Structural characterization of the unusual adduct complex Me_2Bu^tAl–NH[Li(thf)$_3$]($C_6H_3Pr^i_2$-2,6)

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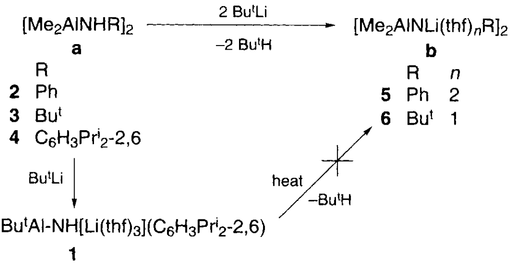
Addition of Bu^tLi to [$Me_2AlNH(C_6H_3Pr^i_2$-2,6)]$_2$ results in the formation of the surprisingly stable adduct, Me_2Bu^tAl–NH[Li(thf)$_3$]($C_6H_3Pr^i_2$-2,6).

Group 13 amide and adduct species {[$R_2MNR'_2$]$_n$ and R_3M—NR'_3, respectively} are ubiquitous in main group chemistry. Beyond their fundamental interest, these types of compounds have been examined for applications in materials science[1] and catalysis.[2] The lithiated analogues of the amides, [R_2ME-$LiNR'$]$_n$, are relatively rare, being known for M, E = B, N[3] and recently reported for M, E = Al, N.[4] However, to date, the only adduct species incorporating a lithium amide are those of formula Me_3M–$NLi(SiMe_3)_2$ (M = Al, Ga)[5] while those incorporating a lithium primary amide are not known. In this communication we report the synthesis and first structural characterization of the trialkylaluminium lithium amide adduct, Me_2Bu^tAl–NH[Li(thf)$_3$]($C_6H_3Pr^i_2$-2,6).

This group has currently been examining the reaction of neutral alkylaluminium primary amides with alkyllithium reagents to form the corresponding lithium amides (Scheme 1, **b**).[2] However, in the case where R = Me, R′ = $C_6H_3Pr^i_2$-2,6 the reaction does not result in deprotonation of the amide but rather in the alkylation of aluminium and lithiation of nitrogen. This results in the formation of the unique adduct complex, **1** which can be isolated in 68% yield, and can be readily recrystallized from toluene.† A molecular structure with atom numbering scheme for **1** is shown in Fig. 1.† Interestingly, the compound crystallized in the non-centrosymmetric space group *Cc* with both the *R* and *S* enantiomers present in the unit cell. The *R* configuration is shown. Compared to the starting material, **4**, several significant changes occur on going to the lithiated species, **1**. Most obviously, lithiation produces a monomeric complex, which possesses idealized tetrahedral angles around Al. In **4**, these angles are distorted as a result of the four-membered Al_2N_2 ring. The greatest deviation from an ideal angular value is demonstrated in the Al–N–C angle [125.9(6)°]. The groups around Al and N adopt a sterically less encumbered staggered arrangement. This leads to a somewhat eclipsed conformation for the N and Li groups. The Al–N bond distance in **1** [1.976(9) Å] is marginally shorter than that observed for **4** (av. 1.986 Å) and reflects a reduction in steric repulsion on going from dimer to monomer. By comparison, the reverse trend is seen in the Al–N bond distances for **5** and **6** which are relatively short [1.873(5) and 1.888(5) Å, respectively].[7] The generally short distances found in **1**, **5** and **6** may be attributed to an increase in the electrostatic attraction between the Al and N atoms resulting from the lithiation. The greater negative charge on **1** compared to **4** is evident from a comparison of the Al–Me ^{1}H chemical shifts (δ −0.60 for **1**, −0.31 for **4**). The N–Li distance in **1** [2.171(21) Å] is similar to that observed for other lithiated amides with the lithium in a tetrahedral coordination geometry.[8]



Scheme 1 General synthesis of **1** and related compounds

Although compound **1** would appear to be an isolated intermediate in the formation of the corresponding aluminium amides (Scheme 1; **a**, **b**), it is surprisingly stable. Heating of **1** to effect this transformation in thf for 24 h results, after work-up, in the isolation of **1** unchanged. This would imply that the formation of such an adduct species is not an intermediate in the synthesis of compounds such as **5** and **6**. Moreover, attempts to isolate adduct species in the synthesis of **5** and **6** (and others) have been unsuccessful. In all cases, this reaction leads directly to the formation of complexes having the general formula **b** shown in Scheme 1. Although **1** is unique, it does bear some similarity to the LiH adduct formed from the reaction of Bu^tLi with R_3Al[9] and the lithium oxide species, $R_3AlOLiAlR_2$ (R = Me, Et, Bu^i).[10]

