Hydroalumination of 1,4-Diazabut-1-enes and 4-Lithio-1,4-diazabut-1-enes: Synthesis of Amidoaluminum Hydride, Lithium Aluminum Hydride, and Lithium Diamidoaluminum Hydride Complexes

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Treatment of the dimeric alkyl-substituted (*E*)-4-lithio-1,4-diazabut-1-ene [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu)]}$_2$], **1**, with 2 equiv of AlH$_3$·NMe$_3$ results in hydroalumination yielding a tetrameric lithium diamidoaluminum hydride complex [{Li[N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)]AlH$_2$}$_4$], **4**, which is associated through both mono- and dibridging hydrides forming a complex Li$_4$Al$_2$H$_6$ 12-membered macrocycle. Treatment of the (*E*)-1,4-diazabut-1-ene HN(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu), **2**, with 2 equiv of AlH$_3$·NMe$_3$ in hexane or 1 equiv of AlH$_3$ in Et$_2$O yields the monomeric internally coordinated secondary amine complexed aminoalane [{HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}-AlH$_2$], **5**, which is stable with respect to loss of hydrogen under reflux in benzene. Treatment of **2** with LiAlH$_4$ gives the imine–secondary amine adduct **2**·LiAlH$_4$, **3**, which decomposes by hydrometalation and metalation on heating to 120 °C in benzene to give **4**. Compound **4** is not accessible *via* lithiation of **5** by MeLi in Et$_2$O. Crystals of **4** are triclinic, of space group $P\bar{1}$ (No. 2), with a = 15.664(6) Å, b = 15.723(7) Å, c = 16.408(6) Å, α = 69.65(3)°, β = 84.98(3)°, γ = 84.22(3)°, V = 3763(3) Å^3, and Z = 2. Crystals of **5** are monoclinic, of space group $P2_1/n$ (No. 14), with a = 9.426(9) Å, b = 12.389(1) Å, c = 15.42(1) Å, β = 103.04(4)°, V = 1754(2) Å^3, and Z = 4.

Introduction

We recently reported the synthesis of thermally stable secondary amine adducts of alane, [CH$_2$(CH$_2$CMe$_2$)$_2$NH·AlH$_3$],[1] and aminoalane species, [{HN(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)}AlHCl],[2] as preliminary reports of ongoing investigations of the metalation and hydrometalation of sterically demanding mono- and difunctional secondary amines and α-diimines by AlH$_3$·NMe$_3$ and alkyllithium species.

The reaction of *N,N*′-di-*tert*-butyl-1,4-diazabuta-1,3-diene with various aluminum hydride sources has been found to be dependent on the reagent used. Paramagnetic products based solely on reduction, [{[HCN(*t*-Bu)]$_2$}$_2$Al], or a combination of reduction and hydrometalation, [{[HCN(*t*-Bu)]$_2$}Al{[N(*t*-Bu)-CH$_2$]$_2$}], have been isolated from the reactions involving LiAlH$_4$ and AlH$_3$·NMe$_3$, respectively.[3]

The metalation of bulky secondary amines by LiAlH$_4$ has been investigated by others.[4] In the case of HN(SiMe$_3$)$_2$, two metastable products proposed as intermediates *en route* to the formation of Al{N(SiMe$_3$)$_2$}$_3$ and LiN(SiMe$_3$)$_2$ were isolated and structurally characterized as the lithium amidoaluminum hydride dimer [{(Me$_3$Si)$_2$NAlH(μ-H)$_2$Li·2Et$_2$O}$_2$], **I**, and the monomeric lithium diamidoaluminum hydride complex [{(Me$_3$-Si)$_2$N}$_2$Al(μ-H)$_2$Li·2Et$_2$O], **II**.

I

II
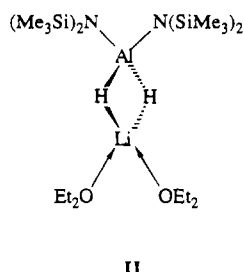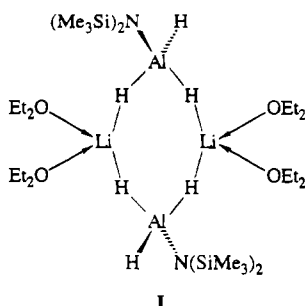
Investigations into the metalation of *N,N*′-di-*tert*-butylethylenediamine by AlH$_3$·NMe$_3$ has been shown[2] to proceed *via* the formation of the metastable secondary-amine-stabilized aminoalane [{HN(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)}AlH$_2$], **III**. Compound **III**

III
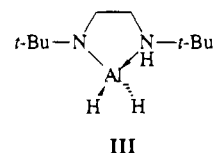
reacts with an additional equiv of AlH$_3$·NMe$_3$ to yield the dibridging aminoalane complex [(CH$_2$-μ-N(*t*-Bu))$_2$(AlH$_2$)$_2$] or a molecule of the diamine to give the triamidoaluminum species [{HN(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)}Al{N(*t*-Bu)CH$_2$}$_2$]. In the absence of excess AlH$_3$·NMe$_3$ or *N,N*′-di-*tert*-butylethylenediamine, **III** eliminates molecular hydrogen to give the dimeric diaminoalane complex [{[μ-N(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)]AlH}$_2$] which is stable toward reaction with either of the reactants, *N,N*′-di-*tert*-butylethylenediamine or AlH$_3$·NMe$_3$.[5] Stable analogues of the intermediate **III** can be made by the replacement of a hydride by a chloride substituent, achieved by using AlH$_2$Cl·NMe$_3$ as the metalating agent.

Herein we report the synthesis of a stabilized analogue of **III**, [{HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)}AlH$_2$], **5**, by hydroalumination of the 1,4-diazabut-1-ene HN(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu), **2**, by AlH$_3$·NMe$_3$. We also report (i) the treatment of the same 1,4-diazabut-1-ene with LiAlH$_4$ yielding the thermally stable imine–secondary amine adduct of LiAlH$_4$, **2**·LiAlH$_4$, **3**,

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(4) Heine, A.; Stalke, D. *Angew. Chem.* **1992**, *104*, 941; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854.
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Table 1. Summary of X-ray Diffraction Data and Overall Refinement Parameters for [{Li[N(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)]-AlH₂}₄], **4**, and [{HN(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)}AlH₂], **5**

	4	5
formula	$C_{56}H_{128}N_8Al_4Li_4$·¹/₂C_6H_6	$C_{14}H_{33}N_2Al$
mol wt	1049.38	256.41
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	15.664(6)	9.426(9)
b, Å	15.723(7)	12.389(1)
c, Å	16.408(6)	15.42(1)
α, deg	69.65(3)	90
β, deg	84.98(3)	103.04(4)
γ, deg	84.22(3)	90
V, Å³	3763(3)	1754(2)
Z	2	4
D(calcd), g cm⁻³	0.960	0.971
F(000), e	1210	576
temp, K	297	297
radiation	Mo Kα (0.710 69 Å, graphite monochromator)	
μ, cm⁻¹	1.04	0.99
2θ limit, deg	50	50
no. of unique rflns	13 223	3098
no. of obsd rflns	4187	1066
[$I > 2.5\sigma(I)$]		
R^a	0.052	0.088
$R_w{}^b$	0.052	0.088
final residual, e Å⁻³	−0.5/0.5	−0.4/0.9
s	1.68	1.81

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

which is relatively stable with respect to formation of the lithium diamidoaluminum hydride complex [{Li[N(*t*-Bu)CH(*t*-Bu)-CH₂N(*t*-Bu)]AlH₂}₄], **4**, *via* hydroalumination and metalation, and (ii) the synthesis of compound **4** by hydroalumination of the latent reactive imine functionality of [*cis*-{Li[μ-N(*t*-Bu)-CH(*t*-Bu)CHN(*t*-Bu)]}₂], **1**, by AlH₃·NMe₃. Mechanistic information has been obtained from these reactions, and the differing reactivities of AlH₃·NMe₃, AlH₃, and LiAlH₄ displayed in their hydrometalation reactions have been rationalized by consideration of the initial complex formed prior to metalation/hydrometalation and the byproducts from the reactions in either case. These findings are of importance in organic synthesis as they relate to the protection of reactive functional groups and the required stoichiometry in aluminum hydride reactions.

