DALTON
PERSPECTIVE

Structural direction by the dominant metal

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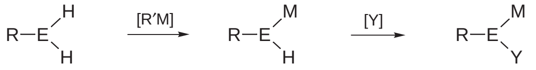
Assessment of the structures of a number of heterometallic alkali metal/p block metal complexes suggests that the p block metals have a dominant role in dictating the structures of these species, since generally greater covalency of the metal–ligand interactions leads to more geometrically rigid metal co-ordination.

1 Introduction

We have recently reported the development of a general synthetic strategy for the preparation of a variety of heterometallic alkali metal/p block metal cage complexes involving the stepwise metallation reactions of primary amines and phosphines (REH_2; E = N or P) with organoalkali metal reagents, producing $[(REH)M]_n$ (M = alkali metal), followed by their deprotonation by various p block metal reagents[1–3] such as $Sb(NMe_2)_3$[4] (Scheme 1). Our principal aims in these studies have been the preparation of a broad range of species containing a variety of mixed-metal stoichiometries and the investigation of the dependence of the cage structures and mixed-metal stoichiometries on the reaction system employed. A large number of these species have now been synthesized and structurally characterised, containing a broad spectrum of Group 13, 14 and 15/alkali metal compositions, and we are now in an appropriate position to assess the central factors governing the structures of these species. This assessment is of primary importance to us since the imido and phosphinidene p block metal anion fragments of these cages are novel ligand systems and can be used as robust synthons in the targeted design of heterobimetallic complexes.[5]



M= alkali metal, Y= p block source

Scheme 1

The purposes of this perspective are (*i*) to highlight the fact that it is the p block metal–ligand frameworks (not the alkali metal–ligand frameworks) which largely control the structures of heterometallic p block metal/alkali metal cage compounds of this type, (*ii*) to clarify the issues concerned in thermodynamic and kinetic control of p block metal/alkali metal cage compounds in general and (*iii*) to address the issue of whether 'ring-stacking' and 'ring-laddering' models[6] are appropriate in the prediction or interpretation of structural influences in systems in which metal valence and covalency provide the fundamental structural influences.

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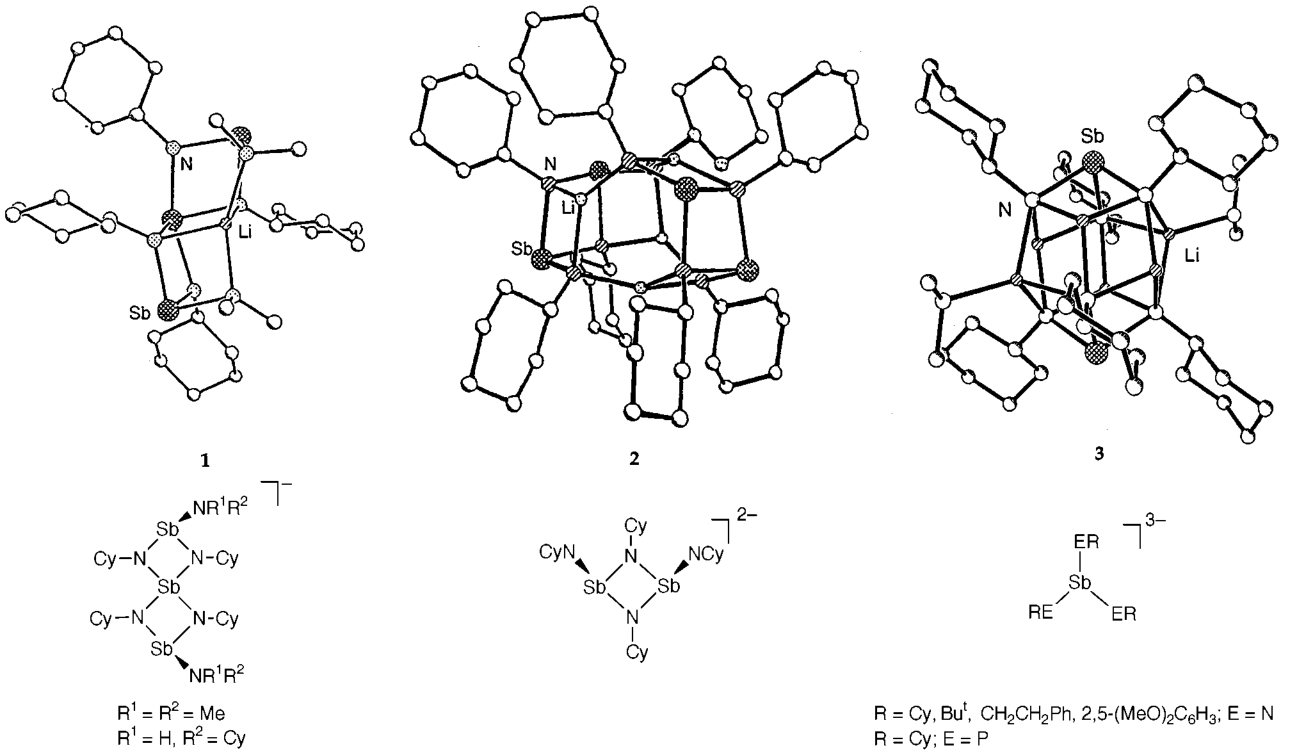


Fig. 1 Structures of [(Me$_2$N)$_2$Sb$_3$(NCy)$_4$Li] **1**, [{Sb$_2$(NCy)$_4$}$_2$Li$_4$] **2** and [{Sb(NCy)$_3$}$_2$Li$_6$]·2Me$_2$NH **3** (top) and imido anion units (bottom)

