Secondary Amine Stabilized Aluminum Hydrides Derived from *N*,*N*′-Di-*tert*-butylethylenediamines

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Received July 29, 1995[⊗]

The metalation of substituted *N*,*N*′-di-*tert*-butylethylenediamines by various aluminum hydride sources has been investigated. HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(H)(*t*-Bu) forms a dimeric lithium chelated adduct of LiAlH$_4$, [{[HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(H)(*t*-Bu)]Li(μ-H)$_2$AlH$_2$}$_2$], **4**, which thermally decomposes to yield the tetrameric lithium diamidoaluminum hydride [{Li[N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)]AlH$_2$}$_4$], **5**. The same diamine reacts with AlH$_3$•NMe$_3$ or AlH$_3$ diethyl etherate to give the secondary amine stabilized amidoaluminum hydride species [{HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], **2**. Similarly, the same aluminum hydride sources react with the diamine *rac*-HN(*t*-Bu)CH(Me)CH(Me)N(H)(*t*-Bu) to yield [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH$_2$], **3**. Compounds **2** and **3** are stable with respect to elimination of hydrogen to form diamidoaluminum hydrides, but can be converted to the alane rich species, [H$_2$Al{N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], **6**, and [H$_2$Al{*rac*-N(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH$_2$], **7**, by reaction with AlH$_3$•NMe$_3$ under special conditions. The varying reactivity of the three aluminum hydride sources in these reactions has enabled mechanistic information to be gathered, and the effect of the different steric requirements in the diamines on the stability of the complexes is discussed. Crystals of **3** are monoclinic, space group $P2_1/n$ (No. 14), with $a = 8.910(4)$, $b = 14.809(1)$, and $c = 12.239(6)$ Å, $\beta = 109.76(2)°$, $V = 1520(1)$ Å^3, and $Z = 4$. Crystals of **4** are orthorhombic, space group *Pbca* (No. 61), with $a = 15.906(9)$, $b = 24.651(7)$, and $c = 9.933(7)$ Å, $V = 3895(3)$ Å^3, and $Z = 4$. Crystals of **6** are monoclinic, space group $P2_1/c$ (No. 14), with $a = 8.392(1)$, $b = 17.513(2)$, and $c = 12.959(1)$ Å, $\beta = 107.098(8)°$, $V = 1820.4(3)$ Å^3, and $Z = 4$.

Introduction

The differing reactivities of various aluminum hydride reagents has been given increased attention recently with regard to nitrogen heteroatom chemistry.[1] As an extension of our research on the reactivity of group 13 metal hydrides[2,3] toward amine and imine functionalities we have investigated the reactions of selected aluminum hydrides with *N*,*N*′-di-*tert*-butylethylenediamines bearing substituents on the ethylene linkage, either a single *t*-Bu group or a Me group on each carbon (*rac* isomer). The reactions have mechanistic implications and highlight the importance of the choice of aluminum hydride to metalate secondary amines. In particular we note (i) the reactions of 2 equiv of the trimethylamine adduct of alane, AlH$_3$•NMe$_3$, in hexane are required for selective monometalation, the by product being the bis(trimethylamine) adduct, AlH$_3$•2NMe$_3$, whereas 1 equiv of ether-solubilized alane affords the same aluminum amido species, and (ii) the reaction of LiAlH$_4$ with the C−*t*-Bu diamine in diethyl ether affords a novel stable, dimeric Lewis base adduct of the lithium cations, which metalates only above *ca.* 120 °C to a tetrameric lithium diamidoaluminum hydride aggregate.[4]

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. Solvents were dried then freeze/thaw degassed prior to use. *rac-N,N*′-Di-*tert*-butyl-2,3-dimethylethylenediamine,[5] *N*,*N*′-di-*tert*-butyl-2-*tert*-butylethylenediamine,[4] and AlH$_3$·NMe$_3$[6] were prepared according to literature procedures. All other reagents were obtained from Aldrich. ^{1}H NMR spectra were recorded on a Varian Gemini-200 spectrometer in deuterated benzene and referenced to the residual ^{1}H resonance of the solvent (δ 7.15). ^{13}C NMR spectra were recorded in deuterated benzene on a Varian Gemini-200 spectrometer operating at 50 MHz using broad band proton decoupling and were referenced to the ^{13}C resonance of the deuterated solvent (δ 128.00). Elemental analyses were performed by the Chemical and Micro Analytical Services Pty. Ltd., Melbourne, Australia. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as thin films or Nujol mulls on NaCl plates, as appropriate, using a Perkin-Elmer 1725X fourier transformed infrared spectrometer. Unless detailed in the following sections, the reactions described in this paper were conducted in sealable NMR tubes under an atmosphere of argon using glovebox techniques. The general procedure adopted for the NMR reactions was the portionwise addition of the aluminum hydride reagent to a Et$_2$O-d_{10}, benzene-d_6, or toluene-d_8 solution of the substrate (*ca.* 20 mg) at 0 °C. Thermal stability investigations were carried out by heating a prepared NMR sample of the compound in a sealed NMR tube at the described temperature. Identification of the products from the NMR reactions/thermal decompositions was by spectroscopic comparison with authentic samples.

