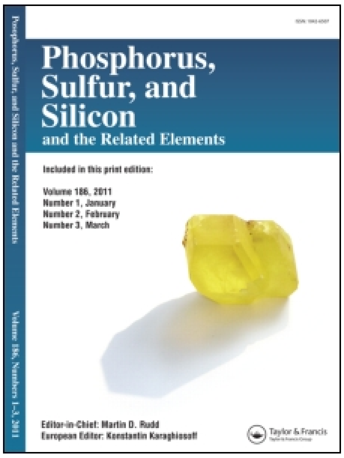

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STRUCTURED ASSEMBLY OF HETEROMETALLIC ARRAYS

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A range of heterometallic cage complexes can be prepared by step-wise metallation reactions of monolithiated primary amines and phosphines ($[REHLi]_n$; E= N, P) with various Group 13, 14 and 15 metal reagents. The p block imido and phosphinidine anions present in these species are novel ligand systems to main group and transition metals. This simple synthetic approach thereby provides a basis for structured assembly of a range of heterometallic cage and ring compounds.

Keywords

Cages, rings, heterometallic, ligands, main group, metallation

INTRODUCTION

Cage complexes of p block metals (Groups 13 to 15) are an extensive and highly structurally varied class of compounds,[1] formed where highly charged, electron rich or multifunctional organic ligands are present. These general ligand requirements contrast with the behaviour of the alkali metals in particular, where essentially ionic metal-ligand bonding is largely responsible for oligomerisation into discrete molecular or extended polymeric arrays for a far broader spectrum of organic ligands.[2] The key difference between the earlier and later main group metals is the greater covalency of metal-ligand bonding in p block compounds, leading to more restricted metal geometries (as a consequence of metal valence requirements) and generally lower coordination numbers. A further broad contrast which can be made between the earlier and later main group metal complexes is the comparative synthetic accessibility of the former. Whereas simple deprotonation of organic acids (such as amines [R_2NH] and alcohols [ROH]) with readily available organo-alkali metal compounds provides a basic and general approach to a diverse family of metallo-organic alkali metal derivatives,[2] there are no general strategies to the p block metal relatives and a variety of approaches (usually involving transmetallation of metal halides or elimination of thermodynamically labile groups) have been used. In addition, the lower polarity of metal-carbon bonds for Group 14 and 15 organometallics makes these species rather unreactive towards organic acids and therefore ineffective as precursors.

A primary goal in our initial studies was to develop a general synthetic approach to metallo-organic derivatives of the p block metals, based on the same synthetic methodology as that most commonly used for the alkali metals, namely, employing basic p block metal reagents (cf ^{n}BuLi) in reactions with organic acids. The dimethylamido reagents [$E(NMe_2)_3$] (E= Sb, Bi) can be readily prepared and earlier investigations of the synthetic utility of the Sb(III) derivative as an organic reagent indicated that this species was a promising candidate for study.[3] We found that this reagent is an extremely potent bases, doubly deprotonating organic primary amines to give imido complexes (containing RN^{2-} ligands).[4]

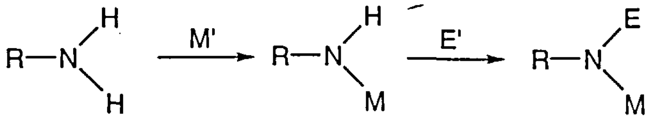
$$2[Sb(NMe_2)_3] + 2[RNH_2] \longrightarrow [(Me_2N)Sb(\mu\text{-}NR)]_2 + 4[Me_2NH]$$

R= Cy (C_6H_{11}), ^{t}Bu, 3,4,5-$MeOC_6H_2$,
2-Pyridyl, 2-$MeOC_6H_4$

The behaviour of [$E(NMe_2)_3$] towards primary amines can be compared to the reactivity of standard alkali metal reagents, such as [^{n}BuLi]. The latter will only generally deprotonate primary amines once even if used in excess, except where conjugative stabilisation within the organic group can occur.[5] In contrast, the Group 15 reagents undergo complete reaction, even in the cases of alkyl amines in which no delocalisation within the organic framework is possible.

