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The crystallographic observation of molecular lithium oxide: synthesis and solid-state structure of $[Me_2AlN(2-C_5H_4N)Ph]_2(O)Li_2·2THF$ †

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Received 18th May 2001, Accepted 24th July 2001
First published as an Advance Article on the web 10th September 2001

The reaction of $Me_2Al[N(2-C_5H_4N)Ph]$, **1**, with 1 equiv. $(Me_3Si)_2NLi$ affords the lithium aluminate $Me_2Al[N(SiMe_3)_2][N(2-C_5H_4N)Ph]Li$, **2**, which exhibits solvent dependent reactivity towards oxygen. In toluene **2** appears to resist oxygenation but in the presence of THF it reacts to afford the new complex $[Me_2AlN(2-C_5H_4N)Ph]_2(O)Li_2·2THF$, **3**. X-Ray diffraction data reveal that **3** has a butterfly-type Al_2Li_2 bimetallic core with two equivalents of reformed **1** stabilising discrete, molecular lithium oxide. The structures of **1**–**3** are probed theoretically.

Introduction

Significant interest has been shown in the structure and reactivity of heteropolymetallic species incorporating lithium. This is by virtue of their ability to induce chemical transformations with selectivities that differ to those affected by homometallic lithiated organics.[1] Hence for example, sterically demanding tricoordinate aluminium tris(2,6-diphenylphenoxide) has been employed as a selective activator of carbonyls towards organolithium-mediated α-alkylation.[2] Lately, it has been noted that in the presence either of the same Lewis acid[3] or of methylaluminium bis(2,6-di-*tert*-butyl-4-alkylphenoxide)[4] organolithium reagents add to α,β-unsaturated ketones at the 1,4- rather than the 1,2-positions,[5] lithium aluminate monomers having been implicated in the process.[6] Further studies into the chemistry of mixed Li–Al systems have led to the report that $Me_2AlN(2-C_5H_4N)Ph$ **1** reacts with Bu^tLi to afford hydride-containing clusters[7] whose formation is critically dependent on the use of organolithium precursors capable of β-eliminating LiH.[8] While this view was supported by the observation that the treatment of **1** with MeLi affords $[Me_3AlN(2-C_5H_4N)Ph]Li$,[9] we wish to report here that the analogous treatment of **1** with $(Me_3Si)_2NLi$ affords a simple lithium aluminate **2**. Moreover, whereas previously reported oxygen scavenging by lithiated homometallic[10–18] and by lithium-containing heterobimetallic[19–25] compounds have previously pointed to the encapsulation of naked O^{2-}, studies into the controlled oxygenation of lithium aluminates have revealed remarkably different behaviour.[26,27] Thus, for example, a selectively oxygenated heterobimetallic mixed-anion ladder $\{[PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li·[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li\}_2$ has lately been isolated and fully characterised[26] with oxo-insertion into Al–C bonds observed.[28] However, we also report here that the controlled oxygenation of **2** follows a new path. Instead of affording a heterobimetallic ladder in which oxo-capture has resulted in the formation of formal Al–O bonds, the treatment of **2** with air (pre-dried over P_2O_5) results in a novel butterfly complex (**3**) in which two equivalents of *in situ* reformed amidoalane, **1**, stabilise a molecule of lithium oxide.

Results and discussion

Reaction of 2-pyridylaniline with $AlMe_3$ in toluene results in the facile evolution of CH_4 and formation of the simple amidoalane **1**. X-Ray crystallography (Fig. 1 and Table 1) reveals that in the solid state **1** is a dimer based on an eight-membered $(NCNAl)_2$ chair [Al1–N1 = 1.8916(18) Å, Al1–N2 = 2.0033(18) Å].

Treatment of the amidoalane **1** with 1 equiv. of $(Me_3Si)_2NLi$ in toluene afforded a yellow solution from which colourless blocks were deposited after storage at 45 °C. Initial NMR spectroscopic studies indicated this to be the simple lithium aluminate $Me_2Al[N(SiMe_3)_2][N(2-C_5H_4N)Ph]Li$ **2**. While con-

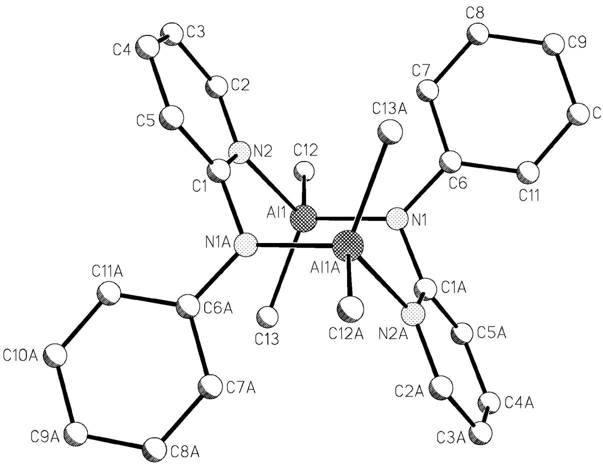

Fig. 1 Molecular structure of dimeric **1**; hydrogen atoms omitted for clarity.

