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Selective oxygen capture by lithium aluminates: a solid state and theoretical structural study †

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Received 21st July 2000, Accepted 9th October 2000
First published as an Advance Article on the web 16th November 2000

Reaction of PhC(O)N(Me)H with AlMe$_3$ in toluene results in facile CH$_4$ evolution and formation of the amidoalane PhC(O)N(Me)AlMe$_2$, **6**. The addition of 1 eq. Bu^{t}Li affords the lithium aluminate [PhC(O)N(Me)Al(Me)$_2$Bu^t]Li, **7**, which on treatment with oxygen yields the mixed-anion species [PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li·[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li, **8**. In the solid state **8** forms a dimer based on a tetranuclear (LiO)$_4$ ladder structure in which terminal mono-oxygenated aluminate ligands and tripodal bis-oxygenated aluminate ligands span end and central Li$^+$ cations. Replacement of PhC(O)N(Me)H in the above reaction sequence with the more sterically congested amide PhC(O)N(Ph)H results in the formation of the amidoalane PhC(O)N(Ph)AlMe$_2$, **9**, which in turn affords the lithium aluminate [PhC(O)N(Ph)Al(Me)$_2$Bu^t]Li, **10**, and upon treatment of this with oxygen, the 70 : 30 **11a** : **11b** mixture [PhC(O)N(Ph)Al(Me)(OR)R′]Li, **11** (R = Bu^t, R′ = Me, **11a**; R′ = Bu^t, R = Me, **11b**). Both **10** and **11** are dimeric in the solid state, suggesting that the selective oxygenation process, and therefore the character of the oxygenated product, is templated by the structure of the precursor aluminate complex. Calculations are presented which corroborate the competitive nature of the inclusion of oxygen atoms into Al–Me and Al–Bu^t groups in species of the type reported here.

Introduction

The syntheses, structures and reactivities of lithium-containing heterobimetallic species are of interest by virtue of their ability to effect organic transformations whose selectivities differ from those afforded by homometallic organolithium species.[1] Hence, whereas organolithium reagents are known to exhibit 1,2-addition towards α,β-unsaturated ketones,[2] the promotion of conjugate addition has more recently been noted in the presence of catalytic quantities of asymmetric heterobimetallic species.[3] More commonly, the non-catalytic addition of sterically congested Lewis acids such as tri-coordinate organoaluminium compounds has been reported to effect 1,4-addition.[4] These observations have led to studies in which bis(aryloxy)methylalanes of the type MeAl(OAr)$_2$ (Ar = aryl) have been reacted with various organolithium reagents to afford lithium aluminate monomers, Me$_2$Al(μ-OAr)$_2$Li, of a type which are implicated in the conjugate addition process.[5] The extension of this work to lithium aluminate complexes involving N-centred ligands[6] has recently shown that various isomers of BuLi react with the alane Me$_2$AlN(2-Pyr)Ph (Pyr = pyridyl), **1**, to yield unique hydride-containing compounds.[7] Thus Bu^{t}Li reacts to afford either the ion-separated compound {Li$_8$(H)[N(2-Pyr)Ph]$_6$}$^+$·[Li(Me$_2$AlBu$^t_2$)$_2$]$^-$, **2**, or Li$_7$(H)[N(2-Pyr)Ph]$_6$, **3**. In order to further investigate the effect which varying the choice of organic residue has on the formation of compounds such as **2** and **3** we have lately undertaken reactions between Bu^{t}Li and a variety of molecules which contain a Me$_2$AlN(R)C(=X)– unit (X = N, O *etc.*) similar to that found in **1**. Whereas for X = N it has been found that the dimethyl(amidinato)alane Me$_2$AlAm, **4** {Am = [PhNC(Ph)NPh]$^-$}, reacts with Bu^{t}Li to yield the compound (Li$_4$Am$_3$)$^+$·{Li[(μ-Me)$_2$Al(Me)Bu^t]$_2$}$^-$, **5**,[8] we report here on the reaction of Bu^{t}Li with various substrates containing the Me$_2$AlN(R)(O=)C– fragment. Reaction of PhC(O)N(Me)AlMe$_2$, **6**, with Bu^{t}Li affords a lithium aluminate, **7**, which in turn reacts with oxygen to afford a heterobimetallic mixed-anion compound, **8**.[9] The related but more sterically congested lithium aluminate [PhC(O)N(Ph)Al(Me)$_2$Bu^t]Li, **10**, reacts with oxygen to give a 70 : 30 **11a** : **11b** mixture of [PhC(O)N(Ph)Al(Me)(OR)R′]Li, **11** (R = Bu^t, R′ = Me, **11a**; R′ = Bu^t, R = Me, **11b**). The products which result from oxo-insertion into Al–C bonds are subjected to a theoretical investigation.

Results and discussion

Solid state study

Reaction of PhC(O)N(Me)AlMe$_2$, **6**, in toluene with 1 eq. Bu^{t}Li affords a solution from which amorphous **7** can be obtained as the only isolable species upon complete removal of the solvent *in vacuo*. It is clear from ^{1}H NMR spectroscopy that rather than being a hydride-containing compound akin to either **2** or **3**, **7** is the simple lithium aluminate [PhC(O)N(Me)Al(Me)$_2$Bu^t]Li. However, the controlled exposure of a solution of **7** to air (pre-dried over P$_2$O$_5$) prior to storage at −30 °C results in the formation of the mixed-metal/mixed-anion compound [PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li·[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li, **8**, as the only isolable product (Scheme 1). In the solid state **8** forms a dimer of this dinuclear formulation (Fig. 1 and Table 1) with the crystal lattice containing two molecules of toluene for each such aggregate (which ^{1}H NMR spectroscopy indicates to be

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† Dedicated to the memory of Ron Snaith.