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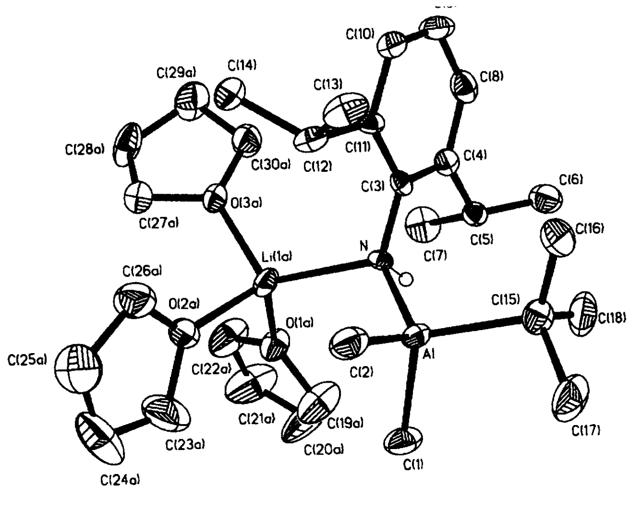

Fig. 1 Molecular structure and atom numbering scheme for **1**. Selected bond lengths (Å) and angles (°): Al–N 1.976(9), Al–C(1) 1.997(13), Al–C(2) 1.988(11), Al–C(15) 2.037(13), N–C(3) 1.396(14), N–H(1a) 1.109, N–Li(1a) 2.171(21), O(1a)–Li(1a) 2.059(20), O(2a)–Li(1a) 1.937(22), O(3a)–Li(1a) 1.979(27); N–Al–C(1) 103.5(5), N–Al–C(2) 117.2(5), C(1)–Al–C(2) 106.2(6), N–Al–C(15) 109.6(5), C(1)–Al–C(15) 109.5(5), C(2)–Al–C(15) 110.4(5), Al–N–C(3) 125.9(6), Al–N–H(1A) 114.9(11), Al–N–Li(1a) 111.9(7), C(3)–N–Li(1a) 113.4(9), C(3)–N–H(1a) 96.2(11).

Footnotes

† *Synthesis of* $Me_2Bu^tAl–NH[Li(thf)_3](C_6H_3Pr^i_2$-2,6) **1**. Amide **4** (1.184 g, 2.54 mmol) was dissolved in 25 ml of freshly distilled, dry thf and stirred at 25 °C. Bu^tLi (2.73 ml, 1.86 mol dm^{-3} in pentane, 5.08 mmol) was added, resulting in a momentary orange colour, which became light yellow upon complete addition. The slightly exothermic reaction was stirred for 1 h at 25 °C, then the volatiles were removed under reduced pressure to give a thick yellow oil. The oil was washed with 50 ml hexane and a yellow solid precipitated. The solvent was removed by filtration to give 1.883 g of a light yellow solid. Recrystallization from toluene at −10 °C yielded 1.767 g of colourless crystals suitable for X-ray analysis (68%): mp 28–34 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.60 (s, 6 H, $AlCH_3$), 1.14 (m, 12 H, thf), 1.17 (d, J 7 Hz, 12 H, CHC*H*$_3$), 1.24 (s, 9 H, CCH_3), 2.90 (br s, 1 H, NH), 3.08 (m, 12 H, thf), 3.47 (m, 2 H, C*H*CH$_3$), 6.72 (t, J 6 Hz, 1 H, Ph-H), 6.95 (d, J 7 Hz, 2 H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −9.02 ($AlCH_3$), 24.2 (*C*CH$_3$), 24.5 (thf), 25.3 (C*C*H$_3$), 27.7 (*C*HCH$_3$), 32.0 (CH*C*H$_3$), 118.3, 123.6, 136.6, 148.5 (Ph); IR (KBr) 3049, 2928, 1462, 1429, 1238, 1167, 1044, 761, 686, 630, 565 cm^{-1}; Anal. Calc for $C_{30}H_{57}AlLiNO_3$: C, 70.18: H, 11.11. Found: C, 69.77; H, 11.38%.

‡ *Crystal data* for **1**: monoclinic, space group *Cc*, a = 18.215(3), b = 10.498(1), c = 18.217(4) Å, β = 106.120(1)°, U = 3347(1) Å^3, Z = 4, 1423 observed reflections [$F > 4.0\sigma(F)$]; R = 0.065, R_w = 0.0611. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/66.

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