Lewis base stabilized lithium TMP-aluminates: an unexpected fragmentation and capture reaction involving cyclic ether 1,4-dioxane†

Joaquín García-Álvarez,* Eva Hevia, Alan R. Kennedy, Jan Klett and Robert E. Mulvey*

Received (in Cambridge, UK) 18th January 2007, Accepted 8th February 2007
First published as an Advance Article on the web 9th March 2007
DOI: 10.1039/b700785j

Three Lewis base variations of the synthetically useful aluminate [L·Li(TMP)(^{i}Bu)Al(^{i}Bu)$_2$], where L is TMPH, Et$_3$N or PhC(=O)N^{i}Pr$_2$, are reported, together with the reaction of the benzamide complex with 1,4-dioxane, which surprisingly leads to fragmentation of the cyclic ether and capture of its alkoxy vinyl ether residue within a novel dilithium dialuminium hexaalkyl aggregate.

Lithium TMP-aluminate "^{i}Bu$_3$Al(TMP)Li" (where TMP is the amide 2,2,6,6-tetramethylpiperidide) was introduced in 2004 by Uchiyama *et al.* as an excellent regio- and chemoselective base for directed alumination of a wide range of functionalized aromatics.[1] Structural information on the reagent itself or on the arylaluminated intermediates it generates (before any electrophilic interception) would help bring about a deeper understanding of this new metallation methodology, thus allowing its future development *a posteriori*. Hitherto, such knowledge has been extremely limited, with our own efforts to synthesize and structurally characterize a TMEDA-stabilized "^{i}Bu$_3$Al(TMP)Li" yielding only an uninformative oily product. That failure notwithstanding, our study did establish, nonetheless, that *in situ* this TMEDA–"^{i}Bu$_3$Al(TMP)Li" mixture reacts with *N*,*N*-diisopropylbenzamide to effect its *ortho*-alumination, as well as methyl-deprotonation of TMEDA in the same product [{PhC(=O)N(^{i}Pr)$_2$}·Li{2-[1-C(=O)N(^{i}Pr)$_2$]C$_6$H$_4$}{Me$_2$NCH$_2$CH$_2$N(Me)CH$_2$}Al(^{i}Bu)$_2$].[2] Here in this paper, we can now report the successful synthesis and crystallographic characterization of three distinct Lewis base-stabilized complexes of ^{i}Bu$_3$Al(TMP)Li. Furthermore, where the Lewis base is *N*,*N*-diisopropylbenzamide, an extraordinary reaction is observed with 1,4-dioxane. In contrast to the situation in the TMEDA system, no *ortho*-alumination of the benzamide occurs, instead the cyclic ether fragments and its alkoxy vinyl ether residue is captured within a novel dilithium dialuminium hexaalkyl aggregate. Evidence is presented that suggests the strong Lewis basicity of the benzamide coordinated to Li is a key factor in this unexpected fragmentation and capture reaction.

Two of the new Lewis base complexes, [L·Li(μ-TMP)(μ-^{i}Bu)Al(^{i}Bu)$_2$] [(**1**), L = TMPH; (**2**), L = Et$_3$N], were synthesized by the same straightforward addition approach.‡ Thus, a hexane solution of freshly prepared LiTMP was first subjected to a molar equivalent of the Lewis base (TMPH or Et$_3$N) before a molar equivalent of the alane ^{i}Bu$_3$Al was introduced. With the third Lewis base complex [{PhC(=O)N^{i}Pr$_2$}·Li(μ-TMP)(μ-^{i}Bu)Al(^{i}Bu)$_2$](**3**), it was found that its crystallization was aided by forming **2** initially, then carrying out a benzamide for triethylamine exchange reaction.‡ The synthesis of **3** may appear straightforward but it must be borne in mind that LiTMP reacts with (deprotonates!) benzamides even at subambient temperatures[3] so the lack of deprotonation here can be ascribed to a retarding (synergic) effect of the mixed-metal system. The isolated, crystalline solids **1–3** were obtained in good yields, ranging from 55–68%.

