ditions near the poles at latitudes equatorward of ±87.5°. This last possibility is supported by the fact that the South Pole of the moon was viewed by Clementine during winter. Areas that appear to be shaded during the winter months may receive sunlight during other times of the year.

However, it is also possible that some of the excess hydrogen inferred from epithermal*-neutron data near the lunar poles is dispersed throughout relatively large areas of the polar regolith, having been delivered to the moon at more equatorial latitudes by the solar wind but transported to the poles through multiple collisionless hops through the lunar exosphere (*2*–*6*). By the method of construction, our polar estimates made from Fig. 6 are additions to the average mass fraction of hydrogen implanted in the regolith by the solar wind at lower latitudes. We believe a solar wind for most of the observed excess hydrogen is unlikely because the lack of a fast-neutron signature rules against a surface deposit.

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Low-Temperature Synthesis of Zintl Compounds with a Single-Source Molecular Precursor

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Thermolysis of the heterobimetallic phosphinidene complex $\{[Sb(PCy)_3]_2Li_6 \cdot 6HNMe_2\}$ (Cy = C_6H_{11}) at 303 to 313 kelvin gives Zintl compounds containing $(Sb_7)^{3-}$ anions. The complex thus constitutes a stable molecular single-source precursor to Zintl compounds and provides a potential low-temperature route to photoactive alkali metal antimonates. The new chemical reaction involved, which is driven thermodynamically by the formation of P–P bonds, has implications in the low-temperature synthesis of other technologically important materials (such as gallium arsenide).

Zintl compounds, which contain polyatomic posttransition metal anions and alkali or alkaline earth metal cations, were discovered over a hundred years ago (*1*). In the 1930s, Zintl and co-workers investigated the composition of solutions of group 14 or 15 elements with alkali metals in liquid NH_3 and showed that, depending on the concentration, a wealth of polyatomic main-group anions are present in equilibrium (*2*). To control their stoichiometry and to obtain single components, direct dissolution of binary alloys of the alkali and posttransition elements (prepared typically at 873 to 1473 K) is required (*3*). Corbett and others have used 2,2,2-crypt-[4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-(8,8,8)hexacosane], which strongly complexes Na^+ and K^+ cations and separates them from the polyatomic anions, to provide stable crystalline materials that are amenable to x-ray structural determination (*4*). Such structural investigations revealed that a wealth of bonding patterns are adopted by the polyatomic posttransition metal anions and these studies have had a fundamental impact on modern bonding theory (*4*).

Recently, by using stepwise metallation of primary amines and phosphines, we showed that a variety of heterometallic alkali metal/Sb(III) imido and phosphinidene complexes are accessible (*5*, *6*). We report here that thermolysis of the heterobimetallic phosphinidine complex $\{[Sb(PCy)_3]_2Li_6 \cdot 6HNMe_2\}$ **1** (Cy = C_6H_{11}) (*6*) in toluene at 303 to 313 K gives the Zintl compound $[Sb_7Li_3 \cdot 6HNMe_2]$ **2** and, with excess TMEDA, it gives $[\{(TMEDA)Li\}_3 Sb_7]$·toluene **3** [TMEDA= $(Me_2NCH_2)_2$] (*7*). The isolation of $(CyP)_4$ from these reactions indicates that this process involves reductive elimination (*7*), with the formation of P–P bonds (having the highest bond energy between any group 15 elements) providing the thermodynamic driving force. Complex **1** thus constitutes a stable molecular single-source precursor to Zintl compounds.

Low-temperature x-ray studies of **2** (Fig. 1) and **3** (Fig. 2) (*8*) show that they consist of discrete heterobimetallic cage molecules in which $(Sb_7)^{3-}$ ions are complexed at the equatorial Sb atoms by three Lewis base solvated Li^+ cations. The Sb–Li bond lengths in both complexes (average 2.92 Å in **2** and 2.89 Å in **3**) are comparable with those found in the other known Sb–Li bonded complexes (*9*–*11*). The minor differences in the bond lengths and angles observed in the $(Sb_7)^{3-}$ anion of **2** and **3** compared with the previously reported ion-separated complexes (*12*, *13*) imply that only weak Sb–Li bonding is occurring here. The recent synthesis of the only other Li/Sb Zintl compound, $[Li(NH_3)_4]_3[(NH_3)_2Li_2Sb_5]$, containing the cyclic $(Sb_5)^{5-}$ anion from the direct reaction of metallic Li and Sb in liquid ammonia is of particular relevance here (*11*). The same $[Sb_7]^{3-}$ ion is formed by thermolysis of **1** as is produced by addition of 2,2,2-crypt or ethyl-

