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Entrapment of *tert*-Butyllithium and Lithium *tert*-Butylamide Monomers by Partially Lithiated Derivatives of Aluminum and Gallium Primary Amide Complexes

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The lithiation of the dimeric trisamido group 13 derivatives $\{M[N(H)t\text{-Bu}]_3\}_2$ (**1a**, M = Al; **1b**, M = Ga) by alkyllithium reagents RLi (R = *t*-Bu or Me), at different stoichiometries, was investigated. On the basis of NMR data, the initial lithiation of **1a** occurs at the bridging N(H)*t*-Bu groups to give the mono- and dilithiated derivatives $Li_x[Al_2(Nt\text{-Bu})_x(NHt\text{-Bu})_{6-x}]$ ($x = 1, 2$). The reaction of **1a** with *t*-BuLi in a 1:3 molar ratio in *n*-pentane at 23 °C produces $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2{\cdot}(t\text{-BuLi})$ (**2**) in 67% yield, whereas the treatment of **1a** with MeLi in diethyl ether at 23 °C yields $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2{\cdot}[LiN(H)t\text{-Bu}]$ (**7**) and $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2$ (**8**). The gallium analogue of **7**, i.e., $\{Li[Ga(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2{\cdot}[LiN(H)t\text{-Bu}]$ (**5**), was obtained in 47% yield by the reaction of **1b** with *t*-BuLi in a 1:3 molar ratio in *n*-pentane at 23 °C. The structures of **2**, **5,** and **7** have been determined by X-ray crystallography and were shown to involve the entrapment of a monomeric *t*-BuLi or LiN(H)*t*-Bu fragment by a dilithiated derivative of **1a** or **1b**. The six fused four-membered rings give rise to a concave, lounge-chair arrangement for the 12-atom $[Li_3Al_2N_6E]$ (E = C or N)] clusters of **2**, **5,** and **7**. Variable-temperature ^1H NMR spectra of **2**, **5,** and **7** in C_7D_8 over the range −90 to 23 °C reveal a fluxional process involving Li−N bond breaking and formation.

Introduction

It is well-established that alkyllithium compounds RLi, which are ubiquitous reagents in organic synthesis, tend to form oligomeric structures in the solid state.[1−6] Common structural motifs include a tetramer $(RLi)_4$ (R = Me,[1] Et,[2] and *t*-Bu[3]), in which each face of the central Li_4 tetrahedron is capped by an alkyl group, and a hexamer $(RLi)_6$ [R = *i*-Pr,[4] *n*-Bu,[3] *c*-C_6H_{11},[5] and CH_2(*c*-$CHCMe_2CMe_2$)[6]], the cluster structure of which is derived from a Li_6 octahedron with six face-coordinating alkyl substituents. The stabilization of smaller oligomers has been achieved by the use of coordinating solvents. For example, the dimers $(t\text{-BuLi}{\cdot}Et_2O)_2$[3] and $(n\text{-BuLi}{\cdot}TMEDA)_2$[7] were obtained by adding diethyl ether or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine to hydrocarbon solutions of *tert*- or *n*-butyllithium, respectively. This method, however, has not led to the isolation and structural characterization of monomeric alkyllithium fragments, which are anticipated to exhibit greater reactivity than their associated counterparts.[1a] In an alternative approach, Williard and Sun[8] demonstrated the utility of the dimeric lithium derivative of *N*-isopropyl-*O*-methylvalinol for trapping the unsolvated fragments *t*-BuLi, *n*-BuLi, and *s*-BuLi. A related example involves the stabilization of two *t*-BuLi monomers via adduct formation at either end of the complex $\{(meso\text{-octaethylcalix[4]pyrrole})Li_4\}$.[9]

Primary lithium alkylamide species LiN(H)R have attracted recent attention as nucleophiles[10] and transamination reagents[11] in the synthesis of main group polyimido and imido/oxo anions. Formally, they differ from RLi only by the presence of an -N(H)- spacer between Li^+ and the alkide group. The solid-state structures have been discussed in a recent review.[12] The octameric $[LiN(H)t\text{-Bu}]_8$ adopts a cyclic ladder structure.[13] Multinuclear (^6Li, ^{13}C, and ^{15}N) NMR studies reveal a single oligomer in toluene solution, but the state of aggregation (tetramer, hexamer, or octamer) is unclear.[14]

In connection with our ongoing investigations of the synthesis and reaction chemistry of homoleptic poly-

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imido anions with *p*-block element centers,$^{10c,d,h-k,15}$ the dimeric trisamido group 13 compounds $\{M[N(H)\mathit{t}\text{-}Bu]_3\}_2$ (**1a**, M = Al;^{16} **1b**, M = Ga^{17}) were chosen as potential candidates to generate the ions $[M(N\mathit{t}\text{-}Bu)_3]^{3-}$ by reaction with alkyllithium reagents. The resulting formation and structural characterization of the unexpected alkyllithium and lithium alkylamide adducts $\{Li[M(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_2]\}_2{\cdot}LiR$ [**2**, M = Al and R = *t*-Bu; **5**, M = Ga and R = N(H)*t*-Bu; **7**, M = Al and R = N(H)*t*-Bu] are described in this account.

Experimental Section

General Comments. Solvents were dried and distilled before use: *n*-hexane, diethyl ether, and *n*-pentane (sodium benzophenone). *n*-Butyllithium (2.5 M solution in hexanes), $\mathit{t}\text{-}BuNH_2$, $AlCl_3$, $GaCl_3$, *tert*-butyllithium (1.7 M solution in pentane), and methyllithium (1.4 M solution in diethyl ether) were commercial samples (Aldrich) used as received. The reagent $[LiN(H)\mathit{t}\text{-}Bu]_8$ was prepared by the addition of *n*-butyllithium to $\mathit{t}\text{-}BuNH_2$ in *n*-hexane at 0 °C. The compounds $\{Al[N(H)\mathit{t}\text{-}Bu]_3\}_2$ (**1a**)^{16} and $\{Ga[N(H)\mathit{t}\text{-}Bu]_3\}_2$ (**1b**)^{17} were prepared by treating a slurry of $[LiN(H)\mathit{t}\text{-}Bu]_8$ in diethyl ether with $AlCl_3$ or $GaCl_3$, respectively, via the literature methods. The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon gas by standard Schlenk techniques or in a glovebox. Chemical shifts in the ^1H and ^{13}C NMR spectra are reported relative to TMS in $CDCl_3$, and those for ^7Li are referenced to LiCl in D_2O. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

