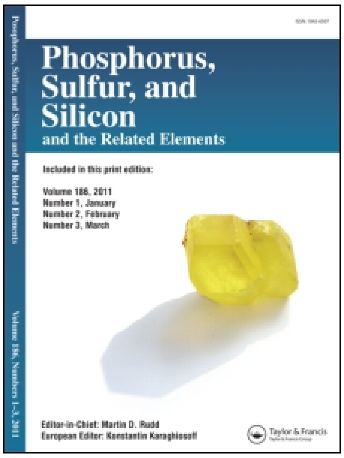

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A NEW LOW-TEMPERATURE SYNTHESIS OF ZINTL COMPOUNDS

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A NEW LOW-TEMPERATURE SYNTHESIS OF ZINTL COMPOUNDS

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In previous work, we have presented synthetic routes to a wide range of heterometallic antimony and alkali-metal complexes.[1] This work centerd on the idea of stepwise deprotonation, exploiting the high basicity of p-block metal dimethylamido reagents which are capable of doubly deprotonating primary amines. This reactivity contrasts with the basicity of standard alkali metal reagents which ordinarily will only singly deprotonate primary amines. This difference provides the key to a general synthetic approach to a range of anionic group 15 imido element frameworks, since stepwise deprotonation of one of the amine protons by organoalkali metal reagents can be followed by deprotonation of the second by $E(NMe_2)_3$ (E = As, Sb, Bi). The three major anionic arrangements that can be prepared using this procedure are shown in Figure 1.

With the above background in mind, we investigated the chemistry of the phosphines. Our initial aims were simply to furnish softer anion ligand arrangements, however, concurrent with this we also had developed an interest in the potential use of the Sb/alkali metal cages as low-temperature sources of alkali metal antimonates for photodiodes.[2] The reaction of $Sb(NMe_2)_3$ with CyPHLi (1:3 equiv. respectively) ca. below 0°C gives $[\{Sb(PCy)_3\}_2Li_6{\cdot}6Me_2NH]$ (**4**) (Figure 2).[3] Complex **4** is structurally very similar to complex **3**, however, if the reaction mix is

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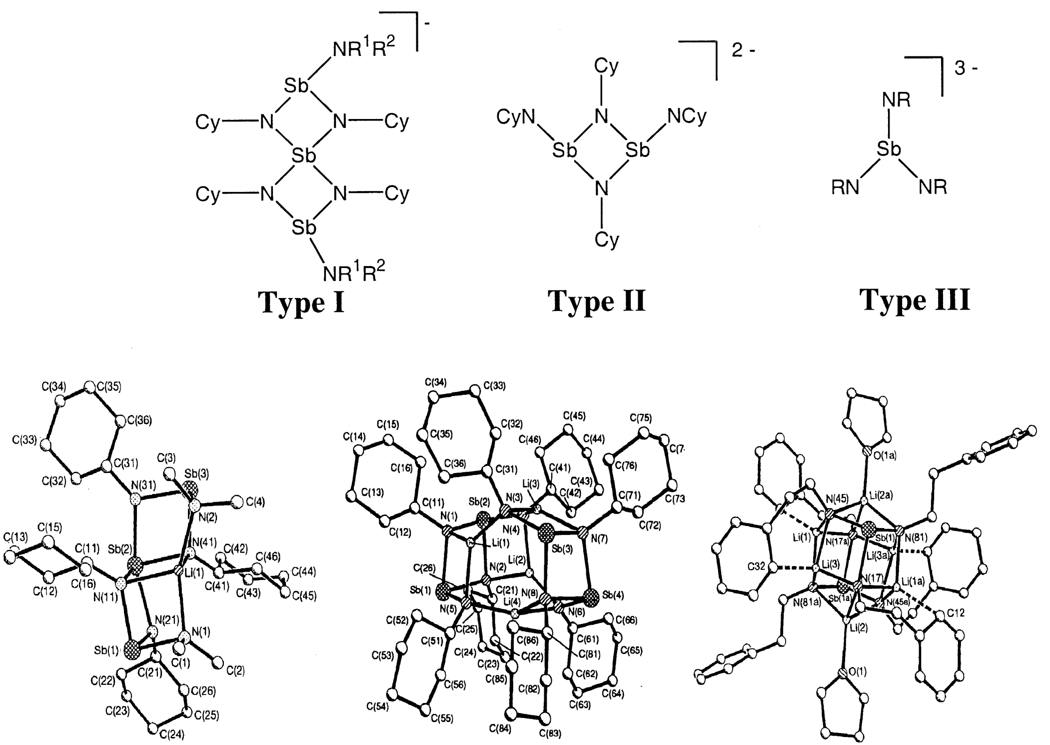

FIGURE 1 The frameworks accessible by stepwise metallation, and the cage structures adopted by [{$Me_2NSb(\mu$-$NCy)\}_2Sb]Li$ (**1**), [{$Sb_2(NCy)_4\}_2Li_4$] (**2**) and [{$Sb(NCy)_3\}_2Li_6\cdot 2HNMe_2$] (**3**).

