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Aluminum Amides Derived from Metalation of *N,N′*-Bis(trimethylsilyl)ethylenediamine

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The reaction of *N,N′*-bis(trimethylsilyl)ethylenediamine with $H_3Al{\cdot}NMe_3$ gives products based on metalation (H_2 elimination), $[\{[CH_2N(SiMe_3)]_2AlH\}_2]$ (**1**) and $[\{CH_2N(SiMe_3)\}_2AlN(SiMe_3)CH_2CH_2N(H)SiMe_3]$ (**2**), as well as products derived from N−Si bond cleavage and metalation, $[\{[CH_2N(SiMe_3)]_2AlH\}_2\{HAlN(SiMe_3)CH_2CH_2NAlH_2\}]$ (**4**) and $[H_2Al\{CH_2N(SiMe_3)\}_2AlN(SiMe_3)CH_2CH_2NAl(H)_2{\cdot}NMe_3\}]$ (**5**). Similarly, $[Me_3SiN(H)CH_2CH_2N(SiMe_3)AlCl_2]$ (**3**) was isolated as the redistributed/metalated product from the reaction of the same diamine with $H_2Al(Cl){\cdot}NMe_3$. The following crystal data were obtained: (**1**) monoclinic, space group $P2_1/c$ (No. 14), $a = 13.636(4)$ Å, $b = 9.565(3)$ Å, $c = 22.683(4)$ Å, $\beta = 105.67(2)°$, $Z = 4$; (**2**) monoclinic, space group $C2/c$ (No. 15), $a = 31.887(3)$ Å, $b = 10.145(6)$ Å, $c = 17.718(3)$ Å, $\beta = 100.36(1)°$, $Z = 8$; (**3**) triclinic, space group $P\bar{1}$ (No. 2), $a = 11.762(3)$ Å, $b = 11.927(3)$ Å, $c = 7.288(2)$ Å, $\alpha = 107.46(2)°$, $\beta = 95.29(2)°$, $\gamma = 110.41(2)°$, $Z = 2$; (**4**) triclinic, space group $P\bar{1}$ (No. 2), $a = 13.884(4)$ Å, $b = 15.379(4)$ Å, $c = 11.044(2)$ Å, $\alpha = 102.11(2)°$, $\beta = 103.85(2)°$, $\gamma = 109.28(2)°$, $Z = 2$; (**5**) triclinic, space group $P\bar{1}$ (No. 2), $a = 10.925(5)$ Å, $b = 11.060(5)$ Å, $c = 12.726(4)$ Å, $\alpha = 92.38(3)°$, $\beta = 95.67(2)°$, $\gamma = 96.90(2)°$, $Z = 2$.

Introduction

The metalation of secondary amines by aluminum hydride and trialkylaluminum complexes has been the subject of several recent studies by us[1] and other workers.[2] We have focused on the reactions of various aluminum and gallium hydride sources with substituted ethylenediamines[3] and related compounds[4] as well as with bulky monofunctional amines.[5] Through this we have developed a detailed understanding of the mechanism for complete alumination and identified unstable intermediate complexes featuring reactive secondary amines coordinating to the aluminum centers. Alternative reaction pathways to metalation have been reported for the reaction of bis(trimethylsilyl)phosphine with dimethylaluminum hydride;[6] products featuring P−Si bond cleavage were identified and isolated, the most noteworthy being trimethylsilane ($HSiMe_3$) by elimination from Me_2AlH and $HP(SiMe_3)_2$. The reaction of silylamines[7] and silylphosphines[8] with group 13 metal chlorides are well-known to yield stable Lewis base adducts or the corresponding metal amides and phosphides *via* the elimination of chlorosilanes.

Herein we report a number of structurally characterized amido−aluminum complexes isolated from the reaction of *N,N′*-bis(trimethylsilyl)ethylenediamine with $H_3Al{\cdot}NMe_3$. Dimeric diamido−aluminum hydride and monomeric triamido−aluminum complexes are reported as products arising from metalation. In addition, the structural characterization of two minor products featuring cleaved N−Si bonds are presented and their possible formation is discussed. Related to this, the reaction of the same amine with $H_2Al(Cl){\cdot}NMe_3$ is reported which gives a monomeric amido−aluminum dichloride complex arising from metalation and ligand redistribution.

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw degassed prior to use. *N,N′*-Bis(trimethylsilyl)ethylenediamine,[9] diethyl ether solvated AlH_3,[10] and $H_3Al{\cdot}NMe_3$[11] were prepared according to adapted literature procedures. $H_2Al(Cl){\cdot}NMe_3$ was prepared by the addition of $HgCl_2$ to $H_3Al{\cdot}NMe_3$ in diethyl ether and sublimed prior to use. $LiAlH_4$ was obtained from Aldrich and purified by recrystallization from diethyl ether. All other reagents were obtained from Aldrich. ^1H NMR spectra were recorded on a Varian Gemini-200 spectrometer in

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(1) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829. Raston, C. L. *J. Organomet. Chem.* **1994**, *475*, 15.

(2) Klein, C.; Nöth, H.; Tacke, M.; Thomann, M. *Angew. Chem.* **1993**, *105*, 923; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 886. Heine, A.; Stalke, D. *Angew. Chem.* **1992**, *104*, 941; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854. Trepanier, S. J.; Wang, S. *J. Chem. Soc., Dalton Trans.* **1995**, 2425.

(3) Atwood, J. L.; Lawrence, S. M.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 73. Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* In press. Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 4868.

(4) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4652. Cloke, F. G. N.; Dalby, C. I.; Henderson, M. J.; Hitchcock, P. B.; Kennard, C. H. L.; Lamb, R. N.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1394. Henderson, M. J.; Kennard, C. H. L.; Raston, C. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1203. Cloke, F. G. N.; Hanson, G. R.; Henderson, M. J.; Hitchcock, P. B.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1002. Jones, C.; Lee, F.-C.; Koutsantonis, G. A.; Gardiner, M. G.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* In press.

(5) Atwood, J. L.; Koutsantonis, G. A.; Lee, F.-C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91. Gardiner, M. G.; Koutsantonis, G. A.; Lee, F.-C.; Lawrence, S. M.; Raston, C. L. *Chem. Ber.* In press.

(6) Krannich, L. K.; Watkins, C. L.; Schauer, S. J. *Organometallics* **1995**, *14*, 3094. Fritz, V. G.; Emül, R. *Z. Anorg. Allg. Chem.* **1975**, *416*, 19.

(7) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, 1980. Nöth, H. *Z. Naturforsch.* **1961**, *16B*, 618.

(8) Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. A.; Woudenberg, R. C.; Jasinski, J. P. *Organometallics* **1993**, *12*, 2832. Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992**, *11*, 221. Wells, R. L.; McPhail, A. T.; Self, M. F., Laske, J. A. *Organometallics* **1993**, *12*, 3333.