Preparation of $\{Li[Al(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_2]\}_2{\cdot}(\mathit{t}\text{-}BuLi)$ (2). *tert*-Butyllithium (1.82 mL, 3.09 mmol) was added slowly to a solution of **1a** (0.50 g, 1.03 mmol) in *n*-pentane (30 mL) at 23 °C and the mixture was stirred for 4 h. Concentration (ca. 5 mL) by removal of solvent in vacuo and subsequent cooling (−20 °C for 24 h) of the resulting solution yielded colorless blocks of **2** (0.39 g, 0.69 mmol, 67%); mp 121−122 °C (decomp). Anal. Calcd for $Al_2C_{28}H_{67}Li_3N_6$: C, 59.77; H, 12.00; N, 14.94. Found: C, 59.35; H, 12.21; N, 14.39. ^1H NMR [in C_6D_6 at 23 °C, 200 MHz]: δ 1.49 (s, 9H, *t*-Bu), 1.39 (s, 18H, N*t*-Bu), 1.34 (s, 18H, N*t*-Bu), 1.27 (s, 18H, N*t*-Bu), 0.36 (br s, 2H, N-H), 0.32 (br s, 2H, N-H). ^1H NMR [in C_7D_8 at 23 °C, 400 MHz]: δ 1.39 (s, 9H, *t*-Bu), 1.38 (s, 18H, N*t*-Bu), 1.33 (s, 18H, N*t*-Bu), 1.28 (s, 18H, N*t*-Bu), 0.36 (br s, 4H, N-H). ^1H NMR [in C_7D_8 at −60 °C, 400 MHz]: δ 1.56 (s, 9H, *t*-Bu), 1.39 (s, 18H, N*t*-Bu), 1.34 (br s, 18H, N*t*-Bu), 1.24 (s, 18H, N*t*-Bu), 0.35 (s, 2H, N-H), 0.29 (s, 2H, N-H). ^{13}C NMR [in C_7D_8 at 23 °C, 300 MHz]: δ 35.19 [$C(\mathit{C}H_3)_3$], 36.02 [$NC(\mathit{C}H_3)_3$], 36.13 [$NC(\mathit{C}H_3)_3$], 37.84 [$NC(\mathit{C}H_3)_3$], 38.89 [$\mathit{C}(CH_3)_3$], 49.84 [$N\mathit{C}(CH_3)_3$], 50.65 [$N\mathit{C}(CH_3)_3$], 51.34 [$N\mathit{C}(CH_3)_3$]. ^7Li NMR [in C_6D_6 at 23 °C, 200 MHz]: δ −0.20 (s), −0.26 (s) (approximate 1:2 relative intensities). IR [KBr (Nujol mull)]: 3182 (br) cm^{-1} [ν(N-H)].

Preparation of $Li[Al_2(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_5]$ (3). *tert*-Butyllithium (0.48 mL, 0.82 mmol) was added slowly to a solution of **1a** (0.40 g, 0.82 mmol) in *n*-pentane (35 mL) at 23 °C and the mixture was stirred for 3 h. Removal of all volatiles in vacuo yielded **3** as a white powder (0.35 g, 0.71 mmol, 87%); mp 120 °C (decomp). Anal. Calcd for $Al_2C_{24}H_{59}LiN_6$: C, 58.51; H, 12.07; N, 17.06. Found: C, 57.37; H, 11.82; N, 16.54. ^1H NMR [in C_6D_6 at 23 °C, 200 MHz]: δ 1.54 (s, 9H, *t*-Bu), 1.45 (s, 18H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.21 (s, 18H, *t*-Bu), 0.76 (s, 1H, N-H), 0.09 (s, 2H, N-H), −0.21 (s, 2H, N-H). ^7Li NMR [in C_6D_6 at 23 °C, 200 MHz]: δ −0.31 (s). IR [KBr (Nujol mull)]: 3401 (br) and 3187 (br) cm^{-1} [ν(N-H)].

Preparation of $\{Li[Ga(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_2]\}_2{\cdot}[LiN(H)\mathit{t}\text{-}Bu]$ (5). *tert*-Butyllithium (1.46 mL, 2.48 mmol) was added slowly to a solution of **1b** (0.48 g, 0.83 mmol) in *n*-pentane (30 mL) at 23 °C and the mixture was stirred for 5 h. Concentration (ca. 4 mL) by removal of solvent in vacuo and subsequent cooling (−20 °C for 3 days) of the resulting solution yielded colorless blocks of **5** (0.26 g, 0.39 mmol, 47% based on **1b**); mp 108 °C (decomp).[18] ^1H NMR [in C_6D_6 at 23 °C, 200 MHz]: δ 1.55 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.41 (s, 18H, *t*-Bu), 1.34 (s, 18H, *t*-Bu), 1.29 (s, 18H, *t*-Bu), 0.88 (s, 1H, N-H), 0.61 (s, 2H, N-H), 0.51 (s, 2H, N-H). ^1H NMR [in C_7D_8 at 23 °C, 400 MHz]: δ 1.49 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.41 (s, 18H, *t*-Bu), 1.33 (s, 18H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 0.59 (s, 2H, N-H), 0.51 (s, 2H, N-H), −0.67 (s, 1H, N-H). ^1H NMR [in C_7D_8 at −80 °C, 400 MHz]: δ 1.69 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.41 (s, 18H, *t*-Bu), 1.32 (br s, 18H, *t*-Bu), 1.24 (s, 18H, *t*-Bu), 0.67 (s, 2H, N-H), 0.49 (s, 2H, N-H), −0.54 (s, 1H, N-H). ^7Li NMR [in C_6D_6 at 23 °C, 200 MHz]: δ 0.40 (s), −0.21 (s) (approximate 2:1 relative intensities). IR [KBr (Nujol mull)]: 3323 (br) and 3247 (br) cm^{-1} [ν(N-H)].

Preparation of $Li[Ga_2(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_5]$ (6). *tert*-Butyllithium (0.51 mL, 0.87 mmol) was added slowly to a solution of **1b** (0.50 g, 0.87 mmol) in *n*-pentane (40 mL) at 23 °C and the mixture was stirred for 3 h. Removal of all volatiles in vacuo yielded **6** as a white powder (0.41 g, 0.71 mmol, 82%); mp 110 °C (decomp).[18] ^1H NMR [in C_6D_6 at 23 °C, 200 MHz]: δ 1.55 (s, 9H, *t*-Bu), 1.47 (s, 18H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.23 (s, 18H, *t*-Bu), 0.34 (s, 2H, N-H), 0.05 (s, 2H, N-H), −0.27 (s, 1H, N-H). ^7Li NMR [in C_6D_6 at 23 °C, 200 MHz]: δ −0.32 (s). IR [KBr (Nujol mull)]: 3385 (br) and 3214 (br) cm^{-1} [ν(N-H)].

Preparation of $\{Li[Al(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_2]\}_2{\cdot}[LiN(H)\mathit{t}\text{-}Bu]$ (7) and $\{Li[Al(N\mathit{t}\text{-}Bu)(NH\mathit{t}\text{-}Bu)_2]\}_2$ (8). Methyllithium (4.41

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(18) Numerous attempts to obtain reasonable CHN analyses for crystalline samples of **5** and **6** were unsuccessful due to the high sensitivity (air and moisture) of these Ga-containing compounds.