Electronic supplementary information (ESI): modelled geometries for **12a**–**f** and **13a**–**h**. Selected bond lengths and angles for (**10**)$_2$ and (**11**)$_2$ (compared with **12a**,**b**,**d**,**f** and **13a**,**b**,**d** respectively) and calculated energies for **12a**–**f** and **13a**–**h**. See http://www.rsc.org/suppdata/dt/b0/b005897l/

DOI: 10.1039/b005897l

Table 1 Selected bond lengths (Å) and angles (°) for dimeric **8**

Al1–O4	1.775(2)	Al2–O3	1.757(2)
Al1–N1	1.943(3)	Al2–O5	1.763(2)
O1–C7	1.262(4)	Al2–N2	1.934(3)
O1–Li1	1.940(5)	O2–C21	1.291(3)
O1–Li2	1.950(5)	O2–Li2	1.957(5)
N1–C7	1.312(4)	O2–Li2A	2.051(5)
Li1–O4	1.900(6)	N2–C21	1.310(4)
Li1–O3	1.935(6)	Li2–O5A	1.896(5)
Li1–O2	2.056(6)	O5–Li2A	1.896(5)
Li1–O1–C7	124.5(2)	O2–Li2–O2A	87.8(2)
O1–C7–N1	122.0(3)	O1–Li1–O3	136.4(3)
C7–N1–Al1	128.8(2)	O2–Li1–O3	96.1(2)
N1–Al1–O4	105.4(1)	O1–Li1–O4	99.3(2)
Li1–O4–Al1	118.0(2)	O2–Li1–O4	116.5(3)
C7–O1–Li2	144.7(2)	O3–Al2–O5	109.5(1)
Li1–O1–Li2	90.0(2)	O3–Al2–N2	103.5(1)
Li1–O2–Li2	86.5(2)	O5–Li2A–O1A	114.3(3)
O1–Li1–O2	90.4(2)	O5–Li2A–O2A	96.8(2)
O1–Li2–O2	93.1(2)	C21–O2–Li2	110.2(2)
Li1–O2–Li2A	123.1(2)	C21–O2–Li1	104.3(2)
Li2–O2–Li2A	92.2(2)	C21–N2–Al2	117.6(2)
O1–Li2–O2A	122.4(3)		

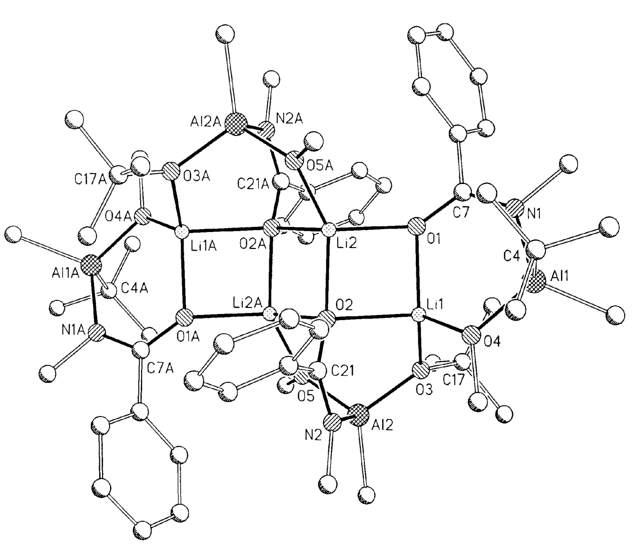
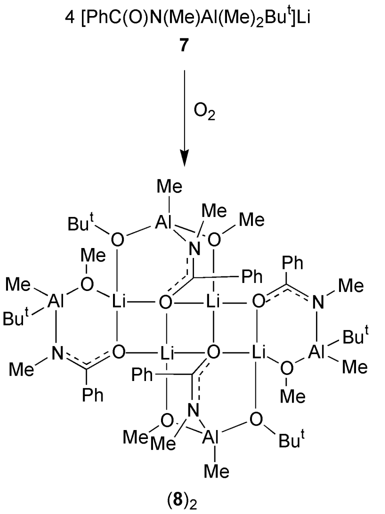


Fig. 1 Molecular structure of (**8**)$_2$; hydrogen atoms and lattice toluene molecules omitted for clarity.



Scheme 1

partially lost upon isolation of the crystals). The resulting tetranuclear structure has, at its core, a (LiO)$_4$ ladder based on three contiguous and precisely planar (LiO)$_2$ rings which utilise the original carbonyl oxygen centres of **7**. Peripheral to this ladder core are the two types of oxygenated aluminate anions which have been produced by aeration. Interestingly, these moieties act in distinct ways. Two terminal mono-oxygenated anions, [PhC(O)N(Me)Al(Me)(Bu^t)OMe]$^-$, use their *in situ* formed methoxy groups to close the 6-membered OCNAlO(Me)Li chelate rings [Li1–O4 = 1.900(6) Å] which stabilise the lithium centres at the ladder ends. In contrast, the two bis-oxygenated [PhC(O)N(Me)Al(Me)(OBu^t)OMe]$^-$ ions span ladder end and central Li$^+$ cations (Li1 and Li2A respectively), interacting with these Group 1 centres *via* both their *tert*-butoxy [Li1–O3 = 1.935(6) Å] and their methoxy [Li2A–O5 = 1.896(5) Å] units, respectively (Fig. 2). The shortness of the Li1–O4 bond in the mono-oxygenated monomer would appear to be responsible for the observation that these Li–OR (R = Me, Bu^t) bonds differ significantly in length. The two bis-oxygenated anions therefore act as tripodal ligands forming fused tricyclic arrangements with the relevant lithium centres (Li1 and Li2A) of the ladder core. It is probably the contiguous nature of these three resultant rings which explains the relatively long Li1–O2 and Li2A–O2 distances (mean = 2.054 Å). Whereas one 6-membered ring involves both types of lithium centre and is based on an approximately symmetrical MO(M′O)$_2$ (M = Al, M′ = Li) heterocycle, the two remaining heterocyclic arrangements incorporate just one Group 1 metal centre each [*i.e.* OCNAlO(Bu^t)Li and OCNAlO(Me)Li stabilise Li1 and Li2 respectively].

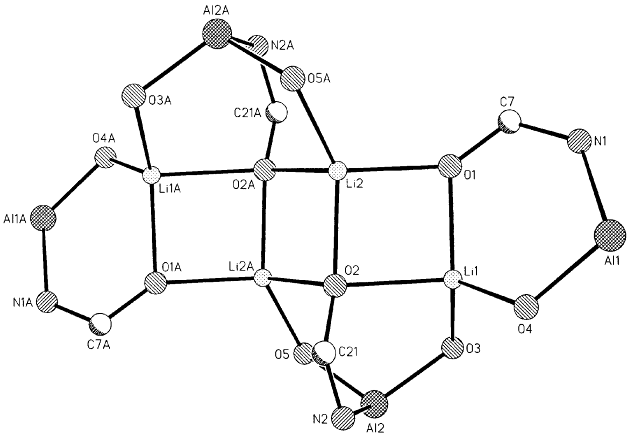
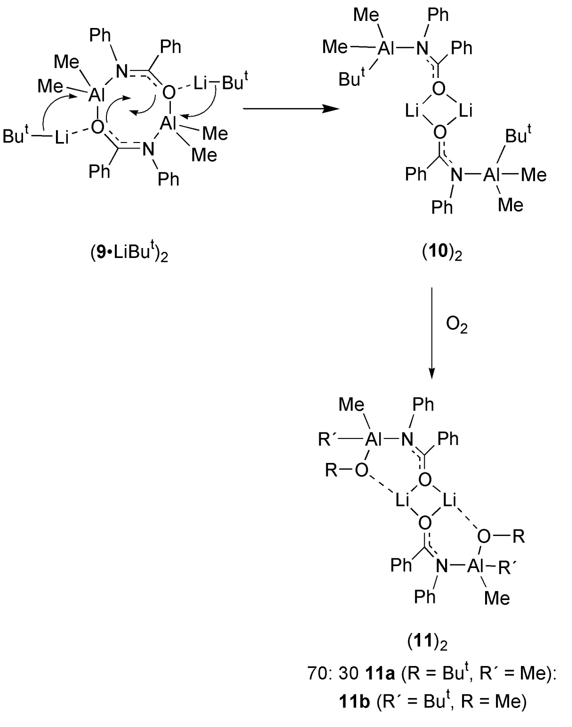