2 Structural Influences in p Block Metal/Alkali Metal Cages

Clearly the outcome of the reactions producing any mixed p block metal/alkali metal cage complex will be highly dependent on the thermodynamic balance between the p block metal–ligand and alkali metal–ligand bond energies. In the case of imido Sb^{III}/Li complexes, all the evidence illustrates that Sb–N bonding dominates the reactions involved. This is witnessed particularly by the formation of alternative imido anions in which the Sb–N frameworks of the antimony precursors are conserved. This point is illustrated in Fig. 1 which depicts the alternative imidoantimony(III) anions formed by the reactions of dimethylamidoantimony(III) reagents with various primary amido or phosphido lithium precursors [Li(REH); E = N or P] and the structures of the heterobimetallic cages resulting. For example, in the reaction of Li$^+$[Sb(HNR)$_4$]$^-$ with Sb(NMe$_2$)$_3$ (1 : 2 equivalents) the (10e) antimony centre of the [Sb(HNR)$_4$]$^-$ anion is preserved in the resulting [(Me$_2$N)$_2$Sb$_3$(NR)$_4$]$^-$ monoanion (*e.g.* in Li[Sb$_3$(NMe$_2$)$_2$(NR)$_4$] **1**[3b]) and in the reaction of the dimer [{Sb(NMe$_2$)(μ-NCy)}$_2$] with [(CyNH)Li]$_n$ (1 : 2 equivalents) the Sb$_2$N$_2$ unit is maintained in [{Sb$_2$(NCy)$_4$}$_2$Li$_4$] **2**, containing the dianion [Sb$_2$(NCy)$_4$]$^{2-}$.[3a] The dominance of the antimony(III) frameworks over the outcome of these reactions is also emphasised by the formation of similar complexes of the type [{Sb(ER)$_3$}$_2$Li$_6$],[3b,f,g] containing [Sb(ER)$_3$]$^{3-}$ trianions (*e.g.* [{Sb(NCy)$_3$}$_2$Li$_6$]·2Me$_2$NH **3**,[3b] Fig. 1), from a broad range of Li(REH) with Sb(NMe$_2$)$_3$ (3 : 1 equivalents), and by the fact that even where the same organic groups are present the outcome of the reactions is dictated by the reaction sequence [*e.g.*, as in the case of **1**, **2** and **3**, all of which contain CyN groups (Cy = C$_6$H$_{11}$)].

Studies of the reactions of heterobimetallic Sb^{III}/Li complexes with metal salts stress the fact that it is the imido antimony(III) monoanion, dianion and trianion units of the cages which are the robust chemical entities.[5] Most dramatically, all six of the Li$^+$ cations of the N$_6$Li$_6$ core of [{Sb(NCy)$_3$}$_2$Li$_6$]·2Me$_2$NH **3** are substituted in the transmetallation reaction with [PbCp$_2$] (Cp = C$_5$H$_5$), giving the heterobimetallic complex [{Sb(NCy)$_3$}$_2$Pb$_3$] **4** (Fig. 2).[5a] In the reaction of **3** with [KOBu^t], cleavage of the N$_6$Li$_6$ core occurs (the weaker N–Li bonds being replaced by stronger O–Li interactions), giving the trimetallic cage [{Sb(NCy)$_3$}$_2$Li$_6$]·3KOBu^t **5** (Fig. 3).[5c] It should be noted that the lability of the Li–N frameworks is in fact a general feature of *all* of the imido Sb^{III}/alkali metal cages shown in Fig. 1,[5] in which the various imido antimony(III) anions are readily transferred (*intact*) to a range of main group and transition metal ions, *e.g.* the reactions of [{Sb$_2$(NCy)$_4$}$_2$Li$_4$] **2** with Group 11 salts give [{Sb$_2$(NCy)$_4$}$_2$M$_4$] (M = Cu **6** or Ag **7**).[5b]

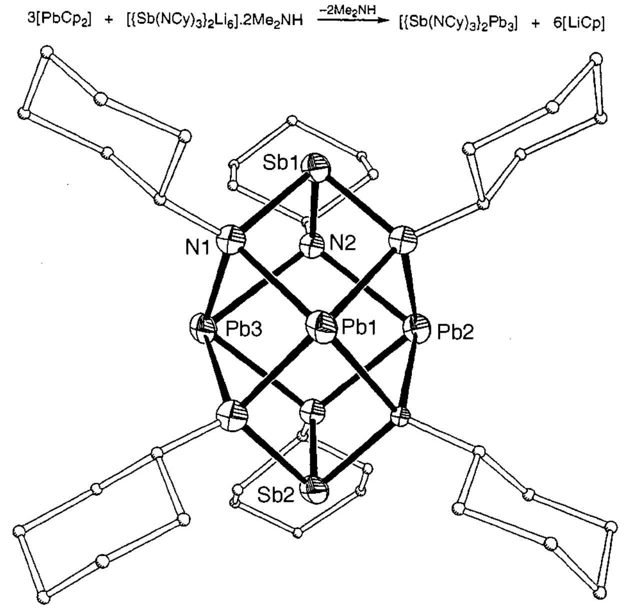


Fig. 2 Conversion of compound **3** into the lead complex [{Sb(NCy)$_3$}$_2$Pb$_3$] **4**

