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Selective oxygen capture to give a unique mixed-anion lithium aluminate: the synthesis and solid-state structure of $\{[PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li\cdot[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li\}_2$

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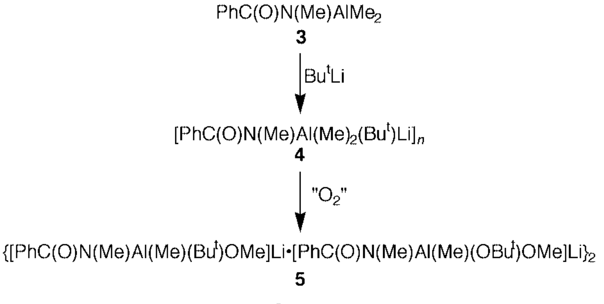
While reaction of a solution of the amidoalane $PhC(O)N(Me)AlMe_2$ 3 with 1 equiv. of Bu^tLi affords the lithium aluminate $PhC(O)N(Me)Al(Me)_2(Bu^t)Li$ 4, deliberate treatment of the reaction mixture with oxygen affords the unique mixed-anion species $\{[PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li\cdot[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li\}_2$ 5; in the solid state 5 has a $(LiO)_4$ ladder structure containing terminal mono-oxygenated aluminate ligands and tripodal bis-oxygenated aluminate ligands spanning end and central Li^+ cations.

There is much current interest in the syntheses, structures and reactivities of lithium-containing heterobimetallic species.[1–3] Recently, we have synthesised lithium aluminate monomers $Me_2Al(\mu_2\text{-}OAr)_2Li$ (Ar = aryl) by treating bis(aryloxy)methylalanes of type $MeAl(OAr)_2$ with RLi reagents (R = Me, Bu^t) and demonstrated the role of such species in 1,4-conjugate additions to α,β-unsaturated ketones.[1] We have also shown that BuLi reagents react with the (amido)methylalane $Me_2AlN(2\text{-}C_5H_4N)Ph$, **1**, to afford remarkable hydride-containing compounds,[2] *e.g.* Bu^tLi reacts with **1** to give $[Li(Me_2AlBu^t{}_2)_2]^-\cdot\{Li_8(H)[N(2\text{-}C_5H_4N)Ph]_6\}^+$ **2**. With a view to investigating the effect that the choice of organic residue has on the formation of species such as **2** we have recently carried out reactions of Bu^tLi with a variety of molecules containing a $Me_2AlN(C{=}X)C–$ unit (X = N, O *etc.*) akin to that found in **1**. We report here, on the reaction of the *N*-methylbenzamidoalane[4] **3** with Bu^tLi to afford the lithium aluminate, **4**, and on the isolation of the unique heterobimetallic mixed-anion ladder, **5**, which results when oxygen is subsequently and deliberately introduced to the reaction mixture (Scheme 1).

