Trapping of *n*-butyllithium dimer by a trilithiated derivative of $\{\mathrm{Al[N(H)Bu^t]_3}\}_2$

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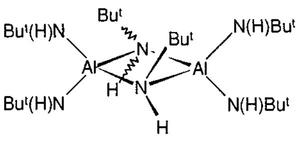
The reaction of $\{\mathrm{Al[N(H)Bu^t]_3}\}_2$, obtained as a 1 : 2 mixture of *cis* and *trans* isomers from the addition of $\mathrm{AlCl_3}$ to three equiv. $\mathrm{LiN(H)Bu^t}$ in diethyl ether, with $\mathrm{LiBu^n}$ generates a complex in which a dimeric *n*-butyllithium fragment is trapped by the trilithiated derivative $\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3}$.

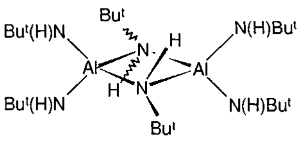
Current interest in amido derivatives of the Group 13 elements is stimulated primarily by possible applications in materials science.[1–3] Although there has been a recent spate of publications describing homoleptic polyimido anions of p-block elements, *e.g.* $\mathrm{E(NBu^t)_3}^{2-}$ (E = Te,[4] Se,[5] S[6]), $\mathrm{Sb(NCH_2CH_2Ph)_3}^{3-}$,[7] and $\mathrm{E(NR)_4}^{x-}$ (E = S, R = $\mathrm{Bu^t}$, $x = 2$;[8] E = P, R = 1-naphthyl, $x = 3$[9]), no examples of trisimido trianions, $\mathrm{E(NR)_3}^{3-}$ (E = Group 13 element, R = alkyl or aryl group) have been reported.

Lithiation has been used to prepare complexes of the type $\mathrm{[R_2AlNLi(thf)_{\mathit{n}}R']_2}$ from $\mathrm{[R_2AlNHR']_2}$ (R, R′ = Me, $\mathrm{Bu^t}$ or $\mathrm{Bu^i}$, Ph; $n = 1$), although adduct formation is observed for very bulky groups, *e.g.* $\mathrm{Me_2Bu^tAlNH[Li(thf)_3](C_6H_3Pr^i_2\text{-}2,6)}$.[10] Nevertheless the trisamido derivatives $\mathrm{[Al(NHR)_3]}_n$ (**1a**, R = $\mathrm{Pr^i}$; **1b**, R = $\mathrm{Bu^t}$) are potential precursors of $\mathrm{Al(NR)_3}^{3-}$. The isopropyl derivative **1a** is obtained by the reaction of $\mathrm{AlCl_3}$ with $\mathrm{LiNHPr^i}$ in a 1 : 3 molar ratio in diethyl ether[11] whereas the analogous reaction with $\mathrm{LiNHBu^t}$ in *toluene* gives $\{\mathrm{LiAl[N(H)Bu^t]_4}\}_2$ rather than **1b**.[1] These observations, and the very recent report of the monomeric complex $\mathrm{Li(thf)Al[N(H)R]_4}$ (R = $\mathrm{2,6\text{-}Pr^i_2C_6H_3}$),[12] prompt us to describe the formation and structure of the unusual cluster $\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3\cdot(LiBu^n)_2}$ (**2**) in attempts to generate $\mathrm{Al(NBu^t)_3}^{3-}$. Complex **2** consists of an *unsolvated n*-butyllithium dimer trapped by a trilithiated derivative of **1b**.

Treatment of $\mathrm{LiN(H)Bu^t}$ with $\mathrm{AlCl_3}$ (3 : 1 molar ratio) in *diethyl ether* gives the dimer **1b** as a *ca.* 1 : 2 mixture of *cis*, **1b′** (C_{2v}), and *trans*, **1b″** (C_{2h}), isomers in 83% yield. The ^{1}H NMR spectrum of **1b** exhibits three equally intense resonances for **1b′** and two resonances in the ratio 1 : 2 for **1b″**.† The gallium analogue $\mathrm{[Ga(NHBu^t)_3]_2}$ has been structurally characterized as the *cis* isomer.[2] The mixture of isomers **1b′** and **1b″** could not be separated by recrystallization.