Further evidence of the integrity of the [Sb(ER)$_3$]$^{3-}$ trianions of the [{Sb(ER)$_3$}$_2$Li$_6$] (E = N or P) cages and of the lability of

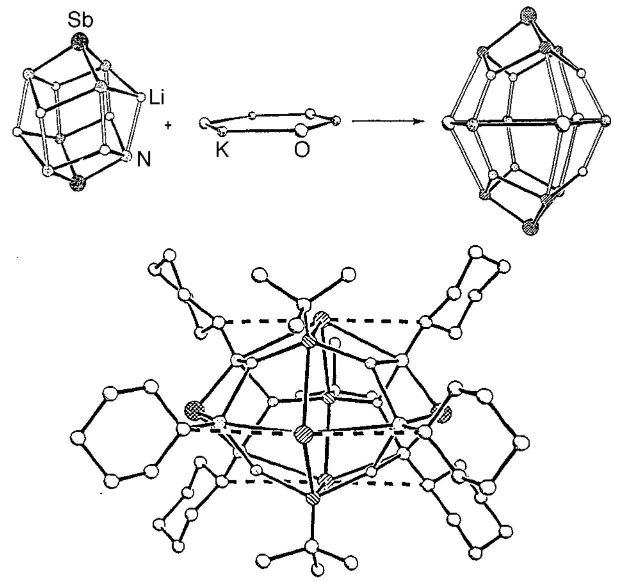


Fig. 3 Cage expansion of compound **3** into the trimetallic [{Sb(NCy)$_3$}$_2$Li$_6$]·3KOBu^t **5**

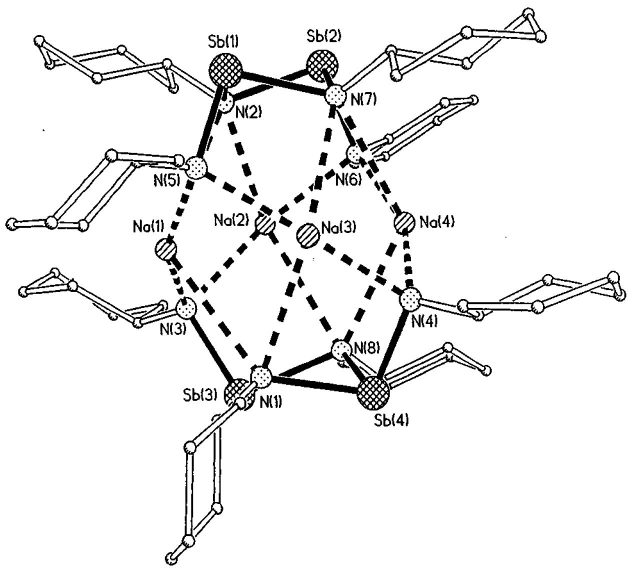


Fig. 5 Structure of [{Sb(NCy)$_4$}$_2$Na$_4$] **9**

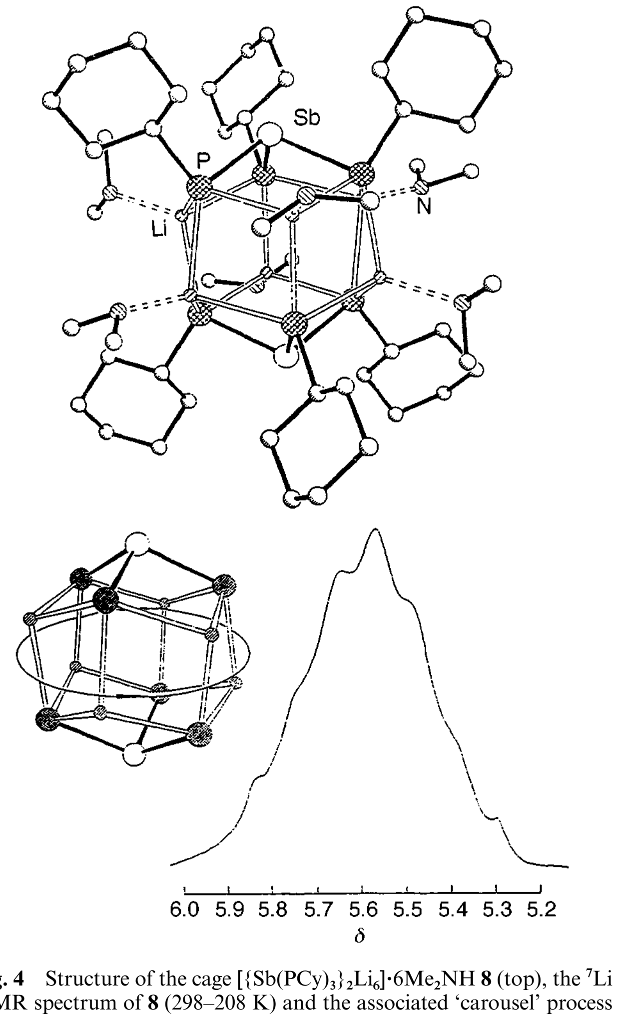


Fig. 4 Structure of the cage [{Sb(PCy)$_3$}$_2$Li$_6$]·6Me$_2$NH **8** (top), the ^{7}Li NMR spectrum of **8** (298–208 K) and the associated 'carousel' process involved (bottom)

their E$_6$Li$_6$ cores comes from variable-temperature ^{7}Li NMR studies of the Me$_2$NH-solvated phosphinidene system [{Sb(PCy)$_3$}$_2$Li$_6$]·6Me$_2$NH **8** in which a binomial septet is observed even at −90 °C (Fig. 4).[3e] Semiempirical MO calculations suggest that the six Li$^+$ cations are involved in a dynamic 'carousel' process by which they are coupled to the six equivalent P centres of the two *intact* [Sb(PCy)$_3$]$^{3-}$ trianions of the core.