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† Electronic supplementary information (ESI) available: modelled geometries of **4a**–**12** and tables of absolute and relative energies for **4a**–**12** and calculated bond lengths and angles. See http://www.rsc.org/suppdata/dt/b1/b104388a/

DOI: 10.1039/b104388a

Table 1 Selected bond lengths (Å) and angles (°) for dimeric $Me_2Al[N(2-C_5H_4N)Ph]$ **1**

Al1–N1	1.8916(18)	N1–C1A	1.403(2)
Al1–N2	2.0033(18)	N1–C6	1.406(2)
Al1–C13	1.958(2)	N2–C1	1.347(2)
Al1–C12	1.968(2)		
N1–Al1–N2	103.59(8)	Al1–N1–C1A	116.32(12)
Al1–N2–C1	120.91(12)	Al1–N1–C6	126.10(12)
N2–C1–N1A	116.67(15)		

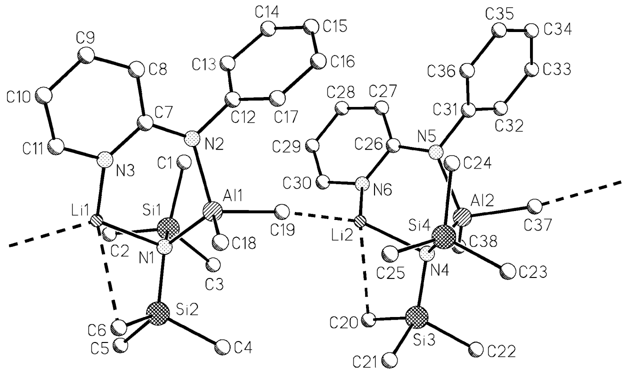


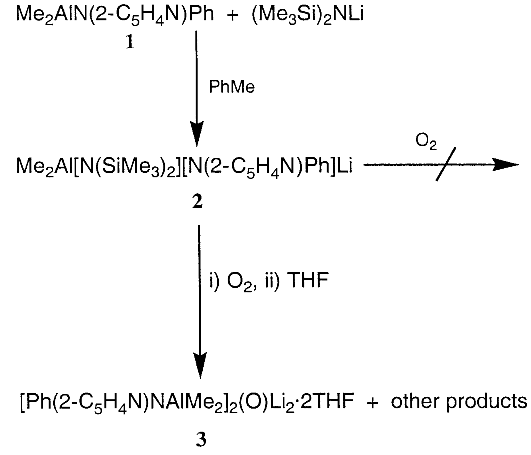
Fig. 2 Molecular structure of the dimeric asymmetric unit of polymer **2**; hydrogen atoms omitted for clarity.