(9) West, R.; Ishikawa, M.; Murai, S. *J. Am. Chem. Soc.* **1968**, *90*, 727.

(10) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.

(11) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141.

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deuterated benzene and referenced to the residual ^{1}H resonances 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 resonances of the deuterated solvent (δ 128.0). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, and the Chemical and MicroAnalytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as Nujol mulls on NaCl plates using a Perkin-Elmer 1725X Fourier transform infrared spectrometer.

Synthesis of [{[CH$_2$N(SiMe$_3$)]$_2$AlH}$_2$] (1). A solution of *N,N′*-bis(trimethylsilyl)ethylenediamine (1.84 g, 9.02 mmol) in diethyl ether (20 mL) was added to a solution of $H_3Al{\cdot}NMe_3$ (1.07 g, 12.04 mmol) in diethyl ether (80 mL) at −80 °C. Vigorous evolution of gas was observed upon addition of the reactants and upon warming to room temperature. The reaction mixture was stirred for 5 h and filtered, and the volatiles were removed from the filtrate *in vacuo*. Compound **1** was recrystallized from hexane on slow cooling to −30 °C (1.60 g, 58% yield): mp 123 °C, 167 °C (dec); ^{1}H NMR (200 MHz, C_6D_6) δ 0.23, 0.26 (2 × 18H, s, Me), 2.69 (2H, m, NCH$_2$), 2.99 (6H, m, NCH$_2$), 4.31 (2H, br, AlH); ^{13}C NMR (50 MHz, C_6D_6) δ 0.39, 0.56, 0.79, 1.10 (Me), 45.29, 45.74, 47.44, 48.09 (CH$_2$); IR ν (cm^{-1}) 1850 (br, AlH). Anal. Found: C, 41.32; H, 10.17; N, 12.33. Calcd: C, 41.70; H, 10.06; N, 12.16.

Synthesis of [{CH$_2$N(SiMe$_3$)}$_2$AlN(SiMe$_3$)CH$_2$CH$_2$N(H)SiMe$_3$] (2). An ethereal solution of HCl (8.16 mL, 0.69 M, 5.63 mmol) was added to a solution of LiAlH$_4$ (3.44 mL, 1.64 M, 5.64 mmol) in diethyl ether (25 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 min. The solution was filtered, and a solution of *N,N′*-bis(trimethylsilyl)ethylenediamine (1.12 g, 5.49 mmol) in diethyl ether (10 mL) was added to the filtrate at −80 °C. Evolution of gas was observed upon addition, and the reaction mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the volatiles were removed from the filtrate *in vacuo*. Compound **2** was recrystallized from hexane (15 mL) on slow cooling to −30 °C (1.17 g, 49% yield): mp 137−138 °C, 167 °C (gas evolution), 290 °C (dec); ^{1}H NMR (200 MHz, C_6D_6) δ 0.04, 0.21, 0.30, 0.35 (4 × 9H, s, Me), 0.68 (1H, br, NH), 2.29 (2H, m, CH$_2$), 2.79 (2H, m, CH$_2$), 3.15 (4H, m, CH$_2$); ^{13}C NMR (50 MHz, C_6D_6) δ −1.43, 0.32, 1.01, 1.37 (Me), 44.23, 45.79, 47.01, 47.38 (CH$_2$); IR ν (cm^{-1}) 3236 (sh, NH). Anal. Found: C, 41.26; H, 10.62; N, 12.31. Calcd: C, 44.39; H, 10.48; N, 12.94.

Synthesis of [Me$_3$SiN(H)CH$_2$CH$_2$N(SiMe$_3$)AlCl$_2$] (3). A hexane (10 mL) solution of *N,N′*-bis(trimethylsilyl)ethylenediamine (0.35 g, 1.73 mmol) was added to a solution of $H_2Al(Cl){\cdot}NMe_3$ (0.21 g, 1.73 mmol) in hexane (40 mL) at −80 °C. The reaction mixture was stirred at −80 °C for $^1/_2$ h until the evolution of gas ceased, warmed to room temperature, and stirred overnight. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo* (*ca*. 25 mL) affording colorless crystals of **2** and **3** (0.15 g, 30% yield) on slow cooling to −30 °C which could be fractionally crystallized. For **3**: mp 132 °C, 154 °C (gas evolution), 224 °C (dec); ^{1}H NMR (200 MHz, C_6D_6) δ −0.03, 0.31 (2 × 9H, s, Me), 0.72 (1H, br, NH), 2.1−2.8 (4H, m, NCH$_2$); ^{13}C NMR (50 MHz, C_6D_6) δ −2.11, 0.00 (Me), 43.50, 46.06 (CH$_2$); IR ν (cm^{-1}) 3166 (sh, NH). Anal. Found: C, 31.71; H, 7.77; N, 9.44. Calcd: C, 31.89; H, 7.69; N, 9.30.

Synthesis of [{[CH$_2$N(SiMe$_3$)]$_2$AlH}$_2${HAlN(SiMe$_3$)CH$_2$CH$_2$NAlH$_2$}] (4). A solution of *N,N′*-bis(trimethylsilyl)ethylenediamine (1.15 g, 5.64 mmol) in hexane (10 mL) was added to a solution of $H_3Al{\cdot}NMe_3$ (1.00 g, 11.24 mmol) in hexane (50 mL) at −80 °C. Evolution of gas was observed upon addition, and the reaction mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the filtrate was concentrated *in vacuo* (*ca*. 20 mL) and stored at −30 °C, yielding crystals of **4**, $H_3Al{\cdot}NMe_3$, and $H_3Al{\cdot}(NMe_3)_2$ (as established by NMR spectroscopy and X-ray crystallography).

Synthesis of [H$_2$Al{CH$_2$N(SiMe$_3$)}$_2$AlN(SiMe$_3$)CH$_2$CH$_2$NAl(H)$_2$·NMe$_3$}] (5). A solution of *N,N′*-bis(trimethylsilyl)ethylenediamine (0.84 g, 4.12 mmol) in diethyl ether (10 mL) was added to a solution of $H_3Al{\cdot}NMe_3$ (0.76 g, 8.55 mmol) in diethyl ether (40 mL) at −80 °C. When the solution was warmed to room temperature, evolution of gas was observed, and the reaction mixture was stirred for 4 h at room temperature. The solution was filtered, and the volatiles were removed from the filtrate *in vacuo*. Compound **5** was recrystallised from hexane at −30 °C.

