[(DippNH)$_2$Al(μ-NHDipp)$_2$Li·thf] and [thf·Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li·thf]·C$_6$H$_5$Me, potential building blocks for heterometallic imido compounds (Dipp = 2,6-Pr$^i{}_2$C$_6$H$_3$)

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[(DippNH)$_2$Al(μ-NHDipp)$_2$Li·thf] 1 and [thf·Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li·thf]·C$_6$H$_5$Me 2 are produced from the reactions of AlCl$_3$ and SnCl$_4$ or MeAlCl$_2$ and MeSn(NMe$_2$)$_3$ with the apporopriate primary amido lithium precursors [RNHLi; R = 2,6-Pr$^i{}_2$C$_6$H$_3$ (Dipp), C$_6$H$_{11}$ (Cy)]; both complexes have ion-paired structures in the solid state with the retention of potentially reactive N–H functionality providing precursors for heterometallic species containing [M(NR)$_x$(NHR)$_{n-x}$]$^{(1+x)-}$ anions (M = Al, n = 4; M = Sn, n = 6).

One area of current interest to us is the investigation of the metallation reactions of primary amido and phosphido p block and transition metal complexes [of the type M(NHR)$_n{}^{x-}$] with a series of main group metal reagents (such as dimethylamido complexes).[1] Some indication of the scope of this approach to the synthesis of heterometallic arrangements is provided by the reaction of the [Sb(NHCy)$_4$]$^-$ (Cy = C$_6$H$_{11}$) with Sb(NMe$_2$)$_3$ which gives the *spiro* anion [(Me$_2$N)Sb(μ-NCy)$_2$Sb]$^-$.[2] However, further in-roads in this area have been hampered by the surprising lack of well defined homoleptic primary amido and phosphido metal complexes which we sought as precursors for metallation. In some cases this situation reflects the ease of formation of imido complexes in the reactions of REHLi with metal halides.[3] We report here the syntheses and X-ray crystal structures of [(DippNH)$_2$Al(μ-NHDipp)$_2$Li·thf] **1** (Dipp = 2,6-Pr$^i{}_2$C$_6$H$_3$) and [thf·Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li·thf]·C$_6$H$_5$Me **2**.

Compounds **1** and **2** can be prepared directly by the reactions of AlCl$_3$ with DippNHLi (1 : 4 equiv., respectively) and SnCl$_4$ with CyNHLi (1 : 6 equiv., respectively) (Scheme 1). The same complexes are also formed in the reactions of MeAlCl$_2$ with DippNHLi (1 : 3 equiv., respectively) and MeSn(NMe$_2$)$_3$ with CyNHLi (1 : 3 equiv., respectively). These reactions presumably involve intra- or inter-molecular deprotonation of RNH– groups by the Me groups of MeAlCl$_2$ and MeSn(NMe$_2$)$_3$.‡

The X-ray study of **1**§ reveals that it exists as an ion-paired complex in the solid state in which an [Al(NHDipp)$_4$]$^-$ anion is attached through two μ-NDipp groups of a thf solvated Li$^+$ cation (Fig. 1). The effect of the bridging of two of the DippNH groups to the Li$^+$ cation is to elongate the associated Al–N bonds (av. 1.95 Å) compared to those made with the terminal DippNH ligands (av. 1.85 Å). The coordination to the Li$^+$ cation also has a large affect on the geometry of the [Al(NHDipp)$_4$]$^-$ anion, with the N–Al–N angle within the Al(μ-N)$_2$Li rings being compressed (av. 93.6°) and the N–Al–N angle between the terminal ligands being expanded (av. 117.7°) as a result. Similar structural variations are found in the related amido complexes [(pyrN)$_2$Al(μ-Npyr)$_2$Li·L$_2$] (pyr = pyrrolidinido; L = pyrNH, thf),[4] although the mono- rather than bis-solvation of the Li$^+$ cation in **1** leads to slightly longer Al–(μ-N) bonds and slightly shorter Li–N bonds. In addition, the resulting planar, three-coordinate geometry of the Li$^+$ cation of **1** gives rise to further α-C–H···Li interactions (range Li···H av. 2.30 Å) with a Pr^i group of each of the bridging DippNH ligands. These