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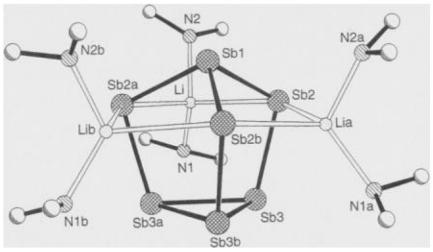

Fig. 1. Molecular structure of **2**. For clarity, H atoms have been omitted. Selected bond lengths (Å) and angles (°): Sb(1)–Sb(2), 2.7838(9); Sb(2)–Sb(3), 2.747(1); Sb(3)–Sb(3a,3b), 2.858(1); Sb(1)–Li, 2.95(2); Sb(2a)–Li, 2.90(2); Li–N(1), 2.04(2); Li–N(2), 2.07(2); Sb–Sb(1)–Sb, 101.20(3); Sb(1)–Sb(2)–Sb(3), 99.16(3); Sb(2)–Sb(3)–Sb(3a,3b), average 105.2; Sb(3a)–Sb(3)–Sb(3b), 60.0(1); Sb(2)–Li–Sb(2a), 94.9(5); N(1)–Li–N(2), 114(1). Symmetry transformations used to generate equivalent atoms: **a**, $-y + 2, x - y, z$; **b**, $-x + y + 2, -x + 2, z$.

enediamine to stoichiometric intermetallic Sb/M alloys (M = Na, K) in liquid NH_3 (*9–11*) and therefore it appears unlikely that the character of the Zintl ions produced may be affected by the choice of Lewis base ligand used. A more plausible explanation is that further reduction of the $(Sb_7)^{3-}$ anion (initially produced in solution) by metallic Li (in the solid state) is responsible for formation of the $(Sb_5)^{5-}$ ion. Therefore, a key feature of the thermolysis reactions of **1** is that the same degree of control of product stoichiometry is offered as is obtained from solvation of a preformed intermetallic alloy.

Although the presence of the $(Sb_7)^{3-}$ anion is not unprecedented and a structural arrangement similar to **2** and **3** has been observed in the $(As_7)^{3-}$ complex $\{[(TMEDA)Li]_3As_7\}$ (*14*), the simple preparation of these complexes using a stable molecular single-source precursor represents an important route to Zintl compounds. Driess has recently shown that a high yield of $\{[(TMEDA)Li]_3As_7\}$ is obtained by addition of TMEDA to the lithium tetraarsanylalanates $[LiAl(AsHR)_4]$ (R = H, Si^iPr_3). However, these thermolabile materials apparently cannot be isolated as solids and are stable only in solution (*14*). Because of the expense of 2,2,2-crypt and the specialized high-temperature techniques required for preparation of the precursor intermetallic alloys (*3*), Zintl compounds, particularly of the heaviest (most metallic) posttransition elements, have generally been prepared only on a very small scale (10 to 50 mg) and therefore have not been broadly accessible to most synthetic chemists (*15*). The use of **1** as a precursor (which is stable in the solid state) allows for cheap and convenient laboratory preparation of the $(Sb_7)^{3-}$ ion on a gram scale.

A final point concerns loss of the labile Me_2NH ligands of **2**. When the complex is placed under vacuum, a lusterous intermetallic phase is formed (probably LiSb and Sb) (*3*), indicating that **1** and related heterometallic compounds may be used as precursors to intermetallic Sb/alkali metal films, with important implications in the manufacture of photodiodes (*16*). Photodiode tubes are normally prepared by deposition of metallic Sb and alkali metals from the vapor, a process that suffers from poor control of the stoichiometry of the alkali metal antimonate film deposited. The use of **1** and related precursors may allow deposition of films of these technologically important materials from solution at low temperature.