1b′



1b″

The reaction of **1b** with six equivalents of $\mathrm{LiBu^n}$ in hexane produces the novel cluster $\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3\cdot(LiBu^n)_2}$ (**2**). Complex **2** is formed as the major product for stoichiometries ranging from 4 : 1 to 8 : 1, even at reflux, but the optimum yield is obtained when 5 equiv. of $\mathrm{LiBu^n}$ are used [eqn. (1)].†

$$5\ \mathrm{LiBu^n} + \underset{\mathbf{1b}}{\{\mathrm{Al[N(H)Bu^t]_3}\}_2} \longrightarrow \underset{\mathbf{2}}{\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3{\bullet}(LiBu^n)_2}} + 3\ \mathrm{HBu^n} \quad (1)$$

The ^{1}H NMR spectrum of **2** shows five unique $\mathrm{Bu^t}$ environments (1 : 2 : 1 : 1 : 1) at 23 °C which resolve into six equally intense resonances at −20 °C, as well as resonances corresponding to $\mathrm{Bu^n}$ groups ($\mathrm{Bu^n}$: $\mathrm{Bu^t}$ ~ 1 : 3). These puzzling observations were clarified by a single crystal X-ray structure determination, which revealed an unsolvated complex in which a trilithiated derivative of **1b** is coordinated to the dimer $\mathrm{(LiBu^n)_2}$ (Fig. 1).‡ *n*-Butyllithium is hexameric in the solid state if crystallized from a non-coordinating solvent,[13] but the dimer is stabilized by coordination of $\mathrm{Li^+}$ ions to TMEDA.[14] A solvated $\mathrm{(LiBu^n)_2}$ moiety has been identified recently in the complex $\mathrm{(Ph_2NLi)[Ph(C_6H_4Li)NLi]_2(LiBu^n)_2(Et_2O)_4}$ (**3**),[15] but **2** is unique in incorporating *unsolvated* $\mathrm{(LiBu^n)_2}$ with three-coordinate $\mathrm{Li^+}$ ions.

The average Li–C bond length in the puckered $\mathrm{Li_2C_2}$ ring is 2.216(12) Å, *cf.* 2.268 Å for the corresponding distances for **3**.[15] Although the three N–H hydrogens in the trilithiated fragment $\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3}$ were not located in the X-ray structural determination, it seems reasonable to associate them with the *three*-coordinate nitrogen atoms N(3), N(4) and N(6). Thus the static structure of **2** contains six inequivalent $\mathrm{NBu^t}$ groups consistent with the ^{1}H NMR spectrum at −20 °C (*vide supra*). However, Li(5) is disordered, with equal occupancies, over two sites in which it is in close contact with either N(1) or N(2). A fluxional process involving Li(5) will give rise to equivalence of the $\mathrm{Bu^t}$ groups attached to N(1) and N(2) as observed in the ^{1}H NMR spectrum at 23 °C. All five $\mathrm{Li^+}$ ions in **2** are three-