X-Ray crystallographic studies reveal that **1–3** adopt a common LiNAlC four-element ring motif with TMP and ^{i}Bu bridges. Two more ^{i}Bu ligands bind terminally to Al, while the relevant Lewis base binds terminally to Li to complete the structures. Due to this similarity, only the molecular structure of **3** (Fig. 1) will be elaborated upon here. Al displays its familiar distorted tetrahedral 'aluminate' coordination [range of bond angles: 102.11(10)–120.65(10)°; mean: 109.32°], with the Al–C terminal bonds (mean: 2.034 Å) marginally shorter than the bridging Al–C bond [2.073(3) Å]. The Li–C bridge is distinctly longer [2.403(5) Å] but there is much less distinction between the Li–N [2.018(5) Å] and Al–N [1.974(2) Å] TMP bridge bonds. Bond angles within the central LiNAlC ring are 90.36(16), 87.74(15), 102.11(10) and 75.96(13)° at the Li, N, Al and C atoms, respectively. Completing a trigonal planar coordination, Li forms a shorter bond [1.872(4) Å] with the benzamide O atom than in the aforementioned TMEDA system [1.916(3) Å],[2] due to its lower coordination number (*i.e.* 3 *versus* 4). Crystallographically characterized complexes with lithium-coordinated, *neutral* tertiary aromatic amide ligands are rare (reflecting mainly the strong propensity of such amides to undergo directed *ortho*-lithiation), with the only precedent seemingly the TMP-zincate [{PhC(=O)N(^{i}Pr)$_2$}·Li(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu)][4] [Li–O bond length: 1.851(3) Å].

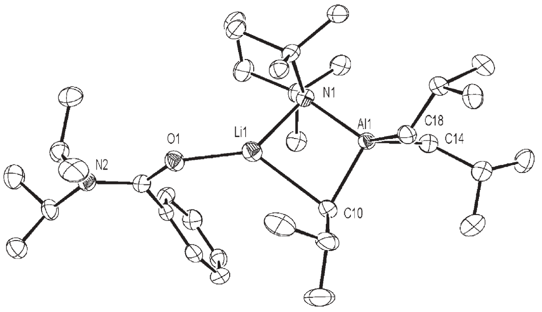


Fig. 1 Molecular structure of **3** with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL. E-mail: r.e.mulvey@strath.ac.uk; Fax: (+44) 141 552 0876

† Electronic supplementary information (ESI) available: Molecular structures of **1**, **2** and **5**; synthesis, NMR spectroscopic characterization and crystal data for **5** (CCDC 634097). See DOI: 10.1039/b700785j

We expected such *ortho*-deprotonation of the benzamide when reacting **3** with a stoichiometric amount of the O Lewis base 1,4-dioxane. Uchiyama *et al.* reported 94% *ortho*-metallation of the benzamide (determined indirectly *via* I_2 interception) using $^i\mathrm{Bu_3Al(TMP)Li}$ in a solution of the related cyclic ether THF.[5] Remarkably, however, the crystalline product isolated from our reaction shows no *ortho*-metallation, but instead contains four metal atoms, six alkyl ligands, two neutral benzamide ligands, one dioxane ligand, and, most significantly and surprisingly, two alkoxy vinyl ether ligands. Despite this witches brew composition of $[\{[\mathrm{PhC(=O)N(^{\mathit{i}}Pr)_2}]\cdot\mathrm{Li[O(CH_2)_2OC(H)=CH_2]Al(^{\mathit{i}}Bu)_3}\}_2\cdot(1,4\text{-dioxane})]$ **4**, its synthesis proved entirely reproducible, with crystalline yields of typically 38%. ^{1}H, ^{13}C, and ^{7}Li NMR spectra recorded in d_6-benzene solutions were obtained for **4**.‡ All of the expected ^{1}H NMR resonances could be assigned easily; most informatively the $\mathrm{OC}H_2$, $\mathrm{OC}H'_2$, $\mathrm{OC}H\mathrm{=CH}_c\mathrm{H}_t$, $\mathrm{OCH=C}H_c\mathrm{H}_t$, and $\mathrm{OCH=CH}_cH_t$ resonances of the alkoxy vinyl ether ligand were located at 3.25, 3.79, 5.86, 3.82, and 3.95 ppm respectively.