Reaction of a prepared solution of **3** with 1 equiv. of Bu^tLi affords a solution from which **4** can be obtained as the only isolable product.‡ ^1H NMR spectroscopy shows that, rather than being a hydride-containing compound, **4** is, in fact, a simple lithium aluminate. However, the controlled treatment of a solution of **4** with air followed by storage at −30 °C affords crystals of the unique mixed-metal/mixed-anion species $[PhC(O)N(Me)Al(Me)(Bu^t)OMe]Li\cdot[PhC(O)N(Me)Al(Me)(OBu^t)OMe]Li$ **5**.§ X-Ray crystallography¶ shows that in the solid state **5** is a dimer of this formulation (Fig. 1) with one molecule of toluene in the lattice. At the core of the solid-state structure is a $(LiO)_4$ ladder composed of three precisely planar edge-fused $(LiO)_2$ rings which incorporate the original carbonyl O-centres of **4**. Supplementary to this core, the two types of oxygenated aluminate anions, which have been afforded by treatment of **4** with air, operate in distinct ways. The two mono-oxygenated anions are terminal, using their generated OMe groups to complete the six-membered OCNAlO(Me)Li chelate rings [Li1–O4 1.900(6) Å] which stabilise the Li^+ centres at the ends of the ladder. In contrast, the two bis-oxygenated anions span ladder end- and central-Li^+ cations (Li1 and Li2A, respectively), coordinating to these metal centres through interactions involving their OBu^t [Li1–O3 1.935(6) Å] and OMe [Li2A–O5 1.896(5) Å] units, respectively. The observation that these Li–OR (R = Me, Bu^t) bonds differ significantly presumably derives from the shortness of the Li1–O4 bond in the mono-oxygenated monomer. Overall, these bis-oxygenated anions act as tripodal ligands forming, with the involved Li^+ centres of the ladder (Li1, Li2A), fused tricyclic arrangements. It is probably the contiguous nature of these three rings which accounts for the relatively long Li1–O2 and Li2A–O2 distances (mean 2.054 Å). While two of the ring systems incorporate one Li^+ centre each [$OCNAlO(Bu^t)Li$ and OCNAlO(Me)Li stabilise Li1 and Li2 respectively], the third six-membered ring, involving two Li^+ centres, is based on a fairly symmetrical $MO(M'O)_2$ (M = Al, M′ = Li) heterocycle.

Aside from the method used for its synthesis, the solid-state stucture of **5** shows a series of particularly noteworthy features. While several structurally characterised lithium aluminates incorporate intramolecular Li–O interactions, these have generally been based either on simple heterobimetallic motifs [$Al(\mu_2\text{-}O)Li$[5,6] or $Al(\mu_2\text{-}O)_2Li$[1,5,7]] or on $(AlO)_n$ rings (*n* = 2,



Scheme 1

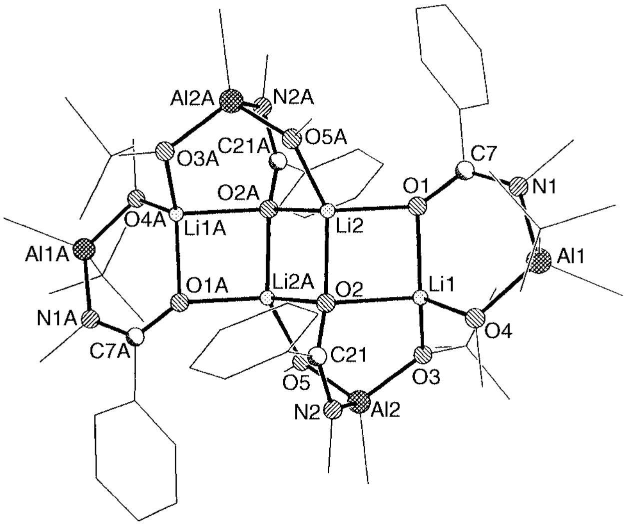


Fig. 1 Molecular structure of **5**; hydrogen atoms and lattice toluene molecule omitted for clarity.

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† Deceased.

3).[6] Here, however, **5** is constructed around a $(LiO)_4$ ladder. Only a very limited number of such homometallic ladders are known,[8] the vast majority of Li–O-containing metallo-organic species (*e.g.* alkoxides, enolates) being pseudo-cubane tetramers,[5] hexamers[5,9] or even higher[10] aggregates in the solid state. It is salient, therefore, that the adoption of an $(LiO)_4$ intercepted-ladder motif by **5** represents the first crystallographic evidence that ladder structures, known for a range of lithiated organic compounds (particularly lithium amides),[5,11] can also pertain for Li–Al heterobimetallic ones. Furthermore, whereas the $(LiO)_4$ core of **5** utilises the original carbonyl *O*-centres, it is clear that the coordinative requirements of the *different* types of Li^+ centre (Li1 and Li2) in the assembled ladder are satisfied by the *variability* of ligand oxygenation.