firming this formulation, single crystal X-ray diffraction revealed a polymeric structure containing two monomeric fragments in the asymmetric unit (Fig. 2 and Table 2). It can be seen that the straightforward 1 : 1 addition of $[N(SiMe_3)_2]^-$ to **1** has afforded the approximately tetrahedral aluminate fragment $\{Me_2Al[N(SiMe_3)_2][N(2-C_5H_4N)Ph]\}^-$, the charge upon which is offset by that on the Group 1 metal centre. The intramolecular coordination of Li^+ arises from its interaction with both the hexamethyldisilazide and pyridyl N-centres [mean Li–N = 2.03 and 1.97 Å, respectively]. The consequent formation of six-membered NCNAlNLi heterocycles renders each monomer in the asymmetric unit chiral at its hexamethyldisilazide N-centre (N1, N4) and means that solid-state **2** is composed of racemic one dimensional chains comprising monomeric units of alternating stereochemistry. The relatively long $Li–N(SiMe_3)_2$ interaction implies that this N-centre adopts a near sp^2-type geometry[29] with its unhybridized p-orbital orientated towards Li^+: a feature borne out by the bond angles around nitrogen [mean Si–N–Si, Si–N–Al and Al–N–Li = 117.78, 114.65 and 94.34°, respectively]. Polymerisation results from the intermolecular stabilisation of Li^+ by Al-bonded methyl groups [mean Li $\cdots$ C = 2.32 Å]. This process, similar to that observed in the polymeric solid-state structures of $Me_3AlN(SiMe_3)_2Li$[30] and $Me_3Al(TMP)Li$ (TMP = 2,2,6,6-tetramethylpiperidide),[31] presumably results from the electron-rich nature of these Me groups. Several reports exist of species which contain Al–N bonds and which incorporate external Lewis bases in the solid state. Hence compounds with the core systems $(PhCH_2)_2N(H)\cdot Li(\mu\text{-}N)Al$,[32] $(THF)_3\cdot Li(\mu\text{-}N)Al$,[33] $[(THF)_n\cdot Li(\mu\text{-}N)Al]_2$ ($n = 1, 2$),[34,35] and $L_n\cdot Li(\mu\text{-}N)_2Al$ ($n = 1$, L = THF, Et_2O, C_5H_5N;[36] $n = 2$, L = HNC_4H_8, THF[35,37]) are all based on an Al–N–Li motif. However, the structure of **2** represents one of only a very limited number of lithium aluminates that incorporate such a bonding pattern in the absence of solvation by external Lewis base.[9,30] It is noteworthy that deaggregation of the solid-state structure of **2** is not induced by the addition of Lewis base, and that polymeric **2** is thus the only species which can be recrystallised from toluene–hexane to which THF has been added after the reaction.

The behaviour of **2** on exposure to oxygen is unusual in two respects. Firstly, there is a propensity for reaction with oxygen which displays a significant dependence upon the choice of solvent. Thus, the treatment of an *in situ* pre-formed solution of **2** in toluene with air (pre-dried over P_2O_5)[26] resulted only in the recrystallisation of unreacted **2**. However, if the sample was treated with THF immediately after dry air had been bubbled through it, and subsequently stored at 5 °C, colourless blocks of **3** were deposited instead. X-Ray crystallography revealed the second novel aspect to the treatment of **2** with oxygen; namely that in the solid state, instead of oxo-insertion into Al–C interactions akin to that observed elsewhere,[26,27] oxygenation has afforded the new trinuclear heterobimetallic adduct $[Me_2AlN(2-C_5H_4N)Ph]_2(O)Li_2\cdot 2THF$ (Fig. 3 and Table 3). This conversion also occurs, with no detectable effect on the yield of **3**, if the order of THF addition and oxygenation is reversed. While these observations imply that the introduced THF (or impurities contained therein) might be directly responsible for the formation of **3**, such a possibility is inconsistent with the observation that the polymeric lithium aluminate **2** is isolable from an anaerobic mixture of **1** and $(SiMe_3)_2NLi$ in toluene–THF (see above).

Table 2 Selected bond lengths (Å) and angles (°) for polymeric $Me_2Al[N(SiMe_3)_2][N(2-C_5H_4N)Ph]Li$ **2**

Li1–N1	2.03(1)	Al2–C37	1.999(3)
Li1–N3	1.96(1)	Al2–C38	1.978(3)
Li2–N4	2.03(1)	Si1–N1	1.757(2)
Li2–N6	1.98(1)	Si2–N1	1.753(2)
Li1 $\cdots$ C37	2.36(1)	Si3–N4	1.749(2)
Li2 $\cdots$ C19	2.28(1)	Si4–N4	1.752(2)
Al1–N1	1.931(2)	N2–C7	1.368(4)
Al1–N2	1.922(2)	N2–C12	1.434(4)
Al2–N4	1.946(2)	N3–C7	1.355(4)
Al2–N5	1.933(3)	N5–C26	1.370(4)
Al1–C18	1.973(3)	N5–C31	1.447(4)
Al1–C19	2.002(3)	N6–C26	1.380(4)
Li1–N1–Al1	96.24(17)	Li2–N4–Al2	92.43(17)
Li1–N3–C7	127.2(2)	Li2–N6–C26	116.7(3)
Li1–N1–Si1	111.2(2)	Li2–N4–Si3	102.9(2)
Li1–N1–Si2	99.69(18)	Li2–N4–Si4	109.3(2)
Al1–N2–C12	117.67(19)	Al2–N5–C31	120.7(2)
N1–Li1–N3	114.8(2)	N4–Li2–N6	116.0(3)
N1–Al1–N2	111.63(10)	N4–Al2–N5	110.95(11)
N2–Al1–C19	108.05(12)	N5–Al2–C37	104.03(12)
N2–C7–N3	116.4(2)	N5–C26–N6	112.9(3)
C7–N2–C12	116.5(2)	C26–N5–C31	112.8(3)
C7–N2–Al1	123.13(18)	C26–N5–Al2	120.8(2)