Further characterization of **4** and elucidation of its molecular structure (Fig. 2) was provided by an X-ray crystallographic study.§ It is a pseudo-dimer with an inversion centre at the centre of a chair-shaped intact dioxane molecule. The dioxane molecule bridges the two Li atoms through terminal Li–O bonds [length: 1.937(4) Å]. Coordinated by a distorted tetrahedron [range of bond angles: 84.78(14)–131.17(19)°; mean: 107.84°] of four chemically distinct O atoms, the Li atom forms the shortest bond to the benzamide [1.867(4) Å], the longest to the weaker donating ether [2.070(4) Å], and a bond of intermediate length to the alkoxide anion [1.898(4) Å]. This alkoxy anion O(2) bridges to the Al atom [bond length: 1.8145(15) Å], the distorted tetrahedral coordination of which [range of bond angles: 99.70(8)–118.90(12)°; mean: 109.52°] is completed by three ^{i}Bu ligands (mean Al–C bond length: 2.003 Å). With a length [1.310(3) Å] reflecting its double bond character, the vinyl C16–C17 bond does not coordinate to any metal atom.

Despite ether cleavage being a common unwanted side reaction in organometallic chemistry[6] and 1,4-dioxane being a common solvent, to the best of our knowledge **4** represents the first fully characterized crystalline product in which an alkoxy vinyl ether residue has been captured from the fragmentation of a 1,4-dioxane molecule. Previously this residue was identified in a single crystal X-ray diffraction study of the magnesium complex $[\mathrm{Mg_6\{2,6\text{-}^{\mathit{i}}Pr_2C_6H_3N(H)\}_4(OCH_2CH_2O)_2\{OCH_2CH_2OC(H)=CH_2\}_4}]$,[7] but no other characterization was reported as its synthesis from $\mathrm{Bu_2Mg}$ and 2,6-diisopropylaniline in 1,4-dioxane solution, in contrast to that of **4**, could not be reproduced. The formation of **4** from **3** suggests that, as is the case with related heteroleptic TMP-aluminates, **3** acts here as an amido, as opposed to an alkyl base. In that regard, it is significant that the homoleptic lithium alkyl gallanate $[\mathrm{Li\{Ga(CH_2SiMe_3)_4\}\cdot 1.5(dioxane)}]_2$[8] does not cleave dioxane. While the TMP basicity of **3** is to be expected, its execution on dioxane in preference to the benzamide is surprising. Such a reversal of the normal reactivity pattern—benzamide is so strong a C-acid that it readily undergoes *ortho*-lithiation even at −78 °C—points to a special contacted ion-pair reaction. Scheme 1 shows a possible pathway. In the first step, **A** could be an intermediate (the aforementioned gallanate has such a dioxane-ligated, four-coordinate Li) or the additional steric strain introduced by dioxane could facilitate its rapid intramolecular deprotonation by the TMP bridge. Alternatively deprotonation could occur intermolecularly on addition of a second dioxane molecule. Either way, the pathway arrives at intermediate **B**. Transformation of **B** to **C** involves an opening of the coordinated deprotonated ether molecule and rearrangement to the vinyl form. In the final step, the alkoxy nucleophile attacks the electrophilic Al and assumes a bridging position between the two metal atoms. This co-operation between metals in this contacted ion-pair system (a synergic effect) thus appears to override the anticipated acidity effect.

Noting that the benzamide appears to be only a spectator in this proposed pathway, starting and finishing as an O Lewis base towards Li, we decided to repeat the same reaction in the absence of the benzamide. Intriguingly, no dioxane fragmentation was detected, instead the isolable product was crystalline $[\{(\mathrm{dioxane})_4\mathrm{Li}\}^+\{\mathrm{Al(^{\mathit{i}}Bu)_4}\}^-]$ **5**, in a yield of 30% (maximum possible: 50%, see ESI†). Presumably **5** forms *via* a disproportionation reaction of "$[(\mathrm{dioxane})_n\cdot\mathrm{Li(TMP)(^{\mathit{i}}Bu)Al(^{\mathit{i}}Bu)_2}]$", with the other product likely to be "$[(\mathrm{dioxane})_n\cdot\mathrm{Li(TMP)_2Al(^{\mathit{i}}Bu)_2}]$". Characterized by ^{1}H, ^{13}C, and ^{7}Li NMR spectroscopic studies in d_6-benzene solutions (see ESI†), **5** was also subjected to an X-ray crystallographic study† and, although the quality of the data obtained was low, they established unequivocally the solvent-separated ion-pair nature of the structure. Thus, it appears that the strong coordinating ability of the benzamide is an essential element in the unexpected fragmentation of dioxane, while the multiple Lewis acidic sites