The dominance of Sb–N bonding over Li–N bonding in these systems allows direct control of the nature of the imidoantimony(III) anions formed and clearly these units will have a direct bearing on the ultimate structures adopted by the heterobimetallic Sb^{III}/alkali metal cages. Although it cannot be taken for granted that the more covalent p block metal–nitrogen bonds will necessarily be stronger than the ionic alkali metal–nitrogen interactions in heterometallic p block metal/alkali metal cages in general, what is certain is that even where there is a closer match in bond energies than appears to be present in the antimony(III) systems the more covalent p block metal–ligand bonding will always exert the greatest influence over the structures adopted, since such bonding imparts directionality in the surrounding ligand framework. These more rigid geometric requirements will dominate the ionic and largely non-directional alkali metal–ligand interactions and the alkali metals will have generally a minor role in dictating the structure.

One consequence of the greater structural influence of the p block metal framework is that the alkali metal–nitrogen frameworks of heterobimetallic imido complexes should be modified at the expense of the more rigid bonding demands of the p block metal. As the difference in the metal–ligand bond energies increases greater distortion of the alkali metal–ligand cores is anticipated. Some evidence for this is seen in the structure of the sodium complex [{Sb(NCy)$_4$}$_2$Na$_4$] **9** (Fig. 5).[7] In contrast to the lithium analogue (**2** in Fig. 1) which has a tetrahedral arrangement of the four Li$^+$ cations at its centre,[3a] the four Na$^+$ cations of **9** are distorted into a square-planar arrangement. This occurs as a consequence of the strain induced by the complexation of the larger Na$^+$ cations by the [Sb$_2$(NCy)$_4$]$^{2-}$ dianions, the weaker and more flexible Na-N core being modified as a result. It is noticeable here that distortion of the imidoantimony(III) dianions only occurs at the μ-N centres and that the pyramidal geometries of the antimony(III) centres are very similar in **2** and **9**.

There is emerging evidence that the p block metal–heteroatom frameworks have a dominant role over the structures of heterometallic cage complexes in general. In the reactions of primary amidolithiums [Li(RNH)] with Sn(NMe$_2$)$_2$ only the imido tin(II) cubanes [Sn(NR)]$_4$ are isolated.[8] For this reason alternative stepwise metallation procedures have to be employed in order to build the desired mixed Sn^{II}/alkali metal arrangements. Using the reactions of Li(REH) (E = N or P) with [Sn(NR)]$_4$[9] (employing the cubane as the base) we showed that heterobimetallic systems are accessible. The fragmentation