Fig. 2 The heterocyclic core of (**8**)$_2$ showing the three edge-fused (LiO)$_2$ rings and emphasising the coordinative modes of the mono- and bis-oxygenated aluminate anions.

Whereas there exist several examples of structurally characterised lithium aluminates incorporating intramolecular Li–O interactions, these species have to date largely been based either on straightforward heterobimetallic motifs [Al(μ-O)Li[3,10–14] or Al(μ-O)$_2$Li[5,10,12,15,16]] or else on LiO(AlO)$_2$[11] or (AlO)$_n$ rings (n = 2, 3).[3,13] Although a 4-membered (LiO)$_2$ ring core [supported by peripheral Al(μ-O)$_2$Li heterocycles] has been noted previously,[16] the observation of a homometallic structural core in (**8**)$_2$ is still highly unusual. Indeed, the dimer of **8**, based as it is on a (LiO)$_4$ ladder, is one of only a very small number of such lithium containing homometallic ladders.[17,18] The great majority of Li–O incorporating metallo-organic compounds are based instead on pseudo-cubane tetramers,[10] hexamers[10,19] or higher[20] aggregates in the solid state. Thus the adoption of a (LiO)$_4$ intercepted-ladder motif by (**8**)$_2$ represents the first crystallographic evidence that ladder structures, observed for a range of lithiated residues (particularly lithium halides,[21] amides[10,22,23] and phosphides,[24] but also lithium thiolates[25] and arsenides[26]), can also be found for heterobimetallic lithium aluminate complexes. Of particular interest is the observation that while the original carbonyl oxygen centres of **7** are utilised in the (LiO)$_4$ core of (**8**)$_2$, the coordinative requirements of the two different types of lithium centre (Li1 and Li2) in the assembled ladder are obviously satisfied by the variability of ligand oxygenation. This relates to the final interesting feature of the oxo-capture process which has afforded $(\mathbf{8})_2$. Previously reported oxygen scavenging by lithiated homometallic [to produce $(\mu_6\text{-O})\text{Li}_6$ fragments][27,28] and by lithium containing bimetallic species [giving $(\mu_4\text{-O})\text{Li}_2\text{Mg}_2\text{O}$,[23,29] $(\mu_5\text{-O})\text{Li}_4\text{Mg}$,[23,30] $(\mu_6\text{-O})\text{Li}_6$,[28] $(\mu_6\text{-O})\text{Li}_2\text{Ru}_4$,[31] $(\mu_8\text{-O})\text{Li}_8$[32] and $(\mu_6\text{-O})\text{Li}_3\text{Zn}_3$[33] units] require O^{2-}-encapsulation. This contrasts with the oxo-insertion which has occurred at the metal–carbon bonds in **7**—a process which is more similar to the formation of the alkoxide–hydroxide containing species[17] $(\text{Bu}^t\text{OLi})_{10}\cdot(\text{LiOH})_6$, to the recently noted behaviour of a lithiated germanium amide in the presence of molecular oxygen[34] and also to the synthesis of $\text{Bu}^t(\mu_3\text{-O})\text{Li}_3(\mu_6\text{-O})\text{Zn}_3[\text{N(2-Pyr)Me}]_6$ (which requires both oxo-insertion and -encapsulation).[33]

In order to gain a better understanding of the processes which are active in the course of oxo-insertion and the factors which govern its duality of behaviour (*viz.* mono- and bis-oxygenation of the two aluminate anions in **8**) the more sterically hindered dimethyl(*N*-phenylbenzamido)alane, **9**, has been studied. Sequential lithiation and oxygenation of this species, itself known to be a dimer based on an 8-membered $(\text{AlNCO})_4$ heterocycle,[35] has the potential advantages of offering an insight into the precise structure of the lithiated oxo-insertion precursor, in addition to the nature and extent of oxo-insertion occurring within a more sterically demanding (and therefore deaggregated) lithium aluminate oligomer.

The reaction of the dimer of PhC(O)N(Ph)AlMe_2, **9**, with 1 eq. Bu^tLi in toluene results in the formation of a colourless solution. Treatment of this with hexane followed by storage at sub-ambient temperature results in the deposition of a single isolable product. ^1H NMR spectroscopy indicates it to be the lithium aluminate $[\text{PhC(O)N(Ph)Al(Me)}_2\text{Bu}^t]\text{Li}$, **10** (Scheme 2).



Scheme 2

Table 2 Selected bond lengths (Å) and angles (°) for dimeric **10**

O1–Li1	1.896(8)	Li1–O2	1.846(9)
O1–Li2	1.911(8)	O2–Li2	1.924(9)
O1–C13	1.270(5)	O2–C32	1.289(5)
N1–C13	1.322(5)	N2–C32	1.291(6)
Al1–N1	1.984(4)	Al2–N2	2.016(5)
Al1–C6	2.033(6)	Al2–C24	1.990(6)
Al1–C5	1.961(5)	Al2–C25	1.973(5)
C4 · · · Li1	2.66(5)	C24 · · · Li2	2.37(1)
C4′ · · · Li1	2.34(5)	C25A · · · Li2	2.45(1)
C6 · · · Li1	2.20(1)		
O1–Li1 · · · C6	106.0(4)	O1–Li2–O2	86.9(4)
O1–Li1 · · · C4	94(2)	Li1–O2–Li2	91.5(4)
Li1 · · · C6–Al1	82.2(3)	O2–Li2 · · · C24	108.1(4)
Li1 · · · C4–C1	88(2)	Li2 · · · C24–Al2	90.8(3)
Li1 · · · C4′–C1	101(2)	C24–Al2–N2	117.0(3)
C4–C1–Al1	125(2)	C24–Al2–C25	105.5(3)
C6–Al1–N1	106.9(2)	Al2A–C25A · · · Li2	160.8(3)
C1–Al1–N1	107.5(2)	O1–Li2–C25	109.5(4)
Al1–N1–C13	118.9(3)	O2–Li2–C25A	107.0(4)
N1–C13–O1	120.2(4)	Al2–N2–C32	118.9(3)
C13–O1–Li1	133.7(4)	N2–C32–O2	121.2(4)
Li1–O1–Li2	90.4(4)	C32–O2–Li1	133.9(4)
C13–O1–Li2	132.8(4)	C32–O2–Li2	134.1(4)
O1–Li1–O2	89.6(4)		