Synthesis of [{HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], 2. To a solution of AlH$_3$·NMe$_3$ (0.32 g, 3.63 mmol) in hexane (40 mL) was added a solution of HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(H)(*t*-Bu) (0.41 g, 1.81 mmol) in hexane (10 mL) at −80 °C. When this mixture was warmed to room temperature, vigorous evolution of gas resulted, and the reaction mixture was then stirred overnight. The solution was filtered, concentrated *in vacuo* whereupon colorless crystals of the *title compound* deposited on slow cooling to room temperature (0.15 g, 33% yield).[4]

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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0020-1669/96/1335-1349$12.00/0

Table 1. Crystal Data for [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH_2], **3**, [{HN(*t*-Bu)CH(*t*-Bu)CH_2N(H)(*t*-Bu)}Li(μ-H)$_2$$AlH_2$], **4**, and [$H_2$Al{N(*t*-Bu)CH(*t*-Bu)$CH_2$N(*t*-Bu)}$AlH_2$] **6**

3: $C_{12}H_{29}N_2Al$	fw 228.36
$a = 8.910(4)$ Å	space group $P2_1/n$ (No. 14)
$b = 14.809(1)$ Å	$T = 25$ °C
$c = 12.239(6)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 109.76(2)°$	$\rho_{calcd} = 0.998$ g cm^{-3}
$V = 1520(1)$ Å^3	$\mu = 1.1$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.045$
	$R_w(F_o)^b = 0.045$(unit weights)
4: $C_{28}H_{72}N_4Al_2Li_2$	fw 532.75
$a = 15.906(9)$ Å	space group *Pbca* (No. 61)
$b = 24.651(7)$ Å	$T = 25$ °C
$c = 9.933(7)$ Å	$\lambda = 0.710\ 69$ Å
$V = 3895(3)$ Å^3	$\rho_{calcd} = 0.909$ g cm^{-3}
$Z = 4$	$\mu = 0.9$ cm^{-1}
	$R(F_o)^a = 0.054$
	$R_w(F_o)^b = 0.054$(unit weights)
6: $C_{14}H_{34}N_2Al_2$	fw 284.40
$a = 8.392(1)$ Å	space group $P2_1/c$ (No. 14)
$b = 17.513(2)$ Å	$T = 25$ °C
$c = 12.959(1)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 107.098(8)°$	$\rho_{calcd} = 1.038$ g cm^{-3}
$V = 1820.4(3)$ Å^3	$\mu = 1.5$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.045$
	$R_w(F_o)^b = 0.051$(sigma weights)

[a] ($R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). [b] ($R_w(F_o) = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$).

Table 2. Non-Hydrogen (and Refined Hydrogen) Atom Coordinates and Isotropic Thermal Parameters for [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH_2], **3**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å2
Al	0.1715(1)	0.40765(7)	0.42017(8)	0.0472(4)[a]
N1	0.1414(3)	0.4459(2)	0.2736(2)	0.046(1)[a]
N4	−0.0604(3)	0.3734(2)	0.3679(2)	0.045(1)[a]
C1	0.2341(4)	0.5082(3)	0.2292(3)	0.052(1)[a]
C2	0.0139(4)	0.3940(3)	0.1900(3)	0.053(1)[a]
C3	−0.1250(4)	0.3858(3)	0.2370(3)	0.052(1)[a]
C4	−0.1205(5)	0.2930(3)	0.4179(3)	0.059(2)[a]
C11	0.3747(5)	0.5404(3)	0.3329(3)	0.067(2)[a]
C12	0.1340(5)	0.5901(3)	0.1700(3)	0.069(2)[a]
C13	0.3025(5)	0.4636(3)	0.1429(3)	0.077(2)[a]
C21	0.0663(5)	0.2998(3)	0.1629(4)	0.079(2)[a]
C31	−0.2278(5)	0.4715(3)	0.2080(3)	0.078(2)[a]
C41	−0.0458(5)	0.3026(3)	0.5501(3)	0.076(2)[a]
C42	−0.0651(6)	0.2054(3)	0.3785(4)	0.096(3)[a]
C43	−0.3018(5)	0.2959(3)	0.3826(4)	0.083(2)[a]
H1	0.192(4)	0.483(2)	0.516(3)	0.059(9)
H2	0.273(3)	0.323(2)	0.468(3)	0.061(9)
H2a	−0.028(3)	0.431(2)	0.117(3)	0.049(9)
H3	−0.196(4)	0.332(2)	0.198(3)	0.052(9)
H4	−0.098(3)	0.418(2)	0.393(2)	0.033(9)

[a] Isotropic equivalent thermal parameters.

Synthesis of [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH_2], 3. To a solution of AlH_3·NMe_3 (0.37 g, 4.12 mmol) in hexane (60 mL) was added a solution of *rac*-HN(*t*-Bu)CH(Me)CH(Me)N(H)(*t*-Bu) (0.41 g, 2.06 mmol) in hexane (10 mL) at −80°C. When the mixture was warmed to room temperature, gas evolved, and the reaction mixture was stirred overnight. The solution was filtered and concentrated *in vacuo* to afford colorless crystals of the *title compound* at −30 °C (0.35 g, 75% yield). Mp: 98−100 °C, 187 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 0.83 (d, ^3J(H,H) = 6.62 Hz, 3H; Me), 0.94 (s, 9H; CMe_3), 1.21 (d, ^3J(H,H) = 6.60 Hz, 3H; Me), 1.36 (s, 9H; CMe_3) 1.84 (br, 1H; NH), 2.41 (m, 1H; NCH), 2.67 (q, ^3J(H,H) = 6.6 Hz, 1H; NCH), 4.40 (br, 2H; AlH). ^{13}C NMR (50 MHz, C_6D_6): δ 24.57, 27.27 (Me), 27.89, 32.80 (C*Me*$_3$), 53.42, 54.75 (*C*Me), 55.49, 58.31 (*C*Me$_3$). IR υ (cm^{-1}): 3156 (w, N−H), 1770 (m, Al−H). Anal. Calcd for $C_{12}H_{29}N_2Al$: C, 63.12; H, 12.80; N, 12.27. Found: C, 62.85; H, 12.87; N, 12.84. Yield using an ethereal solution of AlH_3: 43%.