The final interesting aspects of **5** concern how and why it is formed in the first place. The complex can be obtained repeatedly, albeit so far in moderate yields, from exposure of a pre-formed solution of **4** to either normal (*i.e.* moist) or (P_2O_5) dry air. However, the use of normal air affords samples of **5** which ^{1}H NMR spectroscopy shows to be significantly contaminated with (expected) aluminoxane[12] hydrolysis products. These observations point to oxygen rather than moisture being responsible for the observed multiple oxo-insertion process. In this context, it is known that air-sensitive R_3Al species afford *tris*-oxygenated compounds, $(RO)_3Al$, upon exposure to oxygen.[13] The surprise in the synthesis of **5** is the *controlled* nature and dual s*pecificity* of oxo-insertion. Preliminary ^{1}H NMR spectroscopic evidence suggests that the treatment of **3** alone [having two Al–C(Me) bonds] with pre-dried air fails to afford any detectable reaction and it is only when **3**, Bu^{t}Li and O_2 are combined, *in that order*, that **5** results. Complete *tris*-oxygenation of the Al–C bonds has not occurred in **5**, but rather two of the aluminate anions have each undergone single oxo-insertion and two have each inserted oxygen atoms into two Al–C bonds. In this way, the two types of ligands produced are perfect for provision of additional coordination (terminal and spanning respectively) to the Li^+ centres of the $(LiO)_4$ core of **5**, raising each such centre to a coordination number of four. While the precise mechanism by which **5** is formed is not yet understood, the observations noted above suggest that oxo-insertion is either directly templated [*i.e.* that lithium aluminate **4** is, itself, a $(LiO)_4$ ladder] or else that the conversion of **4** to **5** requires that the processes of ladder formation *and* oxo-insertion occur concurrently.

Attempts to learn the *precise* structural nature of **4**, and to thus better understand the reasons for the dual specificity of oxo-insertion, are ongoing. Further work will also seek to investigate the effects of employing pure oxygen in place of dry air and will attempt to follow the reaction by low-temperature multinuclear NMR spectroscopy. More generally, it is planned to look at related systems of general type R_2AlL and $R'Li$ ($R, R' = $ alkyl, aryl; L = *N*- or *O*-centred ligands) and to deliberately treat these with oxygen. In this way, it is hoped to judge how widespread and how useful the oxo-insertion process, and the concomitant ligand amendments, might be. It is clear already, from this and other work,[3] that deliberate aeration of selected main group organometallic species (usually handled under strictly inert-atmosphere conditions) can produce much interesting new chemistry.

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Notes and references

‡ 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 warmed to room temperature and stirred for 30 min 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 warmed to room temperature whereupon removal of the solvent afforded crude **4** as a white powder. Yield 65%, mp 86–88 °C. Satisfactory C,H,N. ^{1}H NMR spectroscopy (400 MHz, CD_3CN), δ 7.72–6.99 (m, 5H, Ph), 2.87–2.76 (m, 3H, NMe), 0.87–0.66 (m, 9H, Bu^t), −1.21, −1.36, −1.53 (m, 6H, AlMe).

§ As for **4** but upon returning to room temperature the resultant pale yellow solution was treated with dry air (P_2O_5) for 1 min and with hexane (0.5 ml) before being stored at −30 °C for 3 days whereupon colourless microcrystals of **5** were deposited. Yield 15% (based on Bu^{t}Li consumed), mp 128–130 °C. Satisfactory C,H,N. ^{1}H NMR spectroscopy (500 MHz, $[^2H_8]$THF), δ 8.05–7.20 (m, 10H, Ph), 7.19–6.98 (m, 2.5H, C_6H_5Me), 3.51–3.44 (m, 6H, OMe), 3.04–2.66 (m, 6H, NMe), 2.32 (s, 1.5H, C_6H_5Me), 1.20–1.15, 0.86 (m, 18H, Bu^t), −1.02, −1.07 (m, 6H, AlMe).