Table 1. Crystallographic Data for 2, 5, and 7

	2·1a	**5**	**7**
formula	$C_{52}H_{127}Al_4Li_3N_{12}$	$C_{28}H_{68}Ga_2Li_3N_7$	$C_{28}H_{68}Al_2Li_3N_7$
fw	1049.40	663.15	557.67
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$Pca2_1$ (no. 29)	$Pca2_1$ (no. 29)	$Pca2_1$ (no. 29)
a, Å	21.696(4)	18.9693(17)	18.929(7)
b, Å	18.109(3)	10.8903(10)	10.966(4)
c, Å	19.249(3)	18.7885(17)	18.590(7)
V, Å^3	7563(2)	3881.4(6)	3859(2)
Z	4	4	4
T, °C	70(2)	80(2)	70(2)
λ, Å	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	0.922	1.135	0.994
μ, cm^{-1}	0.97	1.413	1.00
F (000)	2336	1440	1280
R1[a]	0.1080	0.0349	0.0688
wR2[b]	0.3220	0.0858	0.1907

[a] $R1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ for $[I > 2\sigma(I)]$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

mL, 6.17 mmol) was added slowly to a solution of **1a** (0.50 g, 1.03 mmol) in diethyl ether (30 mL) at 23 °C and the mixture was stirred for 4 h. Concentration (ca. 3 mL) by removal of solvent in vacuo and subsequent cooling (−20 °C for 24 h) of the resulting solution yielded colorless blocks of **7** (0.26 g, 0.45 mmol, 44% based on **1a**); mp 115 °C (decomp). Storage of the mother liquor at −20 °C for a further 48 h yielded **8** as a white powder (0.10 g, 0.20 mmol, 19% based on **1a**); mp 147−148 °C (decomp at ca. 160 °C). Anal. Calcd for **7**, $Al_2C_{28}H_{68}Li_3N_7$: C, 58.22; H, 11.86; N, 16.97. Found: C, 57.64; H, 11.49; N, 17.21. ^1H NMR for **7** [in C_6D_6 at 23 °C, 200 MHz]: δ 1.54 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.42 (s, 18H, *t*-Bu), 1.36 (s, 18H, *t*-Bu), 1.29 (s, 18H, *t*-Bu), 0.35 (br s, 3H, N-H), 0.31 (s, 2H, N-H). ^1H NMR for **7** [in C_7D_8 at 23 °C, 400 MHz]: δ 1.48 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.41 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 0.32 (br s, 5H, N-H). ^1H NMR for **7** [in C_7D_8 at −80 °C, 400 MHz]: δ 1.66 (s, 9H, *t*-Bu group of [LiN(H)*t*-Bu] moiety), 1.43 (s, 18H, *t*-Bu), 1.38 (br s, 18H, *t*-Bu), 1.26 (s, 18H, *t*-Bu), 0.29 (br s, 5H, N-H). ^7Li NMR for **7** [in C_6D_6 at 23 °C, 200 MHz]: δ 0.24 (s), −0.21 (s) (approximate 2:1 relative intensities). IR for **7** [KBr (Nujol mull)]: 3345 (br) and 3203 (br) cm^{-1} [ν(N-H)]. Anal. Calcd for **8**, $Al_2C_{24}H_{58}Li_2N_6$: C, 57.81; H, 11.72; N, 16.86. Found: C, 57.37; H, 11.43; N, 16.32. ^1H NMR for **8** [in C_6D_6 at 23 °C, 200 MHz]: δ 1.50 (s, 18H, *t*-Bu), 1.43 (s, 36H, *t*-Bu), 0.33 (br s, 4H, N-H). ^7Li NMR for **8** [in C_6D_6 at 23 °C, 200 MHz]: δ −0.62 (s). IR for **8** [KBr (Nujol mull)]: 3255 (br) cm^{-1} [ν(N-H)].

X-ray Analyses. All data were collected on Bruker AX SMART 1000 CCD diffractometers. Crystallographic data are summarized in Table 1.

Compound 2. Colorless crystals of {Li[Al(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·(*t*-BuLi) cocrystallized with a severely disordered molecule, to which the formula {Al[N(H)*t*-Bu]$_3$}$_2$ has been assigned, were obtained in 24 h from an *n*-pentane solution at −20 °C. A flash-cooled crystal (0.20 × 0.20 × 0.20 mm), mounted with viscous oil onto a thin glass fiber, was measured with 0.3° ω-scans at 0°, 90°, and 180° in ϕ in the range 1.46° ≤ θ ≤ 24.71°. Semiempirical absorption corrections ($t_{max}/t_{min} = 1.12$) based on equivalent reflections were applied.[19] Of a total of 59 516 reflections collected, 12 572 were independent ($R_{int} = 0.0920$) and were used to refine 689 parameters, with 7720 reflections considered to be observed [$I > 2\sigma(I)$]. Systematic absences in the data are consistent with $Pca2_1$ (no. 29) and $Pcam$ [$Pbcm$ (no. 57)]. Although the centric option was thoroughly explored, only the solution in $Pca2_1$ yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods,[20a] completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.[20b] The absolute structure parameter refined to nil, indicating that the true hand of the data has been determined.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. One of the Al atoms of the {Al[N(H)*t*-Bu]$_3$}$_2$ molecule was disordered over two positions with equal site occupancy factors. All hydrogen atoms were treated as idealized contributions.

Compound 5. Colorless crystals of {Li[Ga(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·[LiN(H)*t*-Bu] were obtained in 3 days from an *n*-pentane solution at −20 °C. A block crystal with dimensions 0.53 × 0.53 × 0.20 mm, mounted with viscous oil onto a thin glass fiber, was measured with ϕ- (0.5 s/frame, 225° rotation, $\chi = 30°$) and ω-scans (0.5°/frame, two series at $\phi = 0$ and 90° and $\chi = 80°$) in the range 2.16° ≤ θ ≤ 26.37°. Empirical absorption corrections ($t_{max}/t_{min} = 1.27$) based on equivalent reflections were applied.[19] Of a total of 14 656 reflections collected, 7694 were independent ($R_{int} = 0.0385$) and were used to refine 390 parameters, with 5577 reflections considered to be observed [$I > 2\sigma(I)$]. Systematic absences in the data are consistent with $Pca2_1$ (no. 29) and $Pcam$ [$Pbcm$ (no. 57)]. Although the centric option was thoroughly explored, only the solution in $Pca2_1$ yielded chemically reasonable and computationally stable results of refinement. The refined absolute structure parameter [0.36(1)] was neither unity nor nil and was used as the scale parameter in the racemic twin refinement.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl carbon atoms C(51), C(52), and C(53) of one *t*-Bu group were each disordered over two positions with site occupancy factors of 0.75(2) and 0.25(2), respectively. All hydrogen atoms were treated as idealized contributions.

Compound 7. Colorless crystals of {Li[Al(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·[LiN(H)*t*-Bu] were obtained in 24 h from a diethyl ether solution at −20 °C. A flash-cooled crystal (0.20 × 0.20 × 0.20 mm), mounted with viscous oil onto a thin glass fiber, was measured with 0.3° ω-scans at 0°, 90°, and 180° in ϕ in the range 2.15° ≤ θ ≤ 26.39°. Absorption corrections were not required. Of a total of 24 414 reflections collected, 7722 were independent ($R_{int} = 0.0718$) and were used to refine 361 parameters, with 5628 reflections considered to be observed [$I > 2\sigma(I)$]. Systematic absences in the data are consistent with $Pca2_1$ (no. 29) and $Pcam$ [$Pbcm$ (no. 57)]. Although the centric option was thoroughly explored, only the solution in $Pca2_1$ yielded chemically reasonable and computationally stable results of refinement. Structure solution and refinement procedures were the same as those described for **2**.