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. Solvents were dried and then freeze/thaw degassed prior to use. *N,N′*-Di-*tert*-butyl-3-*tert*-butyl-1,4-diazabut-1-ene, bis(*N,N′*-di-*tert*-butyl-3-*tert*-butyl-4-lithio-1,4-diazabut-1-ene),[6] and AlH₃·NMe₃[7] were prepared according to literature procedures. All other reagents were obtained from Aldrich. ¹H NMR spectra were recorded on Bruker WM-250 and Varian Gemini-200 and Unity-400 spectrometers in deuterated benzene or toluene and referenced to the residual ¹H resonances of the solvent (δ 7.15 and 6.98, respectively). ⁷Li NMR spectra were recorded on a Varian Unity-400 spectrometer in deuterated benzene or toluene and referenced to external LiNO₃ (1 M in D₂O, δ 0.00). ¹³C NMR spectra were recorded in deuterated benzene on Bruker WM-250 and Varian Gemini-200 spectrometers operating at 62.8 and 50 MHz, respectively, using broad-band proton decoupling and were referenced to the ¹³C resonance of the deuterated solvents (δ 128.00). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, and the Chemical and Micro Analytical Services Pty. Ltd., Melbourne. 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

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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 Et₂O-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)CHN(*t*-Bu)}·LiAlH₄, 3. To a stirred solution of **2** (0.53 g, 2.35 mmol) in Et₂O (50 mL) was added an ethereal solution of LiAlH₄ (1.43 mL, 1.64 M, 2.35 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The solution was filtered, concentrated *in vacuo* to *ca.* 20 mL, and slowly cooled to −30 °C, yielding colorless crystals of **3** overnight (0.58 g, 93% yield): mp 121 °C (with gas evolution), 192 °C dec; ¹H NMR (200 MHz, C₆D₆) δ 0.75, 1.06, 1.20 (3 × 9 H, s, Me), 1.50 (1 H, br, N−H), 2.78 (1 H, br, N−CH), 7.31 (1H, br, N=CH); ¹³C NMR (50 MHz, C₆D₆) δ 27.46, 29.07, 29.81 (Me), 35.42 (*C*Me₃), 52.57, 58.27 (N−*C*Me₃), 65.98 (N−CH₂), 165.74 (N=C); IR ν (cm⁻¹) N−H 3315 (m), Al−H 1660−1770 (s). Anal. Calc: C, 63.61; H, 12.96; N, 10.60. Found: C, 62.95; H, 12.39; N, 10.40.

Synthesis of [{Li[N(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)]AlH₂}₄], 4. To a stirred solution of **1** (0.44 g, 0.95 mmol) in Et₂O (20 mL) was added an Et₂O (5 mL) solution of AlH₃·NMe₃ (0.17 g, 1.90 mmol) dropwise over 10 min at −50 °C. The pale yellow solution was allowed to warm to room temperature, giving a colorless solution which was stirred for 1 h. The solution was then filtered, and volatiles were removed *in vacuo* to yield a paste which crystallized overnight. Benzene (5 mL) was added, and the solution was filtered and concentrated to *ca.* 1 mL, yielding colorless prisms of **4** after several days. Subsequent cropping of the crystals yielded further product with difficulty (0.34 g, 69% yield): mp 115 °C dec; ¹H NMR (200 MHz, C₆D₆) δ 1.12, 1.31, 1.36 (3 × 9 H, s, Me), 2.79 (1 H, t ³J_{H-H} = 3.3 Hz, N−CH), 3.12 (2 H, d ³J_{H-H} = 3.3 Hz, N−CH₂), 3.8−4.8 (2 H, b, Al−H); ¹³C NMR (50 MHz, C₆D₆) δ 30.0, 31.0, 32.4 (Me), 36.7 (*C*Me₃), 47.7 (N−CH₂), 51.3, 53.5 (N−*C*Me₃), 65.8 (N−CH); ⁷Li NMR (155.5 MHz, C₆D₆) δ 0.99; IR ν (cm⁻¹) Al−H 1735 (s), 1676 (s), 1597 (s). Anal. Calc: C, 64.10; H, 12.29; N, 10.68. Found: C, 63.91; H, 12.39; N, 10.76.

Synthesis of [{HN(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)}AlH₂], 5. Method a. To a stirred solution of AlH₃·NMe₃ (0.42 g, 4.73 mmol) in hexane (40 mL) was added a solution of **2** (0.53 g, 2.35 mmol) in hexane (15 mL) dropwise at 0 °C. Evolution of gas was observed, and the solution was stirred at 0 °C for 1.5 h and then allowed to warm to room temperature, giving a pale yellow solution which was left to stir overnight. The solution was filtered, concentrated *in vacuo*, and cooled to −30 °C, whereupon colorless crystals of **5** deposited overnight. Subsequent cropping of the crystals yielded further product (0.47 g, 78% yield): mp 145 °C, 233 °C dec; ¹H NMR (200 MHz, C₆D₆) δ 0.89, 1.02, 1.41 (3 × 9 H, s, Me), 2.21 (1 H, b, N−H), 2.53 (1 H, t ³J_{H-H} = 3.7 Hz, N−CH), 3.00 (2 H, d ³J_{H-H} = 3.7 Hz, N−CH₂), 4.8 (2 H, b, Al−H); ¹³C NMR (50 MHz, C₆D₆) δ 27.6, 28.4, 30.0 (Me), 34.9 (*C*Me₃), 44.8 (N−CH₂), 51.5, 56.3 (N−*C*Me₃), 64.9 (N−CH); IR ν (cm⁻¹) N−H 3196 (w), Al−H 1780 (s). Anal. Calc: C, 65.58; H, 12.97; N, 10.93. Found: C, 65.38; H, 13.97; N, 12.12.

Method b. To an ethereal solution of LiAlH₄ (3.85 mL, 1.64 M, 6.31 mmol) in Et₂O (40 mL) was added an ethereal solution of HCl (9.14 mL, 0.699 M, 6.31 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and then warmed to room temperature. The ethereal soltuion of AlH₃ was filtered from the LiCl precipitate. To the ethereal solution of AlH₃ was added an Et₂O (20 mL) solution of **2** (0.71 g, 3.14 mmol) slowly at 0 °C. The reaction mixture was warmed to room temperature and was stirred overnight. The solution was filtered, concentrated *in vacuo*, and cooled to −30 °C, whereupon colorless crystals of **5** deposited overnight (0.46 g, 57% yield).