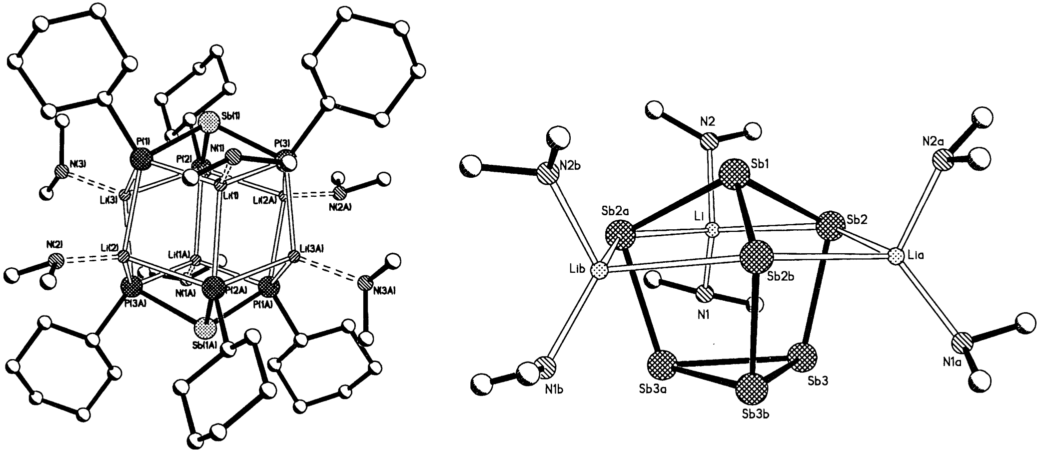

FIGURE 2 Structures of [$\{Sb(PCy)_3\}_2Li_6{\cdot}6Me_2NH$] (**4**) and [$Sb_7Li_3{\cdot}6HNMe_2$] (**5**).

warmed to ca. 30°C another complex may be isolated, the decomposition product [$Sb_7Li_3{\cdot}6HNMe_2$] (**5**) (Figure 2) a Zintl compound containing a nortricyclic Sb_7^{3-} anion coordinated by three Li^+ cations at the equatorial Sb centres.[4]

There have been a number of previous studies on Zintl compounds. Corbett has prepared them from stoichiometric Sb/alkali metal alloys[5] at high temperatures (ca. 1200°C) and then used stabilizing ligands (e.g., 2,2,2-crypt) to produce crystalline Zintl compounds. In the absence of such ligands, the alkali metal cations are easily reduced by the polyatomic Zintl anions, causing reversion to the intermetallic alloys.[5] In the case of **5**, removal of the Me_2NH ligands by placing the complex under vacuum results in the formation of a lustrous metallic phase (Sb and Sb/Li) and so it is, in effect, a metastable source of an alkali metal antimonate alloy.[4] Driess has shown that a high yield of [$\{(TMEDA)Li\}_3As_7$] (**6**) is obtained by the addition of TMEDA to the lithium tetraarsanylalanates [$LiAl(AsHR)_4$] (R=H, Si^iPr_3).[6] However, these thermolabile materials apparently cannot be isolated as solids and are only stable in solution.

The mechanism of this decomposition reaction is far from clear. The isolation of the cyclic compound $[CyP]_4$ from the reaction mix[4] suggests that the thermodynamic driving force could be the formation of P—P single bonds (the strongest homonuclear bonds in group 15).

In order to investigate the influence of the stoichiometry of the precursor on the outcome of the decomposition reaction an attempt was made to prepare the precursor complex [$\{Sb_2(PCy)_4\}_2Na_4$] (**7**), the imido analogue already having been structurally characterized.[7] After warming to ca. 60°C the Zintl compound [$Sb_7Na_3{\cdot}3TMEDA{\cdot}3thf$] (**8**) is isolated in almost quantitative yield[8] showing that the stoichiometry of the precursor bears no relationship to that of the Zintl complex formed. At ca. 0°C a complex [$\{CyP\}_4SbNa{\cdot}TMEDA{\cdot}Me_2NH]_2$ (**9**) is isolated from the reaction mixture, in which two heterocyclic $[\{CyP\}_4Sb]^-$ anions are bridged by two Na^+ cations (Figure 3).[8] This species is a likely intermediate in the formation of compound **9**, the $[\{CyP\}_4Sb]^-$ anion being set up for elimination of $[CyP]_4$.