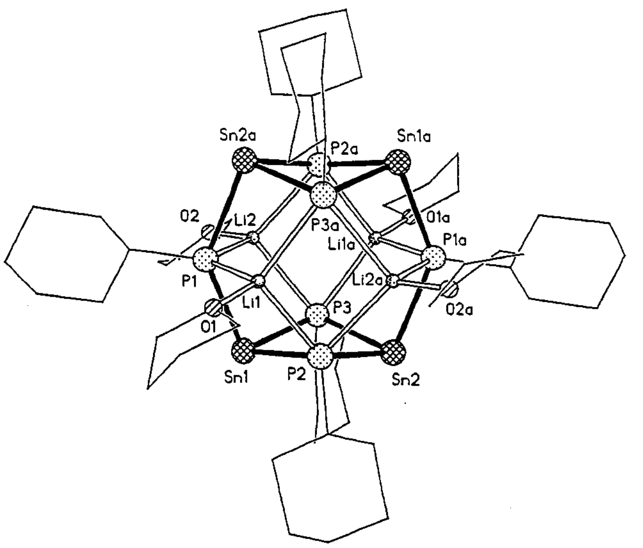


Fig. 6 Structure of [{Sn(μ-PCy)}$_2$(μ-PCy)$_2$(Li·thf)$_4$] **10**

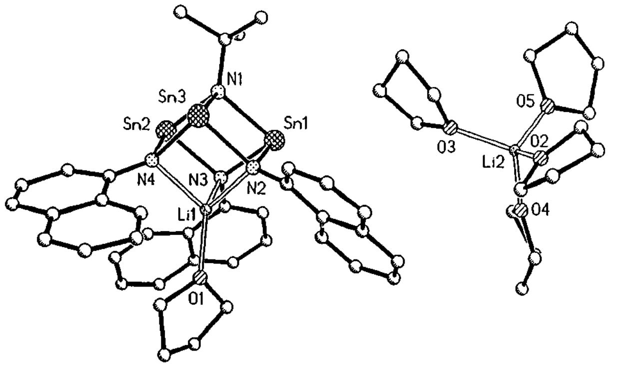


Fig. 7 Structure of [(Li(thf)$_4$][Sn$_3$(Bu^{t}N)(C$_{10}$H$_7$N)$_3$] **11**

of the imido tin(II) cubane arrangement of the precursor in these reactions exhibit a dependency on the acidity of the primary amido or phosphido lithium. Thus, all four of the Bu^{t}N groups of [Sn(NBu^t)]$_4$[9c] are replaced in the reaction with Li(CyPH) (4:6 monomer equivalents), giving the metallacyclic cage complex [{Sn$_2$(μ-PCy)}$_2$(μ-PCy)$_2$(Li·thf)$_4$] **10** (Fig. 6), whereas the reaction of the less acidic Li(C$_{10}$H$_7$NH) with [Sn(NBu^t)]$_4$ gives [Li(thf)$_4$][Sn$_3$(NBu^t)(NC$_{10}$H$_7$)$_3$] **11** (Fig. 7), in which only three of the Bu^{t}N groups are eliminated.[2a] The pattern of reactivity observed for [Sn(NBu^t)]$_4$ and the structures of the products formed strongly suggest that the products are templated by the comparatively thermodynamically robust imido tin(II) cubane. Similar reactivity is observed for the imidoaluminium cubane [MeAl(NMes)]$_4$ (Mes = 2,4,6-Me$_3$-C$_6$H$_2$),[10] the reaction with Li(CyPH) giving [{AlMe(μ-PCy)}$_2$-(μ-PCy)$_2$(Li·thf)$_4$] **12** (the aluminium analogue of **10**).[1]

Although the direct reactions of Sn(NMe$_2$)$_2$ with primary amido lithiums has been unsuccessful in the preparation of heterobimetallic complexes, we have recently shown that the polynuclear dimethylamido reagent [{Sn(NMes)$_2$}-{Sn(μ-NMe$_2$)}$_2$] **13**[8] is more well behaved in this respect. The reaction of the latter with Li(2-MeOC$_6$H$_4$NH) gives the 'pseudo-ladder' [{Sn(MesNH)(μ-NC$_6$H$_4$OMe-2)}$_2$(Li·2thf)$_2$] **14** (composed of a central [Sn(MesNH)(μ-NC$_6$H$_4$OMe-2)}$_2$]$^{2-}$ dianion complex associated with two thf-solvated Li$^+$ cations) (Fig. 8).[2b] The latter appears to result from the deprotonation of the primary amido lithium by the MesN groups of **13** followed by elimination of Sn(NMe$_2$)$_2$ (Scheme 2). It is highly significant that no remnant of any N–Li framework (beyond that of a monomer) is preserved in **14**. Indeed, the structure, which can be regarded as a co-complex between two Li(MesNH) monomers and two SnNC$_6$H$_4$OMe-2 monomers, illustrates from a thermodynamic standpoint that the primary amido lithium precursor is dissembled by lithium solvation and as a result of the preference for Sn–N bonding. The Z-shaped profile of the ladder core of **14** arises directing from the typical pyramidal geometry of the tin(II) centres (N–Sn–N *ca.* 90°). This geometry contrasts with the far flatter ladder arrangements typical of amidolithium ladders,[6,11] such as [{[Li($\overline{C_4H_4N}$)]$_2$·tmen}$_2$][12] and stresses the dominance of Sn–N bonding and tin(II) valence over the structure of **14**.

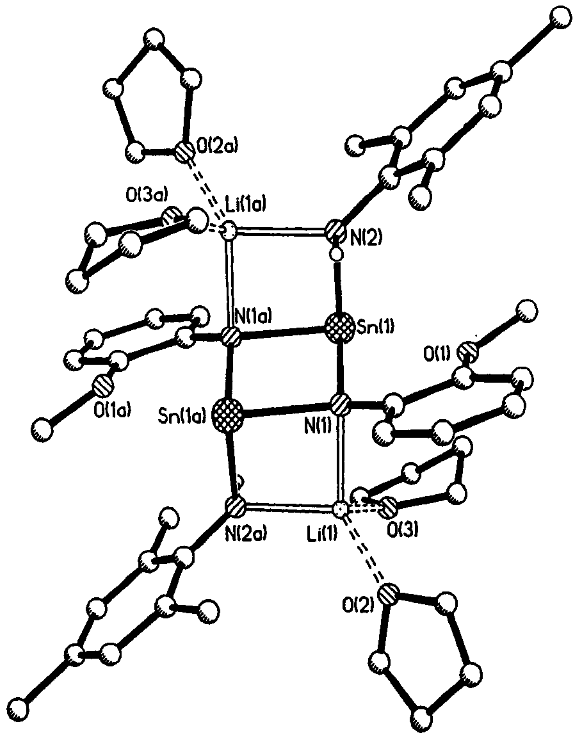
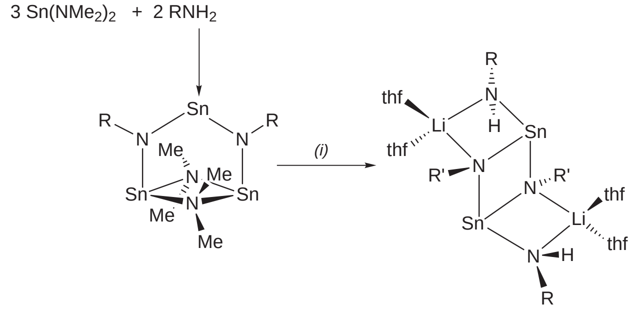


Fig. 8 Structure of [{Sn(MesNH)(μ-NC$_6$H$_4$OMe-2)}$_2$(Li·2thf)$_2$] **14**



Scheme 2 (*i*) +2[Li(2-MeOC$_6$H$_4$NH)], thf, −Sn(NMe$_2$)$_2$

The nature of the reaction producing compound **14** obviously has a profound effect on the stoichiometry of the product since one Sn is eliminated, leading to the observed 2:2 ratio of Sn:Li. As with the related imido Sb^{III}/alkali metal cages, the ultimate structures of the heterobimetallic Sn^{II}/alkali metal cage adopted is thermodynamically controlled by the relative metal–ligand bond energies involved and by the key influence of tin(II) valence. However, comparison of the structures of the complexes formed by the reactions of primary amido and phosphinidene compounds with [Sn(NBu^t)]$_4$ **10** and **11**[2a] and [{Sn(NMes)$_2$}{Sn(μ-NMe$_2$)}$_2$][2b] provides good evidence for our emerging belief that the type and stoichiometry of the basic anion system produced can be influenced by the reaction employed.