Scheme 1

The solid-state structure of **3** has, at its core, an oxo-dianion that is encapsulated in a heterobimetallic environment by virtue of interactions both with Group 1 and Group 13 metal centres. The two Li^+ ions in the complex bond to the O^{2-} centre [Li1–O1 and Li2–O1 = 1.91(2) and 1.88(2) Å, respectively] and the Li1–O1–Li2 angle is, at 76.4(7)°, slightly contracted relative to

Table 3 Selected bond lengths (Å) and angles (°) for $[Me_2AlN(2-C_5H_4N)Ph]_2(O)Li_2{\cdot}2THF$ **3**

Li1–O1	1.91(2)	Al2–N3	1.916(6)
Li1–O2	1.93(2)	Al1–C1	1.96(1)
Li2–O1	1.88(2)	Al1–C2	1.99(1)
Li2–O3	1.89(2)	Al2–C18	1.96(1)
Li1–N2	2.28(2)	Al2–C19	1.98(1)
Li1–N4	2.28(2)	N1–C3	1.45(1)
Li2–N2	2.21(2)	N1–C9	1.38(1)
Li2–N4	2.22(2)	N2–C9	1.37(1)
Al1–O1	1.746(5)	N3–C20	1.44(1)
Al2–O1	1.763(5)	N3–C26	1.37(1)
Al1–N1	1.939(6)	N4–C26	1.38(1)
Li1–O1–Li2	76.4(7)	Li2–N4–C26	104.3(6)
Li1–N2–Li2	63.0(6)	N4–C26–N3	116.3(7)
Li1–N4–Li2	63.0(5)	C26–N3–Al2	127.1(5)
N2–Li1–N4	92.8(6)	N3–Al2–O1	104.3(3)
N2–Li2–N4	96.4(6)	Li1–N2–C9	93.1(6)
O1–Li1–N2	90.5(6)	Li2–N2–C9	131.9(7)
O1–Li1–N4	88.6(6)	N2–C9–N1	115.0(7)
O1–Li2–N2	93.5(6)	C9–N1–Al1	123.9(5)
O1–Li2–N4	91.2(7)	N1–Al1–O1	100.2(3)
Li1–N4–C26	130.9(6)	Al1–O1–Al2	131.2(3)

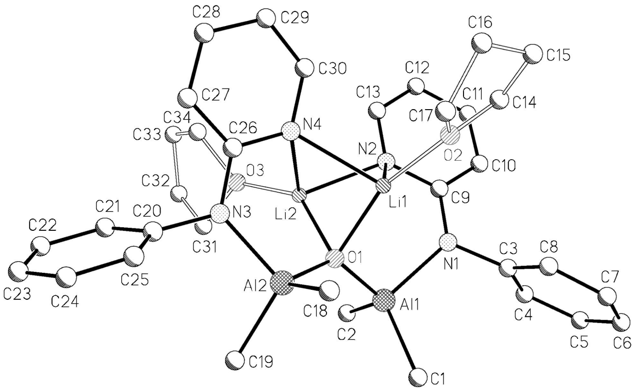


Fig. 3 Molecular structure of **3**; hydrogen atoms and minor THF disorder omitted for clarity.

that typically observed in $(LiO)_2$ rings.[6,38] Compound **3** can therefore be regarded as the lithium salt of an oxo-bridged bis(aluminate). However, it can also be considered to represent a co-complex incorporating a simple, non-linear molecule of lithium oxide. Notably, this view is consistent with the stabilisation of both Li^+ ions by the pyridyl N-centres of two equivalents of *in situ* reformed **1** incurring the formation of a four-membered $(LiN)_2$ ring. That this heterocycle is contiguous with the two concomitantly formed NLi_2O rings (N2–Li1–O1–Li2 and N2–Li1–O1–Li2) results in a tricyclic arrangement of approximately trigonal symmetry, wherein the dihedral angle between the Li1–N2–Li2/Li1–N4–Li2 planes is 119.0° (while those between the Li1–N2–Li2/Li1–O1–Li2 and Li1–N4–Li2/Li1–O1–Li2 planes are 122.2 and 118.6°, respectively). The angles within the $(LiN)_2$ ring itself merit comment. While those about the two metal centres are unremarkable (mean N–Li–N = 94.6°), those about the pyridyl N-centres are dramatically constricted (mean Li–N–Li = 63.0°), reflecting the non-planarity of this heterocycle and its correspondingly long Li–N(pyridyl) interactions (mean 2.247 Å).[39] The final cyclic arrangements to stabilise the Li_2O fragment involve the incorporation of each Li–O bond into two six-membered NCNAlOLi rings (*cf.* the generation of OCNAlOLi rings by selectively oxygenating Al–C bonds)[26,27] formed by virtue of coordination of the approximately tetrahedral (mean N–Al–O = 102.3°) Al centres to the oxo-dianion (mean Al–O = 1.755 Å). Thus, **1** acts not only as a Lewis base through its pyridyl N-atoms, but also as a Lewis acid through its Al-centres. Within the two six-membered rings the small angles about Li^+ (mean N–Li–O = 91.0°) are presumably enforced by strain in the six-membered ring itself and by the inability of the lithium oxide bond angle to collapse any further. Finally, the somewhat distorted tetrahedral coordination spheres of each of the Li^+ centres are completed by mono-THF solvation (mean Li–O = 1.907 Å).

