Direct synthesis of heterocyclic $[(RP)_nE]^-$ anions using $[E(NMe_2)_3]$ (E = Sb, As); implications to the mechanism of formation of Zintl compounds

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The low-temperature reactions of $[Sb(NMe_2)_3]$ with $[CyPH_2]$ and [CyPHNa] (1 : 1 : 1 equiv.) and of $[As(NMe_2)_3]$ with $[^tBuPHLi]$ (1 : 3 equiv.) in TMEDA–thf [TMEDA = $Me_2NCH_2)_2$] produce [{*cyclo*-$(CyP)_4Sb$}$Na\cdot Me_2NH\cdot$TMEDA$]_2$ 1 and [{*cyclo*-$(^tBuP)_3As$}Li·TMEDA·thf] 2, respectively; at higher temperatures these reactions generate Zintl compounds containing Sb_7^{3-} and As_7^{3-} anions.

In earlier work we showed that a variety of dimethylamido Sb(III) reagents can be employed in the syntheses of a range of stable heterometallic imido cages containing Sb(III) anions (such as $[Sb(NR)_3]^{3-}$ and $[Sb_2(NR)_4]^{2-}$).[1] The reaction of $[Sb(NMe_2)_3]$ with [CyPHLi] (1 : 3 equiv. respectively) gives the Sb(III)/Li complex $[\{Sb\{PCy)_3\}_2Li_6\cdot 6Me_2NH]$ (Cy = C_6H_{11}) in which all the Me_2NH produced as a byproduct solvates the six Li^+ cations of the core.[2] Unlike the imido analogue, thermal decomposition of this complex occurs (*ca.* 30–40 °C) to produce the Zintl compound $[Sb_7Li_3\cdot 6Me_2NH]$, the product resulting from elimination of the phosphinidene groups (as is illustrated by the isolation of *cyclo*-$[CyP]_4$).[3] This unique phosphinidene coupling reaction (by which molecular cages are converted into molecular alloys) provides the means for the solution deposition of thin photoemissive alkali metal antimonate films[4] from molecular single-source precursors at low temperatures (*i.e.*, an ‘alloy paint’ approach) rather than using metal vapours.

In order to assess the generality of this approach we decided to investigate a range of reactions of $[E(NMe_2)_3]$ (E = As, Sb) with primary phosphines $[RPH_2]$ and primary phosphido alkali metal complexes (RPHM) (M = Li–Cs) (analogous to those we had used previously for the imido systems[1]). The low-temperature reaction (<0 °C) of $[Sb(NMe_2)_3]$ with $[CyPH_2]$ (Cy = cyclohexyl) (1 : 1 equiv.) followed by addition of [CyPHNa] (1 equiv.) in the presence of excess TMEDA [= $(Me_2NCH_2)_2$] was performed in order to obtain the hetero-bimetallic cage $[\{Sb_2(PCy)_4\}_2Na_4]$, the imido analogue of which ($[\{Sb_2(NCy)_4\}_2Na_4]$) was produced under similar conditions using [CyNHNa] and $[CyNH_2]$.[5] However, the initial product of this reaction is [{*cyclo*-$CyP\}_4SbNa\cdot$TMEDA$\cdot Me_2NH]_2$ **1**,† containing a heterocyclic $[\{CyP\}_4Sb]^-$ anion. Similarly, the low-temperature reaction (*ca.* 25 °C) of $[^tBuPHLi]$ with $[As(NMe_2)_3]$ (3 : 1 equiv.) in the presence of TMEDA–thf leads to the direct formation of [{*cyclo*-$(^tBuP)_3As$}Li·TMEDA·thf] **2**,† containing a related $[\{^tBuP\}_3As]^-$ anion, rather than giving $[\{As(P^tBu)_3\}_2Li_6]$ (*cf.* $[\{Sb(N^tBu)_3\}_2Li_6]$ which is obtained by a similar reaction from $[Sb(NMe_2)_3]$ and $[^tBuNHLi]$[6]). At higher temperatures [*ca.* 60 and 110 °C (in toluene), respectively] Zintl compounds containing As_7^{3-} are isolated.† The almost quantitative yields of the latter and the earlier isolation of $[CyP]_4$ from the thermolysis reaction of $[\{Sb\{PCy)_3\}_2Li_6\cdot 6Me_2NH]$ to the Zintl compound $[Sb_7Li_3\cdot 6Me_2NH]^3$ suggests that elimination of $[RP]_n$ rings from the $[\{CyP\}_4Sb]^-$ and $[\{^tBuP\}_3As]^-$ anions of **1** and **2** is a fundamental step in the formation of these Zintl ions. The precise mechanism of this process is still under investigation.