Synthesis of HN(*t*-Bu)CH(*t*-Bu)CH₂N(H)(*t*-Bu), 6. To a solution of AlH₃·NMe₃ (1.84 g, 21 mmol) in hexane (100 mL) was added a solution of **2** (2.34 g, 10 mmol) in hexane (15 mL) at 0 °C. The solution was allowed to stir at 0 °C for 1 h, warmed to room temperature, and stirred overnight. The reaction mixture was quenched with excess water (120 mL) at 0 °C. The product was extracted with hexane (3 × 30

Table 2. Non-Hydrogen Atom (and Refined Hydrogen Atom) Coordinates and Isotropic Thermal Parameters for [{Li[N(*t*-Bu)CH(*t*-Bu)-CH$_2$N(*t*-Bu)]AlH$_2$}$_4$], **4**

atom	x/a	y/b	z/c	U, Å²	atom	x/a	y/b	z/c	U, Å2
Al1	0.1126(1)	0.1096(1)	0.6920(1)	0.0561(9)^a	C61	0.5290(5)	0.2680(5)	0.5334(5)	0.070(3)^a
Al2	0.3292(1)	0.2968(1)	0.6603(1)	0.0507(8)^a	C62	0.5976(5)	0.2025(5)	0.5906(5)	0.095(4)^a
Al3	0.4633(1)	−0.0253(1)	0.7944(1)	0.065(1)^a	C63	0.4649(5)	0.2123(5)	0.5133(5)	0.080(4)^a
Al4	−0.0064(1)	0.3380(1)	0.8367(1)	0.063(1)^a	C64	0.5782(5)	0.3224(5)	0.4478(5)	0.093(4)^a
Li1	0.0002(8)	0.2041(8)	0.7655(8)	0.081(6)^a	C81	0.1789(5)	0.3868(5)	0.5335(5)	0.092(4)^a
Li2	0.4454(8)	0.1545(8)	0.7099(8)	0.080(6)^a	C82	0.2772(6)	0.4056(7)	0.4033(5)	0.121(5)^a
Li3	0.2978(8)	0.007(1)	0.7577(8)	0.097(7)^a	C83	0.2607(6)	0.5222(6)	0.4754(6)	0.119(5)^a
Li4	0.1491(8)	0.347(1)	0.7511(8)	0.091(7)^a	C91	0.4067(6)	−0.1084(6)	1.0079(5)	0.124(5)^a
N1	−0.0048(3)	0.0950(3)	0.7291(3)	0.058(2)^a	C92	0.3140(6)	0.0276(5)	0.9233(5)	0.097(4)^a
N4	0.0990(3)	0.1103(4)	0.5843(3)	0.061(3)^a	C93	0.2553(6)	−0.1236(6)	0.9806(6)	0.122(5)^a
N5	0.4492(3)	0.2916(3)	0.6695(3)	0.053(2)^a	C101	0.3409(5)	−0.2062(5)	0.7903(6)	0.086(4)^a
N8	0.3320(3)	0.3699(3)	0.5486(3)	0.057(2)^a	C102	0.2427(6)	−0.1886(6)	0.8016(6)	0.121(6)^a
N9	0.3664(3)	−0.0846(3)	0.8556(3)	0.063(3)^a	C103	0.3695(6)	−0.1530(6)	0.6970(6)	0.105(5)^a
N12	0.5293(4)	−0.1253(4)	0.7996(4)	0.070(3)^a	C104	0.3597(6)	−0.3083(6)	0.8062(6)	0.122(5)^a
N13	0.0955(3)	0.3785(3)	0.8568(3)	0.058(2)^a	C121	0.6381(7)	−0.2130(8)	0.7371(9)	0.193(9)^a
N16	−0.0757(3)	0.4279(4)	0.8523(3)	0.062(3)^a	C122	0.6702(7)	−0.171(1)	0.8605(9)	0.219(9)^a
C1	−0.0265(5)	0.0112(5)	0.8025(5)	0.081(4)^a	C123	0.6517(5)	−0.0508(7)	0.7176(7)	0.136(6)^a
C2	−0.0514(4)	0.1096(4)	0.6480(5)	0.061(3)^a	C131	0.2298(5)	0.3619(6)	0.9374(5)	0.092(4)^a
C3	0.0112(4)	0.0874(4)	0.5790(4)	0.065(3)^a	C132	0.1682(5)	0.2280(5)	0.9264(5)	0.086(4)^a
C4	0.1605(5)	0.1025(6)	0.5144(5)	0.077(4)^a	C133	0.0919(5)	0.3093(5)	1.0201(5)	0.095(4)^a
C5	0.4818(4)	0.3232(5)	0.7361(4)	0.066(3)^a	C141	0.0940(6)	0.5496(5)	0.7663(6)	0.090(4)^a
C6	0.4859(4)	0.3368(4)	0.5783(4)	0.060(3)^a	C142	0.0752(6)	0.6448(5)	0.7753(6)	0.119(5)^a
C7	0.4183(4)	0.4026(4)	0.5226(4)	0.064(3)^a	C143	0.0466(6)	0.5486(6)	0.6903(5)	0.116(5)^a
C8	0.2647(5)	0.4211(5)	0.4911(5)	0.072(4)^a	C144	0.1920(6)	0.5391(6)	0.7439(6)	0.122(5)^a
C9	0.3362(5)	−0.0738(5)	0.9420(5)	0.082(4)^a	C161	−0.2047(5)	0.5366(6)	0.8292(5)	0.099(5)^a
C10	0.3873(5)	−0.1813(5)	0.8597(5)	0.074(4)^a	C162	−0.1939(5)	0.4032(6)	0.9666(5)	0.112(5)^a
C11	0.4854(5)	−0.2040(5)	0.8558(5)	0.079(4)^a	C163	−0.2075(5)	0.3812(6)	0.8252(6)	0.115(5)^a
C12	0.6209(5)	−0.1400(6)	0.7798(6)	0.106(5)^a	C211	−0.1223(5)	0.0126(6)	0.8334(5)	0.111(5)^a
C13	0.1451(5)	0.3220(5)	0.9338(4)	0.067(3)^a	C212	−0.0021(6)	−0.0761(5)	0.7818(6)	0.103(4)^a
C14	0.0697(4)	0.4735(4)	0.8550(4)	0.064(3)^a	C213	0.0239(6)	0.0087(5)	0.8797(5)	0.100(4)^a
C15	−0.0257(5)	0.4845(5)	0.8811(5)	0.074(4)^a	C1s	0.539(1)	0.494(1)	0.9265(7)	0.154(8)^a
C16	−0.1679(5)	0.4374(5)	0.8690(5)	0.071(4)^a	C2s	0.4647(9)	0.4523(9)	0.960(1)	0.140(8)^a
C21	−0.0984(4)	0.2059(5)	0.6101(5)	0.068(4)^a	C3s	0.5738(6)	0.5406(8)	0.969(1)	0.123(6)^a
C22	−0.1552(5)	0.2072(6)	0.5368(5)	0.094(4)^a	H1	0.182(3)	0.036(3)	0.743(3)	0.07(2)
C23	−0.1615(5)	0.2254(5)	0.6807(5)	0.089(4)^a	H2	0.123(3)	0.195(4)	0.715(3)	0.08(2)
C24	−0.0383(5)	0.2820(5)	0.5727(5)	0.078(4)^a	H3	0.017(3)	0.327(3)	0.743(3)	0.07(2)
C41	0.1678(5)	0.0077(7)	0.5097(7)	0.131(6)^a	H4	−0.027(3)	0.242(3)	0.873(3)	0.06(2)
C42	0.2487(4)	0.1220(5)	0.5337(5)	0.083(4)^a	H5	0.264(3)	0.335(3)	0.719(3)	0.05(1)
C43	0.1357(6)	0.1727(8)	0.4260(6)	0.137(6)^a	H6	0.316(3)	0.193(3)	0.691(3)	0.04(1)
C51	0.4385(5)	0.2689(5)	0.8244(4)	0.076(4)^a	H7	0.494(3)	0.059(3)	0.812(3)	0.07(2)
C52	0.5782(5)	0.3042(6)	0.7456(5)	0.099(4)^a	H8	0.418(3)	0.041(3)	0.703(3)	0.06(2)
C53	0.4569(6)	0.4251(5)	0.7175(5)	0.096(4)^a					

^{a} Isotropic equiv thermal parameters.

mL), the extract was dried over Na$_2$SO$_4$, and the volatiles were removed *in vacuo*. **6** distilled as a colorless liquid at 60 °C at 1 mmHg (1.41 g, 62% yield): ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 0.92, 1.06, 1.10 (3 × 9 H, s, Me), 1.35 (2 H, br, N—H), 2.27 (1 H, dd $^3J_{H-H}$ = 2.4 Hz $^3J_{H-H}$ = 6.0 Hz, N—CH), 2.51 (1 H, dd $^3J_{H-H}$ = 2.4 Hz, $^2J_{H-H}$ = 11.7 Hz, N—CH$_2$), 2.72 (1 H, dd $^3J_{H-H}$ = 6.0 Hz, $^2J_{H-H}$ = 11.7 Hz, N—CH$_2$); ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 27.81, 29.20, 30.47 (Me), 35.18 (*C*Me$_3$), 46.41 (N—CH$_2$), 50.16, 50.65 (N—*C*Me$_3$), 60.68 (N—CH); IR ν (cm^{-1}) N—H 3335 (w).