Results and Discussion

Lithiation of {Al[N(H)*t*-Bu]$_3$}$_2$ (1a) with *t*-BuLi. The initial objective of this project was the generation of homoleptic polyimido anions containing group 13 element centers. The approach chosen was the lithiation of the dimers {M[N(H)*t*-Bu]$_3$}$_2$ (**1a**, M = Al;[16] **1b**, M = Ga[17]) with alkyllithium reagents, cf. the preparation of {Li[P(N*t*-Bu)$_2$]}$_4$[15c] and {THF·Li$_3$[Si(N*i*-Pr)$_3$(NH*i*-Pr)]}$_2$.[15a] In a preliminary communication, it was demonstrated that reaction of the dimeric primary amido derivative **1a** with 6 equiv of *n*-butyllithium in *n*-hexane gives the adduct Li$_3$[Al$_2$(N*t*-Bu)$_3$(NH*t*-Bu)$_3$]·(*n*-BuLi)$_2$, the formation of which involves trapping of the unsolvated dimer (*n*-BuLi)$_2$ by a trilithiated derivative of **1a**.[16] We report here the unanticipated results of the lithiation of **1a**

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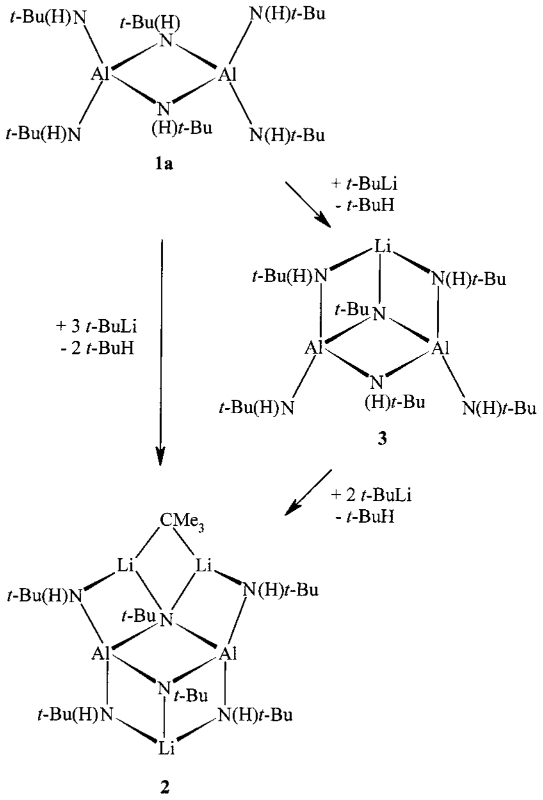
(19) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(20) (a) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**. (b) Sheldrick, G. M. *SHELXL97-2, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(21) (a) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Scheme 1



and, for comparison, **1b** with the more basic reagent *tert*-butyllithium.

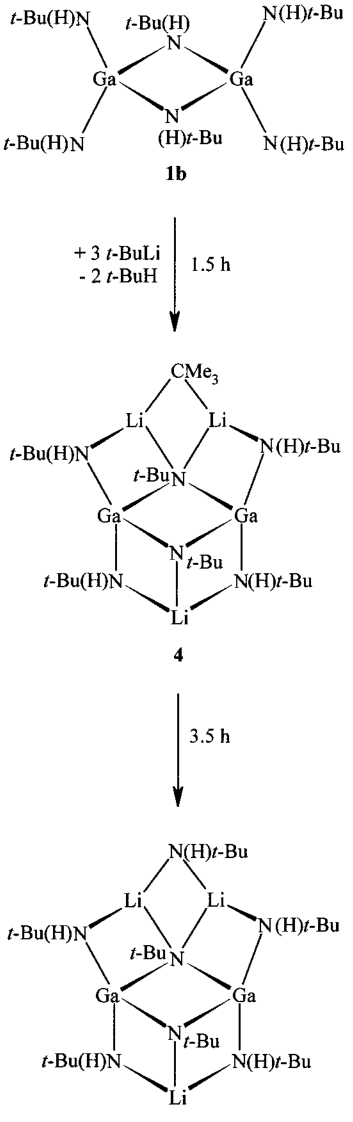
With the intent of hexalithiation, 6 equiv of *tert*-butyllithium was added to an *n*-hexane solution of **1a** and the reaction mixture was heated at reflux for 24 h. The ^{1}H NMR spectrum (benzene-d_6) of the product obtained from this solution revealed the presence of a single compound, which exhibited four *t*-Bu resonances in the ratio 1:2:2:2, as well as approximately 3 equiv of unreacted *tert*-butyllithium. The subsequent treatment of **1a** with 3 equiv of *tert*-butyllithium yielded only the single compound, which was recrystallized as colorless blocks in 67% yield from *n*-pentane. X-ray structure analysis revealed the adduct $\{Li[Al(Nt\text{-}Bu)(NHt\text{-}Bu)_2]\}_2\cdot(t\text{-}BuLi)$ (**2**), in which the monomeric fragment *t*-BuLi is trapped by a dilithiated derivative of **1a** (Scheme 1); *t*-BuLi is tetrameric in the solid state when crystallized from hydrocarbon solvents.[3] The ^{7}Li NMR spectrum of 2 in benzene-d_6 exhibited two resonances at δ −0.20 and −0.26 ppm in an approximate 1:2 ratio, consistent with the solid-state structure. However, the ^{1}H and ^{13}C NMR spectra of **2** suggest fluxional behavior in solution, which was investigated by variable-temperature NMR studies (vide infra). In contrast to the two other known compounds involving trapped *t*-BuLi monomers, i.e., $[c\text{-}LiN(i\text{-}Pr)CH(i\text{-}Pr)CH_2O(Me)]_2\cdot(t\text{-}BuLi)$[8] and $\{(meso\text{-}octaethylcalix[4]pyrrole)Li_4\}\cdot(t\text{-}BuLi)_2$,[9] complex **2** incorporates a *t*-BuLi moiety even in the presence of neighboring acidic protons, i.e., the four remaining N(H)*t*-Bu groups. Surprisingly, addition of the stronger base *tert*-butyllithium to hydrocarbon solutions of **1a** resulted in less extensive lithiation than the analogous reaction with *n*-butyllithium.[16]

To identify the intermediates involved in the formation of **2**, the dimer **1a** was treated with 1 or 2 equiv of *tert*-butyllithium. In the former case, the monolithiated species $Li[Al_2(Nt\text{-}Bu)(NHt\text{-}Bu)_5]$ (**3**) was the only product generated (87% yield). The structure proposed for **3** (Scheme 1) is based on the observation of four *t*-Bu resonances in the ratio 1:2:1:2 in the ^{1}H NMR spectrum. The ^{7}Li NMR spectrum of **3** in benzene-d_6 exhibited a singlet at δ −0.31 ppm. The preferential lithiation of one of the bridging N(H)*t*-Bu groups in **1a**, rather than one of the terminal N(H)*t*-Bu groups, is attributed to an increase in acidity of the H atoms of the bridging N(H)*t*-Bu groups, as compared with their terminal counterparts. Presumably the participation of the bridging N atoms in dative bonding leads to a more stabilized conjugate base via dissipation of the resulting negative charge. The NMR data indicate that **3** exists as a single isomer in solution, whereas the dimer **1a** is obtained and used as a 2:1 mixture of trans and cis isomers,[16] although it is not known if the H atom of the remaining endocyclic N(H)*t*-Bu group is cis or trans to the Li^+ ion (with respect to the Al_2N_2 ring). Treatment of complex **3** with 2 equiv of *tert*-butyllithium gave **2** as the sole product (Scheme 1). This subsequent lithiation of **3** likely involves deprotonation of the second bridging N(H)*t*-Bu group (see complex **8** below). However, the reactions of **1a** or **3** with *tert*-butyllithium in the stoichiometric ratios 1:2 or 1:1, respectively, led to mixtures containing equimolar amounts of **2** and **3**.