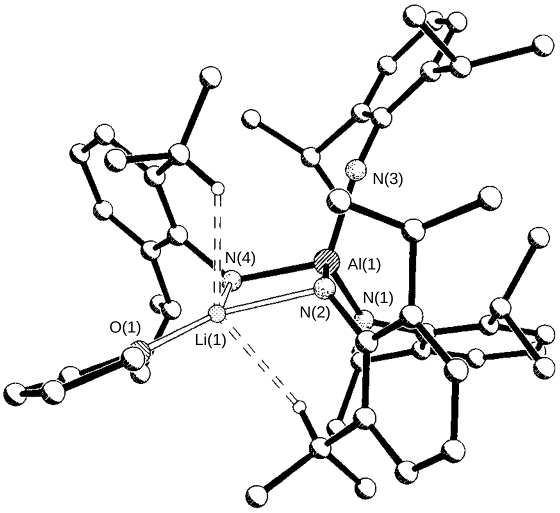

Fig. 1 Crystal structure of [(DippNH)$_2$Al(μ-NHDipp)$_2$Li·thf] **1**. Only one of the independent molecules is shown. H atoms, except those attached to N, have been omitted for clarity. Key bond lengths (Å) and angles (°); molecule A: Al(1)–N(1) 1.846(9), Al(1)–N(2) 1.898(9), Al(1)–N(3) 1.844(9), Al(1)–N(4) 1.91(1), Li(1)–N(2) 2.03(2), Li(1)–N(4) 2.04(2), Li(1)–O(1) 1.81(2), Li(1)···H av. 2.39; N(1)–Al(1)–N(2) 119.5(5), N(1)–Al(1)–N(3) 121.3(5), N(1)–Al(1)–N(4) 98.9(5), N(2)–Al(1)–N(3) 100.6(5), N(2)–Al(1)–N(4) 95.5(5), N(3)–Al(1)–N(4) 119.2(5), Al(1)–N(2)–Li(1) 88.4(6), Al(1)–N(4)–Li(1) 88.4(6), N(2)–Li(1)–N(4) 87.7(8); molecule B: Al(2)–N(5) 1.907(9) Al(2)–N(6) 1.82(1), Al(2)–N(7) 1.830(9), Al(2)–N(8) 1.938(9), Li(2)–N(5) 2.03(2), Li(2)–N(8) 2.04(2), Li(2)–O(2) 1.83(2), Li(2)···H av. 2.36; N(5)–Al(2)–N(6) 99.4(4), N(5)–Al(2)–N(7) 121.4(4), N(5)–Al(2)–N(8) 95.8(4), N(6)–Al(2)–N(7) 121.7(5), N(6)–Al(2)–N(8) 119.0(5), N(7)–Al(1)–N(8) 97.9(4) Al(2)–N(5)–Li(2) 88.1(6), Al(1)–N(8)–Li(2) 87.0(6), N(5)–Li(2)–N(8), 89.1(8).

$$\mathrm{AlCl_3 + 4\,[DippNHLi]} \xrightarrow{\mathrm{thf}} \underset{\mathbf{1}}{\mathrm{[(DippNH)_2Al(\mu\text{-}NHDipp)_2Li{\bullet}thf]}} \mathrm{+\ 3LiCl}$$

$$\mathrm{SnCl_4 + 6\,[CyNHLi]} \xrightarrow[\mathrm{thf}]{\mathrm{toluene}} \underset{\mathbf{2}}{\mathrm{[thf{\bullet}Li(\mu\text{-}NHCy)_3Sn(\mu\text{-}NHCy)_3Li{\bullet}thf]{\bullet}C_6H_5Me}} \mathrm{+\ 4LiCl}$$