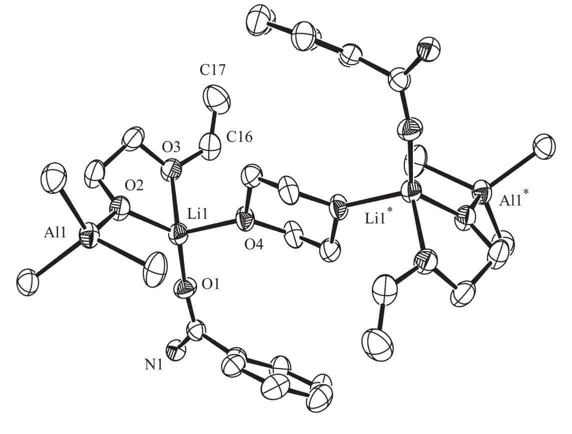
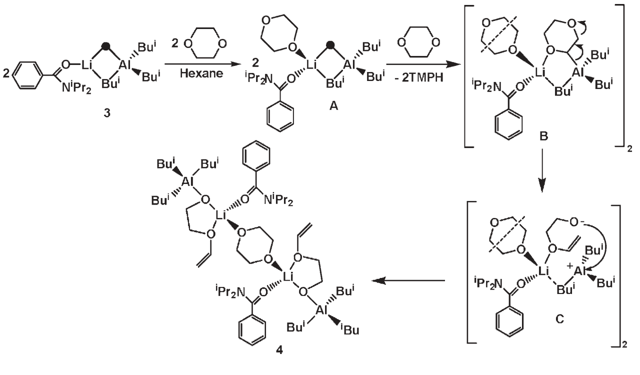


Fig. 2 Molecular structure of **4** with 50% probability displacement ellipsoids. H atoms and ^{i}Pr groups have been omitted for clarity. Where * denotes the equivalent position $-x$, $2-y$, $1-z$.



Scheme 1 Proposed stepwise reaction pathway for the formation of **4**.

offered by the mixed-metal composition of **3** may be a key factor in the subsequent capture of the dioxane fragment. Having established that the benzamide is not merely a spectator but is in fact a crucial reaction directing ligand, future work will investigate whether exploiting the benzamide as a novel Lewis base in **3** and related mixed-metal complexes, with a range of organic substrates, will open the door to other special types of reaction. The general conclusion must be that mixed-metal "synergic" reagents are inherently complicated and thus require careful study as changing variables such as temperature, solvent, stoichiometry and supporting ligands can have a profound effect on their reactivity, but most importantly the synergy can produce reactions inaccessible *via* conventional non-synergic homometallic reagents.

We thank the EPSRC (grant award numbers GR/T27228/01 and EP/D076889/1) for generously sponsoring this research.

