 Å, T = 153(2) K, D_c = 1.428 Mg m⁻³, μ(Mo-Kα) = 1.197 mm⁻¹. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated[5] crystal of dimensions 0.2 × 0.2 × 0.15 mm using the θ–ω method ($8.02 \leqslant 2\theta \leqslant 45.02°$). Of a total of 9143 reflections collected, 8433 were independent. $R1$ = 0.061 ($F > 4\sigma F$), $wR2$ = 0.174 (all data) (weighting scheme, x = 0.0828, y = 16.314).[6] Largest difference in the final difference map, 0.791 and −0.621 e Å⁻³.

2: $C_{60}H_{114}Li_4O_6P_6Sn_4$, M_w = 1619.85, monoclinic, space group $C2/c$, a = 29.159(5), b = 14.981(2), c = 19.235(3) Å, β = 115.253(9)°, U = 7599(2) Å³, Z = 4, λ = 0.71073 Å, T = 153(2) K, D_c = 1.416 Mg m⁻³, μ(Mo-Kα) = 1.467 mm⁻¹. Of a total of 5808 reflections collected, 4966 were independent. $R1$ = 0.066 ($F > 4\sigma F$), $wR2$ = 0.171 (all data) (weighting scheme, x = 0.056, y = 119.94).[6] Largest difference in the final difference map, 0.7682 and −0.495 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/98.

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