STEP-WISE METALLATION

The potency of the Group 15 metal reagents discussed above and the difference between the reactivity of these species and alkali metal organometallics gives rise to the possibility of controlled stepwise deprotonation using a combination of reagents.



M'= alkali metal (M) source; E'= p block metal (E) source

This simple synthetic approach has broad applications to the preparation of heterobimetallic p block/alkali metal complexes containing imido as well as phosphinidine (RP^{2-}) groups.[6]

Group 15 Imido and Phosphinidine Cages

Ligand Synthons

The simplest step-wise metallation reaction which one could envisage is that between $[Sb(NMe_2)_3]$ and three molar equivalents of a primary amido lithium compound [RNHLi]. The reaction where R= $PhCH_2CH_2$ results in the anticipated trianion $[Sb(NR)_3]^{3-}$.[7] Two such anion units are associated by six Li^+ cation in the solid state in to a fourteen-membered spherical cage which can be regarded (conceptually) as resulting from the capping of an imino lithium-type N_6Li_6 'stack', at the open N_3Li_3 faces, by two Sb(III) centres.

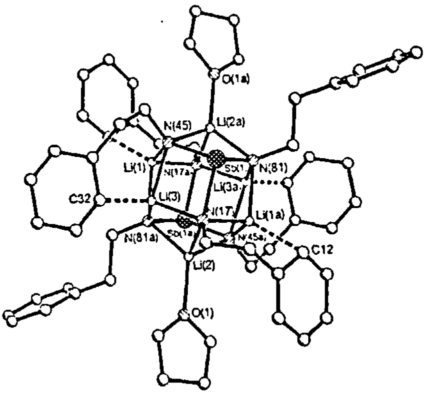


FIGURE 1 Crystal structure of $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6.2THF]$ **1**.

Similar synthetic approaches utilising the dimers $[(Me_2N)Sb(\mu\text{-}NR)]_2$ with $[RNHLi]_n$ and $[Sb(NHR)_4]^-Li^+$ with $[Sb(NMe_2)_3]$ give rise to two additional anion systems, containing $[Sb_2(NR)_4]^{2-}$ dianions and $[\{(Me_2N)Sb(\mu\text{-}NR)_2\}_2Sb]^-$ monoanions, respectively (Figure 2).[7,8]

The major point here is that these reactions are regioselective and that the occurrence of each anion type depends only on the reaction sequence and not, for example, on the nature of R or the structure of the primary amido lithium precursor $[RNHLi]_n$.[9] This conclusion is clear from extensive structural investigations of these species with a broad range of primary amido lithium precursors.[10]

So far, the assignment of the various cage complexes formed as being constructed from imido Sb(III) anions (depicted in Figure 2) which are merely associated by Li^+ cations has been somewhat arbitrary. However, several studies serve to illustrate that this formulation is indeed correct. For example, recent studies of the reaction of $[CyPHLi]_\infty$ (a polymeric ladder in the solid state) with $[Sb(NMe_2)_3]$ gives the $[Sb(PCy)_3]^{3-}$ trianion cage complex $[\{Sb(PCy)_3\}_2Li_6.6HNMe_2]$ **2** in which (unusually) all six of the Li^+ cations of the core are complexed by the byproduct Me_2NH (b.p. 7°C).[11] Semi-empirical MO calculations indicate that a dynamic carousel process is responsible for the equivalence of the six Li^+ cations, as witnessed by variable-temperature ^7Li NMR studies in which a binomial septet is observed (+25- –90°C) (Figure 3).

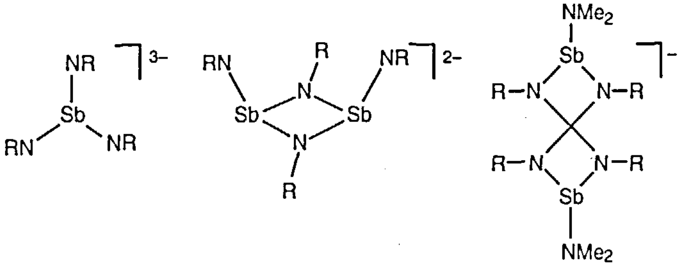


FIGURE 2 Schematic representations of the imido Sb(III) anions generated by stepwise metallation.