Table 3. Non-Hydrogen (and Refined Hydrogen) Atom Coordinates and Isotropic Thermal Parameters for [{[HN(*t*-Bu)CH(*t*-Bu)CH_2N(H)(*t*-Bu)]Li(μ-H)$_2$$AlH_2$}$_2$], **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å2
Li	0.4230(8)	0.5634(4)	0.896(1)	0.057(4)[a]
Al	0.6132(1)	0.51061(9)	0.8546(2)	0.0600(7)[a]
N1	0.3578(4)	0.6004(2)	0.7429(5)	0.044(2)[a]
N4	0.4113(3)	0.6365(2)	1.0065(6)	0.050(2)[a]
C1	0.3803(5)	0.5895(3)	0.5965(6)	0.055(3)[a]
C2	0.3589(5)	0.6583(2)	0.7794(7)	0.052(3)[a]
C3	0.3492(5)	0.6691(2)	0.9328(7)	0.051(3)[a]
C4	0.4911(5)	0.6634(3)	1.0530(8)	0.071(3)[a]
C11	0.3728(5)	0.5273(3)	0.5823(7)	0.076(3)[a]
C12	0.3213(5)	0.6182(3)	0.5007(7)	0.090(3)[a]
C13	0.4714(5)	0.6061(3)	0.5704(7)	0.079(3)[a]
C31	0.2579(4)	0.6643(3)	0.9867(7)	0.055(2)[a]
C32	0.1962(5)	0.6941(3)	0.897(1)	0.110(4)[a]
C33	0.2269(4)	0.6062(3)	1.0026(7)	0.066(3)[a]
C34	0.2542(6)	0.6910(3)	1.1262(9)	0.098(4)[a]
C41	0.5384(5)	0.6205(3)	1.1334(9)	0.092(3)[a]
C42	0.5429(5)	0.6812(3)	0.9337(9)	0.092(4)[a]
C43	0.4740(6)	0.7114(3)	1.147(1)	0.111(4)[a]
H1	0.518(3)	0.526(2)	0.856(5)	0.04(1)
H2	0.379(3)	0.503(2)	0.992(5)	0.05(1)
H3	0.633(4)	0.461(2)	0.772(7)	0.12(3)
H4	0.675(4)	0.560(3)	0.835(7)	0.13(3)
H1a	0.306(3)	0.592(2)	0.750(5)	0.01(1)
H2a	0.315(4)	0.679(2)	0.728(6)	0.06(2)
H2b	0.417(4)	0.670(2)	0.757(6)	0.05(2)
H3a	0.361(3)	0.708(2)	0.946(5)	0.04(2)
H4a	0.389(4)	0.623(2)	1.077(6)	0.05(2)

[a] Isotropic equivalent thermal parameters.

Table 4. Non-Hydrogen (and Refined Hydrogen) Atom Coordinates and Isotropic Thermal Parameters for [H_2Al{N(*t*-Bu)CH(*t*-Bu)CH_2N(*t*-Bu)}AlH_2], **6**

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}
Al1	0.0957(2)	0.21458(7)	0.00316(9)	3.22(3)[a]
Al2	−0.0352(2)	0.17065(8)	0.1642(1)	3.48(3)[a]
N1	0.1848(4)	0.1676(2)	0.1471(2)	2.58(7)[a]
N4	−0.0195(4)	0.2711(2)	0.0906(2)	2.65(7)[a]
C1	0.2974(5)	0.0991(2)	0.1719(3)	3.5(1)[a]
C2	0.2567(5)	0.2385(2)	0.2066(3)	2.74(10)
C3	0.1211(5)	0.3026(2)	0.1872(3)	2.64(9)[a]
C4	−0.1851(5)	0.3129(2)	0.0483(3)	3.5(1)[a]
C11	0.2167(6)	0.0364(3)	0.0923(4)	5.7(1)[a]
C12	0.4691(6)	0.1181(3)	0.1606(4)	5.1(1)[a]
C13	0.3156(6)	0.0714(3)	0.2873(4)	5.1(1)[a]
C31	0.2048(5)	0.3836(2)	0.1906(3)	3.36(10)[a]
C32	0.3638(6)	0.3825(3)	0.2901(4)	5.0(1)[a]
C33	0.0970(6)	0.4478(2)	0.2159(4)	4.8(1)[a]
C34	0.2586(5)	0.4024(2)	0.0911(4)	4.4(1)[a]
C41	−0.1765(5)	0.3812(3)	−0.0234(4)	4.4(1)[a]
C42	−0.3081(6)	0.2562(3)	−0.0248(4)	5.5(1)[a]
C43	−0.2537(5)	0.3361(3)	0.1412(4)	5.2(1)[a]
H1	−0.021(4)	0.160(2)	−0.081(2)	3.6(8)
H2	0.238(4)	0.248(2)	−0.031(2)	3.1(8)
H3	−0.152(5)	0.102(2)	0.106(3)	5.4(10)
H4	−0.050(4)	0.180(2)	0.280(3)	5.1(10)
H2a	0.347(4)	0.252(2)	0.183(2)	1.8(7)
H2b	0.304(4)	0.228(2)	0.288(3)	3.4(9)
H3a	0.079(4)	0.305(2)	0.249(3)	2.5(8)

[a] Isotropic equivalent thermal parameters.