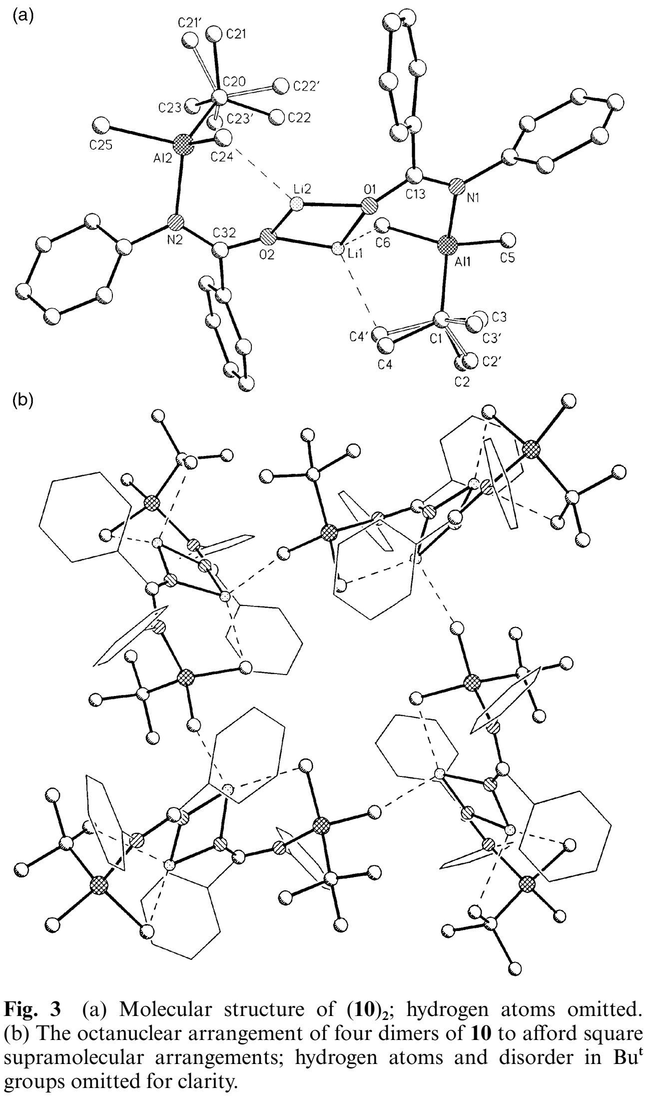


Fig. 3 (a) Molecular structure of $(\mathbf{10})_2$; hydrogen atoms omitted. (b) The octanuclear arrangement of four dimers of **10** to afford square supramolecular arrangements; hydrogen atoms and disorder in Bu^t groups omitted for clarity.

Consistent with the employment of a more sterically congested amide substrate, X-ray crystallography reveals that this aluminate complex, rather than being a tetranuclear ladder analogous to $(\mathbf{8})_2$, has a dimeric formulation for which there exists one molecule of solvent of crystallisation (Fig. 3a and Table 2). The dimer lacks crystallographic inversion symmetry and is based on an essentially planar $(\text{LiO})_2$ ring which utilises the carbonyl oxygen centres of the amidoalane precursor **9**. Dimerisation can be viewed as resulting from the formation of a short Li1–O2 bond [1.846(9) Å] and a rather longer Li2–O1 interaction [1.911(8) Å]. Intramonomer O-stabilisation of the Li^+ ions is supplied by Li1–O1 and Li2–O2 bonds [of 1.896(8) and 1.924(9) Å respectively]. Peripheral to this $(\text{LiO})_2$ ring core, the two aluminate moieties chelate the Group 1 metal centres by

Table 3 Selected bond lengths (Å) and angles (°) for dimeric **11**

Li1–O1A	1.879(8)	Al1–N1	1.963(4)
O1–Li1	1.908(8)	Al1–O2	1.754(4)
O1–C1	1.267(4)	O2–Li1	1.831(8)
N1–C1	1.324(5)		
Li1–O1–Li1A	89.8(3)	C1–N1–Al1	120.6(3)
O1–Li1–O1A	90.2(3)	N1–Al1–O2	105.3(2)
Li1–O1–C1	134.6(3)	O2–Li1–O1	102.9(4)
O1–C1–N1	120.3(3)	O2–Li1–O1A	163.8(5)

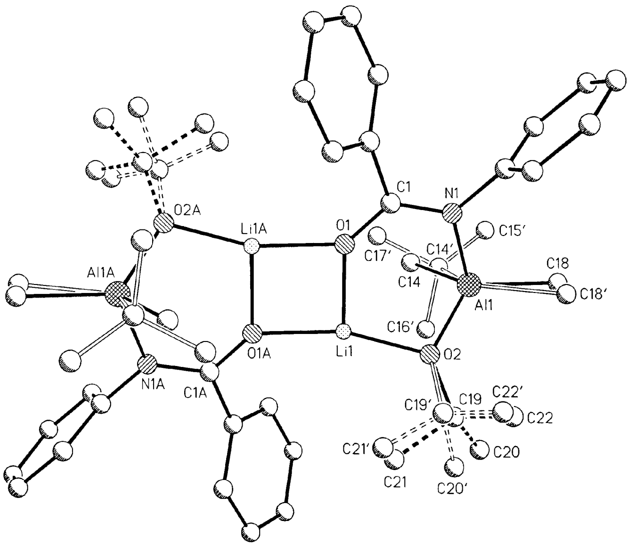


Fig. 4 Molecular structure of $(\mathbf{11})_2$ showing positional disorder in the Bu^t and Me groups; hydrogen atoms and lattice toluene molecules omitted for clarity.