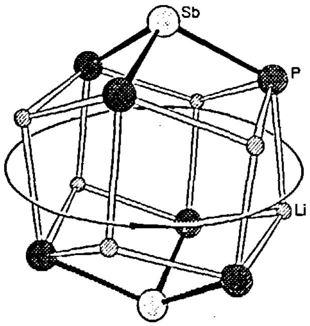


FIGURE 3 The dynamic carousel process occurring in **2**.

Ligand Behaviour

The most striking evidence that the various trianions represented in Figure 2 are the robust chemical entities of the heterobimetallic Sb(III)/alkali metal cages is provided by their coordination behaviour with added metal salts. Two possible outcomes have been identified in these reactions, *(i)* transmetallation and *(ii)* co-complexation. The reaction of $[\{Sb(NCy)_3\}_2Li_6]$ **3** with $[Cp_2Pb]$ eliminates [CpLi] and gives the Pb(II)/Sb(III) cage $[\{Sb(NCy)_3\}_2Pb_3]$ **4** (Figure 4) in which the $[Sb(NCy)_3]^{3-}$ trianions of the precursor survive *intact*.[12] Similar transmetallation reactions are observed between the other imido Sb(III) anions (Figure 2) and a variety of main group and transition metal salts. For example, the reactions of the Sb(III)/ lithium cage $[\{Sb_2(NCy)_4\}_2Li_4]$ (containing the $[Sb_2(NCy)_4]^{2-}$ dianion) with CuCl or [AgAcO] give $[\{Sb_2(NCy)_4\}_2M_4]$ [M= Cu **5** (Figure 5), Ag **6**] in which the M_4 square planar cores are held together by the *intact* dianion units.[12,13]

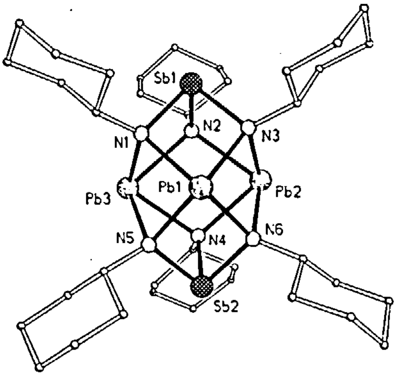


FIGURE 4 Structure of $[\{Sb(NCy)_3\}_2Pb_3]$ **4**.

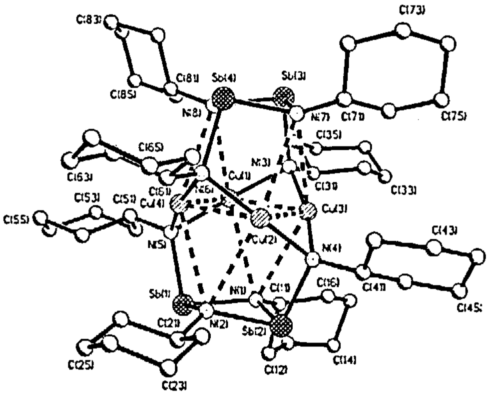


FIGURE 5 Structures of $[\{Sb_2(NCy)_4\}_2Cu_4]$ **5**.

Co-complexation rather than transmetallation occurs when $[\{Sb(NCy)_3\}_2Li_6]$ is mixed with $[KO^tBu]$ (3 equivalents). The product, $[\{Sb(NCy)_3\}_2Li_6].[KO^tBu]_3$ **6** (Figure 6) results from symmetrical cage expansion of the fourteen-membered core and the insertion of a trimeric K_3O_3 ring.[14] Such symmetrical dissociation in solution may well be a general property of the imido Sb(III)/alkali metal cages, as is indicated by solution studies of $[\{Sb_2(NCy)_4\}_2Li_4]$ **7**, which dissociates in arene solutions in to its constituent $[\{Sb_2(NCy)_4\}Li_2]$ cubane halves, and by the isolation of the solvated discrete cubane $[Bi_2(N^tBu)_4Li_2.2THF]$ **8**.[15]