Synthesis of [{[HN(*t*-Bu)CH(*t*-Bu)CH_2N(H)(*t*-Bu)]Li(μ-H)$_2$$AlH_2$}$_2$], 4. To a solution of HN(*t*-Bu)CH(*t*-Bu)CH_2N(H)(*t*-Bu) (0.57 g, 2.50 mmol) in Et_2O (40 mL) was added an ethereal solution of $LiAlH_4$ (1.52 mL, 1.64 M, 2.49 mmol) at 0 °C. After being stirred at room temperature overnight, the solution was filtered and concentrated *in vacuo* (*ca.* 20 mL) to afford colorless crystals of the *title compound* at −30 °C (0.50 g, 73% yield). Mp: 160 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 0.83 (s, 18H; Me), 1.18 (s, 36H; Me), 1.45 (b, 4H; NH), 2.22 (dd, ^3J(H,H) = 5.6 Hz, ^3J(H,H) = 3.4 Hz, 2H; NCH), 2.35 (dd, ^3J(H,H) = 5.6 Hz, ^3J(H,H) = 13.7 Hz, 2H; NCH_2), 2.57 (dd, ^3J(H,H)

Table 5. Selected Structural Parameters for [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH$_2$], **3**

Bond Distances (Å)

Al−N1	1.813(3)	Al−H2	1.54(3)	N4−C3	1.519(4)
Al−N4	2.010(3)	N1−C1	1.459(5)	N4−C4	1.517(5)
Al−H1	1.58(3)	N1−C2	1.464(4)	C2−C3	1.536(6)

Bond Angles (deg)

N1−Al−N4	88.4(1)	N4−Al−H1	105(1)
N1−Al−H1	117(1)	N4−Al−H2	109(1)
N1−Al−H2	120(1)	H1−Al−H2	113(1)

Dihedral Angles (deg)

N1−C2−C3−N4	−37.7(4)

Table 6. Selected Structural Parameters for [{[HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(H)(*t*-Bu)]Li(*μ*-H)$_2$AlH$_2$}$_2$], **4**[a]

Bond Distances (Å)

Li−N1	2.05(1)	Al−H2	1.57(5)	N4−C3	1.469(9)
Li−N4	2.12(1)	Al−H3	1.51(6)	N4−C4	1.505(9)
Li−H1	1.82(4)	Al−H4	1.58(7)	C2−C3	1.55(1)
Li−H2	1.89(5)	N1−C1	1.522(8)		
Al−H1	1.55(4)	N1−C2	1.473(8)		

Contact Distances (Å)

Li−Al′	3.13(1)	Li−Al	3.32(1)

Bond Angles (deg)

N1−Li−N4	87.8(4)	H1−Al−H4	114(3)
N1−Li−H1	119(2)	H1−Al−H2	97(2)
N1−Li−H2	122(2)	H3−Al−H4	116(4)
N4−Li−H1	128(1)	H3−Al−H2	110(3)
N4−Li−H2	112(1)	H4−Al−H2	104(3)
H1−Li−H2	91(2)	Li−H1−Al	159(3)
H1−Al−H3	114(3)	Li−H2−Al	129(3)

[a] The ′ denotes symmetry operator −*x*, −*y*, −*z*.

Table 7. Selected Structural Parameters for [H$_2$Al{N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], **6**

Bond Distances (Å)

Al1-N1	1.974(3)	Al1-H2	1.51(3)	N4-C3	1.548(4)
Al1-N4	1.961(3)	Al2-H3	1.60(4)	N4-C4	1.523(5)
Al2-N1	1.923(3)	Al2-H4	1.54(4)	C2-C3	1.565(5)
Al2-N4	2.024(3)	N1-C1	1.502(5)		
Al1-H1	1.56(3)	N1-C2	1.493(5)		

Bond Angles (deg)

N1-Al1-N4	77.2(1)	N4-Al1-H2	122(1)
N1-Al2-N4	76.9(1)	N1-Al2-H3	113(1)
H1-Al1-H2	114(1)	N1-Al2-H4	117(1)
H3-Al2-H4	108(1)	N4-Al2-H3	123(1)
N1-Al1-H1	113(1)	N4-Al2-H4	113(1)
N1-Al1-H2	109(1)	Al1-N1-Al2	89.3(1)
N4-Al1-H1	113(1)	Al1-N4-Al2	86.8(1)

Dihedral Angles (deg)

Al1-N1-N4-Al2	125.3(1)

= 3.4 Hz, ^3J(H,H) = 13.7 Hz, 2H; NCH$_2$). ^{13}C NMR (50 MHz, C$_6$D$_6$): δ 28.86, 29.28, 29.77 (Me), 34.71 (*C*Me$_3$), 44.85 (NCH$_2$), 51.73, 52.74 (N*C*Me$_3$), 60.01 (NCH). IR υ (cm^{-1}): 3305 cm^{-1} (m, N−H), 3256 (m, N−H), 1770 (s, Al−H). Anal. Calcd for C$_{28}$H$_{72}$N$_4$Al$_2$Li$_2$: C, 61.05; H, 16.47; N, 10.17. Found: C, 63.68; H, 15.05; N, 11.05.

Synthesis of [H$_2$Al{N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], 6. Cooling the mother liquor from the synthesis of **2** to −30 °C afforded colorless crystals of the *title compound* (0.2 g, 40% yield). Mp: 111 °C, 148 °C dec. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.97, 1.16, 1.41 (s, 3 × 9H; Me), 3.04 (d, ^3J(H,H) = 8.7 Hz, 2H; NCH$_2$), 3.69 (t, ^3J(H,H) = 8.6 Hz, 1H; NCH), 4.41 (br, 4H; AlH). ^{13}C NMR (50 MHz, C$_6$D$_6$): δ 29.05, 29.85, 32.65 (Me), 38.27 (*C*Me$_3$), 45.76 (NCH$_2$), 52.49, 53.63 (N*C*Me$_3$), 62.42 (NCH). IR υ (cm^{-1}): 1845 (s, Al−H). Anal. Calcd for C$_{14}$H$_{34}$N$_2$Al$_2$: C, 59.13; H, 12.05; N, 9.85. Found: C, 59.59; H, 12.58; N, 9.96.