Notes and references

‡ All reactions were carried out under a protective argon atmosphere. *Synthesis of* $[L\cdot Li(\mu\text{-}TMP)(\mu\text{-}{}^iBu)Al({}^iBu_2)]$ *[(1) L = TMPH; (2) L = NEt₃]*: in a Schlenk tube, 2 mmol of the ligand L [(**1**) L = TMPH (0.34 mL); (**2**) L = NEt_3 (0.28 mL)] was added to a hexane solution of LiTMP (prepared freshly from a mixture of BuLi (2 mmol, 1.25 mL of a 1.6 M solution in hexane) and TMPH (0.34 mL)) to give a yellow solution. After the solution had been stirred for 30 min, $^iBu_3Al$ (2 mmol, 2 mL of a 1 M solution in hexane) was introduced and the resultant transparent solution was allowed to stir for 1 h. Freezer cooling of this solution at −27 °C afforded colourless crystals of **1** (0.53 g, 55%) and **2** (0.61 g, 68%). (**1**): ^{1}H NMR (400.13 MHz, d_6-benzene, 300 K): 2.28 (septet, 3H, $^3J_{HH}$ = 6.5 Hz, C*H*-^{i}Bu), 1.37 (s, 12H, CH_3-TMP), 1.33 (d, 18H, $^3J_{HH}$ = 6.5 Hz, CH_3-^{i}Bu), 1.22 (m, 2H, γ-TMPH), 1.10 (m, 4H, β-TMPH), 1.03 (s, 12H, CH_3-TMPH), 0.43 (s broad, 1H, NH-TMPH), 0.14 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH_2-^{i}Bu); ^{13}C{H} NMR (100.63 MHz, d_6-benzene, 300 K): 53.32 (α-TMP), 51.74 (α-TMPH), 45.79 (β-TMP), 38.28 (β-TMPH), 37.53 (broad, *C*H_3-TMP), 32.16 (broad, *C*H_3-TMPH), 30.17 (*C*H_3-^{i}Bu), 28.35 (*C*H-^{i}Bu), 19.02 (γ-TMP), 18.45 (γ-TMPH), signal for Al–*C*H_2 was not observed; ^{7}Li NMR (155.50 MHz, d_6-benzene, 300 K, reference LiCl in D_2O at 0.00 ppm): −0.71 ppm. (**2**): ^{1}H NMR (400.13 MHz, d_6-benzene, 300 K): 2.36 (septet, 3H, $^3J_{HH}$ = 6.5 Hz, C*H*-^{i}Bu), 2.26 (q, 6H, $^3J_{HH}$ = 7.1 Hz, CH_2-NEt_3), 1.50 (s, 12H, CH_3-TMP), 1.36 (d, 18H, $^3J_{HH}$ = 6.5 Hz, CH_3-^{i}Bu), 1.26 (m, 4H, β-TMP), 1.20 (m, 2H, γ-TMP), 0.73 (t, 9H, $^3J_{HH}$ = 7.1 Hz, CH_3-NEt_3), 0.20 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH_2-^{i}Bu); ^{13}C{H} NMR (100.63 MHz, d_6-benzene, 300 K): 53.18 (α-TMP), 46.64 (*C*H_2-NEt_3), 45.85 (β-TMP), 30.12 (broad, *C*H_3-TMP and *C*H_3-^{i}Bu), 28.34 (*C*H-^{i}Bu), 18.96 (γ-TMP), 10.72 (*C*H_3-NEt_3), signal for Al–*C*H_2 was not observed; ^{7}Li NMR (155.50 MHz, d_6-benzene, 300 K, reference LiCl in D_2O at 0.00 ppm): −0.31 ppm. *Synthesis of* $[\{PhC(=O)N({}^iPr)_2\}\cdot Li(\mu\text{-}TMP)(\mu\text{-}{}^iBu)Al({}^iBu_2)]$ *(**3**)*: in a Schlenk tube, 2 mmol of the complex $[(Et_3N)\cdot Li(\mu\text{-}{}^iBu)(\mu\text{-}TMP)Al({}^iBu)_2]$ (**2**) in 10 mL of hexane was synthesized by following the procedure described above. *N*,*N*-Diisopropylbenzamide (2 mmol, 0.41 g) was then introduced to give a bright yellow solution. The solution was moved to the freezer to aid the crystallization. A crop (0.74 g, 67%) of clear crystals formed in solution that were suitable for X-ray crystallographic analysis. FT-IR (nujol): 1630 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400.13 