Table 1. Crystallographic Data for Compounds **1**−**5**

1	$C_{16}H_{46}N_4Si_4Al_2$	fw 460.87
	$a = 13.636(4)$ Å	space group $P2_1/c$ (No. 14)
	$b = 9.565(3)$ Å	$T = -100$ °C
	$c = 22.683(4)$ Å	$\lambda = 0.71069$ Å
	$\beta = 105.67(2)°$	$\rho_{calcd} = 1.075$ cm^{-3}
	$V = 2848(1)$ Å^3	$\mu = 2.79$ cm^{-1}
	$Z = 4$	$R^a = 0.040$
		$R_w{}^b = 0.045$
2	$C_{16}H_{45}N_4Si_4Al$	fw 432.88
	$a = 31.887(3)$ Å	space group $C2/c$ (No. 15)
	$b = 10.145(6)$ Å	$T = 25$ °C
	$c = 17.718(3)$ Å	$\lambda = 0.71069$ Å
	$\beta = 100.36(1)°$	$\rho_{cal}/3c_d = 1.020$ g cm^{-3}
	$V = 5638(3)$ Å^3	$\mu = 2.44$ cm^{-1}
	$Z = 8$	$R^a = 0.049$
		$R_w{}^b = 0.043$
3	$C_8H_{23}N_2Si_2AlCl_2$	fw 301.34
	$a = 11.762(3)$ Å	space group $P\bar{1}$ (No. 2)
	$b = 11.927(3)$ Å	$T = 25$ °C
	$c = 7.288(2)$ Å	$\lambda = 0.71069$ Å
	$\alpha = 107.46(2)°$	$\rho_{calcd} = 1.122$ g cm^{-3}
	$\beta = 95.29(2)°$	$\mu = 5.27$ cm^{-1}
	$\gamma = 110.41(2)°$	$R^a = 0.038$
	$V = 891.7(5)$ Å^3	$R_w{}^b = 0.040$
	$Z = 2$	
4	$C_{21}H_{62}N_6Si_5Al_4$	fw 647.11
	$a = 13.884(4)$ Å	space group $P\bar{1}$ (No. 2)
	$b = 15.379(4)$ Å	$T = 25$ °C
	$c = 11.044(2)$ Å	$\lambda = 0.71069$ Å
	$\alpha = 102.11(2)°$	$\rho_{calcd} = 1.048$ g cm^{-3}
	$\beta = 103.85(2)°$	$\mu = 2.73$ cm^{-1}
	$\gamma = 109.28(2)°$	$R^a = 0.042$
	$V = 2051(1)$ Å^3	$R_w{}^b = 0.033$
	$Z = 2$	
5	$C_{16}H_{48}N_5Al_3Si_3$	fw 475.79
	$a = 10.925(5)$ Å	space group $P\bar{1}$ (No. 2)
	$b = 11.060(5)$ Å	$T = 25$ °C
	$c = 12.726(4)$ Å	$\lambda = 0.71069$ Å
	$\alpha = 92.38(3)°$	$\rho_{calcd} = 1.042$ g cm^{-3}
	$\beta = 95.67(2)°$	$\mu = 2.5$ cm^{-1}
	$\gamma = 96.90(2)°$	$R^a = 0.046$
	$V = 1517(1)$ Å^3	$R_w{}^b = 0.047$
	$Z = 2$	

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

Crystal Structure Determinations. Crystals of **1**−**5** suitable for X-ray structure determination were grown from hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere (except crystals of **1** which were coated in oil and transferred directly to the cold stream of nitrogen on the diffractometer for data collection). Unique diffractometer data sets were measured using Rigaku AFC7r and Enraf−Nonius CAD4 (**5** only) diffractometers. Reflections with $I > 3.0\sigma(I)$ (or $2.5\sigma(I)$ **5** only) were considered "observed" and used in the full-matrix least-squares refinements, minimizing $\sum w\Delta^2$ after the 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.[12] Computation used the XTAL 3.0,[13] TEXSAN 1.6,[14] and SHELXS-86[15] program systems implemented on Sun SPARCstation 2 and Silicon Graphics Indy computers. A summary of crystal and solution and refinement data is given in Table 1. Non-

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

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

(14) TEXSAN, version 1.6, Crystal Structure Analysis Package, Molecular Structure Corporation, 1992.

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

Table 2. Non-Hydrogen and Aluminum Hydride Atom Coordinates and Isotropic Thermal Parameters for **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Si(1)	0.32098(8)	−0.1881(1)	0.58536(5)	3.63(2)[a]
Si(4)	0.31467(8)	−0.2238(1)	0.82769(5)	3.09(2)[a]
Si(5)	0.21008(8)	0.2038(1)	0.90066(5)	3.30(2)[a]
Si(8)	0.15587(7)	0.2140(1)	0.64670(5)	2.81(2)[a]
Al(1)	0.22163(7)	−0.1008(1)	0.69338(5)	2.38(2)[a]
Al(2)	0.28021(7)	0.1030(1)	0.78232(4)	2.26(2)[a]
N(1)	0.3184(2)	−0.1101(3)	0.6528(1)	2.82(7)[a]
N(4)	0.3206(2)	−0.0906(3)	0.7744(1)	2.16(6)[a]
N(5)	0.1924(2)	0.1428(3)	0.8272(1)	2.53(6)[a]
N(8)	0.1725(2)	0.0862(3)	0.7049(1)	2.09(6)[a]
C(2)	0.4150(3)	−0.0594(4)	0.6938(2)	3.14(9)[a]
C(3)	0.4233(2)	−0.1006(4)	0.7597(2)	2.72(8)[a]
C(6)	0.0879(3)	0.1525(4)	0.7871(2)	2.89(9)[a]
C(7)	0.0782(2)	0.0696(4)	0.7284(2)	2.60(8)[a]
C(11)	0.3916(3)	−0.3570(4)	0.5988(2)	4.6(1)[a]
C(12)	0.3837(5)	−0.0710(5)	0.5405(2)	7.2(2)[a]
C(13)	0.1879(4)	−0.2256(6)	0.5412(2)	7.4(1)[a]
C(41)	0.1890(3)	−0.2184(4)	0.8445(2)	4.2(1)[a]
C(42)	0.4219(3)	−0.1999(5)	0.8978(2)	6.2(1)[a]
C(43)	0.3251(3)	−0.3972(4)	0.7921(2)	5.3(1)[a]
C(51)	0.3482(4)	0.2067(7)	0.9386(2)	9.3(2)[a]
C(52)	0.1437(5)	0.0942(6)	0.9455(2)	8.1(2)[a]
C(53)	0.1552(4)	0.3811(5)	0.9003(2)	5.7(1)[a]
C(81)	0.1066(3)	0.3785(4)	0.6711(2)	4.9(1)[a]
C(82)	0.0623(3)	0.1472(5)	0.5767(2)	4.7(1)[a]
C(83)	0.2794(3)	0.2521(4)	0.6304(2)	3.84(10)[a]
H(1)	0.133(2)	−0.215(3)	0.680(1)	3.0(7)
H(2)	0.369(2)	0.199(3)	0.785(1)	3.3(7)

[a] Isotropic equivalent thermal parameters.