Another important factor dictating the structures of these heterometallic species is Lewis base solvation. This factor is of

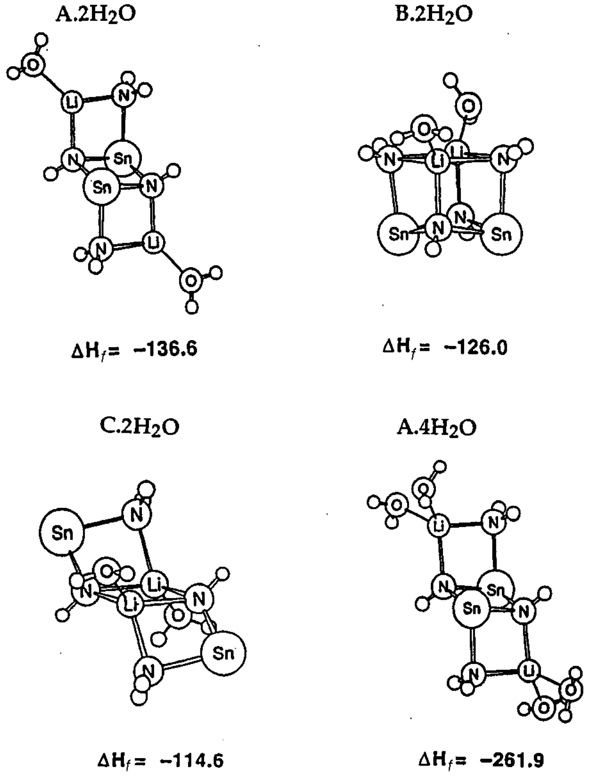


Fig. 9 Semiempirical PM3 calculations of models of compound **14**; heats of formation (ΔH_f) in kcal mol^{-1}, cal = 4.184 J

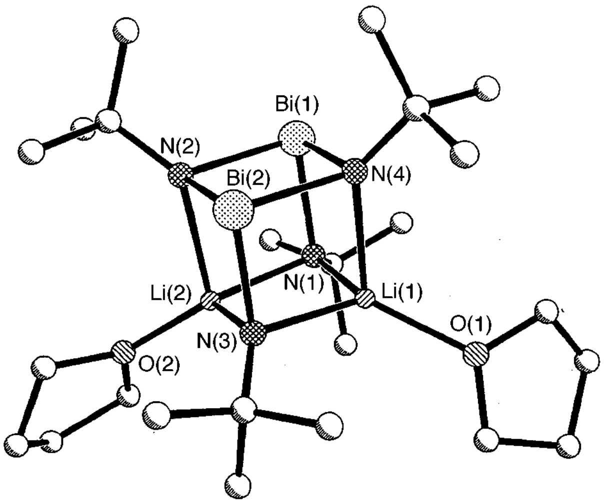


Fig. 10 Structure of [{$Bi_2(NBu^t)_4$}(Li·thf)$_2$] **15**

course in common with the organo and metalloorganic alkali metal complexes, whose structures and association states are well known to be drastically modified by co-ordination of the metal centres.[5,11,13] However, the key difference between the latter and mixed p block metal/alkali metal complexes is that the higher solvation energies for the more electropositive alkali metals and the closed-shell configurations of p block metals will lead to the preferential or exclusive solvation of the alkali metal cations. This will diminish the competition for the ligand electron density by the alkali metal cations and will have the result of strengthening the control of the p block metal ligand framework over the cage structure of the complexes. Semiempirical PM3 calculations on models of the heterobimetallic 'pseudo-ladder' complex [{Sn(MesNH)(μ-NC_6H_4OMe-2)}$_2$(Li·thf)$_2$] **14**[2b] illustrate that the centralised Sn_2N_2 open-ladder arrangement is therefore strongly influenced by solvation of