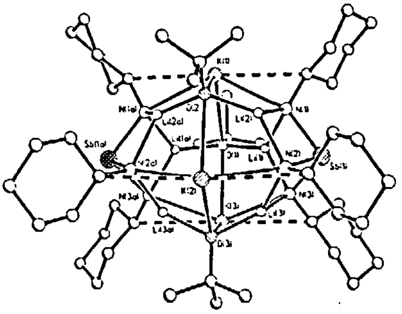


FIGURE 6 Structure of $[\{Sb(NCy)_3\}_2Li_6].[KO^tBu]_3$ **6**

Extensions to Group 13 and 14

The above investigations illustrate the versatility of the new imido Sb(III) ligand systems which have been developed and their scope in the structured assembly of heterometallic arrays. When studies turned to Group 13 and 14, however, it soon became clear that the simple reactivity which had formed the basis of earlier work was no longer to be followed. For example, reactions of $[Sn(NMe_2)_2]$ with $[RNHLi]_n$ (1:2) give rise (somewhat anomolously) to the thermodynamically stable cubanes $[SnNR]_4$ rather than giving species containing $[Sn(NR)_2]^{2-}$[16] anions and the Sn(IV) reagent $[Sn(NMe_2)_4]$ is not only fairly unreactive but also subject to ligand transfer.[16] Instead, of employing the dimethylamido metal species, a new strategy was adopted which utilises the readily prepared $[ENR]_4$ cubanes as the metallating reagents. The reactivity of these species is highly dependent on the steric bulk of the organic group (R), with only less sterically congested precursors being generally useful. In addition, only more acidic primary amido lithiums are sufficiently reactive with these species.

The reaction of $[SnN^tBu]$ with $[C_{10}H_7NHLi]$ ($C_{10}H_7$= 1-naphthyl) and [CyPHLi] give the new imido and phosphinidine cages $[(^tBuN\}Sn_3(NC_{10}H_7)_3Li.THF]^-$ $[Li(THF)_4]^+$ **9** (containing the tripodal

[^{t}BuNSn$_3$(NC$_{10}$H$_7$)$_3$]$^{2-}$ dianion) and [{Sn(μ-PCy)}$_2$(μ-PCy)]$_2$(Li.THF)$_4$ **10** (containing the metallacyclic [{Sn(μ-PCy)}$_2$(μ-PCy)]$_2$$^{4-}$ tetraanion) (Figure 7).[17] The extent of cubane fragmentation observed in the syntheses of **9** and **10** appear to indicate that the acidity of the primary amido or phosphine precursors has a major bearing on these reactions. Recent studies have also shown that imido Group 13 cubanes can be employed as basic precursors, the complex [{MeAl(μ-PCy)}$_2$(μ-PCy)]$_2$(Li.THF)$_4$ **11** being prepared by the reaction of [MeAlNMes]$_4$ with [CyPHLi].[18] The complex has a similar structure to metallacyclic **10**. This approach is of particular value here since the Group 13 dimethylamido reagents are relatively unreactive towards organic acids and there is therefore no obvious advantage in the use of these as opposed to the organo Group 13 reagents.[19]

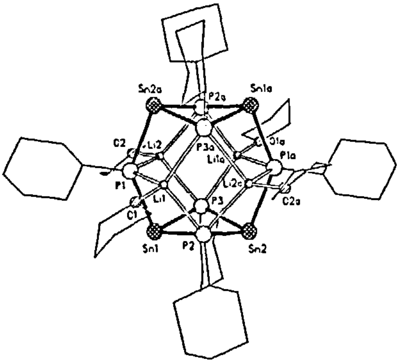


FIGURE 7 Structure of [{Sn(μ-PCy)}$_2$(μ-PCy)]$_2$(Li.THF)$_4$ **10**.