The crystal structure of **3** is rendered unusual in that it demonstrates what is best viewed as the neutral amidoalane entrapment of isolated Li_2O. The solid-state structures of several species have been reported which, it has been suggested, incorporate Li_2O as part of a higher order lithium assembly. Hence, it has been suggested that $(RLi_n)_m{\cdot}Li_2O$ fragments are present in monolithiates $\{(2,6\text{-OMe-}C_6H_3Li)_6{\cdot}Li_2O,$[10] $[(c\text{-}C_5H_9)N(H)Li]_{12}{\cdot}Li_2O,$[13] $[Bu^nC(NBu^t)_2Li]_4{\cdot}Li_2O$[14]$\}$, in the mixed mono- and di-lithiate $\{[PhS(O)(NMe)C(H)(Me)Li]_2{\cdot}[(C_6H_4Li)S(O)(NMe)C(H)(Me)Li]_2{\cdot}Li_2O{\cdot}3TMEDA\}$[14] and in geminal $\{[PhS(O)_2C(SiMe_3)Li_2]_6{\cdot}Li_2O{\cdot}10THF,$[11] $[Pr^i{}_2(Mes)SiPLi_2]_8{\cdot}Li_2O,$[17] $[Me_2(Pr^iMe_2C)SiAsLi_2]_8{\cdot}Li_2O,$[17] $[PhS(O)(NMe)C(H)(Ph)Li]_2{\cdot}Li_2O{\cdot}6THF$[16]$\}$ and vicinal $\{[(salen)Li_2]_3{\cdot}Li_2O{\cdot}TMEDA{\cdot}H_2O$[12] ($H_2$salen = bis(salicylidene)ethylenediamine, TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine)$\}$ dilithiates. However, in all of the above cases, the oxo-dianion has been encapsulated by an octahedral array of Li^+ centres, almost invariably affording O_h symmetry clusters and precluding emphatic identification of the Li_2O unit. In the single lower-symmetry example (C_2 in solid-state $[Bu^nC(NBu^t)_2Li]_4{\cdot}Li_2O$)[14] the Li_2O fragment is considered to be near-linear. Perhaps more importantly, the isolation and solid-state characterisation of both the oxo-encapsulating heterobimetallic cluster $(TMP)_4Mg_2Li_2(O)$[22,23] and of the 2 : 1 adduct $[RuH(SiHPh_2)(CO)X_2]_2{\cdot}[Li_2Ru_4OCl_8X_4]$ (X = $PBu^t{}_2Me$)[19] have been reported.

The solid-state structure of lithium oxide itself[40] reveals an extended lattice in which each oxygen centre is in a cubic coordination environment with three distinct types of Li–O–Li bond angle (70.5, 109.5 and 180.0°). Only two molecular species have been reported in which oxygen is bonded equivalently to eight Li-centres: whereas the geometry at the chalcogen is square antiprismatic in $2TMEDA{\cdot}Li_8K_2(Bu^tO)_8(O)$,[41] a cubic "lattice fragment" has been observed in $Li_8(R)_6(O)$ (R = 4-azabenzimidazole derivative).[42] The X-ray structure of **3** demonstrates the entrapment of a lithium oxide molecule whose geometry at oxygen [76.4(7)°] is comparable with the smallest set of angles in the extended oxide lattice.[40] Lastly, the continued observation of Al–C contacts in the stabilising amidoalane ligands is also noteworthy given the well-known propensity of oxygen for insertion into Al–C bonds.[43]