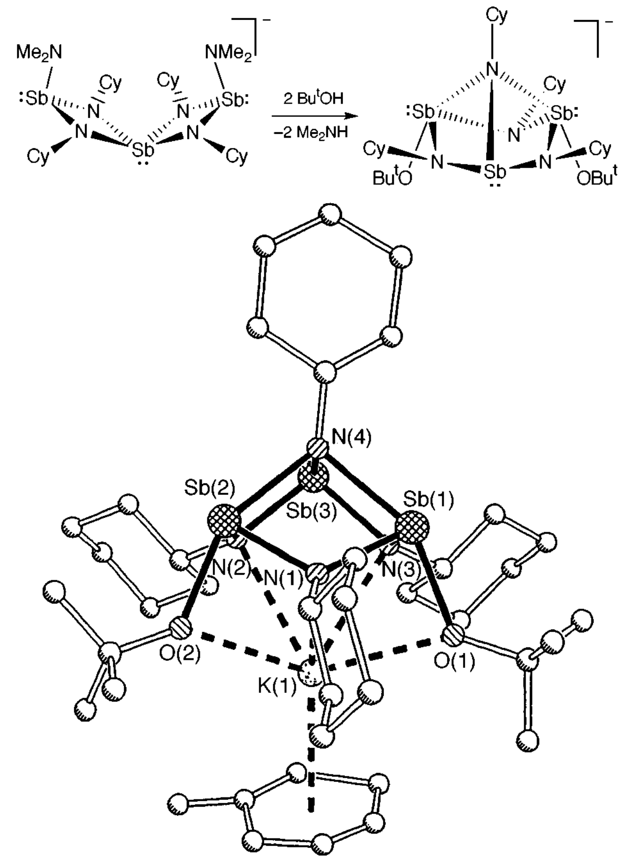


Fig. 11 Conversion of the spiro [{Sb(NMe_2)(μ-NCy)$_2$}$_2$Sb]$^-$ anion of compound **16** into the *nido* anion of K[{Sb(μ-NCy)}$_3$(μ_3-NCy)(OBu^t)·η^6-C_6H_5Me **18**

Li^+. The Sn_2N_2 open ladder [($LiNH_2$){Sn(μ-NH)}$_2$($LiNH_2$)] (akin to **14**) is only marginally more favourable than the cubane [{Sn(μ-NH)}$_2${Li(μ-NH_2)}$_2$] and the Li_2N_2 open ladder [(SnNH){Li(μ-NH_2)}$_2$(SnNH)]. However, the effect of monosolvation of Li^+ by H_2O in these uncomplexed species gives a marked preference for the Sn_2N_2 open ladder structure (**A**·$2H_2O$) over the cubane (**B**·$2H_2O$) or Li_2N_2-centred ladder (**C**·$2H_2O$) (Fig. 9). Notably, there is no thermodynamic preference for further solvation of the tin centres of the Li_2N_2 open ladder, so that the bisolvated Sn_2N_2 open ladder [{$(H_2O)_2LiNH_2$}{Sn(μ-NH)}$_2${$(H_2O)_2LiNH_2$}] **A**·H_2O (Fig. 9) is preferred by 40.5 kcal mol^{-1} to the preservation of the monosolvated Li_2N_2 open ladder. The balance between the relative energies of the Bi–N and Li–N bonds and lithium solvation appears to underlie the structure of the heterobimetallic Bi^{III}/Li cubane [{$Bi_2(NBu^t)_4$}(Li·thf)$_2$] **15** (Fig. 10),[3c] whose arrangement is similar to the monosolvated calculational model **B**·$2H_2O$ (Fig. 9). Presumably, the expected closer energies of the metal–nitrogen bonds leads to greater competition for the nitrogen electron density by Bi and Li. This results in a greater influence of the Li^+ cations over the Bi–N framework of the [$Bi_2(NBu^t)_4$]$^{2-}$ dianion and in a lower solvation energy for Li^+. The monosolvated cubane is now preferred to the bis-solvated open ladder structure.

A recent study also illustrates that the electronegativity of the organic substituents can have a strong influence on the structure of p block metal/alkali metal cages. The reaction of the terminal NMe_2 substituents of [{Sb(NMe_2)(μ-NCy)$_2$}$_2$SbK] **16**, containing a [{Sb(NMe_2)(μ-NCy)$_2$}$_2$Sb]$^-$ monoanion and having a similar structure to the Li^+ complex **1** (Fig. 1), with $CyNH_2$ gives [{Sb(CyNH)(μ-NCy)$_2$}$_2$SbK] **17** in which the spiro structure of **16** is retained.[3g] However, the reaction of **16** with Bu^tOH gives K[{Sb(μ-NCy)}$_3$(μ_3-NCy)]·η^6-C_6H_5Me **18** in which the antimony(III) anion has rearranged into a *nido*-

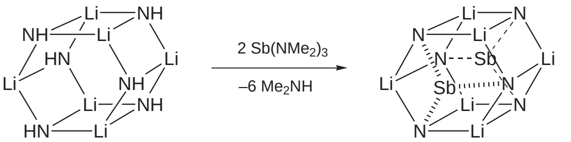


Fig. 12 Proposed structural direction of compound **20** by the supposed cyclic ladder $[(PhCH_2CH_2NH)Li]_6$ precursor

type structure (Fig. 11).[3g] The reason for this transformation is that the greater electronegativity of the alkoxide substituents increases the Lewis acidity of the antimony(III) centres, the *nido* arrangement maximising their co-ordination numbers. This result also reiterates the previous conclusion that the p block metal frameworks provide one of the greatest influences over the structures of such cages.

3 Conclusions and General Remarks

On the basis of the cyclic ladder structure of the primary amido lithium complex $[(Bu^tNH)Li]_8$ **19**,[14] it was suggested recently that the structure of one such species $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2thf]$ **20**,[3b] whose $Sb_2N_6Li_6$ core can be regarded as being constructed from the capping of a hexameric imidolithium stack by two antimony(III) centres, is templated by metallation of a rigid hexameric primary amido lithium precursor $[(RNH)Li]_6$ by $Sb(NMe_2)_3$ (Fig. 12).