The thermal instability of the $[\{CyP\}_4Sb]^-$ anion of **9** (which is not stable above room temperature) means that this compound is not a good candidate for studies on the reactivity of these heterocycles, however, the related As heterocycles being far more thermally stable (owing to the greater As—P bond strengths) are more promising. Reactions of the heterocycle [$\{^tBuP\}_3AsLi{\cdot}2DABCO{\cdot}thf$] (**10**) (DABCO=$N(CH_2CH_2)_3N$) with selected transition metal salts were investigated.[9] While reaction of **10** with [$C_5H_5Fe(CO)_2Cl$] gives the expected substitution at Fe, unexpectedly the only ring substituted products obtained when **10** is reacted

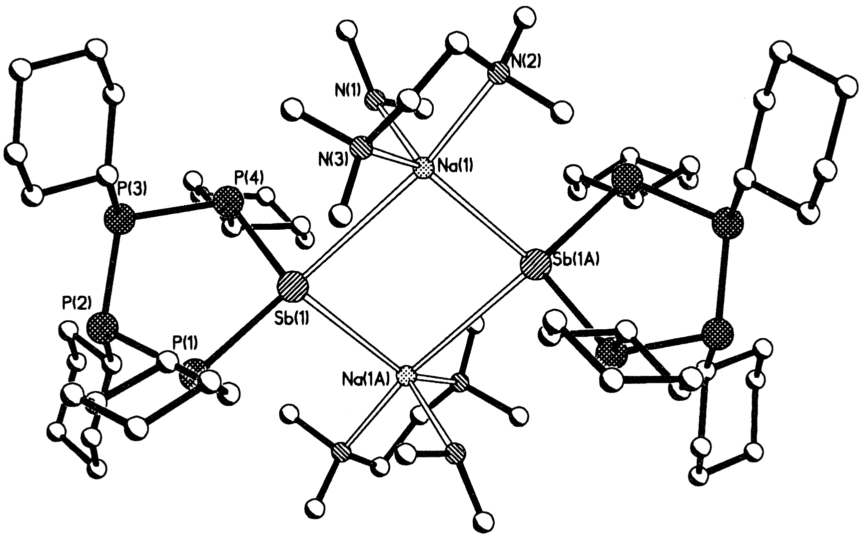

FIGURE 3 Structure of $[\{CyP\}_4SbNa \cdot TMEDA \cdot Me_2NH]_2$ (**9**).

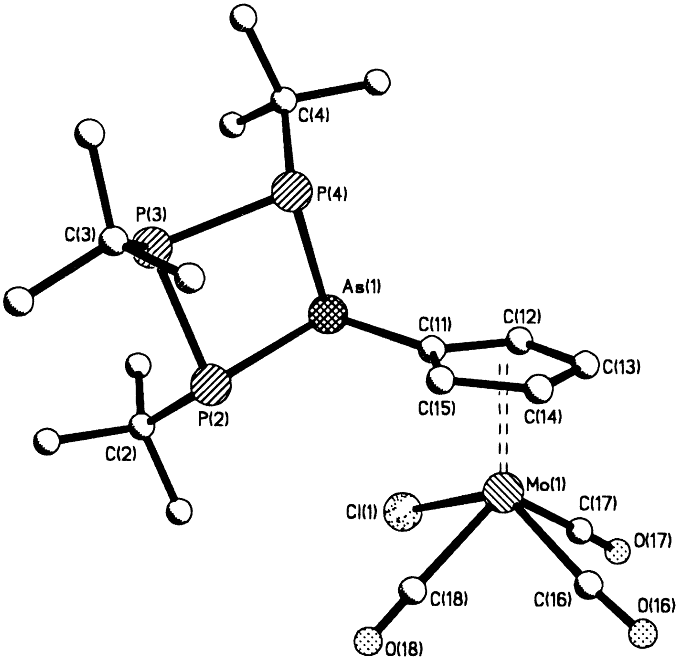

FIGURE 4 Structure of $[\{^tBuP\}_3AsC_5H_4Mo(CO)_3Cl]$ (**11**).

with [$C_5H_5M(CO)_3$)Cl] (M=Mo, W) are [{^{t}BuP}$_3$As$C_5H_4M(CO)_3Cl$] [M=Mo (**11**), W (**12**)] (Figure 4). Previous studies of the reactions of the sandwich compounds [$(C_5H_5)_2MCl_2$] (Mo, W) with various anions have shown that ring substitution can occur,[10] however, this type of reaction never has been observed for sterically less crowded half-sandwich compounds. The substitution of the C_5H_5 ring of [$C_5H_5M(CO)_3Cl$] probably involves the [{^{t}BuP}$_3$As]$^-$ anion adding to the metal followed by transfer to the cyclopentadienyl ring.[10] The adoption of this pathway (as opposed to simple substitution of the Cl ligand) can be attributed to the large steric bulk of the [{^{t}BuP}$_3$As]$^-$ anion.

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