Scheme 1

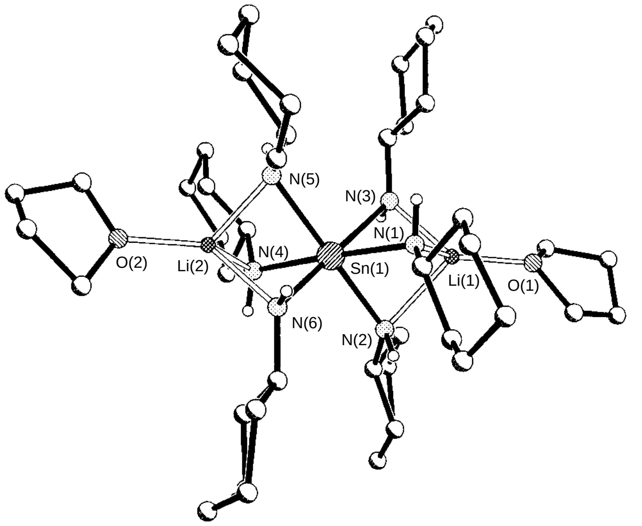

Fig. 2 Crystal structure of [thf·Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li·thf]·C$_6$H$_5$Me **2**. H atoms and the lattice-bond toluene molecule have been omitted for clarity. Key bond lengths (Å) and angles (°); range Sn–N 2.06(2)–2.27(2), range Li–N 1.98(4)–2.17(4), range N–Sn–N [Sn(μ-N)$_3$Li] 81.0(7)–83.6(7), Sn(1)···Li(1) 2.71(4), Sn(1)···Li(2) 2.67(4); N(1)–Sn(1)–N(4) 177(1), N(2)–Sn(1)–N(5) 178.1(9), N(3)–Sn(1)–N(6) 176.4(9), range N–Li–N 81(2)–92(2).

interactions appear to be relatively weak and have no apparent effect on the geometry of the Al(μ-N)$_2$Li rings. Similar interactions are now commonplace in organolithium chemistry[5] and are also found in other lithium aluminate complexes in which the alkali metal cation has a low coordination number.[6]

Although an extensive range of primary amido Al complexes have been reported previously, the vast majority of these have been neutral oligomers of the type [R′$_2$Al(μ-NHR′)]$_n$ prepared by metallation of RNH$_2$ with AlR′$_3$.[7] Complexes containing primary amido Al anions are far rarer and, to our knowledge, the only compounds of this type to be structurally elucidated are the heteroleptic organo-primary amido complexes [(Ph$_3$CNH)$_2$Al-Bu$^t_2$]Li,[8] [(Mes)$_2$Al(NHBu^t)$_2$Li·*n*(thf)] (Mes = 2,4,6-Me$_3$C$_6$H$_2$; *n* = 1, 2),[9] [Li(thf)$_4$] [(DippNH)AlBu$^i_2$Bu^t],[9] and [(DippNH)AlBu^{t}Me$_2$]Li·3thf.[9,10] Although several tetrakis-(amido) complexes adopt similar structures to **1**,[4,11] this complex is the first example containing a primary amido anion of the type [Al(NHR)$_4$]$^-$. The formation of this unit in the reaction of MeAlCl$_2$ with DippNHLi is of particular interest bearing in mind the apparently low basicity of the Me groups in [(DippNH)AlBu^{t}Me$_2$]Li·3thf,[9,10] which even when subjected to prolonged reflux fails to eliminate methane.