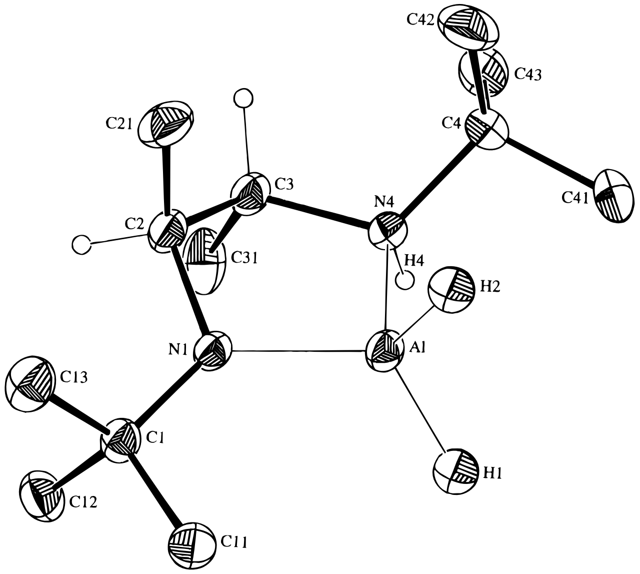

Figure 1. Molecular projection of [{*rac*-HN(*t*-Bu)CH(Me)CH(Me)N(*t*-Bu)}AlH$_2$] **3**, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity methyl hydrogens are omitted. Methine and amine hydrogens are shown as spheres of arbitrary radii. Selected distances (Å) and angles (deg): Al−N1,N4 1.813(3), 2.010(3), Al−H1,H2 1.58(3), 1.54(3); N1−Al−N4 88.4(1), H1−Al−H2 113(1), N1−Al−H1,H2 117(1), 120(1), N4−Al−H1,H2 105(1), 109(1).

Structure Determinations. Crystals of **3** and **4** suitable for X-ray structure determination were grown from hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Crystals of **6** suitable for X-ray structure determination were grown from Et$_2$O solution at −30 °C. Unique diffractometer data sets were measured using Enraf-Nonius CAD4 (**3**) and Rigaku AFC7r (**4** and **6**) diffractometers. Reflections with $I > 2.5\sigma(I)$ (**3** and **4**) or $I > 3.0\sigma(I)$ (**6**) were considered "observed" and used in the full matrix least squares refinements, minimizing $\sum w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on F at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[7] Computation used the XTAL 3.0,[8] teXsan 1.6,[9] and SHELXS-86[10] program systems implemented on Sun SPARCstation 2 and Silicon Graphics Indy computers. Molecular core geometries, atom coordinates and crystal data are given in Tables 1−7, and molecular projections showing numbering schemes are given in Figures 1−3. Averaged structural parameters will be used in the structural comparisons where appropriate and are distinguished by the absence of the least-squares error term from the determined quantity. Anisotropic thermal parameters were refined for all non-hydrogen atoms in all three structure determinations. Methyl hydrogen atoms were calculated and constrained at estimated values (C−H 0.95 Å) and all other hydrogen atoms were located and refined in *x*, *y*, *z* and U_{iso}. Temperature factors for methyl hydrogen atoms were estimated at 1.5U_{ii}(average) (**3** and **4**) and 1.2U_{ii}(average) (**6**) of the attached carbon atom.

Discussion

Synthesis. Reactions of **1**, R = *t*-Bu, R′ = H, and R = R′ = Me (*rac*) are summarized in Scheme 1. All compounds were characterized by NMR spectroscopy and by single-crystal X-ray diffraction studies for **3**, **4**, and **6**. Compound **5**, the thermal degradation product of **4**, and compound **2** have been prepared elsewhere *via* hydroalumination of the amidolithium species

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(7) *International Tables for X-ray Crystallography*; eds. Ibers, J. A., Hamilton, W. C., Ed.; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(8) XTAL User's Manual—Version 3.0. Hall, S. R., Stewart, J. M., Eds.; The Universities of Western Australia and Maryland, 1990.

(9) teXsan—Version 1.6, Crystal Structure Analysis Package. Molecular Structure Corporation, 1992.

(10) SHELXS-86, Program for the Solution of Crystal Structures. University of Göttingen, 1986.