Structure Determinations. Crystals of **4** and **5** suitable for X-ray structure determination were grown from benzene and hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Unique diffractometer data sets were measured using an Enraf-Nonius CAD4 diffractometer. Reflections with I > 2.5σ(I) were considered "observed" and used in the full-matrix least-squares refinements, minimizing $\Sigma w\Delta^2$ 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.[8] Computation used the XTAL 3.0 program system[9] implemented on a Sun SPARCstation 2 computer. Molecular core geometries, atom coordinates, and crystal

(8) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(9) *XTAL User's Manual*, Version 3.0; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1990.

data are given in Tables 1—5, and molecular projections showing numbering schemes are given in Figures 1 and 2. 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 both structure determinations. Methine, methylene, and amine hydrogen atoms were located and refined in (x, y, z, U_{iso}) for **5**, as were the hydrides in **4** and **5**. Methine and methylene hydrogen atoms were located and positionally constrained with fixed temperature factors for **4**. All other hydrogen atoms for **4** and **5** were calculated and constrained at estimated values (C-H 1.0 Å). Temperature factors for methyl hydrogen atoms were estimated at 1.5U_{ii}(average) of the attached carbon atom and 1.25U_{ii}(average) for other hydrogen atoms.

Discussion

Synthesis and Characterization. The lithium diaminoalane and aminoalane complexes **4** and **5** were prepared *via* hydroalumination of the imine functionalities of **1** and **2** by AlH$_3$·NMe$_3$, respectively, as outlined in Scheme 1. Both complexes were isolated in high yield as air- and moisture-sensitive colorless crystalline solids. Hydrolysis of **5** yields the substituted ethylenediamine **6** in high yield as a colorless distillable liquid.

The facile hydroalumination of **2** and **1** by AlH$_3$·NMe$_3$ contrasts to the lack of carbolithiation of **2** by excess MeLi under

Table 3. Non-Hydrogen Atom (and Refined Hydrogen Atom) Coordinates and Isotropic Thermal Parameters for [{HN(*t*-Bu)-CH(*t*-Bu)CH₂N(*t*-Bu)}AlH₂], **5**

atom	x/a	y/b	z/c	U, Å²
Al	0.5661(3)	0.0061(3)	0.6641(2)	0.069(1)ᵃ
N1	0.5111(8)	0.1049(7)	0.7356(5)	0.063(3)ᵃ
N4	0.675(1)	0.1203(6)	0.6121(6)	0.065(4)ᵃ
C1	0.458(1)	0.084(1)	0.8122(8)	0.096(6)ᵃ
C2	0.586(1)	0.208(1)	0.7328(7)	0.071(5)ᵃ
C3	0.621(1)	0.2263(8)	0.6409(8)	0.067(5)ᵃ
C4	0.837(1)	0.1075(9)	0.6270(8)	0.077(5)ᵃ
C11	0.373(2)	−0.021(1)	0.7961(9)	0.139(8)ᵃ
C12	0.341(2)	0.170(2)	0.821(1)	0.19(1)ᵃ
C13	0.568(2)	0.085(2)	0.8956(8)	0.21(1)ᵃ
C31	0.503(1)	0.2809(8)	0.5677(7)	0.072(5)ᵃ
C32	0.475(1)	0.392(1)	0.6025(8)	0.102(6)ᵃ
C33	0.364(1)	0.217(1)	0.5465(9)	0.110(6)ᵃ
C34	0.563(2)	0.3002(9)	0.4845(8)	0.118(7)ᵃ
C41	0.864(1)	−0.005(1)	0.5913(8)	0.105(6)ᵃ
C42	0.909(1)	0.117(1)	0.7232(8)	0.095(5)ᵃ
C43	0.897(1)	0.191(1)	0.5706(9)	0.115(7)ᵃ
H1	0.450(8)	−0.039(6)	0.583(5)	0.06(2)ᵃ
H2	0.692(8)	-0.079(6)	0.713(4)	0.06(2)ᵃ
H2a	0.52(1)	0.27(1)	0.736(7)	0.13(5)ᵃ
H2b	0.69(1)	0.200(7)	0.778(6)	0.08(3)ᵃ
H3	0.696(9)	0.264(7)	0.659(5)	0.05(3)ᵃ
H4	0.639(8)	0.127(7)	0.552(5)	0.06(3)ᵃ

ᵃ Isotropic equiv thermal parameters.

forcing conditions.[6] Rather, the secondary amine of **2** is lithiated preferentially and the imine functionality of **1** fails to add MeLi to give the dilithio species.

Complex **5** is obtained from the reaction of **2** with AlH₃•NMe₃ or AlH₃ in a 1:1 stoichiometric ratio or either a 2-fold excess or deficiency of the hydride source. This indicates the stability of **5** with respect to loss of hydrogen to form a diaminoalane complex and stability with respect to reaction of **5** with both **2** and AlH₃•NMe₃ or AlH₃. Isolated samples of **5** show no trace of decomposition *via* metalation of the remaining acidic amine proton even under reflux in benzene. This contrasts[2] with the behavior of the less substituted analogue of **5**, **III**, which is stable only at low temperatures, eliminating hydrogen at ambient temperatures to form the diaminoalane complex [{[μ-N(*t*-Bu)-CH₂CH₂N(*t*-Bu)]AlH}₂][5] and reacting with *N*,*N*′-di-*tert*-butyl-ethylenediamine and AlH₃•NMe₃ to give triamidoaluminum and dibridging aminoalane species, [{HN(*t*-Bu)CH₂CH₂N(*t*-Bu)}-Al{N(*t*-Bu)CH₂}₂] and [(CH₂-μ-N(*t*-Bu))₂(AlH₂)₂], respectively.

Complex **5** contains two chiral centers, but only one of the two possible diastereoisomers is present in solution. Presumably the carbon-centered *t*-Bu substituent is stereodirecting, dictating the configuration of the N(amine)-*t*-Bu substituent to be *trans* to the *t*-Bu substituent attached to the carbon atom. This configuration is also present in the solid state structures of complexes **1**[6] and **4**.

The imine−secondary amine adduct of LiAlH₄, **3**, was prepared according to Scheme 1. The complex can be isolated in high yield as an air- and moisture-sensitive colorless crystalline solid. Crystals of **3** obtained from Et₂O were sensitive to loss of solvent, and attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful. The compound is stable with respect to hydroalumination and metalation in the solid state and in solution at room temperature. The chemical reactivity displayed by **3** suggests that the imine and amine nitrogen centers are bound to the lithium centers in chelating fashion. Coordination of these nitrogen atoms to the aluminum center is unlikely, given the coordination saturation of the aluminum center by the four hyrides, although coordination numbers of up to 6 have been reported for a form of

polymeric AlH₃.[10] In the event of aluminum coordination, facile hydroalumination and/or metalation is likely, giving rise to amido species. A dimeric structure containing a Li₂Al₂H₄ ring containing the two [AlH₄]⁻ units bridging the lithium centers, **IV**, is the most likely structure for **3**. This structural type has been established for (a) the bis(secondary amine) adduct of LiAlH₄[11] [{Li[HN(*t*-Bu)CH(*t*-Bu)CH₂N(H)*t*-Bu]AlH₄}₂], (b) the amidoaluminum complex **I**,[4] and (c) the alkylaluminum species [{(Me₂PhSi)₃CAlH(μ-H)₂Li•2THF}₂][12] recently reported by Eaborn *et al.* The alternative monomeric structure for **3**, **V**, cannot be ruled out at this stage, given that this coordination mode has been established for lithium aluminum hydride species, e.g., **II**.[4] In addition, higher oligomers are possible for **3**.