virtue of the formation of weak agostic interactions comparable in length to those in previously reported lithium aluminate complexes in which the lithium centres were merely two-coordinate {*c.f.* Li $\cdots$ C = 2.787 Å (mean) in $[(Me_3Si)_2NLi]_2$,[36] 2.482 Å (mean) in $[(Me_3Si)_2NLi]_3$,[36] and 2.82–3.05 Å in *anti*-$[(Bu^t)_6Al_6(O)_6Me_2](Li{\cdot}OEt_2)_2]$}.[37] Notably, different coordinative modes are adopted by each lithium centre in $(\mathbf{10})_2$ with respect to the aluminium bonded alkyl groups. Hence Li1 is intramolecularly stabilised by agostic bonds which involve both AlMe [Li1 $\cdots$ C6 = 2.20(1) Å] and $AlBu^t$ [Li1 $\cdots$ C4 and Li1 $\cdots$ C4′ = 2.66(5) Å and 2.34(5) Å respectively] groups, whereas Li2 is internally bonded to only a single AlMe fragment [Li2 $\cdots$ C24 = 2.37(1) Å]. The coordination sphere of this metal centre is completed by the formation of a 2.45(1) Å interaction with an AlMe group in an adjacent dimer in the crystal lattice, a bond which presumably explains the significant difference between the intra-dimer bonds in which Li1 and Li2 participate (see above). The association of four dimeric units in the manner discussed affords an octanuclear arrangement (Fig. 3b). The mechanistic basis for the structure of $(\mathbf{10})_2$ is of some interest. Both the known solid state structure of $(\mathbf{9})_2$ and that of $(\mathbf{10})_2$ reveal a significant azaenolate contribution (Table 2),[35] and it seems reasonable to suppose that a combination of this effect, along with the predilection of lithium for intra-dimer agostic stabilisation as discussed above, lead to the observation of *cis*- rather than (normally preferred) *trans*-isomerism[38] about the N$\overset{\cdots}{-}$C bond.

The selective oxygenation of $[PhC(O)N(Ph)Al(Me)_2Bu^t]Li$ has been achieved by the treatment of a pre-formed solution of this compound with P_2O_5 pre-dried air to afford a colourless solution from which micro-crystals of **11** deposit (Scheme 2). Refinement of the X-ray crystal structure of this species presented some problems, including positional disorder in the aluminium bonded alkyl groups, the presence of disordered lattice solvent, and ambiguity in the exact site of oxygenation (see below). Nevertheless, the important features in compound **11** are unambiguous (Table 3 and Fig. 4). Unlike the tetranuclear ladder structure observed for $(\mathbf{8})_2$, and presumably by virtue of the steric constraints associated with the N-phenyl groups, the solid state structure reveals the new complex to be a dimer for which there are two equivalents of toluene in the lattice (^1H NMR spectroscopy indicating that they are readily removed upon isolation *in vacuo*). The dimer is based on a centrosymmetric $(LiO)_2$ core similar to that in $(\mathbf{10})_2$ [(intermonomer) Li1–O1A = 1.879(8) Å]. Again, unlike in $(\mathbf{8})_2$ where both mono- and bis-oxygenation of ligands was observed, the anionic moieties in $(\mathbf{11})_2$ have been only mono-oxygenated. Nevertheless, they utilise their *in situ* formed alkoxy groups in the formation of the 6-membered OCNAlO(R)Li (R = Bu^t or Me, see below) rings which chelate the Group 1 metal centres [Li1–O1 = 1.908(8) Å] in a manner comparable to the terminal singly oxygenated monomers in tetranuclear $(\mathbf{8})_2$. A close consideration of the Fourier difference map of $(\mathbf{11})_2$ indicates, however, that the crystallographic dimer is composed of two different structural isomers generated by the oxygenation process. Similarly ^1H NMR spectroscopy suggests that the crystalline material isolated is composed of an isomeric mixture. The complex signal observed at δ 3.57–3.17, consistent with the presence of 0.3OMe, taken in conjunction with the multiplet at δ −0.88 to −1.23 (0.85AlMe), suggests that $(\mathbf{11})_2$ is composed of a 70:30 **11a**:**11b** mixture of $[PhC(O)N(Ph)Al(Me)(OR)R']Li$ where R = Bu^t, R′ = Me for **11a** and R′ = Bu^t, R = Me for **11b**. This ratio is borne out crystallographically with the most suitable model of the dimer having the Bu^t group disordered over one site (C14′) on Al1 with occupancy 0.312(2) and two sites on O2 (C19 and C19′) with occupancies of 0.480(5) and 0.208(5) respectively. Conversely, one Me group is disordered over two sites (C14, C14″) on Al1 with occupancies 0.517(4) and 0.171(5) and one site (C19″) on O2 with occupancy 0.312(2). Since crystallography provides a description of the molecule which is time- and space-averaged over the complete unit cell, it is not possible to determine by analysis of the scattering factors whether the dimers comprise molecules with the same R and R′ groups in both halves.

Both $(\mathbf{8})_2$ and $(\mathbf{11})_2$ are reproducibly obtainable, albeit thus far in moderate yields, from the treatment of lithium aluminates **7** and **10** to either normal (*i.e.* moist) or (P_2O_5) pre-dried air. Instructively, however, the use of moist air affords samples of oxo-insertion product which ^1H NMR spectroscopy shows to contain significant amounts of contamination. This suggests the hydrolytic formation[39] of alkylaluminoxanes[40] and leads to the conclusion that it is molecular oxygen, rather than moisture, which is active in the oxo-insertion processes that yield both $(\mathbf{8})_2$ and $(\mathbf{11})_2$. It is, therefore, interesting to compare these results with the previously reported observation that air-sensitive R_3Al species react to give tris-oxygenated compounds, $(RO)_3Al$, upon exposure to molecular oxygen.[39,41] While the syntheses of $(\mathbf{8})_2$ and $(\mathbf{11})_2$ clearly demonstrate that controlled oxo-insertion is viable, they pose significant questions about the precise mechanism by which oxygen is introduced to the lithium aluminate precursors.

Discussion of the formation of the structural isomers of **11** in the context of a templated oxo-insertion process into the lithium aluminate precursor suggests that the order of combination of alane, organolithium reagent and molecular oxygen is crucial. Importantly, therefore, it has been established by ^1H NMR spectroscopy that the treatment of $PhC(O)N(R)AlMe_2$ (R = Me, **6**; Ph, **9**) alone with pre-dried air fails to afford any detectable reaction. It is only the sequential combination of $PhC(O)N(R)AlMe_2$ (R = Me, Ph), Bu^tLi and O_2 that selective oxygenation of the type discussed here results. Neither $(\mathbf{8})_2$ nor $(\mathbf{11})_2$ show complete tris-oxygenation of the aluminium centres. Rather, in $(\mathbf{8})_2$ two of the aluminate anions have each undergone single oxo-insertion and two have each inserted oxygen atoms into two Al–C bonds whereas in $(\mathbf{11})_2$ each aluminate anion has been singly oxygenated. In each case ligands are afforded in the respective products which are ideal for the provision of additional coordination to the alkali metal centres in the $(LiO)_n$ core [$n = 4$ in $(\mathbf{8})_2$ and 2 in $(\mathbf{11})_2$]. Whereas the mechanistic details surrounding the formation of $(\mathbf{8})_2$ are unclear, largely because **7** failed to crystallise adequately for a full (X-ray) characterisation, the observations discussed above suggest that oxo-insertion is either directly templated [in which case **7** is based on a $(LiO)_4$ ladder core] or else that the synthesis of $(\mathbf{8})_2$ requires that the processes of ladder formation *and* oxo-insertion occur concurrently. The study of compounds $(\mathbf{10})_2$ and $(\mathbf{11})_2$, however, sheds light on the processes active in oxygenation and the relationship between species before and after exposure to dry air. Crucially, the isolation and structural characterisation of both $(\mathbf{10})_2$ and $(\mathbf{11})_2$ point to the activity of a template effect with the essential features of the dimeric structure observed for $(\mathbf{10})_2$ being retained in $(\mathbf{11})_2$. The amount of oxygen captured is exactly that necessary for the complete removal of agostic stabilisation of the Group 1 metal centres and their subsequent stabilisation by all of the *in situ* generated alkoxy fragments while retaining the $(LiO)_2$ ring core of the precursor.