¶ *Crystal data* for **5**: $C_{31.5}H_{50}Al_2Li_2N_2O_5$; $M = 604$, triclinic, space group $P\bar{1}$, $a = 12.333(3)$, $b = 13.439(3)$, $c = 14.021(4)$ Å, $\alpha = 109.87(1)$, $\beta = 91.58(2)$, $\gamma = 114.21(1)°$, $U = 1955.2(9)$ Å^3, $Z = 2$, $D_c = 1.105$ g cm^{-3}, Cu-Kα ($\lambda = 1.54178$ Å), $\mu = 0.972$ mm^{-1}, $T = 180(2)$ K. 8243 reflections (4837 unique, $\theta < 54.98°$, $R_{int} = 0.0301$), data were collected on a Stoe Siemens four-circle diffractometer. Refinement on F^2 values of all data gave $wR2 = 0.1766$, conventional $R = 0.0640$ on F values of 4242 reflections with $F^2 > 2\sigma(F^2)$, 428 parameters. Residual electron density extrema are 0.69 and −0.24 Å^{-3}. CCDC 182/1509. See http://www.rsc.org/suppdata/cc/a9/a909135a/ for crystallographic files in .cif format.

1 W. Clegg, E. Lamb, S. T. Liddle, R. Snaith and A. E. H. Wheatley, *J. Organomet. Chem.*, 1999, **573**, 305.

2 W. Clegg, R. P. Davies, S. T. Liddle, D. J. Linton, P. R. Raithby, R. Snaith and A. E. H. Wheatley, *Angew. Chem., Int. Ed.*, 1999, **38**, 3367.

3 A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *Angew. Chem., Int. Ed.*, 1998, **37**, 3180; A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *J. Am. Chem. Soc.*, 1998, **120**, 7816; A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts and R. B. Rowlings, *Chem. Commun.*, 1999, 353.

4 For the analogous *N*-phenylbenzamidoalane, see: Y. Kai, N. Yasuoka, N. Kasai and M. Kakudo, *J. Organomet. Chem.*, 1971, **32**, 165.

5 *Lithium Chemistry: A Theoretical and Experimental Overview*, ed. A. M. Sapse and P. von R. Schleyer, John Wiley and Sons, New York, 1995.

6 See, for example: W. Uhl, I. Hahn, M. Kock and M. Layh, *Inorg. Chim. Acta*, 1996, **249**, 33; T. Arai, H. Sasai, K. Aoe, K. Okamura, T. Date and M. Shibasaki, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 104; J. Storre, C. Schnitter, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, R. Fleischer and D. Stalke, *J. Am. Chem. Soc.*, 1997, **119**, 7505.

7 See, for example: T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco and S. H. Strauss, *Organometallics*, 1996, **15**, 3776; A. G. Avent, W.-Y. Chen, C. Eaborn, I. B. Gorrell, P. B. Hitchcock and J. D. Smith, *Organometallics*, 1996, **15**, 4343; H. Nöth, A. Schlegel, J. Knizek and H. Schwenk, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2640.

8 See, for example: C. Lambert, F. Hampel, P. von R. Schleyer, M. G. Davidson and R. Snaith, *J. Organomet. Chem.*, 1995, **487**, 139; M. Montevalli, D. Shah and A. C. Sullivan, *J. Organomet. Chem.*, 1996, **513**, 239; N. A. Khanjin and F. M. Menger, *J. Org. Chem.*, 1997, **62**, 8923.

9 See, for example: T. Maetzke, C. P. Hidber and D. Seebach, *J. Am. Chem. Soc.*, 1990, **112**, 8248.

10 See, for example: T. Maetzke and D. Seebach, *Organometallics*, 1990, **9**, 3032.

11 K. Gregory, P. von R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; W. Clegg, L. Horsburgh, F. M. Mackenzie and R. E. Mulvey, *J. Chem. Soc., Chem. Commun.*, 1995, 2011; R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167; R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339; W. Clegg, S. T. Liddle, R. E. Mulvey and A. Robertson, *Chem. Commun.*, 1999, 511.

12 J. J. Eisch, *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 1, p. 462.

13 J. P. Oliver, R. Kamur and M. Taghiof, *Coordination Chemistry of Aluminium*, ed. G. H. Robinson, Wiley-VCH, New York, 1993, p. 171.

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