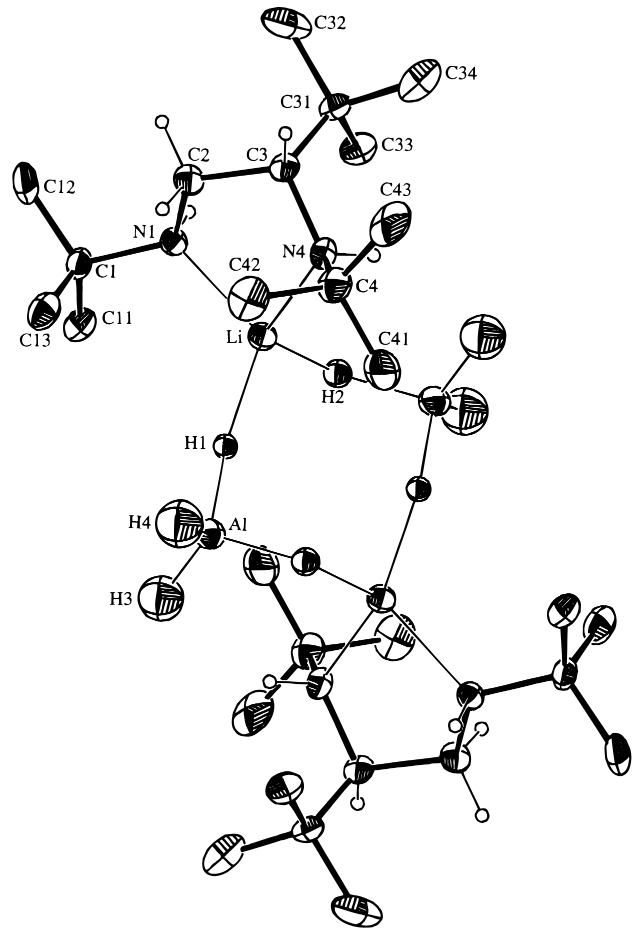

Figure 2. Molecular projection of [{HN(*t*-Bu)CH(*t*-Bu)CH_2N(H)(*t*-Bu)}Li(μ-H)$_2$AlH_2], **4**, showing atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity methyl hydrogens are omitted. Methine, methylene and amine hydrogens are shown as spheres of arbitrary radii. Selected distances (Å) and angles (deg): Li−N1,N4 2.05(1), 2.12(1), Li−H1,H2 1.82(4), 1.89(5), Al−H1,H2′,H3,H4 1.55(4), 1.57(5), 1.51(6), 1.58(7); Li−Al,Al′ 3.32(1), 3.13(1); N1−Li−N4 87.8(4), H1−Li−H2 91(2), Li−H1−Al 159(3), Li−H2′−Al′ 129(3). (The ′ denotes symmetry operator −*x*, −*y*, −*z*).

[*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu)]}$_2$] or the 1,4-diazabut-1-ene HN(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu) using $AlH_3 \cdot NMe_3$.[4]

The need for 2 equiv of $AlH_3 \cdot NMe_3$ to generate **2** and **3** relates to the preference for alane to readily form bis(tertiary amine) adducts.[11] Metalation most likely involves complexation of the least hindered secondary amine with $AlH_3 \cdot NMe_3$ as the primary process, followed by hydrogen extrusion/intramolecular complexation then elimination of trimethylamine. Competitive complexation of unreacted $AlH_3 \cdot NMe_3$ with free trimethylamine would coordinatively saturate the metal center and block complexation with unreacted **1**. However, removal of solvent *in vacuo* followed by addition of fresh solvent results in the formation of the bis(amido)−alane-rich species, **6**, possibly arising from the coordinatively unsaturated monoamine adduct, $AlH_3 \cdot NMe_3$, forming some intimate contact with **2**. Similarly **3** is converted to alane-rich **7**, as established by NMR spectroscopy.[12] Alternatively, the conversion of **2** and **3** into **6** and **7** is achieved by extended reaction times of several days. We have noted that the reaction of the parent amine, **1**, R = R′ = H,[13] with 2 equiv of $AlH_3 \cdot NMe_3$ yields directly the alane rich species. In that instance the diminished steric hindrance facilitates the second metalation by $AlH_3 \cdot NMe_3$ rather than forming the bis(trimethylamine) adduct. Steric hindrance associated with the *C*-alkyl substituents in compounds **2** and **3** is responsible for blocking dimetalation and is also responsible for the stability of these compounds relative to the elimination of hydrogen, which occurs in the solid at 233 and 187 °C respectively. In contrast the compound derived from one equivalent of $AlH_3 \cdot NMe_3$ and **1**, R = R′ = H, [{HN(*t*-Bu)CH_2CH_2N(*t*-Bu)}AlH_2], eliminates hydrogen at room temperature affording a dimeric species, [{[μ-N(*t*-Bu)CH_2CH_2N(*t*-Bu)]AlH}$_2$],[14] which fails to react with $AlH_3 \cdot NMe_3$ to form the alane rich species [H_2Al{N(*t*-Bu)CH(*t*-Bu)CH_2N(*t*-Bu)}AlH_2].

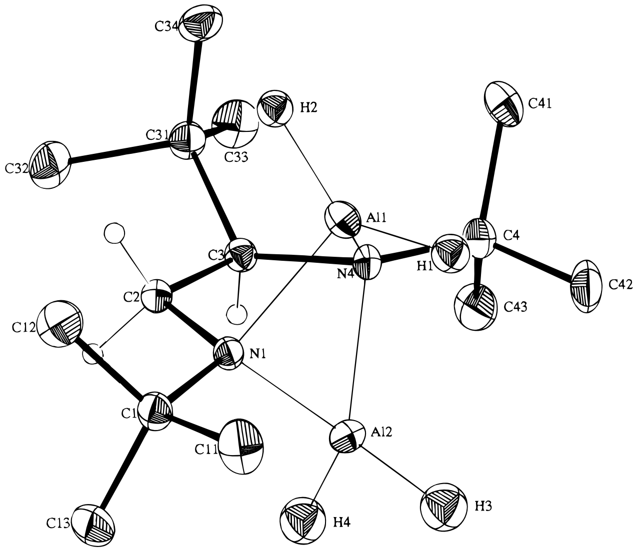

Figure 3. Molecular projection of [H_2Al{N(*t*-Bu)CH(*t*-Bu)CH_2N(*t*-Bu)}AlH_2], **6**, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity methyl hydrogens are omitted. Methine and methylene hydrogens are shown as spheres of arbitrary radii. Selected distances (Å), angles (deg) and dihedral angles (deg): Al1−N1,N4 1.974(3), 1.961(3), Al2−N1,N4 1.923(3), 2.024(3), Al1−H1,H2 1.56(3), 1.51(3), Al2−H3,H4 1.60(4), 1.54(4); N1−Al1,Al2−N4 77.2(1), 76.9(1), H1−Al1−H2 114(1), H3−Al2−H4 108(1), Al1−N1−N4−Al2 125.3(1).

Only 1 equiv of ether-solubilized alane is required to generate **2** and **3**, which is consistent with the weaker donor strength of diethyl ether toward alane. Indeed, the only well-characterized ether adducts are mono- and bis(tetrahydrofuran)alane.[15] Interestingly the use of 2 equiv of ether solubilized alane with **1** results in indiscriminate monometalation of the diamine, yielding *ca.* 30% of **2** and 70% of the product derived from metalation at the other amine center (NMR spectroscopy).[16] We have also noted that the reaction of excess **1**, R = *t*-Bu, R′ = H, with $AlH_3 \cdot NMe_3$ affords a complex mixture of **2** and an undefined species (NMR spectroscopy).

