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Heterobimetallic lithium alkyltriimido aluminate cages containing the $[R'Al(NR)_3]^{4-}$ tetraanion ($R' = Bu^n$, Et; $R = 2\text{-}OMeC_6H_4$)†

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Attempted metallation of a triamidoaluminane gives a complex containing the $[R'Al(NR)_3]^{4-}$ anion whose formal tetranegative charge is the highest charge observed crystallographically for a simple mononuclear imido main group anion system.

Imido p-block anion chemistry is a field that has blossomed in the last decade.[1,2] Most attention has focused on complexes where the central atom is from groups 15 and 16 of the periodic table, with imido analogues of the phosphite,[3] phosphate,[4,5] sulfite[6] and sulfate[7] anions being among the analogues of more common oxoanions that have been identified. Related imido group 13 anions have received somewhat less attention. Metallation studies on triamidoboranes, $B\{N(H)R\}_3$, in our own group[8] and in the groups of Chivers[9] and Nöth[10] have shown competition between alkyllithium reagents acting as a base giving imidoborates, and the alkyllithium acting as a nucleophile to give organoimido borates. Imido anions of the heavier group 13 elements are limited to three reports, despite the extensive number and fascinating structural variety in neutral imido group 13 complexes that are known.[11] Two reports from the group of Chivers describe reactions of the triamido group 13 dimers, $[M\{N(H)Bu^t\}_3]_2$ (M = Al, Ga), with organolithium reagents. This results in partial lithiation to produce imido group 13 anions that display the unusual property of trapping unreacted organolithium reagent.[12,13] A further report from Henderson *et al.* describes the hetero-adamantanyl imidoalane anion, $[(HAl)_4(NPh)_6\{Li(OEt_2)\}_3]^-$, produced from reaction of the primary amidolithium LiN(H)Ph with the alane adduct $H_3Al{\cdot}N(Me)C_5H_8$.[14] In this report, we describe the syntheses of lithium organotriimidoaluminate complexes using two alternative routes and contrast this with the corresponding imido borate chemistry.

Reaction of $AlCl_3$ with 3 equivalents of LiN(H)R {R = $(2\text{-}OMe)C_6H_4$} in THF results in the formation of the triamidoaluminane $[Al\{N(H)R\}_3]_n$ (**1**). We have been unable to unequivocally assign the degree of oligomerisation, but the ^1H NMR spectrum of **1** in d^8-toluene shows several overlapping singlets for the methoxy groups which we have interpreted in terms of a dimeric Al_2N_6 structure exhibiting *cis* and *trans* isomers, similar to that reported for $[Al\{N(H)Bu^t\}_3]_2$ by Chivers *et al.*[12] and in agreement with the observations of dimeric tris(primary amido)gallanes by Cowley and Jones.[15] Treatment of **1** with $LiBu^n$ (3 equiv. per monomer unit of **1**) leads to metallation of all three N–H protons and nucleophilic addition of the *n*-butyl moiety to give the lithium organotriimidoaluminate, $[Li(thf)_4]_2[Li_6\{Bu^nAl(NR)_3\}_2]$ (**2**). A similar compound, $[Li(THF)_4]_2[Li_6\{EtAl(NR)_3\}_2]$ (**3**), was prepared by reaction of ethylaluminium dichloride with three equivalents of LiN(H)R {R = $(2\text{-}OMe)C_6H_4$} followed by metallation of the remaining N–H protons with three equivalents of $LiBu^n$. These are the first reported examples of trimetallated products of triamidoaluminanes. An interesting contrast between the reactivity of amidoaluminanes and amidoboranes is seen in the equivalent reaction using $PhBCl_2$ in place of $EtAlCl_2$ which gives the dimeric $[Li_2PhB(NR)_2]_2{\cdot}3THF$ {R = $(2\text{-}OMe)C_6H_4$, **4**} as the only crystalline product.