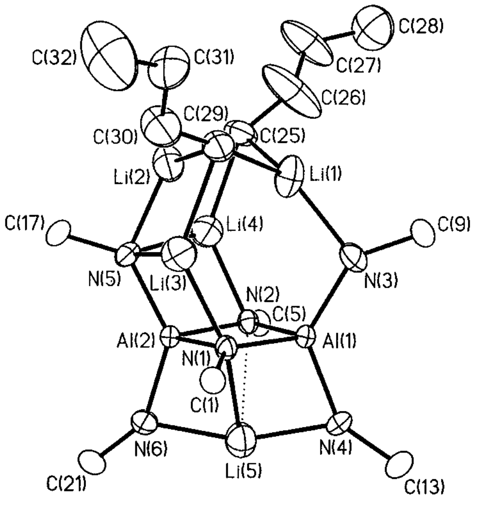


Fig. 1 Molecular structure of $\mathrm{Li_3Al_2[N(H)Bu^t]_3[NBu^t]_3\cdot(LiBu^n)_2}$ **2** (30% thermal ellipsoids). For clarity only α-carbon atoms of $\mathrm{Bu^t}$ groups are shown and a second, disordered position of Li(5) is omitted. The hydrogen atoms attached to N(3), N(4) and N(6) were not located. Selected bond distances (Å) and angles (°): Li(1)–C(25) 2.262(12), Li(1)–C(29) 2.187(11), Li(1)–N(3) 2.043(12), Li(2)–C(25) 2.181(12), Li(2)–C(29) 2.236(12), Li(2)–N(5) 2.031(12), Li(3)–C(29) 2.238(11), Li(3)–N(1) 2.041(10), Li(3)–N(5) 2.080(11), Li(4)–C(25) 2.157(12), Li(4)–N(2) 2.037(10), Li(4)–N(5) 2.052(11), Li(5)–N(2) 2.303(19), Li(5)–N(4) 2.064(10), Li(5)–N(6) 2.069(11), Al(1)–N(3)–Li(1) 110.3(4), Al(2)–N(5)–Li(2) 127.4(4).

coordinate and the Li–N distances are in the normal range of 2.031(12)–2.075(10) Å with the exception of those involving Li(5) [Li(5)–N(2) = 2.303(19), Li(5)′–N(1) = 2.296(16) Å]. The geometry at aluminium is distorted tetrahedral with NAlN bond angles in the range 87.96(13)–127.90(19)° and 87.14(13)–134.80(17)° for Al(1) and Al(2), respectively. The smallest bond angle ($<90°$) is found within the Al_2N_2 ring. The significant difference between the values of N(5)–Al(2)–N(6) and N(3)–Al(1)–N(4) [134.80(17)° *vs.* 127.90(19)°] presumably reflects the coordination of N(5) to Li(3) and Li(4). The Al–N distances [average value = 1.872(4) Å, range 1.833(3)–1.895(3) Å] are comparable to the values found for related lithiated AlN complexes.[10a]

Although $LiBu^n$ has been employed successfully for the dilithiation of the dimer $[Bu^tN(H)P(\mu\text{-}NBu^t)]_2$[16] and the trilithiation of $MeSi(NHBu^t)_3$,[17] the use of alternative metallating reagents will be necessary for the generation of $Al(NR)_3{}^{3-}$, an isoelectronic analogue of $AlO_3{}^{3-}$.

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Notes and references

† *Synthesis of* **1b**: A solution of $AlCl_3$ (1.22 g, 9.15 mmol) in diethyl ether (10 mL) was added dropwise to a stirred slurry of $LiN(H)Bu^t$ (2.17 g, 27.4 mmol) in diethyl ether (30 mL) cooled to −78 °C. After 0.5 h at −78 °C the reaction mixture was stirred for a further 1.5 h at 23 °C and subsequently filtered to give a colourless solution. Removal of solvent *in vacuo* yielded white microcrystalline **1b** (1.84 g, 3.78 mmol, 83%); mp 170 °C (decomp.). Anal. calc. for $AlC_{12}H_{30}N_3$: C, 59.22; H, 12.42; N, 17.27. Found: C, 59.24; H, 12.48; N, 17.16%. ^1H NMR (C_6D_6, 23 °C, 200 MHz): δ 1.48 (18 H, Bu^t), 1.46 (36 H, Bu^t), 1.37 (18 H, Bu^t), 1.35 (72 H, Bu^t), 1.28 (18 H, Bu^t). ^{27}Al NMR [C_7D_8, 23 °C, 52.12 MHz, $Al(NO_3)_3$ in D_2O]: δ 98.5 ($\Delta\nu_{1/2}$ = 2.08 kHz). IR (KBr, Nujol mulls): 3358 (br) and 3250 (br) cm^{-1} [ν(N–H)]. X-Ray quality crystals (blocks) were obtained in 4 days (23 °C) *via* recrystallization from hexane.