Table 3. Non-Hydrogen and Amine Hydrogen Atom Coordinates and Isotropic Thermal Parameters for **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Si(1)	0.20194(6)	0.2623(2)	0.1708(1)	4.75(6)[a]
Si(4)	0.08657(7)	0.2290(2)	−0.1452(1)	5.63(6)[a]
Si(5)	0.16383(7)	−0.1326(2)	0.0159(1)	5.09(6)[a]
Si(8)	0.05136(7)	0.2925(2)	0.1148(1)	5.39(6)[a]
Al(1)	0.12715(7)	0.1603(2)	0.0406(1)	3.81(5)[a]
N(1)	0.1725(1)	0.2630(5)	0.0802(3)	4.0(1)[a]
N(4)	0.1281(2)	0.2407(6)	−0.0624(3)	6.6(2)[a]
N(5)	0.1281(2)	−0.0183(5)	0.0345(3)	4.1(1)[a]
N(8)	0.0768(2)	0.1710(5)	0.0741(3)	4.4(2)[a]
C(2)	0.1852(2)	0.3528(7)	0.0243(4)	5.7(2)[a]
C(3)	0.1522(3)	0.3576(8)	−0.0474(4)	6.4(2)[a]
C(6)	0.0911(3)	−0.0640(8)	0.0663(5)	7.7(3)[a]
C(7)	0.0610(3)	0.0369(8)	0.0756(5)	8.4(3)[a]
C(11)	0.1840(2)	0.1231(8)	0.2246(4)	6.8(2)[a]
C(12)	0.2597(2)	0.2446(9)	0.1676(4)	7.5(2)[a]
C(13)	0.1955(3)	0.4177(8)	0.2234(4)	8.3(3)[a]
C(41)	0.0755(5)	0.0589(10)	−0.1625(6)	20.0(5)[a]
C(42)	0.1043(4)	0.303(1)	−0.2273(5)	18.0(5)[a]
C(43)	0.0416(4)	0.317(1)	−0.1245(5)	21.1(6)[a]
C(51)	0.1403(3)	−0.2577(8)	−0.0562(4)	8.4(3)[a]
C(52)	0.1881(3)	−0.2268(9)	0.1025(4)	10.2(3)[a]
C(53)	0.2071(3)	−0.0457(8)	−0.0213(6)	10.2(3)[a]
C(81)	0.0731(3)	0.4562(7)	0.0909(4)	7.0(3)[a]
C(82)	−0.0074(2)	0.2906(8)	0.0786(5)	8.7(3)[a]
C(83)	0.0594(3)	0.2790(9)	0.2212(4)	9.2(3)[a]
H(4)	0.1478	0.1887	−0.0779	7.9583

[a] Isotropic eqivalent thermal parameters.

Table 4. Non-Hydrogen and Amine Hydrogen Atom Coordinates and Isotropic Thermal Parameters for **3**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Cl(1)	0.0991(1)	0.2893(2)	0.5702(2)	7.39(5)[a]
Cl(2)	0.4162(1)	0.4280(1)	0.7149(2)	7.01(4)[a]
Si(1)	0.2630(2)	0.0409(2)	0.2744(3)	7.65(6)[a]
Si(4)	0.2205(2)	0.5418(2)	0.3159(3)	6.18(5)[a]
Al(1)	0.2646(1)	0.3183(2)	0.4631(2)	4.91(4)[a]
N(1)	0.2745(4)	0.1879(4)	0.2782(6)	6.1(1)[a]
N(4)	0.2819(4)	0.4212(4)	0.2955(6)	4.6(1)[a]
C(2)	0.2982(8)	0.2210(7)	0.103(1)	7.6(2)[a]
C(3)	0.2465(7)	0.3192(7)	0.0936(9)	6.5(2)[a]
C(11)	0.4009(8)	0.0128(7)	0.214(1)	15.1(4)[a]
C(12)	0.2512(9)	0.0344(7)	0.522(1)	14.2(4)[a]
C(13)	0.1279(8)	−0.0870(7)	0.096(1)	15.7(3)[a]
C(41)	0.0517(6)	0.4606(6)	0.2357(9)	8.7(2)[a]
C(42)	0.2722(7)	0.6475(6)	0.5765(10)	9.3(2)[a]
C(43)	0.2859(7)	0.6287(6)	0.153(1)	9.3(2)[a]
H(4)	0.358(4)	0.459(4)	0.319(6)	3(1)

[a] Isotropic equivalent thermal parameters.

Table 5. Non-Hydrogen and Aluminum Hydride Atom Coordinates and Isotropic Thermal Parameters for **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Si(1)	0.6827(1)	0.1850(1)	1.0033(2)	5.75(4)[a]
Si(4)	0.8700(1)	0.3665(1)	0.6833(2)	5.54(4)[a]
Si(5)	0.2500(1)	0.0519(1)	0.6207(2)	5.85(4)[a]
Si(9)	0.3224(1)	0.4252(1)	0.7390(1)	4.98(4)[a]
Si(12)	0.1988(1)	0.1915(1)	0.1961(2)	7.07(5)[a]
Al(1)	0.6540(1)	0.2306(1)	0.7258(1)	4.36(4)[a]
Al(2)	0.6495(1)	0.3915(1)	0.6614(2)	4.64(4)[a]
Al(3)	0.4311(1)	0.27133(10)	0.6987(1)	3.88(4)[a]
Al(4)	0.2389(1)	0.2221(1)	0.5040(1)	4.52(4)[a]
N(1)	0.6816(3)	0.2531(3)	0.9006(4)	4.9(1)[a]
N(4)	0.7647(3)	0.3587(3)	0.7495(4)	4.28(10)[a]
N(5)	0.3204(3)	0.1492(2)	0.5703(3)	4.07(9)[a]
N(8)	0.5415(3)	0.2653(2)	0.6330(3)	3.80(9)[a]
N(9)	0.3539(3)	0.3451(2)	0.6281(3)	3.75(9)[a]
N(12)	0.2548(3)	0.2530(3)	0.3608(3)	4.8(1)[a]
C(2)	0.7264(5)	0.3594(4)	0.9581(6)	5.7(2)[a]
C(3)	0.8075(5)	0.4067(4)	0.8967(6)	5.5(2)[a]
C(6)	0.3812(5)	0.1174(4)	0.4854(6)	5.2(2)[a]
C(7)	0.4814(4)	0.2015(4)	0.4938(5)	4.7(1)[a]
C(10)	0.3983(4)	0.3953(4)	0.5371(5)	4.4(1)[a]
C(11)	0.3174(5)	0.3581(5)	0.3989(6)	5.8(2)[a]
C(12)	0.6421(5)	0.0577(4)	0.9047(6)	9.2(2)[a]
C(13)	0.5902(5)	0.1917(5)	1.0982(6)	9.5(2)[a]
C(14)	0.8201(5)	0.2268(5)	1.1244(6)	10.0(2)[a]
C(41)	0.9577(4)	0.3127(4)	0.7680(6)	8.4(2)[a]
C(42)	0.9508(4)	0.4967(4)	0.7080(6)	8.4(2)[a]
C(43)	0.8114(4)	0.2977(4)	0.5059(5)	7.6(2)[a]
C(51)	0.1455(4)	−0.0473(4)	0.4741(6)	7.9(2)[a]
C(52)	0.1860(5)	0.0929(4)	0.7362(6)	8.4(2)[a]
C(53)	0.3477(5)	0.0084(4)	0.7081(6)	9.6(2)[a]
C(91)	0.4474(4)	0.5365(4)	0.8362(5)	7.3(2)[a]
C(92)	0.2672(4)	0.3649(4)	0.8498(5)	6.4(2)[a]
C(93)	0.2182(4)	0.4589(4)	0.6431(5)	7.3(2)[a]
C(121)	0.3069(6)	0.1879(5)	0.1229(6)	10.8(3)[a]
C(122)	0.1228(5)	0.2501(6)	0.1048(6)	11.8(3)[a]
C(123)	0.1093(6)	0.0664(5)	0.1787(6)	13.8(2)[a]
H(1)	0.651(2)	0.131(2)	0.631(3)	3.0(7)
H(2)	0.636(2)	0.475(2)	0.770(3)	2.3(7)
H(3)	0.652(2)	0.405(2)	0.524(3)	2.8(7)
H(4)	0.446(2)	0.284(2)	0.839(3)	3.6(8)
H(5)	0.128(3)	0.185(2)	0.530(3)	4.6(9)