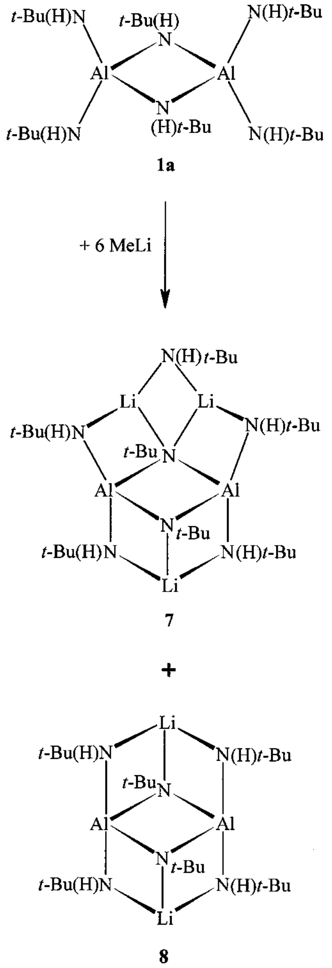
Lithiation of $\{Ga[N(H)t\text{-}Bu]_3\}_2$ (1b) with *t*-BuLi. For comparison with the behavior of the aluminum system **1a**, the gallium analogue **1b** was treated with 3 equiv of *tert*-butyllithium in *n*-pentane. The ^{1}H NMR spectrum of an aliquot taken from the reaction mixture after 1.5 h revealed the presence of a single compound with *t*-Bu resonances in the ratio 1:2:2:2 at δ 1.48, 1.37, 1.32, and 1.28 ppm (cf. δ 1.49, 1.39, 1.34, and 1.27 ppm for **2**). This observation is consistent with the formation of $\{Li[Ga(Nt\text{-}Bu)(NHt\text{-}Bu)_2]\}_2\cdot(t\text{-}BuLi)$ (**4**), isostructural with $\{Li[Al(Nt\text{-}Bu)(NHt\text{-}Bu)_2]\}_2\cdot(t\text{-}BuLi)$ (**2**). Surprisingly, the ^{1}H NMR spectrum of the same sample after 5 h revealed a new major product with four *t*-Bu resonances at δ 1.55, 1.41, 1.34, and 1.29 ppm in the ratio 1:2:2:2, respectively, along with minor, unidentified species that exhibited multiple peaks in the *t*-Bu region. X-ray-quality crystals of the major product were obtained in 47% yield by concentrating and, subsequently, cooling the reaction mixture (−20 °C for 3 days). A structural determination revealed the adduct $\{Li[Ga(Nt\text{-}Bu)(NHt\text{-}Bu)_2]\}_2\cdot[LiN(H)t\text{-}Bu]$ (**5**) in which the monomeric fragment LiN(H)*t*-Bu is trapped by a dilithiated derivative of **1b** (Scheme 2); LiN(H)*t*-Bu is octameric in the solid state.[13] The ^{7}Li NMR spectrum of **5** in benzene-d_6 exhibited two resonances at δ 0.40 and −0.21 ppm in an approximate 2:1 ratio, consistent with the solid-state structure.

The driving force for the formation of **5** from **4** (Scheme 2) is not well understood. However, degradation of a portion of **4** is clearly required to provide LiN(H)*t*-Bu and thus generate **5**, but the other product(s) of this reaction have not been identified. In contrast to the related aluminum system, treatment of **1b** with 6 equiv of *tert*-butyllithium led to the generation of $[LiN(H)t\text{-}Bu]_8$[22] as the major product, along with unidentified species that exhibited many resonances in the *t*-Bu region of the ^{1}H NMR spectrum. In an attempt to

Scheme 2



Scheme 3



develop a directed preparation of **5**, 2 equiv of *tert*-butyllithium was added to an 8:1 mixture of **1b** and [LiN(H)*t*-Bu]$_8$ in *n*-pentane. However, a variety of products, including the complexes **4**, **5,** and **6** (vide infra), were generated.

The only other identifiable product from the reaction of **1b** with various stoichiometric amounts of *tert*-butyllithium is the monolithiated complex Li[Ga$_2$(N*t*-Bu)(NH*t*-Bu)$_5$] (**6**), which can be isolated in 82% yield if only 1 equiv of *tert*-butyllithium is utilized. The observation of *t*-Bu resonances in the ratio 1:2:1:2 in the ^{1}H NMR spectrum and of a single resonance at δ −0.32 ppm in the ^{7}Li NMR spectrum for **6** indicate that this complex is isostructural with the analogous aluminum species Li[Al$_2$(N*t*-Bu)(NH*t*-Bu)$_5$] (**3**) (vide supra).

Lithiation of {Al[N(H)*t*-Bu]$_3$}$_2$ (1a) with MeLi. For comparison with the corresponding reactions of *tert*- and *n*-butyllithium,[16] **1a** was treated with 6 equiv of methyllithium in diethyl ether. X-ray-quality crystals of {Li[Al(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·[LiN(H)*t*-Bu] (**7**) were obtained in 44% yield by concentrating and, subsequently, cooling the reaction mixture (−20 °C for 1 day). The ^{1}H NMR spectrum of **7** in benzene-d_6 showed four signals in the *t*-Bu region at δ 1.54, 1.42, 1.36, and 1.29 ppm with relative intensities of 1:2:2:2, respectively. The ^{7}Li NMR spectrum exhibited two resonances at δ 0.24 and −0.21 ppm in an approximate 2:1 ratio. These values are similar to those obtained for the ^{1}H and ^{7}Li NMR spectra of the complex {Li[Ga(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·[LiN(H)*t*-Bu] (**5**). The structure of **7**, in which the monomer LiN(H)*t*-Bu is trapped by a dilithiated derivative of **1a**, cf. **5**, was confirmed by X-ray crystallography (Scheme 3).

After a further 2 days at −20 °C, the mother liquor from the reaction mixture yielded a white amorphous powder (19% yield). The ^{1}H NMR spectrum of this product in benzene-d_6 revealed two *t*-Bu resonances at δ 1.50 and 1.43 ppm and a broad N-H resonance at δ 0.33 ppm with integrations of 9:18:2, respectively. The ^{7}Li NMR spectrum in benzene-d_6 exhibited a singlet at δ −0.62 ppm. These NMR data indicate the formation of {Li[Al(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$ (**8**) by the lithiation of both bridging N(H)*t*-Bu groups (Scheme 3). The CHN analyses are consistent with this conclusion.