IV   **V**
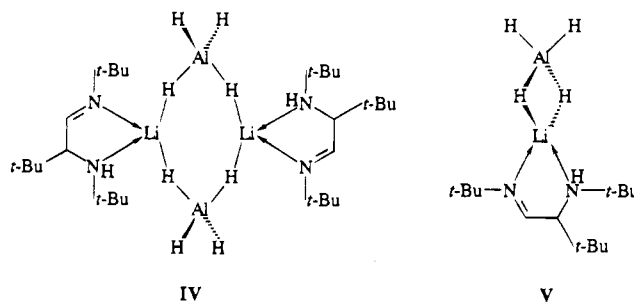
Complex **3** is converted to the lithium diamidoaluminum hydride complex **4** under reflux in benzene with some selectivity for metalation of the secondary amine prior to hydrometalation of the imine functionality. The mechanism for hydrometalation reactions of carbonyls and imines is generally believed to involve the initial coordination of the metal to the heteroatom followed by hydride transfer to the carbon atom *via* a cyclic four-membered, or similar, transition state.[13] Rationalization of the selectivity shown for LiAlH₄ metalating the secondary amine in preference to adding to the imine functionality of **2** follows from the proposed structures for **3**, **IV**, **V**, and higher oligomers. Coordination of the imine nitrogen of **2** to the lithium atom prevents coordination to the aluminum center, effectively blocking the reaction pathway for hydroalumination. Hydrolithiation of the imine is not observed; instead the acidity of the amine proton is enhanced by the coordination of the secondary amine to the lithium center, and metalation to give the metastable imine-functionalized lithium amidoaluminum hydride complex {Li[N(*t*-Bu)CH(*t*-Bu)CHN(*t*-Bu)]AlH₃}ₙ is the preferred process. A direct amidoaluminum bond for this complex increases the likelihood that the species adopts a structure with the aluminum center being chelated by the ligand, expelling the lithium atom from that position it held in **3**. This complex, exhibiting an aluminum−imine dative bond, would then undergo facile intramolecular hydroalumination to give the observed lithium diamidoaluminum hydride complex **4**.

Complex **4** was not accessible *via* lithiation of **5** by MeLi in Et₂O, the reaction giving a product tentatively formulated on the basis of IR and NMR spectroscopic data as {Li[N(*t*-Bu)-CH(*t*-Bu)CH₂N(*t*-Bu)]AlHMe}₂, formed by the elimination of H₂ from the reactants.

The hydroalumination of **2** by AlH₃•NMe₃ to yield the internally coordinated aminoalane complex **5** has mechanistic

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(13) (a) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560. (b) Coxon, J. M.; Luibrand, R. T. *Tetrahedron. Lett.* **1993**, *34*, 7093, 7097.

Table 4. Selected Structural Parameters for [{Li[N(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)]AlH$_2$}$_4$], **4**

		Bond Distances (Å)					
Al1−N1	1.896(5)	Al3−H8	1.67(4)	Li3−H1	1.84(5)	N8−C8	1.457(8)
Al1−N4	1.795(6)	Al4−H3	1.62(6)	Li3−H8	2.05(5)	N9−C9	1.52(1)
Al2−N5	1.891(5)	Al4−H4	1.48(5)	Li4−H3	2.14(5)	N9−C10	1.502(9)
Al2−N8	1.792(5)	Li1−N1	2.01(2)	Li4−H5	1.85(5)	C10−C11	1.54(1)
Al3−N9	1.884(5)	Li2−N5	2.03(1)	N1−C1	1.490(8)	N12−C11	1.457(8)
Al3−N12	1.772(6)	Li3−N9	2.05(1)	N1−C2	1.510(9)	N12−C12	1.46(1)
Al4−N13	1.871(6)	Li4−N13	2.05(2)	C2−C3	1.54(1)	N13−C13	1.497(8)
Al4−N16	1.771(6)	Li1−H2	2.03(5)	N4−C3	1.473(9)	N13−C14	1.498(9)
Al1−H1	1.56(4)	Li1−H3	1.88(6)	N4−C4	1.46(1)	C14−C15	1.53(1)
Al1−H2	1.55(6)	Li1−H4	2.05(6)	N5−C5	1.49(1)	N16−C15	1.46(1)
Al2−H5	1.56(5)	Li2−H6	2.07(4)	N5−C6	1.505(7)	N16−C16	1.448(9)
Al2−H6	1.56(4)	Li2−H7	1.97(4)	C6−C7	1.523(8)		
Al3−H7	1.57(6)	Li2−H8	1.92(6)	N8−C7	1.470(8)		

		Contact Distances (Å)					
Al1−Li1	2.67(1)	Al2−Li2	2.67(1)	Al3−Li2	2.68(1)	Al4−Li1	2.73(2)
Al1−Li3	3.25(2)	Al2−Li4	3.23(1)	Al3−Li3	2.67(1)	Al4−Li4	2.69(1)

		Bond Angles (deg)			
N1−Al1−N4	94.5(3)	Al2−H5−Li4	143(3)	Al2−N5−C5	118.7(4)
N1−Al1−H1	119(2)	Li1−H3−Li4	112(2)	Al2−N5−C6	105.6(4)
N1−Al1−H2	98(2)	Li2−H8−Li3	112(3)	Li2−N5−C5	112.8(5)
N4−Al1−H1	114(2)	N1−Li1−H2	80(2)	Li2−N5−C6	116.5(6)
N4−Al1−H2	125(2)	N1−Li1−H3	153(2)	C5−N5−C6	114.3(5)
H1−Al1−H2	106(3)	N1−Li1−H4	139(1)	N5−C6−C7	110.6(5)
N5−Al2−N8	94.4(2)	N5−Li2−H6	80(1)	N8−C7−C6	111.2(5)
N5−Al2−H5	122(2)	N5−Li2−H7	130(2)	Al2−N8−C7	109.4(4)
N5−Al2−H6	100(1)	N5−Li2−H8	156(2)	Al2−N8−C8	132.5(4)
N8−Al2−H5	113(1)	N9−Li3−H1	133(1)	C7−N8−C8	115.3(4)
N8−Al2−H6	124(2)	N9−Li3−H8	83(1)	Al3−N9−Li3	85.5(4)
H5−Al2−H6	105(2)	N13−Li4−H3	80(2)	Al3−N9−C9	118.7(5)
N9−Al3−N12	96.4(3)	N13−Li4−H5	128(2)	Al3−N9−C10	103.4(4)
N9−Al3−H7	121(2)	H2−Li1−H3	85(2)	Li3−N9−C9	110.0(6)
N9−Al3−H8	99(2)	H2−Li1−H4	121(2)	Li3−N9−C10	121.6(7)
N12−Al3−H7	125(2)	H3−Li1−H4	68(2)	C9−N9−C10	114.6(5)
N12−Al3−H8	122(2)	H6−Li2−H7	126(2)	N9−C10−C11	110.9(6)
H7−Al3−H8	92(3)	H6−Li2−H8	85(2)	N12−C11−C10	110.8(5)
N13−Al4−N16	96.4(3)	H7−Li2−H8	74(2)	Al3−N12−C11	108.8(4)
N13−Al4−H3	101(2)	H1−Li3−H8	144(2)	Al3−N12−C12	131.8(5)
N13−Al4−H4	123(2)	H3−Li4−H5	151(2)	C11−N12−C12	116.9(6)
N16−Al4−H3	124(2)	Al1−N1−Li1	86.0(4)	Al4−N13−Li4	86.6(5)
N16−Al4−H4	123(2)	Al1−N1−C1	118.0(4)	Al4−N13−C13	119.4(4)
H3−Al4−H4	90(3)	Al1−N1−C2	105.9(4)	Al4−N13−C14	103.6(4)
Al1−H2−Li1	95(3)	Li1−N1−C1	113.6(6)	Li4−N13−C13	107.5(5)
Al4−H3−Li1	103(2)	Li1−N1−C2	116.9(5)	Li4−N13−C14	123.8(5)
Al4−H4−Li1	100(2)	C1−N1−C2	113.6(6)	C13−N13−C14	113.8(6)
Al2−H6−Li2	94(2)	N1−C2−C3	109.8(5)	N13−C14−C15	111.2(6)
Al3−H7−Li2	98(3)	N4−C3−C2	111.5(6)	N16−C15−C14	111.2(6)
Al3−H8−Li2	96(3)	Al1−N4−C3	109.5(4)	Al4−N16−C15	108.6(4)
Al3−H8−Li3	91(2)	Al1−N4−C4	132.4(5)	Al4−N16−C16	132.0(5)
Al1−H1−Li3	145(3)	C3−N4−C4	115.3(6)	C15−N16−C16	115.8(6)
Al4−H3−Li4	90(3)	Al2−N5−Li2	86.0(4)		