Theoretical calculations

The GAUSSIAN 94[44] computer program was used to probe the observed structures of **1**–**3** by both *ab initio* (with the 6-31G* basis set[45] at the RHF level) and DFT (6-31G* basis set[45] with B3LYP method[46]) calculations. Details of modelled mono- and dimeric $Me_2AlN(2-C_5H_4N)Me$ (**4a** and **4b**, respectively) and $Me_2AlN(2-C_5H_4N)Ph$ (**5a** and **5b**, respectively), monomeric $(Me_3Si)_2NLi$ **6a/b** and $Me_2Al[N(SiMe_3)_2][N(2-C_5H_4N)R]Li$ (R = Me, **7**, R = Ph, **8**) and of unsolvated and OMe_2-solvated $[Me_2AlN(2-C_5H_4N)R]_2(O)Li_2$ (**9** and **10a/b**, respectively for R = Me and **11** and **12**, respectively for R = Ph) have been submitted as ESI.†

The calculated structures of **4/5a** and **4/5b** reveal stabilisation of the metal centre by both the deprotonated and pyridyl N-centres. Whereas in a monomeric context this results in the formation of a four-membered NCNAl ring, the dimer is based on an eight-membered $(NCNAl)_2$ ring core with intermolecular Al–N(pyridyl) interactions akin to that observed for **1**. Whereas a small aggregation enthalpy of 3.1 kcal mol^{-1} is noted for **4a/b** it is surprising to note that **5a** is 1.7 kcal mol^{-1} more stable than the corresponding dimer (**5b**). However, the energy difference is sufficiently small as to resist meaningful interpretation.

The favourable formation of $Me_2Al[N(SiMe_3)_2][N(2\text{-}C_5H_4N)\text{-}R]Li$ is pointed to by the theoretical finding of a 30.3 kcal mol^{-1} (R = Me, **7**) and a 30.5 kcal mol^{-1} (R = Ph, **8**) enthalpy of formation for the lithium aluminate relative to the combined energies of its components (**4a** + **6a** and **5a** + **6b**, respectively). The resultant monomeric complexes both reveal a six-membered NCNAlNLi core of the type noted in polymeric **2**, in which the alkali metal centre is stabilised both by hexamethyldisilazide and by pyridyl N-centres. The approximately sp^2 hybridization noted for the hexamethyldisilazide N-centre in polymeric **2** is also replicated in the calculated structures of monomeric **7** and **8**. Moreover, calculations suggest that this phenomenon is attributable to intramolecular agostic interactions. Thus, theory reveals a single agostically bonding hexamethyldisilazide C-centre (Li···C = 2.54 Å in **7** and 2.44 Å in **8**) which corresponds to the carbon atom which most closely approaches the alkali metal centre in each of the crystallographically independent molecules in the asymmetric unit of **2**. However, an interatomic distance of 2.937 Å (mean for Li1···C6 and Li2···C20) suggests only very weak intramolecular agostic bonding in the aggregated solid-state structure.[6,47]

The crystal structure of **3** reveals weak[39] Li–N(pyridyl) bonds (mean 2.247 Å; Table 3) and non-bonding [Li2···N1 = 2.281(17) Å; remaining Li···N($AlMe_2$) > 2.5 Å] distances with the distorted tetrahedral coordination spheres of each of the Li^+ centres being completed by mono-THF solvation (see above). Calculations on unsolvated and OMe_2-solvated $[Me_2AlN(2\text{-}C_5H_4N)R]_2(O)Li_2$ (**9** and **10a/b**, respectively for R = Me and **11** and **12**, respectively for R = Ph) point to these solvent molecules being of structural importance with THF-coordination evidently prevailing over the formation of Li–N($AlMe_2$) interactions by buckling of the NCNAlOLi rings. The calculated structure of **11** reveals the coordination of each pyridyl N-centre to just a single alkali metal ion (Li–N = 2.042 Å, Li···N = 2.841 Å). This is compensated for by the modification of both six-membered NCNAlOLi rings, the result being the formation of four-membered OAlNLi and six-membered NCNLiOLi rings, which are edge-fused by virtue of both Li–O and the new Li–NMe interactions (1.867 and 2.112 Å, respectively). The introduction of two molecules of OMe_2 results in several structural modifications, which make the calculated structure (**10a** with C_2 symmetry imposed, **10b** without) more closely approach that of **3**. The favourability of solvation is revealed by formation enthalpies of −22.2 kcal mol^{-1} for both species (relative to **9** + two free OMe_2 molecules). Further, **10a** and **10b** each show the interaction of pyridyl N-centres with both Li centres [mean 2.283 Å (**10a**), mean 2.284 Å (**10b**)] and the formation of six-membered NCNAlOLi rings of the type noted in **4**. Calculations on unsolvated (**11**) and OMe_2-solvated (**12**) $[Me_2AlN(2\text{-}C_5H_4N)Ph]_2(O)Li_2$ reiterate the observations noted for **9** and **10a/b**. The modelled structure of **11** shows each pyridyl N-centre bonding to one Li^+ ion (Li–N = 2.009 Å). The lack of a second lithium–pyridyl nitrogen bond (Li···N = 2.894 Å) is compensated for by stabilisation of the alkali metal centres by edge-fused four-membered OAlNLi and six-membered NCNLiOLi rings (Li–O and Li–NPh = 1.859 and 2.128 Å, respectively). The introduction of solvation by two molecules of OMe_2 results in the calculated structure (**12**) closely resembling the observed structure of **3**. A calculated formation enthalpy of −25.8 kcal mol^{-1} for **12** (relative to **11** + two free OMe_2 molecules) points to the preference for solvation by an etherate solvent. While modelled **12** reveals widely variable behaviour of the pyridyl N-centres with respect to each alkali metal ion [2.13–2.46 Å *cf.* 2.21(2)–2.28(2) Å in **3**], bond angles in the calculated $(LiN)_2$ ring core nevertheless agree excellently with observation. Finally, external solvation is accompanied by dislocation of the Li–NPh bonds noted in **11**, and the emergence of NCNAlOLi rings of the type noted in **3**, albeit with slightly exaggerated non-bonding Li···N distances.