Apparently, two competing processes occur when **1a** is treated with an excess of methyllithium: the dimer **1a** is (a) dilithiated to form **8** and (b) consumed via nucleophilic attack by the alkyllithium reagent to form LiN(H)*t*-Bu and unidentified aluminum-containing prod-

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[22] [LiN(H)*t*-Bu]$_8$: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 1.36 ppm (s, *t*-Bu); X-ray, monoclinic, *P*2/*n*, $a = 12.043(2)$ Å, $b = 12.547(2)$ Å, $c = 18.365(4)$ Å, $\beta = 105.481(3)°$, $V = 2674.5(9)$ Å^3 (cf. ref 13).

Table 2. Selected Bond Lengths and Bond Angles for 2, 5, and 7

	2[a]	**5**[b]	**7**[c]
	Bond Lengths, Å		
M(1)−N(1)	1.853(5)	1.933(3)	1.865(3)
M(1)−N(2)	1.906(5)	1.970(3)	1.888(3)
M(1)−N(3)	1.875(6)	1.938(3)	1.884(3)
M(1)−N(4)	1.896(6)	1.930(3)	1.880(3)
M(2)−N(1)	1.888(5)	1.938(3)	1.860(3)
M(2)−N(2)	1.906(5)	1.972(3)	1.905(3)
M(2)−N(5)	1.882(5)	1.943(3)	1.877(3)
M(2)−N(6)	1.879(5)	1.931(3)	1.863(3)
N(1)Li(3)	2.055(12)	2.033(8)	2.129(8)
N(2)Li(1)	2.264(11)	2.239(8)	2.306(7)
N(2)Li(2)	2.232(11)	2.245(8)	2.294(7)
N(3)Li(3)	2.077(11)	2.086(8)	2.102(7)
N(4)Li(1)	2.041(13)	2.031(9)	2.066(8)
N(5)Li(3)	2.116(12)	2.069(8)	2.097(8)
N(6)Li(2)	2.054(11)	2.054(8)	2.067(8)
Li(1)−E	2.136(13)	1.941(8)	1.925(8)
Li(2)−E	2.160(13)	1.923(8)	1.925(8)
Li(1)···Li(2)	2.395(15)	2.394(10)	2.386(10)
	Angle, deg		
N(1)−M(1)−N(2)	89.8(2)	88.88(13)	89.19(13)
N(1)−M(1)−N(3)	104.8(3)	100.81(14)	106.05(15)
N(1)−M(1)−N(4)	113.0(3)	116.17(14)	114.47(15)
N(2)−M(1)−N(3)	107.1(2)	107.47(13)	106.80(13)
N(2)−M(1)−N(4)	107.2(2)	104.81(14)	108.23(14)
N(3)−M(1)−N(4)	128.1(3)	130.69(15)	125.74(15)
N(1)−M(2)−N(2)	88.8(2)	88.70(13)	88.81(13)
N(1)−M(2)−N(5)	104.2(2)	100.47(15)	105.63(15)
N(1)−M(2)−N(6)	115.6(2)	116.52(13)	114.19(14)
N(2)−M(2)−N(5)	108.0(2)	108.93(14)	107.87(14)
N(2)−M(2)−N(6)	107.4(2)	104.61(15)	108.57(14)
N(5)−M(2)−N(6)	126.3(2)	129.95(16)	125.51(17)
M(1)−N(1)−M(2)	90.4(2)	91.13(10)	90.81(11)
M(1)−N(1)Li(3)	81.1(3)	82.2(2)	80.0(2)
M(2)−N(1)Li(3)	81.6(4)	81.7(2)	80.1(2)
M(1)−N(2)−M(2)	88.3(2)	89.04(11)	88.73(11)
M(1)−N(2)Li(1)	78.0(3)	78.1(2)	78.2(2)
M(1)−N(2)Li(2)	123.0(4)	122.9(2)	120.4(2)
M(2)−N(2)Li(1)	121.7(4)	123.5(2)	121.6(2)
M(2)−N(2)Li(2)	78.2(3)	78.7(2)	77.5(2)
Li(1)N(2)−Li(2)	64.4(4)	64.6(3)	62.5(3)
M(1)−N(3)Li(3)	80.0(3)	80.7(2)	80.3(2)
M(1)−N(4)Li(1)	84.1(4)	84.3(3)	84.8(2)
M(2)−N(5)Li(3)	80.1(3)	80.7(2)	80.5(2)
M(2)−N(6)Li(2)	83.4(3)	84.6(3)	84.5(2)
N(2)Li(1)−N(4)	90.5(4)	92.6(3)	88.4(3)
N(2)Li(1)−E	113.1(5)	107.3(4)	108.8(4)
N(4)Li(1)−E	141.3(7)	147.0(4)	145.9(4)
N(2)Li(2)−N(6)	90.7(4)	91.7(3)	89.0(3)
N(2)Li(2)−E	113.4(5)	107.7(4)	109.3(3)
N(6)Li(2)−E	140.2(6)	148.3(4)	147.9(4)
N(1)Li(3)−N(3)	91.3(4)	92.8(3)	90.1(3)
N(1)Li(3)−N(5)	91.0(4)	93.3(3)	89.6(3)
N(3)Li(3)−N(5)	116.2(5)	119.8(4)	120.2(3)
Li(1)−E−Li(2)	67.8(4)	76.6(4)	76.6(3)

[a] M = Al and E = C(25). [b] M = Ga and E = N(7). [c] M = Al and E = N(7).

uct(s). A portion of complex **8** thus generated traps 1 equiv of LiN(H)t-Bu to form **7**, which is the first product to crystallize from solution. The remaining unreacted **8** is obtained as an amorphous white powder. The proposed formation of **8** as an intermediate in the production of {Li[Al(Nt-Bu)(NHt-Bu)$_2$]}$_2$·(t-BuLi) (**2**) (vide supra) is supported by the observation that **2** is produced quantitatively when **8** is treated with 1 equiv of *tert*-butyllithium in *n*-pentane (^{1}H NMR). By contrast, **7** is not formed when **8** is treated with 1 equiv of LiN(H)t-Bu under similar conditions.

X-ray Structure of {Li[Al(Nt-Bu)(NHt-Bu)$_2$]}$_2$·(t-BuLi) (2). The X-ray structural determination for complex **2** revealed that it is cocrystallized with a severely disordered aluminum-containing species for which a molecule of {Al[N(H)t-Bu]$_3$}$_2$ (**1a**) fits the difference map (five different crystals from two unique batches were measured and shown to be the same). Since the ^{1}H NMR spectrum of crystalline samples of **2** showed no evidence for the presence of **1a**, we assume that **1a** must have been formed during the transportation and/or mounting of the crystals. Despite the high *R*-values resulting from the inherent disorder in the crystal, the esds associated with the structural parameters for the ordered molecule of **2** are reasonable (Table 2).

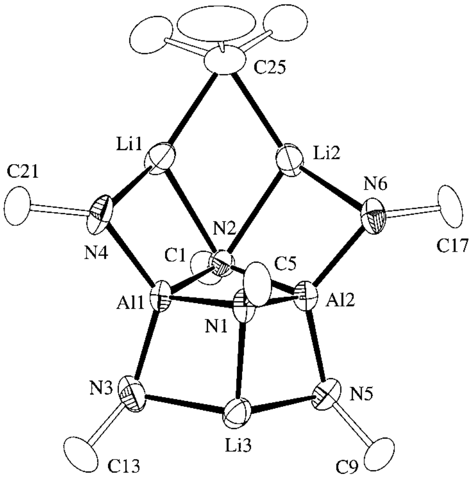

Figure 1. Molecular structure of {Li[Al(Nt-Bu)(NHt-Bu)$_2$]}$_2$·(t-BuLi) (2). For clarity, only the α-carbon atoms of the N-bonded t-Bu groups are shown and hydrogen atoms are omitted. Displacement ellipsoids are plotted at the 40% probability level.