Theoretical calculations

The observation that templated oxo-insertion in $(\mathbf{10})_2$ afforded structural isomers by virtue of competition between the oxygenation of Al–C(Bu^t) and Al–C(Me) bonds (**11a** and **11b** respectively) prompted a theoretical investigation of the relative energies of the mono- and di-meric substrate, as well as the two monomeric and the various permutations of dimeric product [$(\mathbf{11a})_2$, $(\mathbf{11b})_2$ and (**11a11b**)]. *Ab initio* calculations[42] were performed on $\{[HC(O)N(H)Al(Me)_2Bu^t]Li\}_n$, $\{[HC(O)N(H)Al(Me)(Bu^t)OMe]Li\}_n$, $\{[HC(O)N(H)Al(Me)_2OBu^t]Li\}_n$ ($n = 1$, 2) and the mixed dimer $\{[HC(O)N(H)Al(Me)(Bu^t)OMe]Li{\cdot}[HC(O)N(H)Al(Me)_2OBu^t]Li\}$ using the 6-31G* basis set at the RHF level. Tables of calculated absolute and relative energies and also schematic representations of the modelled structures have been supplied as Electronic Supplementary Information.†

The simplified monomeric precursor to oxo-insertion $[HC(O)N(H)Al(Me)_2Bu^t]Li$ was modelled in two geometries (**12a/b**). Calculations indicate little theoretical difference in the predilection of lithium for stabilisation both by a Me and a Bu^t group [**12a**, absolute energy (E) = −653.754891 au (au = arbitrary/absolute units)] and by only two Me groups (**12b**, $E = -653.754282$ au)—the latter model being the more stable by a mere 0.38 kcal mol^{-1} (1 kcal = 4.186 kJ). Dimerisation has been modelled for both $(\mathbf{12a})_2$ [as **12c** (C_2-symmetry) and **12d** (C_i-symmetry)] and $(\mathbf{12b})_2$ [as **12e** (C_2) and **12f** (C_i)]. Both **12c/d** and **12e/f** demonstrate a nominal preference for inversion symmetry. The most stable dimer (**12d**) has a calculated enthalpy of aggregation (ΔH_{agg}) of −37.10 kcal mol^{-1} relative to two molecules of **12a**. This compares very closely with ΔH_{agg} of −36.32 kcal mol^{-1} (relative to two molecules of **12b**) for the most stable dimer of **12b**. In each instance the calculated bonding interactions correlate extremely well with the experimentally observed structure of $(\mathbf{10})_2$.

Theoretical study of the monomeric oxo-insertion product $[HC(O)N(H)Al(Me)(OR)R']Li$ yields structures **13a** (R = Me, $R' = Bu^t$, $E = -728.688697$ au) and **13b** ($R = Bu^t$, R′ = Me, $E = -728.712250$ au). Importantly, with respect to the known competition between OMe and OBu^t formation in tetranuclear $(\mathbf{8})_2$ and—more significantly—the structural isomerism observed in $(\mathbf{11})_2$ (see above), the relative stabilities of the calculated structures suggest that the *tert*-butoxy isomer (**13b**) is 14.78 kcal mol^{-1} more stable than the methoxy one (**13a**) at the level of computational sophistication used. While the reasons for this require further clarification, two possibilities appear to present themselves. The first is that minimisation of steric crowding around the tetra-coordinate Al centre is achieved in the *tert*-butoxy isomer. The observation that in the calculated methoxy monomer (**13a**) Al–C(Bu^t) is 2.022 Å [0.028 Å longer than Al–C(Me) in the same structure] whereas O–C(Bu^t) in **13b** is 1.412 Å [only 0.012 Å longer than O–C(Me) in **13a**] supports this view. The second possible explanation derives from inductive stabilisation of the inserted oxygen atom. The lithium centre in methoxy isomer **13a** has a more positive charge (+0.65e) than that in *tert*-butoxy isomer **13b** (+0.61e) with the carbonyl O-centres having the same charge (+0.72e) in both structures. In spite of this the relative charges on the methoxy and *tert*-butoxy O-centres in **13a/b** are −0.92e and −0.96e, respectively. It is of note that **13b** (OBu^t) incorporates (at 1.820 Å) a longer alkoxy–lithium interaction than does **13a** (OMe) (1.807 Å).

Dimeric oxy-insertion products have been modelled as both symmetric and asymmetric types. In the former category $(\mathbf{13a})_2$ and $(\mathbf{13b})_2$ have been computed with both C_2- (**13c** and **13e** respectively) and C_i-symmetry (**13d** and **13f** respectively). The asymmetric dimer (**13a13b**) has been modelled with both aluminium centres (and also both alkoxy centres) relatively *syn*- (**13g**, *viz.* C_2-symmetry) and relatively *anti*- (**13h**, *viz.* C_i-symmetry) disposed. These six computed species (**13c–h**) are all based on almost identical $(LiO)_2$ ring cores in which, consistent with the solid state structure of $(\mathbf{11})_2$, Li–O inter-monomer bonds are shorter than their Li–O intra-monomer counterparts. Hence the respective observed distances of 1.879(8) and 1.908(8) Å in $(\mathbf{11})_2$ correlate well with the calculated ones of 1.885 Å and 1.934 Å (mean for **13c–h**). Noticeably, however, the preference for *tert*-butoxy formation over methoxy formation is maintained (compare **13c/e** and also **13e/f**) as is the preference for inversion symmetry (compare **13c/d** and also **13e/f**) or *anti*-isomerism (compare **13g/h**). Consequently **13f** is the most stable theoretical dimer, its inversion symmetry making it 0.39 kcal mol^{-1} more stable than **13e** (C_2) and giving it a calculated ΔH_{agg} value of −34.52 kcal mol^{-1}. **13d** (C_i-symmetry dimer of **13a**) and **13c** (its C_2 analogue) are respectively 28.09 and 28.52 kcal mol^{-1} less stable than **13f**. It should be noted, however, that these energetic pairs are extremely close and that their exact ordering should not be over-interpreted. Relative to the calculated methoxy dimers (**13c/d**) and their *tert*-butoxy counterparts (**13e/f**), the mixed dimers **13g/h** are energetically intermediate with **13g** (*syn*-Al/*syn*-alkoxy) being a mere 0.40 kcal mol^{-1} less stable than **13h** (*anti*-Al/*anti*-alkoxy).