The formation of a stable secondary amine lithium adduct of $LiAlH_4$, **4**, clearly relates to the overall steric congestion at the

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(11) Atwood, J. L.; Bennett, F. R.; Jones, C.; Koutsantonis, G. A.; Raston, C. L.; Robinson, K. D. *J. Chem. Soc., Chem. Commun.* **1992**, 541.

(12) NMR data for **7**: ^{1}H NMR (200 MHz, C_6D_6) δ 1.19 (s, 18H; CMe_3), 1.15 (d, 6H; Me), 3.04 (m, 2H; NCH); ^{13}C NMR (50 MHz, C_6D_6) δ 20.90 (Me), 31.12 (C*Me*$_3$), 52.72, (*C*Me) 57.27(*C*Me$_3$).

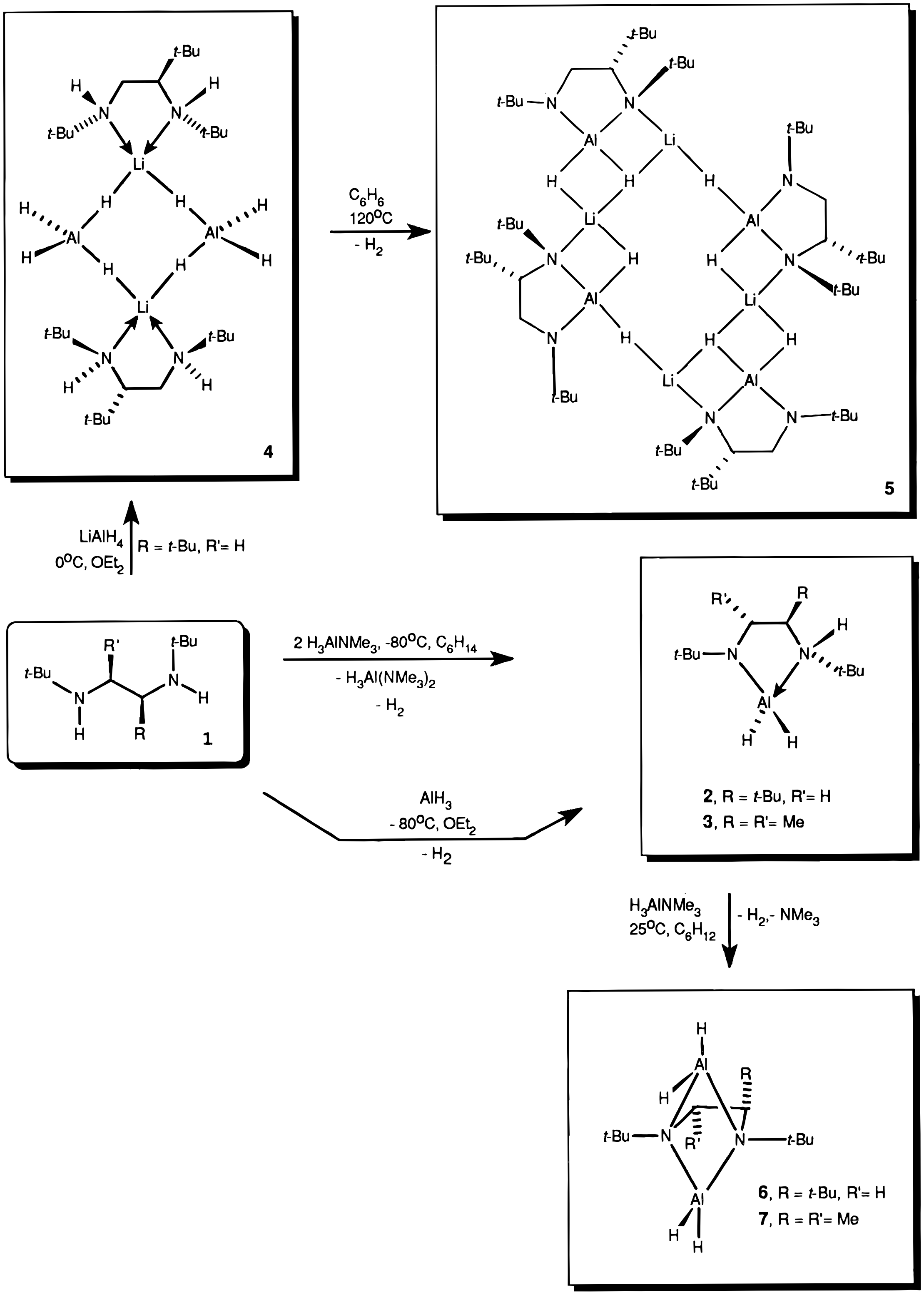
(13) Atwood, J. L.; Lawrence, S. M.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 73.

(14) [{[μ-N(*t*-Bu)CH_2CH_2N(*t*-Bu)]AlH}$_2$] was incorrectly identified in reference (13) as the amidoaluminum hydride species [{HN(*t*-Bu)-CH_2CH_2N(*t*-Bu)}AlH_2].

(15) Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1993**, 189.

(16) NMR data: ^{1}H NMR (200 MHz, C_6D_6) δ 0.89 (s, 9H; Me), 0.98 (s, 9H; Me), 1.36 (s, 9H; Me), 2.35 (b, 1H; NH), 2.48 (t, 1H; NCH), 2.94 (d, 2H; NCH_2); ^{13}C NMR (50 MHz, C_6D_6) δ 27.71, 28.39, 30.32 (Me), 35.02 (*C*Me$_3$), 44.49 (NCH_2), 51.48, 56.99 (N*C*Me$_3$), 63.94 (NCH).