Complexes **1–4** were characterised by elemental analysis, ^1H NMR and IR spectroscopies. Additionally, single crystal X-ray diffraction studies were carried out on **2, 3** and **4**.‡The structures of **2** and **3** showed them to be ion-separated and dimeric, consisting of two $[Li(THF)_4]^+$ cations and a $[Li_6\{R'Al(NR)_3\}_2]^{2-}$ dianion {$R' = Bu^n$ (**2**), Et (**3**)}. There are additional molecules of THF that crystallise in the lattice that are removed upon isolation of the material and do not feature in the spectroscopic data. Complexes **2** and **3** are isostructural save for the alkyl chain attached to the aluminium centre and the number of molecules of lattice THF (1 per unit cell of **2**, 3 per unit cell of **3**). Structural data are only presented for **3** (see Fig. 1).

The 14 membered $Al_2N_6Li_6$ core of the dianion of **3** adopts a rhombododecahedral arrangement that has been commonly

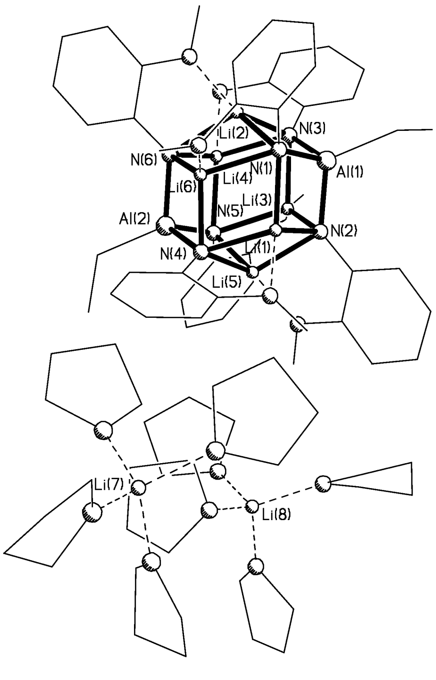

Fig. 1 Crystal structure of **3**. Hydrogen atoms and the thf molecules of crystallisation have been omitted for clarity. Selected bonds (Å) and angles (°): Al(1)–N(3) 1.882(1), Al(1)–N(1) 1.886(1), Al(1)–N(2) 1.887(1), Al(1)–C(51) 2.010(2), Al(2)–N(5) 1.878(1), Al(2)–N(4) 1.878(1), Al(2)–N(6) 1.887(1), Al(2)–C(27) 2.004(2), Li(1)–N(1) 2.048(3), Li(1)–N(2) 2.054(3), Li(1)–N(4) 2.095(3), Li(5)–N(4) 2.020(3), Li(5)–N(5) 2.059(3), Li(5)–N(2) 2.110(3), Li(4)–N(6) 2.050(3), Li(4)–N(5) 2.054(3), Li(4)–N(3) 2.117(3), Li(2)–N(3) 2.034(3), Li(2)–N(1) 2.092(3), Li(2)–N(6) 2.112(3), Li(6)–N(6) 2.038(3), Li(6)–N(4) 2.074(3), Li(6)–N(1) 2.115(3), Li(3)–N(2) 2.036(3), Li(3)–N(3) 2.037(3), Li(3)–N(5) 2.108(3), av. N–Al(1)–N 101.0, av. N–Al(2)–N 101.1, av. N–Al(1)–C 117.0, av. N–Al(2)–C 116.9, av. N–Li–N 90.3 (when both N atoms are bound to the same Al centre), av. N–Li–N 107.9 (when the N atoms are bound to different Al centres), av. Li–N–Li 117.2 (when both Li atoms are associated with the same Al centre), av. Li–N–Li 69.7 (when both Li atoms are associated with different Al centres).

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† Electronic supplementary information (ESI) available: syntheses of **1–4**. See http://www.rsc.org/suppdata/cc/b3/b307589c/

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observed for related neutral $E_2N_6Li_6$ imido group 14 and 15 complexes.[1,2] It is interesting that the dianion adopts an Al/N/Li motif commonly seen in imido p-block anion chemistry with imidoaluminium units linked by Li cations, rather than forming an Al/N cage anion with separate Li cations as may be anticipated from the rich structural chemistry observed in imidoalanes.