Our knowledge of the solid state structure of $(\mathbf{8})_2$ demonstrates the shortness of Li–OMe interactions relative to Li–OBu^t ones. Hence, within each ladder-spanning tripodal arrangement the salient distances are 1.895(5) Å and 1.935(6) Å respectively whereas the terminal (mono-oxygenated) aluminate anions stabilise the ladder-end alkali metal centres by virtue of forming a Li–OMe interaction which is, at 1.900(6) Å, not dissimilar to the former value. This propensity for the formation of shorter bonds between lithium and methoxy O-centres, though unobservable in $(\mathbf{11})_2$ by virtue of its structural isomerism, is nonetheless reflected theoretically. The crystallographically determined value of 1.831(8) Å [for Li1–O2 in $(\mathbf{11})_2$] compares with the values of 1.837 Å and 1.869 Å predicted for **13d** (C_i OMe dimer) and **13f** (the significantly more stable C_i OBu^t dimer) respectively. Correlation is also shown with the Li–OMe and Li–OBu^t distances (1.838 Å and 1.867 Å respectively) calculated for the mixed *anti*-dimer **13h**.

Conclusion

Attempts to better understand why the structure of $(\mathbf{8})_2$ reveals two types of anion (mono- and bis-oxygenated) are ongoing, and centre on efforts to learn the precise structural nature of **7**. The close structural relationships between $(\mathbf{9})_2$, $(\mathbf{10})_2$ and $(\mathbf{11})_2$ are striking. The preference of both $(\mathbf{9})_2$ and $(\mathbf{10})_2$ for *cis*-isomerism about $N \overset{...}{-} C$ bonds and also agostic stabilisation of the alkali metal centres in the latter complex point to its self-assembly from (**9**)$_2$. Meanwhile the observation that both (**10**)$_2$ and (**11**)$_2$ are based on a $(LiO)_2$ dimer core with both lithium centres being stabilised by virtue of the selectivity with which oxygenation occurs is also consistent with a templating effect on the part of the lithium aluminate precursor. Calculations predict very similar energies—the exact ordering of which should therefore be treated with caution—for a variety of structural models. However, they do strongly support the experimentally observed preference for oxo-insertion into Al–Bu^t bonds over Al–Me interactions in the conversion of (**10**)$_2$ to (**11**)$_2$ with a 14.8 kcal mol^{-1} gain in stabilisation upon oxygenation of the Al–Bu^t bond relative to that of an Al–Me one in monomeric $[HC(O)N(H)Al(Me)_2Bu^t]Li$. Further work will seek to eliminate the structural isomerism which plagues the organic periphery of (**11**)$_2$ by reacting a solution of **9** with Bu^{t}OLi in an attempt to yield (**11a**)$_2$. More generally, it will be profitable to study systems of the form R_2AlL and $R'Li$ (R, R' = alkyl, aryl; L = N- or O-centred ligands) under stringently anaerobic conditions and in the deliberate presence of pre-dried air, pure oxygen or chemical sources of oxygen.[44] Thus, it is hoped to judge how widespread and how useful the templated oxo-insertion process, and the concomitant ligand amendments, might be.

Experimental

Syntheses and characterisation

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen or argon, using standard double manifold and glove-box techniques. Where appropriate the treatment of air sensitive reaction mixtures with oxygen was achieved using air which had been pre-dried over P_2O_5 (Lancaster). All other chemical reagents (Aldrich) were used as received without further purification. Toluene and hexane were distilled from sodium and sodium–potassium amalgam, respectively, immediately prior to use.

NMR data were collected on either a Bruker DPX 400 (operating at 400.12 MHz for ^{1}H) or a Bruker DRX 500 (operating at 500.05 MHz for ^{1}H and 125.01 MHz for ^{13}C) FT NMR spectrometer. Chemical shifts are quoted relative to TMS at δ 0.00.

Synthesis of $[PhC(O)N(Me)Al(Me)_2Bu^t]Li$, 7. Toluene (1 ml) was added to *N*-methylbenzamide (0.14 g, 1 mmol) at −78 °C under nitrogen and the resultant suspension treated with $AlMe_3$ (0.5 ml, 1 mmol, 2 M in hexane). The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes whereupon it was returned to −78 °C and Bu^{t}Li (0.59 ml, 1 mmol, 1.7 M in pentane) was added. The resultant solution was returned to room temperature and the solvent was removed *in vacuo* to afford **7** as a white powder. Yield 0.17 g (65%), mp 86–88 °C. Found: C 64.94, H 8.94, N 6.41%. Calcd. for $C_{14}H_{23}AlLiNO$: C 65.88, H 9.02, N 5.49%. ^{1}H NMR spectroscopy (400.12 MHz, $[^2H_8]$THF), δ 7.61–6.93 (m, 5H, Ph), 2.81–2.79 (m, 3H, NMe), 0.79–0.71 (m, 9H, Bu^t), −1.38, −1.53 (m, 6H, AlMe).

Synthesis of $\{[PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li\cdot[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li\}_2\cdot 2PhMe$, (8)$_2$·2PhMe. As for **7** but after allowing to warm to room temperature the pale yellow solution was sequentially treated with dry air (P_2O_5) for 1 min. and with hexane (0.5 ml). Storage at −30 °C for 3 days resulted in the deposition of colourless micro-crystals of (**8**)$_2$·2PhMe. Yield 0.05 g (15%) (assuming excess oxygen), mp 128–130 °C. Found: C 63.21, H 8.80, N 4.79%. Calcd. for $C_{35}H_{54}Al_2Li_2N_2O_5$: C 64.62, H 8.31, N 4.31%. ^{1}H NMR spectroscopy (500.05 MHz, $[^2H_8]$THF), δ 8.05–7.20 (m, 10H, Ph), 7.19–6.98 (m, 2.5H, tol.), 3.51–3.44 (m, 6H, OMe), 3.04–2.66 (m, 6H, NMe), 2.32 (s, 1.5H, tol.), 1.20–1.15, 0.86 (m, 18H, Bu^t), −1.02, −1.07 (m, 6H, AlMe).