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

	Bond Distances (Å)		
Al−N1	1.799(9)	N1−C2	1.47(2)
Al−N4	2.02(1)	C2−C3	1.54(2)
Al−H1	1.57(6)	N4−C3	1.51(1)
Al−H2	1.63(7)	N4−C4	1.50(1)
N1−C1	1.41(2)		

|	Bond Angles (deg)		
N1−Al−N4	90.6(4)	Al−N1−C2	111.7(7)
N1−Al−H1	119(3)	C1−N1−C2	116.8(9)
N1−Al−H2	116(2)	N1−C2−C3	110.9(9)
N4−Al−H1	105(3)	N4−C3−C2	107.6(9)
N4−Al−H2	105(3)	Al−N4−C3	104.9(7)
H1−Al−H2	116(3)	Al−N4−C4	117.2(6)
Al−N1−C1	126.4(8)	C3−N4−C4	116.4(8)

implications, Scheme 2. On the basis of steric hindrance and donor strength arguments of the sp^2 and sp^3 hybridized nitrogen donors of **2**, the primary process in the reaction is almost certainly coordination of AlH$_3$·NMe$_3$ by the imine functionality

of **2** to give the 5-coordinate trigonal bipyramidal bis(nitrogen donor) adduct of AlH$_3$, **VI**. Loss of NMe$_3$ from this intermediate to give 5-coordinate chelated bis(nitrogen donor) adducts of AlH$_3$, **VIII** and **IX**, is unlikely. *Ab initio* molecular orbital calculations on AlH$_3$·2NH$_3$ species have revealed minima only for trigonal bipyramidal coordinated aluminum centers with the nitrogen donors in apical positions; starting geometries having one or both amine donors in equatorial coordination sites lead to fragmentation, giving AlH$_3$·NH$_3$ and NH$_3$.[14] Ligand bite angle constraints in **VIII** and **IX**, N−Al−N *ca.* 90−95°, necessitate the nitrogen donors to occupy equatorial and apical positions, shown to be unstable by theoretical molecular orbital calculations. Hydrometalation and loss of NMe$_3$ may be a concerted process for the intermediate **VI**; alternatively the reaction pathway to **5** may proceed *via* the four-coordinate tertiary-amine-coordinated aminoalane **VII** (*cf.* structurally authenticated [{CH$_2$(CH$_2$CMe$_2$)$_2$N}AlH$_2$·NMe$_3$]^1), which can

(14) Gardiner, M. G.; Raston, C. L. Unpublished theoretical molecular orbital calculations.
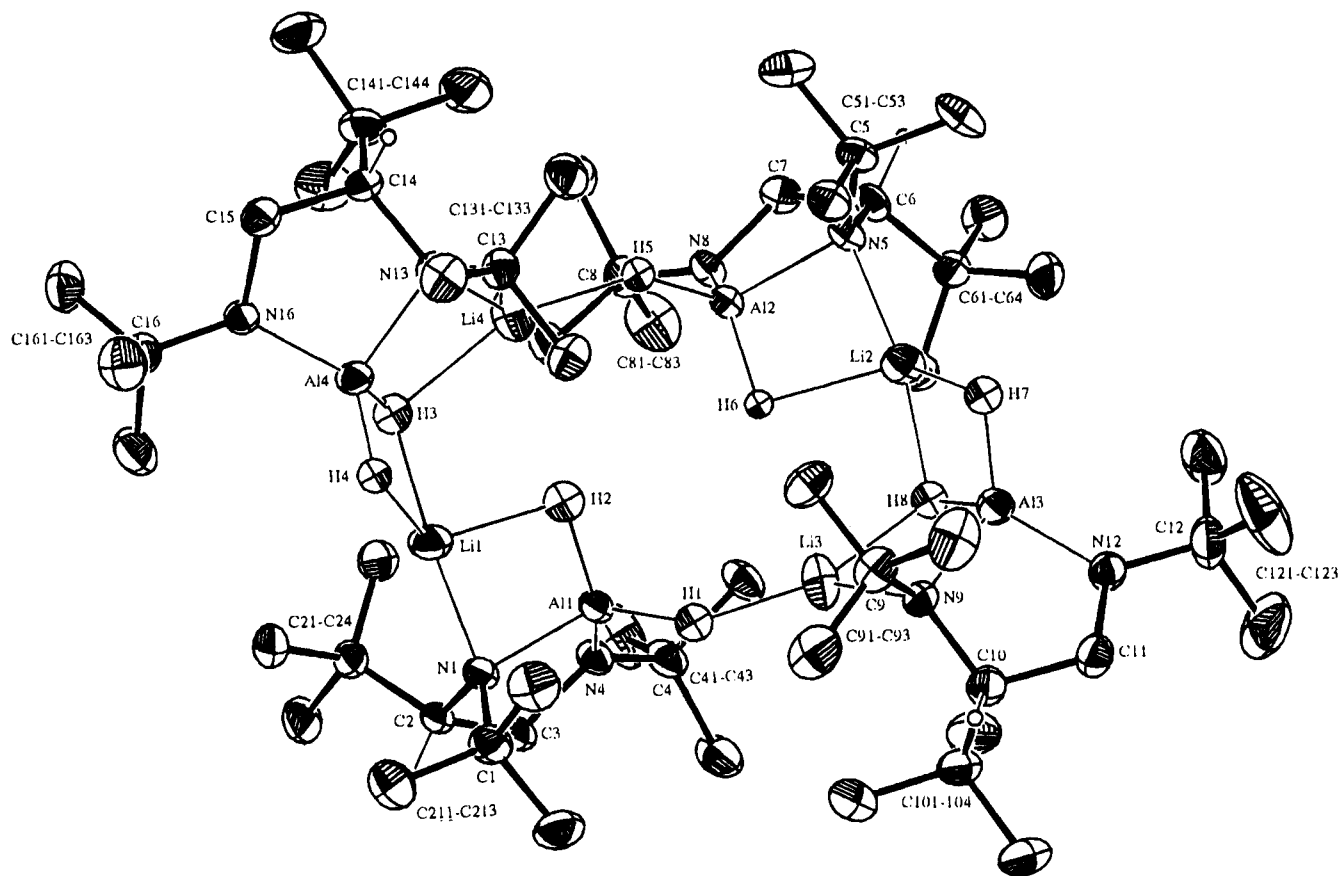
Figure 1. Molecular projection of [{Li[N(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)]AlH₂}₄], **4**, showing the labeling scheme and 20% thermal ellipsoids. For clarity only the methylene and methine hydrogens are shown in addition to the hydrides. Methylene and methine hydrogens have arbitrary radii.
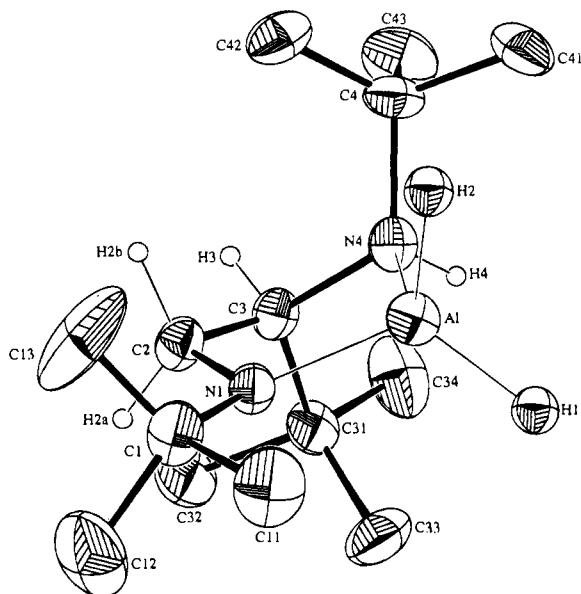