X-Ray crystallographic studies of **1** and **2** were undertaken at low temperature.‡ Complex **1** (Fig. 1) consists of centrosymmetric dimers [{*cyclo*-$CyP\}_4SbNa\cdot$TMEDA$\cdot Me_2NH]_2$, in which two heterocyclic $[\{CyP\}_4Sb]^-$ anions are associated by two Na^+ cations. The central Sb_2Na_2 ring has a planar, rhombic shape [Sb(1)–Na(1)–Sb(1a) 87.0(1), Na(1)–Sb(1)–Na(1a) 93.0(1)°], with the pattern of alternating Sb–Na bond lengths [Sb(1)–Na(1) 3.617(4), Sb(1)–Na(1a) 3.229(4) Å] indicating that the two monomer units are only loosely associated (*cf.* estimated 2.98 Å for the Sb–Na bond). Although a similar metallacyclic $[(^tBuP)_4Ni]$ fragment has been observed in the structure of [{(*cyclo*-$^tBuP)_4Ni\}(\eta^2$-$^tBuP)_2]$,[7] the closest p block relatives to **1** are the neutral heterocycle $[SbP(2,4,6$-$^tBu_3C_6H_2)]_2$ (composed of a four-membered P_2Sb_2 ring with an endocyclic Sb–Sb bond)[8] and complexes containing the cyclic $[P_5]^-$ anion.[9] Alkali metal Li–Sb bonded complexes have been reported previously;[10] however, **1** is the first containing a Na–Sb bond.

Complex **2** consists of discrete monomers [{*cyclo*-$(^tBuP)_3As$}Li·TMEDA·thf], in which a heterocylclic [{*cyclo*-$(^tBuP)_3As\}]^-$ anion is bonded by its anionic centre to a Lewis base solvated Li^+ cation (Fig. 2). The As–Li bond length in **2** [2.62(2) Å] is within the range observed in other complexes of this type (2.46–2.76 Å).[11] The formation of a four-membered P_3As anion in **2**, as opposed to a five-membered unit similar to that found in the related Sb(III) system **1**, may simply result from the smaller covalent radius of As (the shorter As–P bonds being accommodated into a four membered ring unit without inducing excessive strain). The closest relative of **2** is $[(^tBuP)_3As]_2$, a principal product of the Wurtz coupling reaction

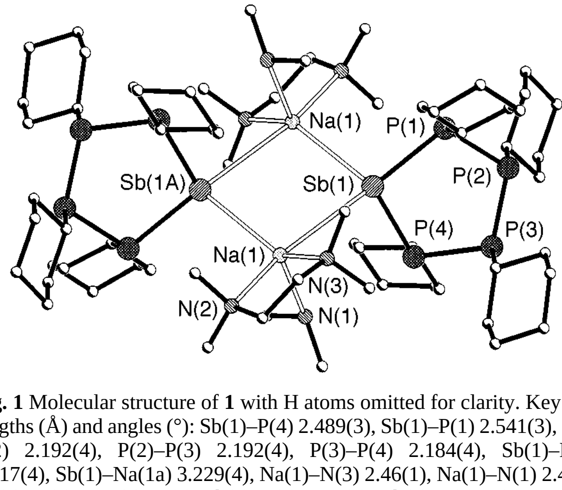

Fig. 1 Molecular structure of **1** with H atoms omitted for clarity. Key bond lengths (Å) and angles (°): Sb(1)–P(4) 2.489(3), Sb(1)–P(1) 2.541(3), P(1)–P(2) 2.192(4), P(2)–P(3) 2.192(4), P(3)–P(4) 2.184(4), Sb(1)–Na(1) 3.617(4), Sb(1)–Na(1a) 3.229(4), Na(1)–N(3) 2.46(1), Na(1)–N(1) 2.49(1), Na(1)–N(2) 2.49(1); P(1)–Sb(1)–P(4) 99.7(1), Sb(1)–P(1)–P(2) 105.7(1), P(3)–P(2)–P(1) 110.9(2), P(4)–P(3)–P(2) 109.4(2), Sb(1)–P(4)–P(3) 105.6(2), Na(1)–Sb(1)–Na(1a) 93.0(1), Sb(1)–Na(1)–Sb(1a) 87.0(1). Symmetry transformations used to generate equivalent atoms $-x + 2$, $-y + 1$, $-z$.