The structure of **2** can be described as a 12-atom ($Li_3Al_2N_6C$) open-framework quaternary cluster comprised of six fused four-membered rings (Figure 1). Although no crystallographic symmetry is imposed on the molecule, **2** displays near C_s symmetry with the mirror plane bisecting the atoms Li(3), N(1), N(2), and C(25). The generation of **2** is formally envisaged to occur via adduct formation between monomeric t-BuLi and the dilithium derivative of **1a**, i.e., the complex {Li[Al(Nt-Bu)(NHt-Bu)$_2$]}$_2$ (**8**), which is proposed to contain a $Li_2Al_2N_6$ “deck-chair” core.[23] The expansion of this deck chair to incorporate the t-BuLi fragment results in the formation of a larger concavity on one end of the molecule and, hence, a “lounge-chair” arrangement for **2** (Scheme 4). The Li$^+$ ion of the trapped t-BuLi unit cannot be distinguished, i.e., Li(1) or Li(2), on the basis of the structural parameters. The mean Li−C distance of 2.148(13) Å [involving Li(1), Li(2), and C(25)] is significantly shorter than the value of 2.246 Å found for (t-BuLi)$_4$,[3] presumably due to reduced coordination numbers for both the lithium and carbon atoms in **2**. The presence of a Li(1)···Li(2) contact with a distance of 2.395(15) Å, which falls in the range of 2.383(9)−

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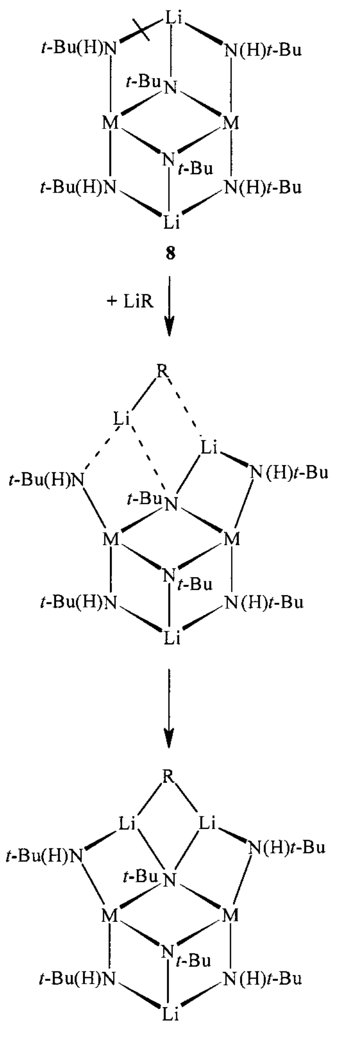
[23] Other examples of complexes containing 10-atom deck-chair cluster structures include (a) {(THF)$_2$Mg[OS(Nt-Bu)(NPh)]}$_2$; Brask, J. K.; Chivers, T.; Parvez, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 958; and (b) Li[Sb$_3$(NCy)$_4$(NMe$_2$)$_2$]; Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1277.

Scheme 4[a]



2: M = Al, R = *t*-Bu
5: M = Ga, R = N(H)*t*-Bu
7: M = Al, R = N(H)*t*-Bu

[a] The slashed and dashed bonds indicate bond breaking and bond formation, respectively.

2.431(8) Å for the Li_4 tetrahedron in $(t\text{-BuLi})_4$,[3] results in a particularly acute Li(1)−C(25)−Li(2) angle of 67.8(4)°.

The aluminum atoms in **2** are four-coordinate with distorted tetrahedral geometries [N−Al(1)−N, mean 108.3(3)°, range 89.8(2)−128.1(3)°; N−Al(2)−N, mean 108.4(2)°, range 88.8(2)−126.3(2)°] and both participate in the formation of three four-membered rings. The smallest bond angles at the aluminum centers occur in the Al_2N_2 core, while the exocyclic bond angles N(3)−Al(1)−N(4) and N(5)−Al(2)−N(6) are the largest. The Al−N distances [mean 1.886(5) Å, range 1.853(3)−1.906(5) Å] are comparable to those found for the related complex $Li_3[Al_2(Nt\text{-Bu})_3(NHt\text{-Bu})_3]\cdot(n\text{-BuLi})_2$.[16]

The H atoms of the four remaining N(H)*t*-Bu groups were not located in the Fourier map; however, it seems reasonable to associate them with the three-coordinate nitrogen atoms N(3), N(4), N(5), and N(6). Thus all nitrogen atoms are four-coordinate with the exception of N(2), which is five-coordinate. Accordingly, the longest Li−N distances in **2** [2.264(11) and 2.232(11) Å] involve N(2), cf. Li−N distances not involving N(2), mean 2.067(12) Å, range 2.041(13)−2.116(12) Å.

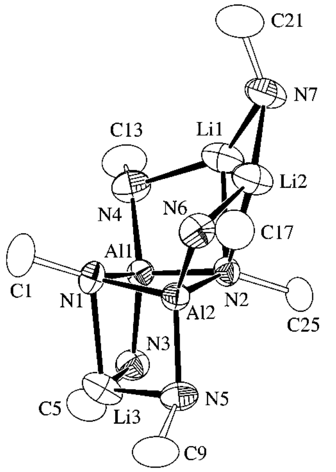


Figure 2. Molecular structure of $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2\cdot[LiN(H)t\text{-Bu}]$ (7) as viewed side-on. For clarity, only the α-carbon atoms of the *t*-Bu groups are shown and hydrogen atoms are omitted. Displacement ellipsoids are plotted at the 50% probability level.

X-ray Structures of the Complexes $\{Li[M(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2\cdot[LiN(H)t\text{-Bu}]$ (7, M = Al; 5, M = Ga). By analogy with the formation of the complex $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2\cdot(t\text{-BuLi})$ (**2**), generation of the open cluster **7** is viewed to proceed via incorporation of the monomer LiN(H)*t*-Bu into $\{Li[Al(Nt\text{-Bu})(NHt\text{-Bu})_2]\}_2$ (**8**) (Scheme 4). With the exception of an -N(H)- spacer between the *t*-Bu moiety and the adjacent Li^+ ions, i.e., Li(1) and Li(2), the pseudo-C_s-symmetric complex **7** is isostructural with **2** (Figure 2). Indeed, the structural parameters for the $Li_3Al_2N_6$ component [N(7) excluded] in the $Li_3Al_2N_7$ lounge-chair core of **7** are almost identical to those found for the analogous component in **2** (Table 2). Interestingly, the Li−N(7) distances are both 1.925(8) Å, which is a considerably smaller value than those found for the other Li−N bonds in **7** [mean 2.152(8) Å, range 2.066(8)−2.306(7) Å] and in the Li_8N_8 octagonal prism of $[LiN(H)t\text{-Bu}]_8$ [range 2.028−2.068 Å].[13] Although the H atoms of the N(H)-*t*-Bu groups were not located, it is reasonable to associate them with the three-coordinate nitrogen atoms N(3), N(4), N(5), N(6), and N(7).