Scheme 1



secondary amine centers and that metalation occurs under rather forcing conditions, albeit without selective mono-metalation of one site of the diamine before the other. The stability of **4** is comparable to that of the alane adduct of a bulky amine, $[AlH_3{\cdot}(H)N\{C(Me)_2CH_2\}_2CH_2]$.[17]

X-ray Structure Commentary

Structure of 3. Complex **3** crystallises as prismatic crystals in the monoclinic space group $P2_1/n$ with four molecules in the unit cell, the asymmetric unit comprising one discrete molecule, Figure 1. The complex is best described as an intramolecularly coordinated secondary amine adduct of an amidoaluminum hydride. The monometalated ethylenediamine acts as a bidentate ligand, chelating the aluminum atom achieving 4-fold coordination for the aluminum atom which has a distorted tetrahedral $N(amine)N(amido)H_2$ coordination environment. The molecule is devoid of symmetry.

Selected geometrical parameters are given in Table 5. The Al−N(amido) and Al−N(amine) distances, 1.813(3) and 2.010-

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(17) Atwood, J. L.; Koutsantonis, G. A.; Lee, F. -C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91.

(3) Å, are typical, as are the Al−H distances of 1.58(3) and 1.54(3) Å. The larger N−Al−H angles to the amido- nitrogen atom (117(1) and 120(1)° vs 105(1) and 109(1)°) reflect the distorted tetrahedral coordination of the metal center, which is tending toward trigonal pyramidal with the datively bound nitrogen donor in the apical position. The molecule exhibits a nearly eclipsed $H1^{\delta-}$−Al−N4−$H4^{\delta+}$ (17(2)°) geometry which is stable toward elimination of molecular hydrogen.[4,13] The ligand bite angle, N1−Al−N4, measures 88.4(1)°. Other bond angles within the molecule are unexceptional and do not require comment.

Structure of 4. Complex **4** crystallizes as prismatic crystals in the orthorhombic space group *Pbca* with four dimers in the unit cell, the asymmetric unit containing half of the dimer, with molecules lying on inversion centers (0, 0, 0), Figure 2. The structure is best described as a solvated lithium tetrahydroaluminate dimer with the diamine chelating the lithium cations, which complement their coordination environment with a μ_2-bridging hydride from each of two $[AlH_4]^-$ units. This results in a cyclic $Li_2Al_2H_4$ membered ring, of the type recently established for the lithium amido-aluminum hydride and lithium alkylaluminum hydride complexes $[\{(Me_3Si)_2NAlH(\mu\text{-}H)_2Li(Et_2O)_2\}_2]$[18] and $[\{(Me_2PhSi)_3CAlH(\mu\text{-}H)_2Li(THF)_2\}_2]$.[19]

Selected geometrical parameters are given in Table 6. The Li−N(amine) distances of 2.05(1) and 2.12(1) Å and the Li−H distances, 1.82(4) and 1.89(5) Å are not atypical, as are the Al−H distances which range from 1.51(6) to 1.58(7) Å and show no difference between terminal and bridging Al−H distances. The lithium atoms are in distorted tetrahedral environments, with the ligand bite angle, N1−Li−N4, of 87.8(4)° and small H1−Li−H2 angle, 91(2)°, being the largest deviations. The dimer exhibits two distinct non-linear Li−H−Al angles of 159(3) and 129(3)° which stems from the puckered chelate ring of the solvated cation. The $Li_2Al_2H_4$ ring is nonplanar, in contrast to other lithium aluminates which have been structurally characterized and is again presumably a consequence of the bidentate Lewis base. Other bond angles within the molecule are unexceptional and do not require comment.

Structure of 6. Complex **6** crystallizes as prismatic crystals in the monoclinic space group $P2_1/c$ with four molecules in the unit cell, the asymmetric unit comprising one discrete molecule of **6**, Figure 3. Compound **6** was shown to be monomeric, exhibiting a butterflied Al_2N_2 ring owing to the perturbing influence of the ethylene bridge which folds the planar four membered ring typically observed in Al_2N_2 rings along the N1-N4 vector.[13] The AlH_2 units form a dibridging structure which attains four fold, distorted tetrahedral $N(amido)_2H_2$ coordination environment for the metal centers, analogous to the unsubstituted aluminum and gallium complexes $[(CH_2\text{-}\mu\text{-}N(t\text{-}Bu))_2(MH_2)_2]$, M =Al and Ga.[13,20] The molecule has no symmetry, broken from noncrystallographic C_2 symmetry only by the carbon centered *t*-Bu substituent.

Selected geometrical parameters are given in Table 7. The Al−N distances cover a broad range, 1.923(3)-2.024(3) Å, which is presumably a consequence of the torsion in the ethylene linkage, N1−C2−C3−N4. The distortion from tetrahedral coordination of the aluminum atoms is most notable by the acute N−Al−N angles, which measure 76.9(1) and 77.2(1)°. The Al−N···N−Al torsion angle measures 125.3(1)°. Other bond angles within the molecule are unexceptional and do not require comment.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council and we thank Colin Kennard and Karl Byriel for collecting some of the X-ray diffraction data.

Supporting Information Available: Tables giving full crystallographic experimental details, non-hydrogen atom thermal parameters, hydrogen atom parameters, bond distances and angles for compounds **3**, **4**, and **6** (11 pages). Ordering information is given on any current masthead page.

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[18] Heine, A.; Stalke, D. *Angew. Chem.* **1992**, *104*, 941; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854.

[19] Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D.; Tavakkoli, K. *Organometallics* **1994**, *13*, 4143.

[20] Henderson, M. J.; Kennard, C. H. L.; Raston, C. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1203.