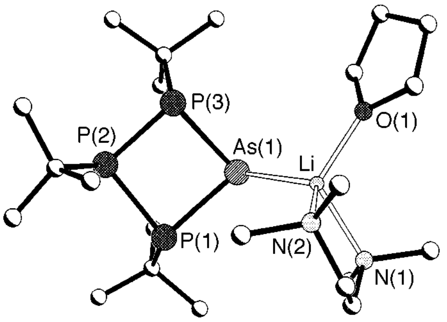

Fig. 2 Molecular structure of **2** with H atoms and the disorder on the thf and TMEDA ligands omitted for clarity. Key bond lengths (Å) and angles (°): As(1)–P(1) 2.333(4), As(1)–P(3) 2.324(3), As(1)–Li 2.62(2), P(1)–P(2) 2.203(4), P(2)–P(3) 2.198(4), Li–N(1,2) av. 2.10, Li–O(1) 1.92(2); P(1)–As(1)–P(3) 85.1(1), P–As–Li av. 107.5, As(1)–P(1)–P(2) 88.2(1), As(1)–P(3)–P(3) 88.5(1), P(1)–P(2)–P(3) 91.4(2).

of $AsCl_3$, ${}^tBuPCl_2$ and Mg, which consists of two $[({}^tBuP)_3As]$ rings linked by their As centres.[12]

In conclusion, the aforementioned reactions provide direct access to a unique family of group 15 heterocyclic anions (**1** and **2** being the first examples of this type to be characterised). The application of these species as sources of $[\{RP\}_nE]^-$ (E = Sb, As) ligands to other main group and transition metals and the thermolysis of the resulting complexes is an interesting prospect.

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Notes and references

† *Synthesis* of **1**: $[Sb(NMe_2)_3]$ (5.1 ml, 1.74 mol dm^{-3} in toluene, 8.8 mmol) was added dropwise to a chilled solution of $CyPH_2$ (1.17 ml, 8.8 mmol) in hexane (20 ml). The solution was allowed to warm to room temperature and stirred (10 min). The orange solution produced was transferred by syringe into a chilled (*ca.* −20 °C) solution of [CyPHNa] [prepared *in situ* by the reaction of $PhCH_2Na$ (1.0 g, 8.8 mmol) with $CyPH_2$ (1.17 ml, 8.8 mmol) in hexane (10 ml)–thf (5 ml)]. The reaction mixture was allowed to warm to *ca.* 0 °C. An excess of TMEDA (*ca.* 3.0 ml, 20 mmol) was added and the solution was filtered while cold. Crystallisation at −35 °C (24 h) gave red plates of **1**. Yield 1.1 g (16% on the basis of Sb supplied). Decomp. 75 °C to black solid. ${}^1H$ NMR (+25 °C, 250 MHz, $[{}^2H_8]$toluene), δ 1.0–2.0 (overlapping m, 40H, $\{CyP\}_4$), 2.22 (d, 4H (${}^2J_{31_{P-H}}$ *ca.* 6.4 Hz), C(α)-H of $\{CyP\}_4$), 2.10 (br s, 16H, TMEDA), 2.46 (s, 6H, Me_2NH). Elemental analysis. Calc. C, 50.4; H, 8.8; N, 5.5; P, 16.3. Found: C, 49.0; H, 8.6; N, 5.2; P 15.1%.