A similar neutral cyclic arrangement is found in the twenty-four membered neutral metallacycle [Sb$_{12}$(Nma)$_{18}$] **12** (ma= 2-MeOC$_6$H$_4$),[20] the surprising product of the attempted metallation reaction of the primary tris(amido) stannate [(maN)Sn(μ-NHma)$_2$Li.2THF] **13** with [Sb(NMe$_2$)$_3$] (Figure 8). Metallacyclic arrangements of main group and transition metals are rare and these arrangements in the anions of **10** and **11** and in the structure of the neutral complex **12** give exciting prospects for their application to selective metal complexation of metal ions. In this context, the configuration of the six endo OMe groups of **12** produces an octahedral metallacyclic cavity (*ca.* 3Å from the centre to each donor O) which should in principle be well suited to cation scavenging.

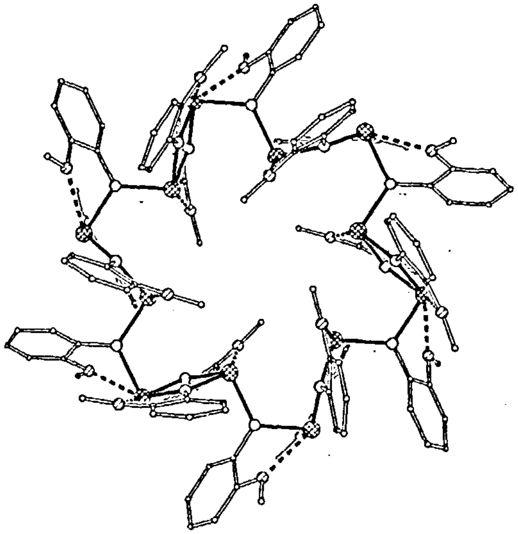


FIGURE 8 Metallacyclic structure of $[Sb_{12}(Nma)_{18}]$ **11.**

Although the simplest mononuclear Group 14 reagents are not well-behaved in terms of their reactions with $[REHLi]_n$ (E= N, P), recent reinvestigation of the metallation of primary amines (RNH_2) with $[Sn(NMe_2)_2]$ has furnished some valuable new polynuclear reagents. Unlike reactions of $[Sn(NMe_2)_2]$ with sterically unencumbered primary amines, which give cubanes $[SnNR]_4$, reactions with sterically bulky aromatic amines give the basket compounds $[\{SnNR\}_2(Sn\mu\text{-}NMe_2)_2]$ [R= 2,4,6-$Me_3C_6H_2$ **14** (Mes), 2,6-$^iPr_2C_6H_3$ **15** Dipp)].[21] The latter are model intermediates in the formation of the cubanes, the steric bulk of the organic groups present preventing completion of these reactions. These species, which contain formal acceptor (two-coordinate) Sn and donor (three-coordinate) Sn centres, are of some structural interest. Although the steric bulk of the Dipp groups of **15** prevents association between the molecular units, cyclisation of six molecules of **14** occurs in the solid state, in which short contacts are made between the formally donor and acceptor Sn centres (Figure 10).

Complexes **12** and **13** have potential applications as reagents for the preparation of mixed-ligand cubanes and novel Group 14 anion systems. These species can be regarded as analogous (in a synthetic sense) to the dimers $[(Me_2N)Sb(\mu\text{-}NR)]_2$. However, reactions of these with [RNHLi] follow a very different reaction pathway in the formation of imido Sn(II) anions.[22]

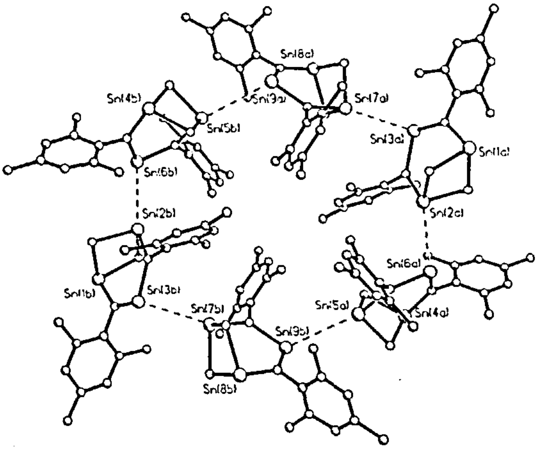


FIGURE 9 Association of [{SnNMes}$_2$(Snμ-NMe$_2$)$_2$] **14**.

Acknowledgements
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