[a] Isotropic equivalent thermal parameters.

hydrogen and important hydrogen atom coordinates are given in Tables 2–6. Molecular projections showing numbering schemes are given in Figures 1–5. Selected geometrical parameters are given in the figure captions. Important molecular geometries appear in the figure captions. Thermal ellipsoids are drawn at the 20% probability level. For clarity, only aluminum hydride and amine hydrogen atoms are shown as spheres of arbitrary radii or with their isotropic temperature factor thermal ellipsoids. Anisotropic thermal parameters were refined for all non-hydrogen atoms in each structure. All aluminum hydride, amine, and methylene hydrogen atoms were located and refined in x, y, z, and U_{iso} for all five structures with the exception of the amine hydrogen in **2** (which was located and constrained in x, y, z, and U_{iso}) and the methylene hydrogens in **2** and **5**. Calculated methyl and methylene hydrogen atoms were included as invariants at estimated values (C–H 0.95 or 1.0 Å).

Table 6. Non-Hydrogen and Aluminum Hydride Atom Coordinates and Isotropic Thermal Parameters for **5**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å^2
Al(1)	0.7704(1)	0.7987(1)	0.2653(1)	0.0440(5)^a
Al(2)	0.8565(2)	0.6761(2)	0.4325(1)	0.0660(6)^a
Al(3)	0.5772(1)	0.7460(1)	0.4334(1)	0.0576(6)^a
Si(1)	0.8777(1)	1.0650(1)	0.1885(1)	0.0561(5)^a
Si(2)	1.0213(1)	0.6654(1)	0.2383(1)	0.0680(6)^a
Si(3)	0.5269(1)	0.7525(1)	0.0950(1)	0.0593(5)^a
N(1)	0.8408(3)	0.9555(3)	0.2743(3)	0.051(1)^a
N(2)	0.7417(3)	0.7943(3)	0.4130(3)	0.050(1)^a
N(3)	0.8720(3)	0.6642(3)	0.2805(3)	0.053(1)^a
N(4)	0.6593(3)	0.7193(3)	0.1645(3)	0.052(1)^a
N(5)	0.5578(4)	0.7428(4)	0.5895(3)	0.066(2)^a
C(1)	0.8770(5)	0.9880(5)	0.3878(4)	0.070(2)^a
C(2)	0.7852(5)	0.9240(5)	0.4543(4)	0.064(2)^a
C(3)	0.7818(5)	0.5604(4)	0.2281(4)	0.069(2)^a
C(4)	0.6981(5)	0.6008(5)	0.1361(4)	0.077(2)^a
C(5)	0.6415(6)	0.6649(6)	0.6448(4)	0.092(3)^a
C(6)	0.5777(7)	0.8667(5)	0.6439(5)	0.104(3)^a
C(7)	0.4279(6)	0.6888(6)	0.5960(5)	0.100(3)^a
C(11)	1.0458(5)	1.1264(5)	0.2091(5)	0.084(2)^a
C(12)	0.8358(5)	0.9995(5)	0.0516(4)	0.077(2)^a
C(13)	0.7922(6)	1.1991(5)	0.2088(5)	0.098(3)^a
C(21)	1.1251(6)	0.7997(6)	0.3002(6)	0.116(3)^a
C(22)	1.0854(6)	0.5229(6)	0.2750(6)	0.111(3)^a
C(23)	1.0121(6)	0.6745(7)	0.0919(5)	0.116(3)^a
C(31)	0.4964(5)	0.9079(5)	0.1391(4)	0.079(2)^a
C(32)	0.3906(5)	0.6404(6)	0.1183(5)	0.094(3)^a
C(33)	0.5416(6)	0.7442(6)	−0.0505(4)	0.090(3)^a
H(1)	0.798(4)	0.545(4)	0.463(3)	0.07(1)
H(2)	0.999(3)	0.714(3)	0.511(2)	0.020(8)
H(3)	0.479(3)	0.845(3)	0.398(3)	0.05(1)
H(4)	0.535(3)	0.613(3)	0.394(3)	0.06(1)

[a] Isotropic equivalent thermal parameters.