With the obvious exception of the subtle consequences of longer M−N distances in complex **5**, as compared with those observed for **7** [mean 1.944(3) Å (M = Ga), 1.878(3) Å (M = Al)], **5** is isostructural with **7** (Figure 3). Additionally, **5** and **7** are isomorphic, both crystallizing in the space group $Pca2_1$. Selected bond distances and angles are included in Table 2. Interestingly, the range of Ga−N distances measured for **5** [1.930(3)−1.972(3) Å] is considerably narrower than that reported for the precursor $\{Ga[N(H)t\text{-Bu}]_3\}_2$ (**1b**) [1.813(10)−2.008(8) Å], for which the shortest Ga−N distances involve the three-coordinate exocyclic nitrogen atoms.[17] The central Ga_2N_2 ring in **1b** is exactly planar, whereas the same ring in **5** exhibits a torsion angle of 11.41(15)°. This anomaly is presumably due to the asymmetry inherent in the lounge-chair arrangement for **5**.

Complexes **5** and **7** provide the first examples of the entrapment of an unsolvated LiN(H)*t*-Bu monomer. However, related complexes involving a THF-solvated

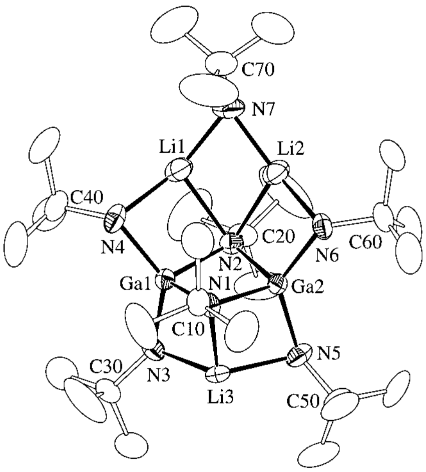


Figure 3. Molecular structure of {Li[Ga(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·[LiN(H)*t*-Bu] (**5**). For clarity, only one orientation of the disordered *t*-Bu group at N(5) is shown and hydrogen atoms are omitted. Displacement ellipsoids are plotted at the 50% probability level.

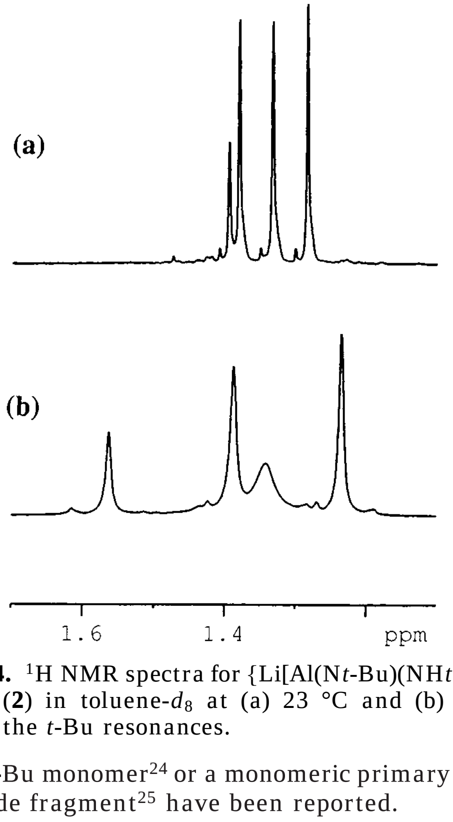
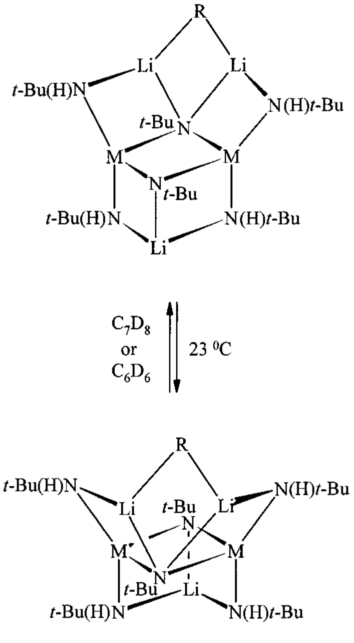


Figure 4. ^{1}H NMR spectra for {Li[Al(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·(*t*-BuLi) (**2**) in toluene-d_8 at (a) 23 °C and (b) −60 °C showing the *t*-Bu resonances.

LiN(H)*t*-Bu monomer[24] or a monomeric primary lithium arylamide fragment[25] have been reported.

Solution Studies of the Complexes {Li[M(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·LiR [2, M = Al and R = *t*-Bu; 5, M = Ga and R = N(H)*t*-Bu; 7, M = Al and R = N(H)*t*-Bu]. The ^{1}H NMR spectra for **2**, **5,** and **7** in benzene-d_6 or toluene-d_8 exhibit four *t*-Bu resonances in the ratio 1:2:2:2, rather than five resonances in the ratio 1:1:1:2:2 expected for the solid-state structures of these compounds. However, when toluene-d_8 solutions of **2**, **5,** or **7** are cooled to −90 °C (by increments of −10 °C), the middle resonance (of those with an integration of 2) broadens and collapses significantly in comparison with the other resonances (see Figure 4 for a representative example). The original spectra are regenerated upon warming the solutions back to 23 °C, indicating the occurrence of a facile fluxional process. The middle signal is assigned to the endocyclic N*t*-Bu groups [involving N(1) and N(2)], which can be made equivalent via the rearrangement illustrated in Scheme 5. Related examples that invoke facile Li−N bond breaking and formation to explain unexpectedly simple ^{1}H NMR spectra include the complexes {Li$_2$[Te(N*t*-Bu)$_3$]}$_2$[10h] and Li$_3$[Al$_2$(N*t*-Bu)$_3$(NH*t*-Bu)$_3$]·(*n*-BuLi)$_2$.[16]

Scheme 5



2: M = Al, R = *t*-Bu
5: M = Ga, R = N(H)*t*-Bu
7: M = Al, R = N(H)*t*-Bu

Conclusions

Treatment of the dimeric trisamido compounds {M[N(H)*t*-Bu]$_3$}$_2$ (1a, M = Al; **1b**, M = Ga) with an excess of *tert*-butyllithium or methyllithium yielded the complexes {Li[M(N*t*-Bu)(NH*t*-Bu)$_2$]}$_2$·LiR [**2**, M = Al and R = *t*-Bu; **5**, M = Ga and R = N(H)*t*-Bu; **7**, M = Al and R = N(H)*t*-Bu], in which monomeric *t*-BuLi or LiN(H)-*t*-Bu units are trapped by a dilithiated M$_2$N$_6$ template. In contrast to the behavior of *n*-BuLi,[16] lithiation of **1a** or **1b** by RLi (R = *t*-Bu or Me) occurred only at the endocyclic N(H)*t*-Bu groups. In solution, complexes **2**, **5,** and **7** undergo a fluxional process involving concerted Li−N bond breaking and formation.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **2**, **5,** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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