MHz, d_6-benzene, 300 K): 7.03 (m, 3H, 2H *m*-C_6H_5 and 1H *p*-C_6H_5), 6.93 (m, 2H, *o*-C_6H_5), 3.42 and 2.96 (m, 1H each, C*H*-^{i}Pr), 2.35 (septet, 3H, $^3J_{HH}$ = 6.5 Hz, C*H*-^{i}Bu), 1.52 (s, 6H, CH_3-TMP), 1.42 (m, 4H, β-TMP), 1.36 (s overlapping d, 24H, 18H, $^3J_{HH}$ = 6.5 Hz, CH_3-^{i}Bu and 6H CH_3-TMP), 1.26 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH_3-^{i}Pr), 1.20 (m, 2H, γ-TMP), 0.54 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH_3-^{i}Pr), 0.38 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH_2-^{i}Bu); ^{13}C{H} NMR (100.63 MHz, d_6-benzene, 300 K): 173.27 (*C*=O), 137.55 (*i*-C_6H_5), 130.36 (*p*-C_6H_5), 129.64 (*m*-C_6H_5), 125.32 (*o*-C_6H_5), 52.68 (α-TMP and *C*H-^{i}Pr), 47.08 (β-TMP), 44.56 (*C*H-^{i}Pr), 35.94 and 30.25 (*C*H_3-TMP), 29.96 (*C*H_3-^{i}Bu), 28.18 (*C*H-^{i}Bu), 20.82 and 20.08 (*C*H_3-^{i}Pr), 18.90 (γ-TMP), signal for Al–*C*H_2 of ^{i}Bu was not observed. ^{7}Li NMR (155.50 MHz, d_6-benzene, 300 K, reference LiCl in D_2O at 0.00 ppm): 0.89 ppm. *Synthesis of* $[\{(PhC(=O)N({}^iPr)_2)\cdot Li(\kappa^2\text{-}O,O\text{-}O(CH_2)_2\text{-}OCH{=}CH_2)Al{}^iBu_3\}_2\cdot(dioxane)]$ *(**4**)*: in a Schlenk tube, 2 mmol of the complex $[(PhC(=O)N({}^iPr)_2\cdot Li(\mu\text{-}{}^iBu)(\mu\text{-}TMP)Al({}^iBu)_2]$ (**3**) in 10 mL of hexane, was synthesized by following the procedure described above. 1,4-Dioxane (4 mmol, 0.34 mL) was introduced and the resultant transparent solution was allowed to stir for 1 h. The solution was moved to the freezer to aid crystallization. A crop (0.39 g, 36%) of colourless crystals formed in solution that were suitable for X-ray crystallographic analysis. FT-IR (nujol): 1608 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400.13 MHz, d_6-benzene, 300 K): 7.13 (m, 6H, 4H *m*-C_6H_5 and 2H *p*-C_6H_5), 7.06 (m, 4H, *o*-C_6H_5), 5.86 (dd, 2H, $^3J_{HH}$ = 14.1 and 3.7 Hz, OC*H*=CH_2), 3.95 (d, 2H, $^3J_{HH}$ = 14.1 Hz, *trans*-H of OCH=CH_2), 3.82 (d, 2H, $^3J_{HH}$ = 6.7 Hz, *cis*-H of OCH=CH_2), 3.79 and 3.25 (t, 4H each, $^3J_{HH}$ = 4.1 Hz, O(CH_2)$_2$O), 3.41 (s, 8H, OCH_2-dioxane), 3.45 and 3.00 (septet, 2H each, $^3J_{HH}$ = 6.8 Hz, C*H*-^{i}Pr), 2.40 (septet, 6H, $^3J_{HH}$ = 6.5 Hz, C*H*-^{i}Bu), 1.46 (d, 36H, $^3J_{HH}$ = 6.5 Hz, CH_3-^{i}Bu), 1.39 and 0.59 (broad s, 12H each, CH_3-^{i}Pr), 0.32 (d, 12H, $^3J_{HH}$ = 6.5 Hz, CH_2-^{i}Bu); ^{13}C{H} NMR (100.63 MHz, d_6-benzene, 300 K): 172.73 (*C*=O), 142.51 (O*C*H=CH_2), 138.53 (*i*-C_6H_5), 130.04 (*p*-C_6H_5), 129.47 (*m*-C_6H_5), 126.41 (*o*-C_6H_5), 88.95 (OCH=*C*H_2), 72.60 and 60.56 (O(*C*H_2)$_2$O), 67.65 (O*C*H_2-dioxane), 52.03 and 46.49 (*C*H-^{i}Pr), 30.19 (*C*H_3-^{i}Bu), 28.77 (*C*H-^{i}Bu), 21.67 and 21.10 (*C*H_3-^{i}Pr), signal for Al–*C*H_2 of ^{i}Bu was not observed. ^{7}Li NMR (155.50 MHz, d_6-benzene, 300 K, reference LiCl in D_2O at 0.00 ppm): 0.11 ppm.