Synthesis of $\{[PhC(O)N(Ph)Al(Me)_2Bu^t]Li\}_2$, (10)$_2$. Toluene (1 ml) was added to *N*-phenylbenzamide (0.19 g, 1 mmol) at −78 °C under nitrogen and the resultant suspension treated with $AlMe_3$ (0.5 ml, 1 mmol, 2 M in toluene). The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes whereupon it was returned to −78 °C and Bu^{t}Li (0.59 ml, 1 mmol, 1.7 M in pentane) was added. The resultant colourless solution was returned to room temperature whereupon the solvent was reduced to half-volume prior to the addition of hexane (0.3 ml). Storage at −30 °C for 2 days afforded colourless needles of (**10**)$_2$. Yield 0.13 g (40%), mp 167–169 °C. Found: C 70.58, H 8.18, N 4.60%. Calcd. for $C_{19}H_{25}AlLiNO$: C 71.92, H 7.89, N 4.42%. ^{1}H NMR spectroscopy (500.05 MHz, $[^2H_8]$THF), δ 8.07–6.80 (m, 10H, Ph), 0.56 (s, 9H, Bu^t), −1.32 (s, 6H, AlMe). ^{13}C NMR spectroscopy (125.01 MHz, $[^2H_8]$THF), δ 151.2, 140.8 (*i*-Ph), 128.8 (*o*-, *m*-Ph), 128.0 (*p*-Ph), 127.3, 126.6, 124.5 (*o*-, *m*-Ph), 120.7 (*p*-Ph), 30.4 (Bu^t), −9.5 (AlMe).

Synthesis of 70:30 $\{[PhC(O)N(Ph)Al(Me)(OR)R']Li\}_2\cdot 2PhMe$, (11)$_2$·2PhMe (R = Bu^t, R′ = Me, 11a; R′ = Bu^t, R = Me, 11b). As for (**10**)$_2$ but upon returning to room temperature the solution was treated with dry air (P_2O_5) for 45 s and then with hexane (0.5 ml). Storage at −30 °C for 3 days yielded colourless micro-crystals of (**11**)$_2$·2PhMe. Yield 0.04 g (10%) (assuming excess oxygen), mp 220–222 °C. Found: C 69.36, H 8.01, N 4.42%. Calcd. for $C_{52}H_{66}Al_2Li_2N_2O_4$: C 73.24, H 7.74, N 3.29%. ^{1}H NMR spectroscopy (500.05 MHz, $[^2H_8]$THF), δ 9.29–6.68 (m, 10H, Ph), 3.57–3.17 (m, 0.9H, 0.3OMe), 1.32–1.14, 0.91–0.83 (m, 9H, Bu^t), −0.88 to −1.23 (m, 5.1H, 0.85AlMe). ^{13}C NMR spectroscopy (125.01 MHz, $[^2H_8]$THF), δ 129.0 (*o*-, *m*-Ph), 128.6 (*p*-Ph), 128.4 (*o*-, *m*-Ph), 34.1, 33.9, 32.0, 31.2 (Bu^t, Me).

X-Ray crystallography

Essential crystallographic details for compounds (**8**)$_2$·2PhMe, (**10**)$_2$ and (**11**)$_2$·2PhMe are given in Table 4. In (**10**)$_2$, disorder in the Me carbon atoms of the Bu^t groups was modelled with two positions of half occupancy (C2–C4, C2′-C4′ and C21–C23, C21′–C23′). In (**11**)$_2$·2PhMe, disorder in the Bu^t groups was modelled with one site on Al1 (C14′–C16′) and two sites on O2 (C19–C22 and C19′–C22′), and the corresponding Me group over 3 positions (C14, C14″ and C19″). The coordinates and displacement parameters of C14′, C14″ and C19, C19″ were constrained to be equal. In addition, the other Me group was disordered over two positions, C18 and C18′. The occupation factors were refined in each case and restrained to sum to unity. The toluene solvent molecules in (**11**)$_2$·2PhMe were modelled as being disordered over two sites of half occupancy and all disordered C atoms in this structure were refined with isostropic displacement parameters.

CCDC reference number 186/2224.

See http://www.rsc.org/suppdata/dt/b0/b005897l/ for crystallographic files in .cif format.

Theoretical calculations

Ab initio calculations were carried out using the GAUSSIAN 94[42] computer program. Calculations employed the 6-31G* basis set[43] at the RHF level and the resulting geometries were subjected to a frequency analysis to verify the presence of a local minimum.

Acknowledgements

We wish to thank the UK EPSRC (D. J. L., P. S.) and the CCDC (G. P. S.) for financial support and St. Catharine's (R. P. D.) and Gonville & Caius (A. E. H. W) Colleges for Research Fellowships.

Table 4 Crystallographic data for $(\mathbf{8})_2\cdot 2\mathrm{PhMe}$, $(\mathbf{10})_2$ and $(\mathbf{11})_2\cdot 2\mathrm{PhMe}$

	$(\mathbf{8})_2\cdot 2\mathrm{PhMe}$	$(\mathbf{10})_2$	$(\mathbf{11})_2\cdot 2\mathrm{PhMe}$
Formula	$C_{35}H_{54}Al_2Li_2N_2O_5$	$C_{38}H_{50}Al_2Li_2N_2O_2$	$C_{52}H_{66}Al_2Li_2N_2O_4$
M_r	650.64	634.64	851.91
Crystal system	Triclinic	Tetragonal	Triclinic
Space group	$P\bar{1}$	$I4_1/a$	$P\bar{1}$
a/Å	12.333(3)	33.134(2)	9.787(5)
b/Å	13.439(3)	33.134(2)	11.779(5)
c/Å	14.021(4)	14.4150(4)	14.112(3)
α/°	109.87(1)		108.20(3)
β/°	91.58(2)		101.91(3)
γ/°	114.21(1)		108.08(3)
V/Å^3	1955.2(9)	15826(1)	1384(1)
Z	2	16	1
Radiation, Å	Cu-K$_\alpha$, 1.54178	Mo-K$_\alpha$, 0.71069	Mo-K$_\alpha$, 0.71069
μ/mm^{-1}	0.972	0.105	0.092
T/K	180(2)	180(2)	180(2)
Measured reflections	8243	12299	8491
Unique reflections	4837	6920	5395
R_{int}	0.0301	0.0515	0.0394
Final $R(F)$, $wR(F^2)$	0.0640, 0.1766	0.0926, 0.2922	0.1029, 0.3455

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