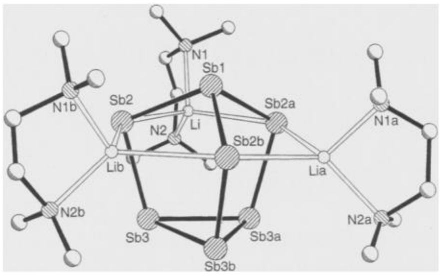

Fig. 2. Molecular structure of **3**. For clarity, H atoms, the disorder about the TMEDA ligands, and the lattice-bound toluene molecule have been omitted. Selected bond lengths (Å) and angles (°): Sb(1)–Sb(2), 2.805(2); Sb(1)–Sb(2a), 2.790(1); Sb(2)–Sb(3), 2.759(2); Sb(2a)–Sb(3a), 2.752(2); Sb(3)–Sb(3a), 2.847(2); Sb(3a)–Sb(3b), 2.863(2); Sb(2a)–Li(a), 2.90(2); Sb(2a)–Li, 2.90(2); Sb(2)–Li, 2.86(2); Sb(2)–Li(b), 2.86(2); Li–N, average 2.12; Sb–Sb(1)–Sb, average 101.0; Sb(1)–Sb(2)–Sb(3), 98.51(6); Sb(1)–Sb(2a)–Sb(3a), 99.46(5); Sb(2)–Sb(3)–Sb(3a), 105.92(6); Sb(2a)–Sb(3a)–Sb(3,3a), average 105.1; Sb(3)–Sb(3a)–Sb(3b), 59.81(3); Sb(3a)–Sb(3)–Sb(3b), 60.38(6); Sb–Li–Sb, average 96.6; N–Li–N, average 88.4. Symmetry transformations used to generate equivalent atoms: **b**, $x, -y + 3/2, z$.

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8. X-ray data for **2**, $C_{12}H_{42}Li_3N_6Sb_7$, molecular weight = 1143.58, trigonal, space group P^3 (unit cell dimensions), a = 11.508(1), c = 14.954(2) Å, Z (number of formula units) = 1, $\rho_{calc.}$ (crystal density) = 2.214 Mg m^{-3}, λ (wavelength used) = 0.71073 Å, T (temperature) = 198(2) K, μ(Mo–Kα) (absorption coefficient) = 5.438 mm^{-1}. Data were collected on a Siemens P4 diffractometer with an oil-coated rapidly cooled crystal (*17*) of dimensions 0.10 × 0.36 × 0.48 mm by the $\omega/2\theta$ method ($1.36° \leq \theta \leq 25.00°$). Of a total of 4482 collected reflections, 2004 were independent. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1[F > 4\sigma(F)] = 0.053$ and $wR2 = 0.168$ (all data) (*18, 19*); largest peak and hole in final difference map, 2.038 and –1.402e Å^{-3}. X-ray data for **3**: $C_{32}H_{64}Li_3N_6Sb_7$, M = 1407.97, monoclinic, space group $P21/m$, a = 10.192(1), b = 20.944(3), c = 11.967(2) Å, β= 92.22(1)°, Z = 4, $\rho_{calc..}$ = 1.829 Mg m^{-3}, λ = 0.71073 Å, T = 213(2) K, μ(Mo–Kα) = 3.673 mm^{-1}. Data were collected on a Siemens P4 diffractometer with an oil-coated rapidly cooled crystal (*17*) of dimensions 0.20 × 0.35 × 0.40 mm by the $\omega/2\theta$ method ($1.94° \leq \theta \leq 25.00°$). Of a total of 5803 collected reflections, 4636 were independent. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1[F > 4\sigma(F)] = 0.066$ and $wR2 = 0.241$ (all data) $\{R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{0.5}$, $w = 1/[\sigma^2(F_o{}^2) + (yP)^2 + xP]$, $P = F_o{}^2 + (2F_c{}^2/3)\}$ (*18, 19*); largest peak and hole in final difference map, 1.772 and –2.419 eÅ^{-3}. The $-CH_2-$ and Me groups of all the TMEDA ligands are disordered over two 1:1 sites. The disordered toluene molecule is disordered over two sites about a twofold axis.
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