Synthesis of **2**: to a stirred, chilled suspension of $[LiPH{}^tBu]_n$ (6.0 mmol of monomer) in toluene (20 ml) and TMEDA (1.0 ml) was added a solution of $[As(NMe_2)_3]$ (2.0 mmol, 0.92 cm^3, 2.17 mol dm^{-3} in toluene). The suspension was stirred and gradually allowed to warm to 0 °C, at which stage an orange precipitate was observed. Then thf (20 ml) was added and the mixture stirred for 48 h after which an orange solution (with a fine precipitate) remained. This was filtered off and the solvent reduced to *ca.* 8 ml, the solid produced was redissolved by the addition of thf (*ca.* 1 ml) and storage at −18 °C (12 h) gave orange crystals of **2** suitable for X-ray diffraction studies. Isolated samples of **2** (placed *in vacuo* for *ca.* 15 min, 10^{-1} atm) contain no thf solvate. The following data refer to this material; yield 0.27 g (2% on the basis of As supplied to the reaction); mp. 115 °C to clean orange oil; IR (Nujol), major bands at 1260 m, 1032 s cm^{-1}; ${}^1H$ NMR (250 MHz, +25 °C, $[{}^2H_8]$thf), δ 2.39 (s, 4H, CH_2, TMEDA), 2.13 (s, 12H, Me_2N, TMEDA), 1.07 (d, 18H, ${}^3J_{P-H}$ 11.5 Hz), 1.01 (d, 9H, $J_{31_{P-H}}$ 10.5 Hz); ${}^{31}P$ NMR (101.256 MHz, +25 °C, $[{}^2H_8]$thf; rel. to 80% H_3PO_4–D_2O), δ 7.87 (t), −74.50 (d) (ratio 1 : 2, ${}^2J_{31_P-31_P}$ 179.4 ± 0.8 Hz); Elemental analysis. Calc. C, 46.8; H, 9.3; N, 6.1; P, 20.1. Found: C, 46.0; H, 9.3; N, 7.2; P, 17.6%.

The syntheses and structures of $[Sb_7Na_3\cdot 3TMEDA\cdot 3thf]$ **3** and $[As_7Li_3\cdot 3TMEDA]\cdot PhMe$ **4** (see last ref. 11) obtained in the high temperature reactions will be discussed in a later paper.

‡ *Crystal data*: for **1**: $C_{64}H_{134}N_6Na_2P_8Sb_2$, M = 1525.02, monoclinic, space group $P2_1/n$, a = 11.168(3), b = 22.420(4), c = 16.468(3) Å, β = 92.71(2)°, U = 4118.6(14) Å^3, Z = 2, D_c = 1.230 Mg m^{-3}, λ = 0.71073 Å, T = 223(2) K, μ(Mo-Kα) = 0.859 mm^{-1}. Data were collected on a Siemens P4 diffractometer. The crystal diffracted very weakly at high angle; of a total of 5646 data collected (1.82° $\leqslant \theta \leqslant$ 21.00°) 4439 were independent (R_{int} = 0.0532). Relatively high thermal displacement parameters indicated some disorder of the cyclohexyl rings but it was not possible to resolve this. Empirical absorption corrections were applied after initial refinement with isotropic displacement parameters.[13] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1[F > 4\sigma(F)]$ = 0.069 and $wR2$ = 0.214 (all data);[14] largest peak and hole in the final difference map 0.772 and −0.843 e Å^{-3}.

For **2**: $C_{22}H_{51}AsLiN_2OP_3$, M = 534.42, monoclinic, space group $P2_1/n$, a = 12.238(7), b = 15.574(12), c = 16.27(1), β = 105.23(5)°, U = 2993(4) Å^3, Z = 4, D_c = 1.186 Mg m^{-3}, T = 180(2) K, μ(Mo-Kα) = 1.311 mm^{-1}, $F(000)$ = 1144. Data were collected on a Siemens-Stoe diffractometer using ω–θ scans (3.56 $\leqslant \theta \leqslant$ 22.50). Of a total of 7645 reflections, 3900 were independent (R_{int} = 0.1036). The structure was solved using direct methods and refined by full matrix least squares on F^2 to final R indices of $R1$ = 0.086 $[F > 4\sigma(F)]$ and $wR2$ = 0.200 (all data);[14] largest peak and hole in the final difference map 1.269 and −0.622 e Å^{-3}. The C atoms of the thf ligand and one of the C atoms of each of the Me_2N groups of the TMEDA were disordered over two sites and were refined with half occupancy. CCDC 182/1045.

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