Figure 2. Molecular projection of [{HN(*t*-Bu)CH(*t*-Bu)CH₂N(*t*-Bu)}-AlH₂], **5**, showing the labeling scheme and 20% thermal ellipsoids. For clarity only the methylene, methine, and amine hydrogens are shown in addition to the hydrides. Methylene, methine, and amine hydrogens have arbitrary radii.

then lose NMe₃ to yield the observed 4-coordinate internally coordinated aminoalane complex **5** through chelation by the secondary amine functionality. Further evidence for the reaction mechanism not proceeding *via* intermediates **VIII** and **IX** is given by the kinetics of the 1:1 and 1:2 stoichiometric reactions of **2** and AlH₃·NMe₃. The latter reaction is facile and proceeds to completion within 30 min. In contrast, the former reaction

is rapid only for the 50% conversion of **2** to the aminoalane **5** and proceeds slowly from that point to *ca.* 80% after 12 h. This suggests that the liberated NMe₃ coordinates to the unreacted AlH₃·NMe₃ to form AlH₃·2NMe₃ as the byproduct. The rate-determining step is then the competitive complexation of **2** to AlH₃·2NMe₃ which is not favored by the chelation stability of the **2**·AlH₃ adduct, **VIII** or **IX**. The bis(trimethylamine) adduct of alane has been isolated from the reaction of **2** with 1 or 2 equiv of AlH₃·NMe₃ and was identified spectroscopically. The reaction of **2** with either 1 or 2 equiv of AlH₃ in Et₂O leads to the facile, complete conversion to hydrometalated species. This is consistent with the proposed mechanism for the reaction of **2** with AlH₃·NMe₃. In that case, the initially formed adduct is likely to be a 4-coordinate species, **VI·NMe₃**, which undergoes intramolecular hydrometalation followed by chelate ring formation to give the observed product, **5**. Ethers bind only weakly to alane in solution and are readily displaced by nitrogen donor Lewis bases.[15]

The importance of these mechanistic findings for organic chemistry is 2-fold. First, the source of aluminum hydride in reduction/metalation reactions can lead to chemoselectivity, altering the course of the reaction. In that sense, the metalation of secondary amines in the presence of reactive imines can be achieved by "protecting" the imines by the *in situ* coordination of the imines in their reactions with LiAlH₄. Second, up to a 2-fold equiv of the hydride source can be necessary for the complete, facile conversion of substrates in their reactions with aluminum hydrides under mild conditions, i.e., 6 equiv of active hydride. In this regard, we are currently pursuing the utility of

(15) For examples of ether-monocoordinated and dicoordinated AlH₃ adducts see: Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1993**, 189.
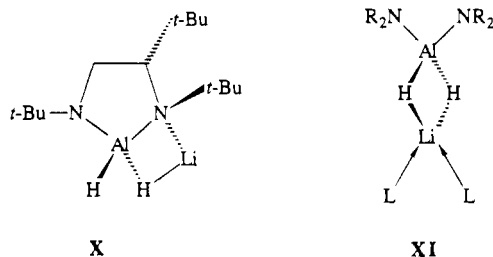
Scheme 1
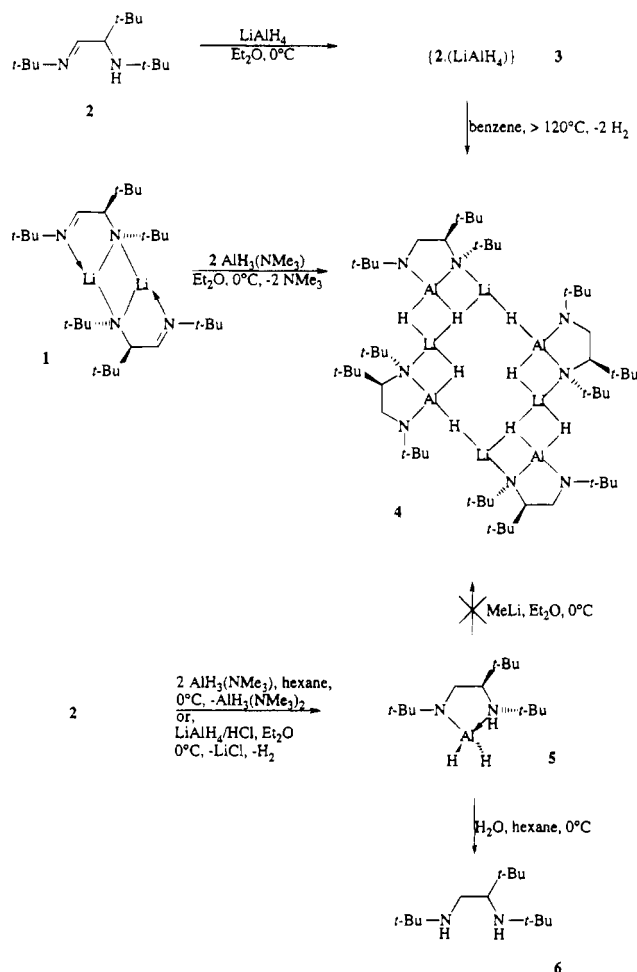
Scheme 2
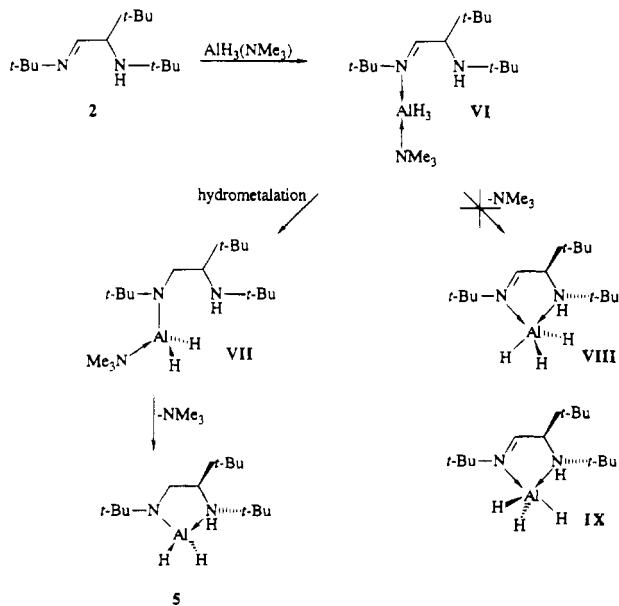
group 1 metal hydroaluminates as protecting agents for imines in reduction and metalation reactions.