Conclusions

Compound **3** is reproducibly obtained from the exposure of a pre-formed solution of **2** to dry air (pre-dried over P_2O_5). Although the presence of trace moisture cannot be entirely ruled out, previous work with lithium aluminates,[26,27] the isolation and characterisation of **2** [inconsistent with LiOH contamination of the $(Me_3Si)_2NLi$ substrate], and the absence of any isolable aluminoxane[28,48] hydrolysis products, points to molecular oxygen being responsible for the formation of Li_2O. NMR spectroscopic investigations into the formation of **3** are ongoing and will focus particularly on the nature of any by-products since the observation of $(Me_3Si)_2NH$ would clearly suggest the presence of moisture whereas the reaction of O_2 requires generation of the hydrazine $[(Me_3Si)_2N]_2$.[22] Also of mechanistic interest is the observation that neither the amidoalane[43] component of **3** nor the lithium aluminate[26,27] **2** has demonstrated thermodynamic oxo-insertion into Al–C bonds.[28,43] The reasons why the oxygenation of **2** is solvent dependent are also the subject of continued study, with calculations already suggesting that the way in which the alkali metal centres in **3** are stabilised varies with the choice of solvent.

Experimental

Methods and materials

All reactions and manipulations were carried out under an inert atmosphere, using standard Schlenk 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, THF and hexane were distilled off sodium or sodium–potassium amalgam immediately prior to use.

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

Crystallographic data for complexes **1**–**3** were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling device.

Syntheses and characterisation

$Me_2Al[N(2\text{-}C_5H_4N)Ph]$, 1. Trimethylaluminium (0.5 ml, 2.0 M in hexane, 1.0 mmol) was added to 2-pyridylaniline (0.17 g, 1.0 mmol) in toluene (0.3 ml) at −78 °C under nitrogen and the resultant slurry was warmed to room temperature. Gentle heating gave complete dissolution and the resultant yellow solution was stirred for 1 h prior to filtration and storage at −30 °C. After 1 week yellow blocks of **1** were deposited. Yield = 54%, mp = 100–102 °C. Found: C, 70.19; H, 6.93; N, 11.11. Calc. for $C_{26}H_{30}Al_2N_4$: C, 69.03; H, 6.64; N, 12.39%. ^1H NMR spectroscopy (400 MHz, 27 °C, [$^2H_6$]benzene): δ 7.26–5.83 (m, 9H, Ar), −0.12 (s, 6H, AlMe).

$Me_2Al[N(SiMe_3)_2][N(2\text{-}C_5H_4N)Ph]Li$, 2. *Method (i).* Treatment of the amidoalane **1** (0.11 g, 1 mmol) with 1 equiv. $(SiMe_3)_2NLi$ (0.08 g, 1 mmol) (both pre-weighed) in toluene (2 ml) at −78 °C under nitrogen afforded a slurry which was warmed to room temperature. Gentle heating gave complete dissolution and the resultant yellow solution was stored at 45 °C for 1 day whereupon colourless blocks were deposited. Yield = 20%, mp = 190–192 °C. Found: C, 55.42; H, 7.58; N, 11.10. Calc. for $C_{18}H_{33}AlLiN_3Si_2$: C, 56.69; H, 8.66; N, 11.02%. ^1H NMR spectroscopy (400 MHz, 27 °C, CD_3CN): δ 7.96–5.70 (m, 9H, Ar), 0.04 (s, 18H, $SiMe_3$), −1.20, −1.27, −1.37 (m, 6H, AlMe).