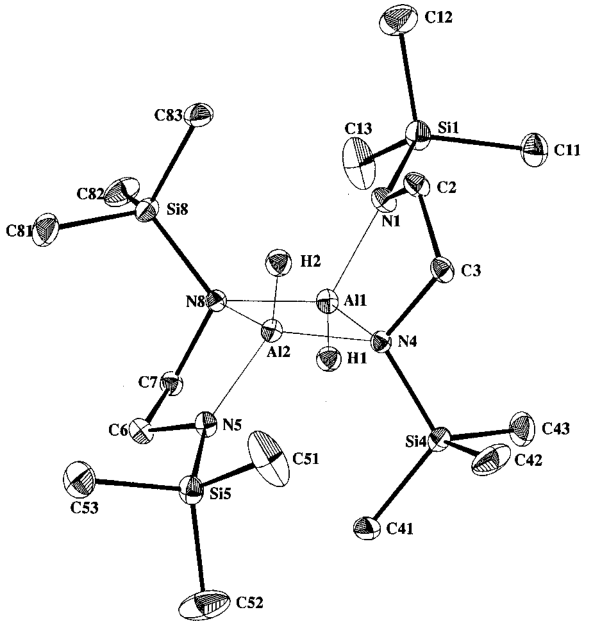


Figure 1. Molecular projection of **1**. Selected interatomic distances (Å) and angles (deg): Al1−N1,N4,N8 1.804(3), 1.967(3), 1.952(3); Al2−N4,N5,N8 1.955(3), 1.810(3), 1.968(3); Al1−H1 1.59(3), 1.51(3); Si1−N1, 1.710(3); Si4−N4 1.774(3); Si5−N5 1.719(3); Si8−N8 1.769(3); N1−Al1−N4,N8 93.9(1), 116.0(1); N4−Al1−N8 90.2(1); H1−Al1−N1,N4,N8 119(1), 120(1), 113(1); N4−Al2−N5,N8 119.8(1), 90.1(1); N5−Al2−N8 94.1(1); H2−Al2−N4,N5,N8 110(1), 120(1), 119(1).

Results

Synthesis. The dimeric diamido−aluminum hydride and monomeric triamido−aluminum complexes **1** and **2** were prepared *via* alumination of the substituted ethylenediamine *N*,*N*′-bis(trimethylsilyl)ethylenediamine by $H_3Al{\cdot}NMe_3$ and diethyl ether solvated AlH_3. The attempted synthesis of the alane rich species $[(CH_2\text{-}\mu\text{-}NSiMe_3)_2(AlH_2)_2]$ using $H_3Al{\cdot}NMe_3$ in the appropriate stoichiometric ratio proved unsuccessful, yielding only **1** and unreproducible yields of compounds **4** and **5** which preferentially crystallized from solution. Similarly, the amido−aluminum complex $[Me_3SiN(H)CH_2CH_2N(SiMe_3)AlH_2]$ could not be obtained, presumably due to the instability of this compound with respect to loss of hydrogen to yield the dimeric diamido−aluminum hydride **1**. Compounds **1**−**4** were isolated as air and moisture sensitive colorless crystalline solids. Compounds **1** and **2** have been characterized using ^1H and ^{13}C NMR spectroscopies, infrared spectroscopy, microanalysis, and X-ray structure determinations. The characterization of compounds **4** and **5** was based solely on X-ray structure determinations.

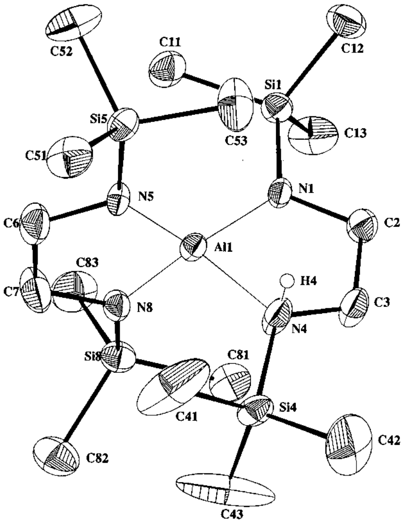
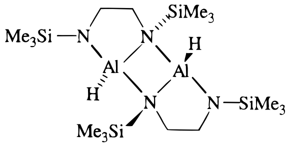
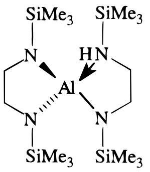


Figure 2. Molecular projection of **2**. Selected interatomic distances (Å) and angles (deg): Al1−N1,N4,N5,N8 1.818(5), 2.004(6), 1.816(5), 1.812(6); N1,N4,N5,N8−Si1,Si4,Si5,Si8 1.708(5), 1.795(6), 1.698(6), 1.705(6); N1−Al1−N4,N5,N8 88.7(2), 125.0(2), 122.0(2); N4−Al1−N5,N8 110.4(3), 115.7(3); N5−Al1−N8 96.0(3).



1



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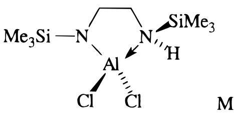

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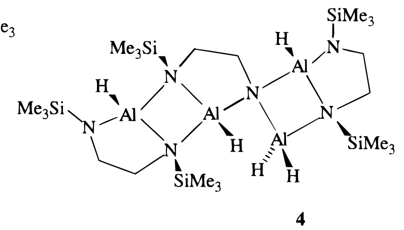
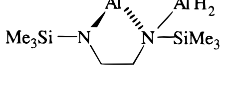


4



5

The results obtained herein relate to those of the analogous reactions of *N*,*N*′-di(*tert*-butyl)ethylenediamine with $H_3Al{\cdot}NMe_3$ in which the *tert*-butyl-substituted analogues to **1** and **2** could be isolated in addition to $[(CH_2\text{-}\mu\text{-}N\text{-}t\text{-}Bu)_2(AlH_2)_2]$.[3] Those

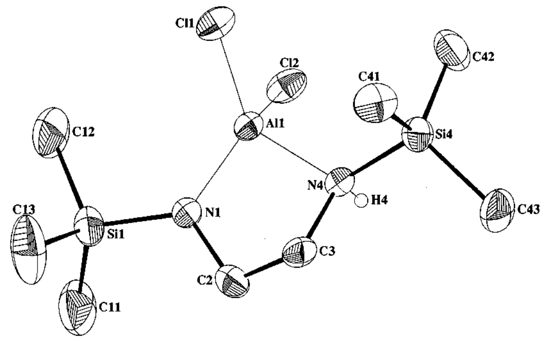


Figure 3. Molecular projection of **3**. Selected interatomic distances (Å) and angles (deg): Al1−N1,N4,Cl1,Cl2 1.774(4), 1.952(4), 2.120(2), 2.142(2); N1,N4−Si1,Si4 1.703(4), 1.796(5); N1−Al1−N4,Cl1,Cl2 93.6(2), 118.7(2), 118.3(2); N4−Al1−Cl1,Cl2 112.2(2), 106.1(2); Cl1−Al1−Cl2 106.68(9).