§ Crystal data for **1**, CCDC 634093: $C_{30}H_{64}AlLiN_2$, M_r = 486.75, monoclinic, space group $P2_1$, a = 8.5631(2), b = 18.6410(5), c = 10.6743(3) Å, β = 105.995(2)°, V = 1637.92(7) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.080 mm^{-1}, T = 200 K; 23 836 reflections, 7415 unique, R_{int} 0.050; final refinement to convergence on F^2 gave $R1$ = 0.0559 (F, 5436 obs. data only) and w$R2$ = 0.1321 (F^2, all data), GOF = 1.041. Crystal data for **2**, CCDC 634094: $C_{27}H_{60}AlLiN_2$, M_r = 446.69, triclinic, space group $P\bar{1}$, a = 10.5683(7), b = 11.0648(3), c = 14.9605(7) Å, α = 96.822(4), β = 105.870(3), γ = 113.030(3)°, V = 1497.42(15) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.083 mm^{-1}, T = 123 K; 10 472 reflections, 5850 unique, R_{int} 0.0588; final refinement to convergence on F^2 gave $R1$ = 0.0582 (F, 3535 obs. data only) and w$R2$ = 0.1165 (F^2, all data), GOF = 1.010. Crystal data for **3**, CCDC 634095: $C_{34}H_{64}AlLiN_2O$, M_r = 550.79, orthorhombic, space group $Pna2_1$, a = 18.9601(5), b = 16.2475(4), c = 11.5036(3) Å, V = 3543.73(16) Å^3, Z = 4, λ = 0.71073 Å, μ = 0.083 mm^{-1}, T = 123 K; 7772 reflections, 4255 unique, R_{int} 0.057; final refinement to convergence on F^2 gave $R1$ = 0.0427 (F, 3189 obs. data only) and w$R2$ = 0.0843 (F^2, all data), GOF = 1.015. Crystal data for **4**, CCDC 634096: $C_{62}H_{114}Al_2Li_2N_2O_8$, M_r = 1083.4, triclinic, space group $P\bar{1}$, a = 11.8338(4), b = 11.8351(3), c = 13.8446(4) Å, α = 111.793(2), β = 95.568(2), γ = 101.398(2)°, V = 1733.71(9) Å^3, Z = 1, λ = 0.71073 Å, μ = 0.089 mm^{-1}, T = 150 K; 39 049 reflections, 7639 unique, R_{int} 0.060; final refinement to convergence on F^2 gave $R1$ = 0.0566 (F, 4855 obs. data only) and w$R2$ = 0.1489 (F^2, all data), GOF = 1.030. Two butyl groups were each treated as disordered over two sites. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700785j

1 M. Uchiyama, H. Naka, Y. Matsumoto and T. Ohwada, *J. Am. Chem. Soc.*, 2004, **126**, 10526.
2 J. García-Álvarez, D. V. Graham, A. R. Kennedy, R. E. Mulvey and S. Weatherstone, *Chem. Commun.*, 2006, 3208.
3 J. Clayden, *Organolithiums: Selectivity for Synthesis*, Elsevier Science Ltd, Oxford, 2002.
4 W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2006, **45**, 2370.
5 Note that in our hands we found that $^iBu_3Al(TMP)Li$ metallates the benzamide to a negligible extent in a stoichiometric amount of THF and not at all in neat hexane.
6 For a review, see: A. Maercker, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 972.
7 J. A. Rood, B. C. Noll and K. W. Henderson, *Inorg. Chem. Commun.*, 2006, **9**, 1129.
8 W. Uhl, K.-W. Klinkhammer, M. Layh and V. Massa, *Chem. Ber.*, 1991, **124**, 279.