The $[Li_6\{R'Al(NR)_3\}_2]^{2-}$ dianion unit can be thought of as being built from two $[R'Al(NR)_3]^{4-}$ tetraanions which sandwich six Li^+ cations. The formal tetranegative charge on the $R'Al(NR)_3$ unit is to our knowledge the highest charge observed crystallographically for a simple mononuclear imido main group anion system. The two tetrahedral aluminium centres each have a terminal ethyl chain and use the three imido arms to bind the Li centres that hold the dimeric cage together. Oxygen atoms from the anisyl moiety additionally solvate each Li centre in the cage such that each Li has distorted tetrahedral geometry. It is interesting to note that all eight lithium centres are not incorporated into a single dimeric unit. There may be several reasons for this. Firstly, the 14 membered dianion of **3** contains a hexagonal prismatic Li_6N_6 framework similar to those commonly seen in lithium amide chemistry. The high thermodynamic stability of this unit may be of critical importance in stabilising this heterobimetallic core. Secondly, steric constraints may preclude incorporation of all the Li centres into a single cage structure. Lastly, there remains a question as to whether a hypothetical 16 membered $Li_8Al_2(NR)_6$ cage geometry is possible that allows sufficient favourable Li^+–N^- contacts to outweigh the accompanying repulsive Li^+–Li^+ and N^-–N^- contacts.

The reaction to form **2** provides an interesting contrast to the observations of Chivers *et al.* on metallation studies of triamidoaluminanes and gallanes, $[E\{N(H)Bu^t\}_3]_2$.[12,13] This group found that only partial lithiation occurs to produce mixed amido/imido group 13 anions that trap excess organolithium reagent. In forming **2** full deprotonation of the imido groups has occurred followed by nucleophilic addition of the organolithium reagent. There are many possible reasons for this difference in reactivity, notably the fact that arylamido groups are more readily deprotonated than alkylamido groups and that the methoxy sidearms of **2** help stabilise the Li^+ counter cations. In addition, the differences in steric bulk between the two systems is likely to be a significant feature.

Another intriguing aspect of the system is revealed from a comparison of related aluminium and boron systems. Hence, whereas reaction of $EtAlCl_2$ with three equivalents of 2-methoxyanilido lithium and subsequent metallation with $LiBu^n$ (3 equiv.) produces $[Li(THF)_4]_2[Li_6\{EtAl(NR)_3\}_2]$ (**3**) containing the *tetraanionic* $[EtAl(NR)_3]^{4-}$ unit, the corresponding reaction of $PhBCl_2$ with 2-methoxyanilido lithium (3 equiv.) and $LiBu^n$ (3 equiv.) gives $[Li_2PhB(NR)_2]_2\cdot 3THF$ (**4**) containing the *dianionic* $[PhB(NR)_2]^{2-}$ fragment. It is interesting to note that the ^{11}B NMR spectrum of the reaction mixture used to form **4** shows a broad peak at δ = 33.5 ppm corresponding to **4** and another sharp peak at δ = 2.2 ppm that corresponds to a tetrahedral boron environment that is probably due to tetrahedral borate anions present in solution where an anion $\{$probably either Bu^{n-} or free $N(H)R^-\}$ complexes the boron centre. However, the only crystalline material isolated is composed solely of **4** which forms a dimeric cage in the solid state with four lithium centres sandwiched between two $[PhB(NR)_2]^{2-}$ dianions. This possesses the same components as have been seen in related studies by Chivers *et al.*[16] The differences in the observed products from similar boron and aluminium chemistry can be accounted for by the fact that the boron atoms in **4** adopt planar geometries whereas the aluminium centres in **3** readily adopt tetrahedral geometries. This may be explained by the relatively strong π-bonding found for the second period elements B and N. Thus, reaction stops before nucleophilic addition of an extra formal Li_2NR fragment can occur, which is conceptually what occurs to give the corresponding aluminium product. However, the observation of tetrahedral borate anions in the reaction solution illustrates the very fine thermodynamic balance present in the boron system between the planar and tetrahedral forms.

In conclusion, we have found two routes towards alkyltriimido aluminium tetraanions and have found an interesting contrast to the related boron chemistry.

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Notes and references

‡ CCDC 214484. See http://www.rsc.org/suppdata/cc/b3/b307589c/ for crystallographic data in .cif or other electronic format.

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