X-ray Structure Commentary. Structure of 4. Complex 4 crystallizes as prismatic crystals in the triclinic space group $P\bar{1}$ with two tetramers in the unit cell, the asymmetric unit containing one discrete molecule of 4 and a half molecule of a centrosymmetric molecule of benzene centered on ($^1/_2$, $^1/_2$, 0), Figure 1. Selected geometrical parameters are given in Table

4. The tetramer is associated *via* both mono- and dihydride bridging, so that the basic repeat unit in the structure has the N,N'-dimetalated ethylenediamine chelating the (AlH_2) units. The lithium atom is displaced from the position it held in the lithium amide percursor to now be bound only to the nitrogen atom which was formally the amido nitrogen atom in the same precursor.[6] One of the aluminum hydrides forms a bridge to the lithium atom to form a N—Li—H—Al four-membered ring, **X**. The structural framework in the related monomeric Et_2O-

disolvated complex **II** is shown for comparison,[4] **XI**. The monomeric unit of 4 associates to form the cyclic tetramer *via* alternating mono- and dihydride bridging between the aluminum hydrides and the lithium atoms, attaining both 3- and 4-fold coordination for the lithium atoms, respectively. The coordination environments of the lithium atoms are {N(amido)LiH_2} and {N(amido)LiH_3}, respectively. The aluminum atoms are all 4-coordinate, having {N(amido)_2AlH_2} coordination environments.

The $Al(\mu-H)_2Li$ fragment found in the related monomeric lithium diamidoaluminum hydride complex $\{(Me_3Si)_2N\}_2Al(\mu-H)_2Li\cdot2Et_2O$,[4] **II**, is represented in two places in 4, as is the $Al(\mu-H)Li$ fragment which holds together the lithium amidoaluminum hydride dimer $\{(Me_3Si)_2NAlH(\mu-H)_2Li\cdot2Et_2O\}_2$,[4] **I**. In both **I** and **II**, the Et_2O-disolvated lithium atoms are not associated with the amidonitrogen atoms, unlike in the structure of 4. Only in the linear polymeric lithium triamidoaluminum hydride complex $\{(\mu-NEt_2)_2Al(\mu-NEt_2)(\mu-H)Li\}_n$[16] is there any interaction observed between the amido nitrogen atoms and the lithium atoms as part of a four-membered $Al(\mu-H)(\mu-NR_2)Li$ ring; this structure is the only other example of this structural fragment. The lithium—aluminum contacts for the $Al(\mu-H)Li$, $Al(\mu-H)_2Li$, and $Al(\mu-H)(\mu-NR_2)Li$ linkages in 4 measure 3.23(1)—3.25(2), 2.68(1)—2.72(2), and 2.67(1)—2.69(1) Å, respectively, providing benchmark standards for lithium amidoaluminum hydride complexes in which the hydrides cannot be located. These compare with the same measured quantities seen in **I**, **II**,[4] and $\{(\mu-NEt_2)_2Al(\mu-NEt_2)(\mu-H)Li\}_n$,[16] 3.33, 2.621, and 2.71 Å, respectively.

The Li—N distances in 4 cover a small range, 2.03(1)—2.05(2) Å, and are not influenced by the different coordination numbers of the lithium atoms. The distances are typical for Li—N(dibridging amido) bonds. The Al—N distances in 4 are in two distinct groupings, those to the 3-coordinate sp^2 hybridized amido nitrogen atoms being shorter, 1.771(6)—1.795(6) Å, than those to the 4-coordinate dibridging sp^3 hybridized amido nitrogen atoms, 1.871(6)—1.896(5) Å.

The Al—H distances are not atypical, being in the range 1.48(5)—1.67(4) Å, as are the Li—H distances of 1.84(5)—2.14(5) Å, which compare with the Li—H distances in LiH,[17] 2.04 Å, and LiAlH_4,[18] 1.88—2.16 Å. There is no correlation between the metal—H bond distances and the coordination number of the metals or the hydride itself which bridge one

(16) Linti, G.; Noth, H.; Rahm, P. *Z. Naturforsch., B* **1988**, *43*, 1101.
(17) Zintl, E.; Harder, A. *Z. Phys. Chem., B.* **1935**, *28*, 478.
(18) Sklar, N.; Post, B. *Inorg. Chem.* **1967**, *6*, 669.

aluminum and either one or two lithium atoms. The lithium atoms exhibit Li···H agostic type contacts, with Li···H distances as close as 2.86(1) Å (Li4−C132), corresponding to calculated Li···H contacts of *ca.* 2.11 Å.

The Al−H−Li bond angles for the 2-coordinate hydrides measure 143(3)−145(3) and 94(2)−103(2)° for the Al(μ-H)Li and Al(μ-H)$_2$Li moieties. The former angle compares with the average Al−H−Li angle in **I**,[4] 157(3)°, indicative of the preference for nonlinear monohydride bridging between these metals. The position of the bridging hydride was not reported for the lithium trialkylaluminum hydride complex [{MeN(CH$_2$-CH$_2$)$_2$NMe}Li(μ-H)Al(*t*-Bu){CH$_2$(SiMe$_3$)$_2$}$_2$].[19] However, the Li···Al distance of 3.26 Å in that complex is similar to that found for the Al(μ-H)Li distance in **4** and would indicate a similar Al−H−Li angle.

The H−Al−H angles are influenced greatly by their incorporation into the Al(μ-H)$_2$Li ring. When involved in this "kite-shaped" ring, the H−Al−H angle is markedly decreased relative to the case when it is not, the angles measuring 90(3)−92(3) and 105(2)−106(3)°, respectively, in those cases. The ligand bite angles, N−Al−N, in **4** range from 94.4(2) to 96.4(3)°. Other bond angles within the molecule are unexceptional and do not require comment.

Structure of 5. Complex **5** crystallizes as prismatic crystals in the monoclinic space group *P*2$_1$/*n* with four molecules in the unit cell, the asymmetric unit comprising one discrete molecule of **5**, Figure 2. The complex is best described as a monomeric intramolecularly coordinated secondary amine adduct of an aminoalane complex. The N-aluminated ethylenediamine acts as a bidentate ligand, chelating the aluminum atom which achieves 4-fold coordination for the aluminum atom. The molecule is devoid of symmetry.

Selected geometrical parameters are given in Table 5. The N(amine){N(amido)}AlH$_2$ coordination environment of the aluminum atom in **5** is also seen in {CH$_2$(CH$_2$CMe$_2$)$_2$N}-AlH$_2$·NMe$_3$,[1] where the dative Al−N bond belongs to a tertiary amine. Complex **5** represents the only example of this coordination environment where there is a secondary amine possessing an acidic N−H atom. The chloroalane species [{HN(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)}AlHCl][2] has been previously reported, and in that case the decreased activity of the hydride was responsible for the stability of the adduct. In **5** the added steric hindrance afforded by the carbon-centered *t*-Bu group presumably leads to the stability of the complex with respect to loss of hydrogen to form the diaminoalane complex, noting that **III** is stable only at low temperature.

Compound **5** has the same structural features as [{HN(*t*-Bu)-CH$_2$CH$_2$N(*t*-Bu)}AlHCl],[2] albeit with a chloride replaced by a hydride substituent. The comparative bond lengths to the aluminum centers in the two complexes do not reflect the expected enhanced Lewis acidity of the aluminum atom upon chloride substitution, the Al−N(amido) and Al−N(amine) distances measuring 1.799(9) and 2.02(1) Å, for **5** and 1.80(1) and 2.00(1) Å for the chloro species. The Al−H distances for **5** are unexceptional at 1.57(6) and 1.63(7) Å. The acidic amine nitrogen is eclipsed with respect to the *cis*-aluminum hydride (H4−N4−Al−H1 = 0(6)°). However, the N−H$^{\delta+}$···$^{\delta-}$H−Al distance is not notably short, 2.8(1) Å. In the diastereomer of the chloroalane species which was structurally authenticated, the chloro group was *cis* to the amine proton. The ligand bite angle, N1−Al−N4, in **5** measures 90.6(4)°, being unaltered from that of the chloroalane species, 90.6(6)°. Other bond angles within the molecule are unremarkable and do not require comment.

(19) Uhl, W.; Schnepf, J. E. O. *Z. Anorg. Allg. Chem.* **1991**, *595*, 225.

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