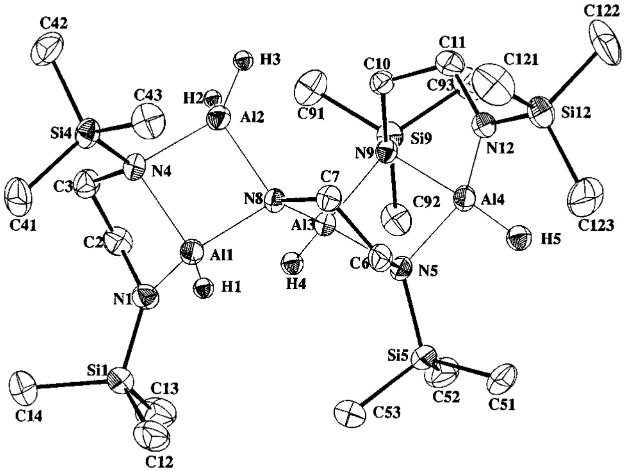


Figure 4. Molecular projection of **4**. Selected interatomic distances (Å) and angles (deg): Al1−N1,N4,N8,H1 1.809(4), 1.975(4), 1.945(4), 1.65(3); Al2−N4,N8,H2,H3 1.939(4), 1.927(3), 1.66(3), 1.58(3); Al3−N5,N8,N9,H4 1.958(3), 1.867(4), 1.953(4), 1.47(3); Al4−N5,N9,N12,H5 1.964(4), 1.968(4), 1.787(4), 1.57(3); Si1−N1 1.699(4); Si4−N4 1.766(4); Si5−N5 1.775(4); Si9−N9 1.786(3); Si12−N12 1.710(4); N1−Al1−N4,N8,H1 93.2(2), 117.1(2), 122(1); N4−Al1−N8,H1 90.1(1), 121(1); N8−Al1−H1 110(1); N4−Al2−N8,H2,H3 91.7(2), 109(1), 114(1); N8−Al2−H2,H3 110(1), 109(1); H2−Al2−H3 119(1); N5−Al3−N8,N9,H4 94.8(2), 91.3(2), 118(1); N8−Al3−N9,H4 114.9(2), 121(1); N9−Al3−H4 113(1); N5−Al4−N9,H12,H5 90.7(1), 117.0(2), 107(1); N9−Al4−N12,H5 94.6(2), 118(1); N12−Al4−H5 125(1); Al1−N4−Al2 88.5(1); Al3−N5−Al4 88.9(2); Al1−N8−Al2,Al3 89.7(1), 120.7(2); Al2−N8−Al3 112.9(2); Al3−N9−Al4 88.9(1).

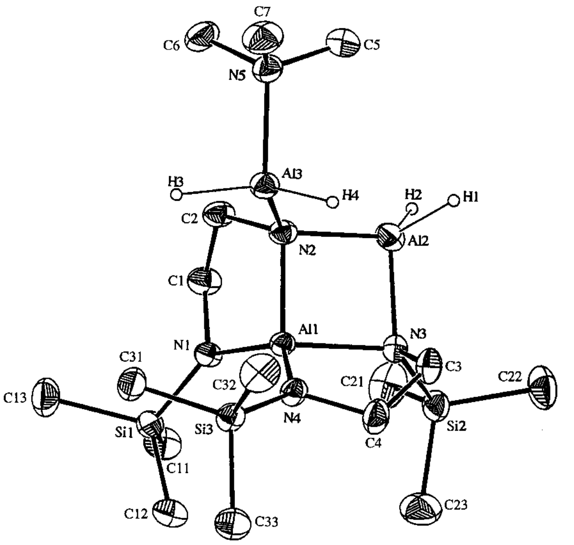


Figure 5. Molecular projection of **5**. Selected interatomic distances (Å) and angles (deg): Al1−N1,N2,N3,N4 1.806(4), 1.938(4), 1.965(4), 1.798(3); Al2−N2,N3,H1,H2 1.924(4), 1.959(4), 1.60(4), 1.76(3); Al3−N2,N5,H3,H4 1.859(4), 2.020(5), 1.66(4), 1.53(4); Si1−N1 1.703(4); Si2−N3, 1.766(4); Si3−N4 1.707(4); N1−Al1−N2,N3,N4 95.2(2), 121.1(2), 129.4(2); N2−Al1−N3,N4 90.7(2), 120.7(2); N3−Al1−N4 94.8(2); N2−Al2−N3,H1,H2 91.3(2), 115(2), 120(1); N3−Al2−H1,H2 107(1), 114(1); H1−Al2−H2 108(2); N2−Al3−N5,H3,H4 110.2(2), 115(1), 112(1); N5−Al3−H3,H4 100(1), 103(1); H3−Al3−H4 116(2); Al1−N2−Al2,Al3 89.6(2), 113.4(2); Al2−N2−Al3 117.7(3); Al1−N3−Al2 87.8(2).

reactions were shown to proceed *via* the unstable intermediate [HN(*t*-Bu)CH_2CH_2N(*t*-Bu)AlH_2], which could be stabilized by alkyl substitution of the ethylenediamine or chloride substitution of a hydride substituent, [HN(*t*-Bu)CH(R)CH(R′)N(*t*-Bu)AlHX] (where R = R′ = Me, X = H or R = *t*-Bu, R′ = H, X = H or R = R′ = H, X = Cl). Presumably here the intermediate [$Me_3SiN(H)CH_2CH_2N(SiMe_3)AlH_2$] is also thermally unstable and converts to **1** in the absence of an excess of the starting materials. Seemingly, the intermediate also lacks sufficient stability to react with an additional equivalent of $H_3Al{\cdot}NMe_3$ or diethyl ether solvated AlH_3 to give [$(CH_2$-μ-$NSiMe_3)_2$-$(AlH_2)_2$]; however, the intermediate does react with additional *N,N*′-bis(trimethylsilyl)ethylenediamine to give **2**. These differences can be attributed to either the different steric requirements of the substituents (*t*-Bu > $SiMe_3$) or electronic factors.

The reaction pathway to yield compounds **4** and **5** involves, in addition to metalation of the secondary silylamine, the cleavage of a silyl group from one of the nitrogen centers in the compounds which are represented as dimetalated primary amines or imino−aluminum functionalities. The elimination of $HSiMe_3$ highlights the added complexity of this system relative to the analogous *tert*-butyl system. At present, we offer only the possible suggestion of trimethylsilane ($HSiMe_3$) elimination from either the secondary amine or metalated secondary amine along the lines established for aluminum hydrides reacting with silylphosphines.[6] It is well established that primary amines form the aggregated imino complexes $(HAlNR)_n$ in reactions with aluminum hydride reagents.[16] However, the presence of *N*-(trimethylsilyl)ethylenediamine as an impurity in the sample of *N,N*′-bis(trimethylsilyl)ethylenediamine en route to compounds **4** and **5** was not indicated by NMR spectroscopy.