Table 4 Crystallographic data for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{26}H_{30}Al_2N_4$	$C_{19}H_{33}AlLiN_3Si_2$	$C_{34}H_{46}Al_2Li_2N_4O_3$
M_r	452.50	393.58	626.59
Crystal system	Triclinic	Orthorhombic	Cubic
Space group	$P\bar{1}$	$P2_1/n$	$Pna2_1$
a/Å	8.198(4)	13.8140(4)	20.16(1)
b/Å	8.531(4)	17.6740(5)	9.986(4)
c/Å	9.462(6)	19.7500(5)	18.129(4)
α/°	107.85(4)	90	90
β/°	106.44(5)	99.557(2)	90
γ/°	94.05(4)	90	90
U/Å^3	595.1(6)	4755.0(2)	3540(2)
Z	1	8	4
Radiation/Å	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
μ/mm^{-1}	0.144	0.913	0.120
T/K	180(2)	180(2)	180(2)
Measured refl.	3828	16045	4101
Unique refl.	2095	8324	3440
R_{int}	0.0270	0.0379	0.0593
$R1$,[a] $R1$[b]	0.037, 0.040	0.054, 0.079	0.070, 0.145
$wR2$,[a] $wR2$[b]	0.1060, 0.1106	0.148, 0.166	0.123, 0.151

[a] Value of the residual considering only the reflections for which $I > 2\sigma(I)$. [b] Value of the residual for all reflections.

Method (ii). As for route (i) with the yellow solution obtained at room temperature being treated with air (pre-dried over P_2O_5)[26] for 45 s. This afforded a dark brown suspension which reverted to a yellow solution at reflux. Filtration, reduction of the solvent volume by one half and storage at room temperature resulted in the deposition of crystalline **2** [by mp and NMR spectroscopy; yield = 20% (first batch); while the yield of material obtained, which had identical spectroscopic properties, could be increased to 82% by removal of all the solvent *in vacuo* after reflux, the mp of this material (at only 91–93 °C) suggested that polymerisation had not occurred].

$[Me_2AlN(2\text{-}C_5H_4N)Ph]_2(O)Li_2\cdot 2THF$, 3. A preformed solution of **2** in toluene (see above) was treated with air (pre-dried over P_2O_5)[26] for 45 s. THF (0.3 ml) was then added before the solution was reduced to half volume. The resultant yellow solution was stored at 5 °C for 3 days whereupon colourless blocks of **3** were deposited. Yield 11% [by $(Me_3Si)_2NLi$ consumed], mp 175–177 °C. Found: C, 63.25; H, 7.15; N, 8.86. Calc. for $C_{34}H_{46}Al_2Li_2N_4O_3$: C, 65.18; H, 7.35; N, 8.95%. ^1H NMR spectroscopy (500 MHz, 27 °C, CD_3CN): δ 8.15–6.74 (m, 9H, Ar), 3.64 (m, 4H, THF), 1.80 (m, 4H, THF), −1.10 (s, br, 6H, AlMe).

Crystallographic structure solution and refinement

Crystallographic data for complexes **1**–**3** are given in Table 4. The positions of some of the non-hydrogen atoms were determined by direct methods and refined against F^2 using SHELXL-97.[49] All of the non-hydrogen atoms were found by successive iterations of least-squares refinement. Hydrogen atoms were added in calculated positions and allowed to ride on their parent atoms unless they appeared in difference maps. For crystalline **1**–**3**, all of the non-hydrogen atoms were refined anisotropically. For crystalline **2**, one of the two THF molecules was disordered. This was modelled over two sites and the atoms refined at half occupancy.

CCDC reference numbers 165070–165072.

See http://www.rsc.org/suppdata/dt/b1/b104388a/ for crystallographic data in CIF or other electronic format.

Theoretical calculations

The GAUSSIAN 94[44] program was used to undertake *ab initio* calculations using the 6-31G* basis set[45] at the RHF level and also DFT calculations employing the 6-31G* basis set[45] with B3LYP method.[46]

Acknowledgements

We thank the UK EPSRC (D. J. L. & P. S.) and Gonville & Caius College (A. E. H. W.) for financial support.

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