The idea that the structures of the cage complexes $[\{Sb(NR)_3\}_2Li_6]$ are 'directed' by the common hexameric structure of a cyclic primary amido lithium precursor[6] assumes that the N_6Li_6 units of these species are thermodynamically robust enough to template the eventual cage arrangement and that this unit is sustained during metallation by $Sb(NMe_2)_3$. In effect, the mechanism and the structure of the product are dominated by a single thermodynamic factor. Although we agree that thermodynamic considerations generally play the greatest role in dictating the outcomes of the variety of reactions discussed above and the structures of the heterometallic complexes formed, our conclusion is that structural direction by the primary amido lithium complexes is unlikely and that the bonding demands of the p block metals dominate the kinetics and thermodynamics involved. In this regard, it is noteworthy that the infinite ladder structure of the primary phosphido lithium complex $[(CyPH)Li\cdot thf]_\infty$ **21** (which has previously been structurally characterised)[15] has no bearing on the structure of $[\{Sb(PCy)_3\}_2Li_6]\cdot 6Me_2NH$ **8** formed in its reaction with $Sb(NMe_2)_3$[3e] and that the reaction of the cyclic ladder $[(Bu^tNH)Li]_8$ itself with $Sb(NMe_2)_3$ gives $[\{Sb(NBu^t)_3\}_2Li_6]$ **22**, containing the expected $Sb_2N_6Li_6$ core (Fig. 13).[3f] In complexes of the type $[\{Sb(ER)_3\}_2Li_6]$[3b,e,f] (E = N or P) the eight electron, pyramidal antimony(III) centres have the greatest influence on the molecular architecture of the core (not the ionically bonded, flexible E_6Li_6 framework) (Fig. 14). Their overall structures are constrained by the rigid geometry of the $[Sb(ER)_3]^{3-}$ trianions and the appearance of a E_6Li_6 cyclic ladder motif, which simply maximises ionic interactions between the chemically robust anion units, has no necessary mechanistic significance.

In a general sense, the nature of the p block metal anion units formed in an individual reaction system obviously has a primary role in dictating the ultimate structure of the heterometallic cage formed with alkali metal cations. The structure adopted relies mainly on the interplay between the p block metal–ligand and alkali metal–ligand bond energies, on the different (ionic and covalent) bonding requirements of the alkali and p block metals and on the presence of Lewis base solvation. Assessment of these structures shows the geometric rigidity of the p block metal frameworks, which results from greater covalency and the requirements of metal valence, is a predominant structural factor. Since the alkali metal–ligand frameworks present in these complexes are almost entirely ionic in nature, it is clear that the alkali metal cations will exert a lesser influence. The dominance of the p block metal frameworks is reinforced by preferential Lewis base solvation of the alkali metal cations.

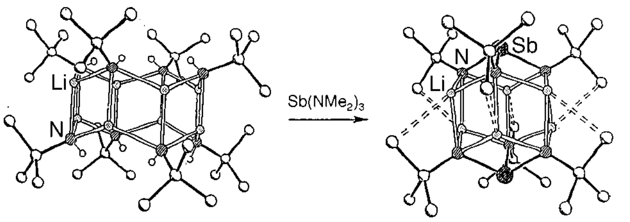


Fig. 13 Reaction of $[(Bu^tNH)Li]_8$ with $Sb(NMe_2)_3$ and the formation of $[\{Sb(NBu^t)_3\}_2Li_6]$ **22**

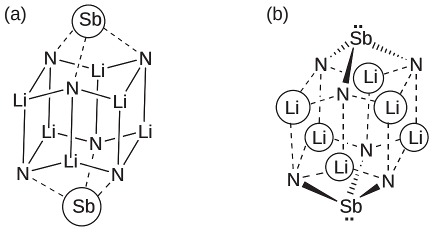


Fig. 14 An 'ionic' formulation (a) in which the Sb^{3+} ions reside in the N_6Li_6 'bed'[6] and a 'covalent' formulation (b) in which the $[Sb(NR)_3]^{3-}$ anions are associated by six Li^+ cations

Bearing in mind the complicated factors governing the formation and structures of these heterometallic cage arrangements, no one global theory is appropriate in their general rationalisation or prediction. In this context, although the 'ring-stacking' and 'ring-laddering' models have been of immense value in the prediction of the structures of a large range of metalloorganic and organoalkali metal complexes,[6] it should be noted that all these systems are dominated by ionic interactions. In mixed p block/alkali metal arrangements, in which there is a large disparity between the character and bonding demands of the metals, it should not be expected that related or similar structural arrangements will be adopted because (*i*) the p block metal valence generally places large demands on structure, (*ii*) the geometries of the p block metal centres will not be modified significantly by non-directional alkali metal–ligand interactions and (*iii*) the alkali metal–ligand frameworks are generally the weakest and the most readily solvated and are therefore subject to breakdown and distortion. A key point here is that the formulation of the 'ring-stacking' and 'ring-laddering' models deliberately ignores whether the alkali metal–ligand bonds are ionic or covalent. Indeed, in the analysis of ring, stack or ladder options consideration of ionicity or covalency is largely irrelevant since the structures and the detailed variations in metal–ligand bond lengths within them can be rationalised equivalently either by assuming overlap between the metal and ligand orbitals or that the most favourable ionic interactions occur by the alignment of the ligand lone pairs towards the Li^+ cations.[7] It is precisely this point, however, which will lead to the breakdown of these models as predictive tools in heterometallic p block/alkali metal systems where the directionality and rigidity of the p block metal–ligand bonding outweights the propensity for the alignment of the ligand lone pairs towards the alkali metal cations. Thus, it is not just the relative strengths of the alkali metal–ligand and p block metal–ligand bonds which affect the outcome of the conflict between the two metals for ligand electron density and the resulting dominance of either metal over the structure, but unfavourable distortion and electronic rearrangement of the p block metal also provide potent contributions to the thermodynamic balance.

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