Synthesis of **2**: A 2.5 M solution of $LiBu^n$ in hexanes (2.06 mL, 5.15 mmol) was added dropwise to a stirred solution of **1b** (0.50 g, 1.03 mmol) in hexane (30 mL) cooled to −78 °C. After 0.5 h at −78 °C the reaction mixture was stirred for a further 4 h at 23 °C. Concentration (*ca.* 2 mL) and subsequent cooling (0 °C) of the resulting solution yielded colourless cubes of **2** (0.61 g, 0.97 mmol, 94%); mp 175 °C (decomp.). Anal. calc. for $Al_2C_{32}H_{75}Li_5N_6$: C, 60.75; H, 11.95; N, 13.28. Found: C, 60.14; H, 12.06; N, 13.07%. ^1H NMR (C_7D_8, 23 °C, 400 MHz): δ 1.73 [m, 8 H, $CH_2(CH_2)_2CH_3$], 1.50 (9 H, Bu^t), 1.42 (18 H, Bu^t), 1.38 (9 H, Bu^t), 1.34 (9 H, Bu^t), 1.32 (9 H, Bu^t), 1.14 [t, 6 H, $CH_2(CH_2)_2CH_3$], −0.52 [m, 4 H, $CH_2(CH_2)_2CH_3$]. ^1H NMR (C_7D_8, −20 °C, 400 MHz): δ 1.73 [m, 8 H, $CH_2(CH_2)_2CH_3$], 1.53 (9 H, Bu^t), 1.43 (9 H, Bu^t), 1.41 (9 H, Bu^t), 1.38 (9 H, Bu^t), 1.35 (9 H, Bu^t), 1.31 (9 H, Bu^t), 1.14 [t, 6 H, $CH_2(CH_2)_2CH_3$], −0.52 [m, 4 H, $CH_2(CH_2)_2CH_3$]. ^7Li NMR (C_7D_8, 23 °C, 155.51 MHz, 1 M LiCl in D_2O): δ 0.29 (br), 0.18, −1.16 (approximately 3 : 1 : 1). ^{27}Al NMR [C_7D_8, 23 °C, 52.12 MHz, $Al(NO_3)_3$ in D_2O]: δ 98.0 ($\Delta\nu_{1/2}$ = 762 Hz). IR (KBr, Nujol mulls): 3227 (br) cm^{-1} [ν(N–H)].

‡ *Crystallographic data* for **2**: Colourless cubic crystals of **2** (0.3 × 0.3 × 0.4 mm) were obtained from hexane and mounted on a thin glass fibre. Data were collected on a SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å) at 20 °C in the range $1.98° < 2\theta < 23.50°$ (10471 reflections collected, 6241 independent reflections, R_{int} = 0.0457). The structure was solved by direct methods and refinement, based on F^2, was by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms for the Bu^t groups were treated as idealized contributions. Attempts to locate the NH hydrogen atoms were unsuccessful and were ignored. Atomic scattering factors were obtained from the SHELXTL (5.1) program library. $C_{32}H_{75}Al_2Li_5N_6$, M = 632.66, monoclinic, $P2_1/c$, a = 17.872(5), b = 11.472(3), c = 20.606(5) Å, β = 91.896(5)°, V = 4222(2) $Å^3$, D_c = 1.045 g cm^{-3}, Z = 4, μ = 0.099 mm^{-1}. Refinement converged at $R1$ = 0.0936, $wR2$ = 0.2962. CCDC 182/1063. See http://www.rsc.org/suppdata/cc/1998/2543, for crystallographic files in .cif format.

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