The X-ray structure of **2**§ shows that the complex is the ion-paired species [thf·Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li·thf]·C$_6$H$_5$Me, composed of a central [Sn(NHCy)$_6$]$^{2-}$ dianion which uses all six of its NHCy groups to bond to two thf solvated Li$^+$ cations (Fig. 2). There is one lattice-bound molecule of toluene per formula unit. The coordination of the two Li$^+$ cations gives rise to a contraction in the skeletal N–Sn–N angles of the resulting Sn(μ-N)$_3$Li units (av. 82.3°) and introduces considerable distortion in the geometry of the Sn^{IV} centre away from pure octahedral. Despite the apparent similarity of the geometries of two Li$^+$ cations of **2**, they are crystallographically different. The large variation in the Sn–N bond lengths within the [Sn(NHCy)$_6$]$^{2-}$ dianion [range 2.06(2)–2.27(2) Å] roughly mirrors the different degrees of interaction of the bridging NHCy groups with each Li$^+$ cation, the longest Sn–N bonds being associated with the shortest Li–N interactions and the shortest Sn–N bonds with longer Li–N contacts. The distortions within the framework of **2** suggest that this arrangement is highly strained. Although the structure of **2** is comparatively simple, few related Sn–N bonded compounds appear to have been structurally characterised. The closest relatives to **2** are ion-separated species containing inorganic EX$_6$$^{2-}$ anions (E = Si–Pb; X = N$_3$$^-$, SCN$^-$, SeCN$^-$, CN$^-$).[12] Complex **2** contains the first example of a hexa(amido) group 14 dianion to be characterised in the solid state.

Our studies of the reactions of homoleptic complexes of groups 13 and 14 with a range of metallating reagents [such as E(NMe$_2$)$_x$ (E = Sb, *x* = 3; E = Sn, *x* = 2)] are still at an early stage. However, there are good reasons for thinking that complexes like **1** and **2** (containing reactive N–H functionalities) will be of value as precursors in the synthesis of heterometallic species containing [M(NR)$_x$(NHR)$_{n-x}$]$^{(1+x)-}$ anions (M = Al, *n* = 4; M = Sn, *n* = 6). Recent work by Rutherford and Atwood has shown that deprotonation of species of the type [R$_2$AlNHR′] can be easily accomplished with organolithium reagents[9,10] and our own studies have revealed that various p block metal bases readily deprotonate primary amido metal complexes.[1,2] Further studies will be aimed at the synthesis of such ‘multianion’ species and the applications of these as new ligands to a range of main group and transition metals.

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Note added at proof. During the proof stage another example of a primary amido Al^{III} complex was reported (J. S. Silverman, C. J. Carmalt, D. A. Neumayer, A. H. Cowley, B. G. Burnett and A. Decken, *Polyhedron*, 1998, **17**, 977).

Notes and References

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‡ Synthetic details will be reported in a full paper.

§ *Crystal data*: C$_{52}$H$_{76}$AlLiN$_4$O **1**, *M* = 807.09, monoclinic, space group *P*2$_1$/*c*, *a* = 23.913(4), *b* = 20.756(3), *c* = 22.833(3) Å, *β* = 116.25(1)°, *U* = 10 164(3) Å^3, *Z* = 8, *D*$_c$ = 1.055 Mg m^{-3}, *λ* = 0.71 073 Å, *T* = 293(2) K, *μ*(Mo-Kα) = 0.078 mm^{-1}, *F*(000) = 3520. 11 986 collected reflections, 10 190 independent (*R*$_{int}$ = 0.098). *R*1 [*F* > 4*σ*(*F*) = 0.099 and *wR*2 = 0.425 (all data).[13] C$_{51}$H$_{93}$Li$_2$N$_6$O$_2$Sn **2**, *M* = 954.88, monoclinic, space group *Cc*, *a* = 14.81(2), *b* = 16.574(1), *c* = 23.24(2) Å, *β* = 106.48(8)°, *U* = 5473(9) Å^3, *Z* = 4, *D*$_c$ = 1.159 Mg m^{-3}, *λ* = 0.710 73 Å, *T* = 203(2) K, *μ*(Mo-Kα) = 0.507 mm^{-1}, *F*(000) = 2052. 6227 collected reflections, 6051 independent (*R*$_{int}$ = 0.048). *R*1[*F* > 4*σ*(*F*)] = 0.094 and *wR*2 = 0.438 (all data).[13] CCDC 182/880.

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