Attempts to prepare a stable monochloride-substituted analogue of [$Me_3SiN(H)CH_2CH_2N(SiMe_3)AlH_2$] by the reaction of *N,N*′-bis(trimethylsilyl)ethylenediamine with $H_2Al(Cl){\cdot}NMe_3$ yielded the redistributed dichloride species [$Me_3SiN(H)CH_2$-$CH_2N(SiMe_3)AlCl_2$] and **2**. Presumably the monochloride [$Me_3SiN(H)CH_2CH_2N(SiMe_3)AlHCl$] exchanges to yield a mixture of **3** and the dihydride species, and the dihydride then reacts with additional *N,N*′-bis(trimethylsilyl)ethylenediamine to yield **2**, thus driving the equilibrium further in favor of the dichloride species **3**. Compound **3** was isolated in high yield as an air and moisture sensitive colorless crystalline solid and has been characterized using ^1H and ^{13}C NMR spectroscopies, infrared spectroscopy, microanalysis, and X-ray structure determination. In the case of the synthesis of the analogous *tert*-butyl chloride [HN(*t*-Bu)CH_2CH_2N(*t*-Bu)AlHCl], no products resulting from redistribution processes were observed.

X-ray Structure Commentary. A. Structure of 1. Complex **1** crystallizes as prismatic crystals in the monoclinic space group $P2_1/c$ with four molecules in the unit cell and the

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(16) See, for example: Del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281. Del Piero, G.; Cesari, M.; Perego, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1977**, *129*, 289. Del Piero, G.; Cucinella, S.; Cesari, M. *J. Organomet. Chem.* **1979**, *173*, 263.

asymmetric unit comprising one discrete dimeric molecule (Figure 1). The complex is best described as an amido-bridged diamido−aluminum hydride. The dimetalated ethylenediamine acts as a bidentate ligand, chelating the aluminum atom with a nitrogen center bridging the aluminum atoms to achieve a 4-fold coordination for the aluminum atom which has a distorted tetrahedral N(amido){μ-N(amido)$_2$}H$_2$ coordination environment. The dimer possesses noncrystallographic centrosymmetry and is not isomorphous with the *tert*-butyl analogue.[17]

The bridging and terminal Al−N(amido) distances 1.952(3)−1.968(3) and 1.804(3)−1.810(3) Å are typical, as are the Al−H distances of 1.51(3) and 1.59(3) Å. The ligand bite angles (93.9(1) and 94.1(1)°) and the N−Al−N angles of the four-membered Al_2N_2 ring represent the largest distortion of the geometries about the metal centers from ideal tetrahedral coordination. Other bond angles within the molecule are unexceptional and do not require comment.

B. Structure of 2. Complex **2** crystallizes as prismatic crystals in the monoclinic space group *C*2/*c* with eight molecules in the unit cell and the asymmetric unit containing one discrete molecule (Figure 2). The structure is best described as a monomeric triamido−aluminum species featuring intramolecular coordination of the aluminum center by the secondary amine of the monometalated ethylenediamine. Both ethylenediamine ligands are chelating, achieving a distorted tetrahedral, 4-fold coordination sphere for the metal center. The molecule is devoid of symmetry and is not isomorphous with the *tert*-butyl analogue.[17]

The position of the secondary amine is defined unambiguously by the coordination geometry of the nitrogen and the aluminum centers and was confirmed by the location of the secondary amine proton in the crystal structure. The Al−N(amido) and Al−N(amine) distances are clearly distinct at 1.812(6)−1.818(5) and 2.004(6) Å, as are the N−Si distances of the secondary amine and amido nitrogen centers (1.795(6) and 1.698(6)−1.708(5) Å). The geometry about the amido nitrogen centers is planar ($\sum$(C−N−Si,Al;Si−N−Al) range from 359−360°) and set apart from that of the tetrahedral-coordinated secondary amine (351.8°). The ligand bite angles of the mono- and dimetalated ethylenediamine ligands are 88.7(2) and 96.0(3)°, respectively.

C. Structure of 3. Complex **3** crystallizes as prismatic crystals in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and the asymmetric unit comprising one discrete molecule (Figure 3). The complex is best described as a monomeric intramolecularly coordinated secondary amine adduct of an amido−aluminum dichloride 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.

The Al−N(amido) and Al−N(amine) distances of 1.774(4) and 1.952(4) Å are typical, as are the terminal Al−Cl distances of 2.120(2) and 2.142(2) Å. These Al−N distances are significantly reduced compared to those of the related compounds [HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(*t*-Bu)AlH$_2$][4] and [HN(*t*-Bu)CH$_2$CH$_2$N(*t*-Bu)AlHCl][3] (1.799(9) and 2.02(1) Å, and 1.80(1) and 2.00(1) Å) in either consequence of the silyl substituents or the expected enhanced Lewis acidity of the aluminum atom upon chloride substitution. The larger N−Al−Cl angles to the amido nitrogen atom (118.3(2) and 118.7(2)° *versus* 106.1(2) and 112.2(2)°) 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 Cl−Al−Cl angle is not constrained by ligand geometry constraints and approximates to ideal tetrahedral geometry (106.68(9)°). The ligand bite angle N−Al−N measures 93.6(2)°. Other bond angles within the molecule are unexceptional and do not require comment.

D. Structure of 4. Complex **4** crystallizes as prismatic crystals in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and the asymmetric unit comprising one discrete molecule (Figure 4). The amido−aluminum complex comprises three ligands. Two of which are dimetalated and chelate an aluminum center bearing one hydride and bridge another aluminum center through a nitrogen center with the other nitrogen center being three coordinate. These structural fragments of compound **4** are represented in the dimeric structure of **1**. The third ligand has had one of the trimethylsilyl groups removed and is trimetalated. This central ethylenediamine also chelates an aluminum hydride moiety and is involved in multiple bridge bonding which serves to link the former two fragments together. The molecule is devoid of symmetry.

The geometrical parameters for compound **4** will not be discussed in detail owing to their structural similarity to those found in compound **1**, with the exception of those regarding the dimetalated primary amine/imino nitrogen. The nonchelating Al−N bond lengths to the nitrogen center Al1 and Al2−N8 are marginally shorter than those in related complexes in this work (1.945(4) and 1.927(3) Å), and the Al−N distance within the chelate ring Al3−N8 at 1.867(4) Å is much shorter than normally found for amido−aluminum complexes with four-coordinate nitrogen centers.

E. Structure of 5. Complex **5** crystallizes as prismatic crystals in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and the asymmetric unit comprising one discrete molecule (Figure 5). The amido−aluminum hydride complex contains two ligands: one being dimetalated with both trimethylsilyl substituents retained and the other having had a single trimethylsilyl substituent removed (formally trimetalated). Both ligands chelate a common aluminum center, which is devoid of auxiliary ligands, and each also bridges an AlH$_2$ unit through one of the amido nitrogen centers, the other nitrogen being planar three-coordinate. The dimetalated primary amine nitrogen binds to a terminal AlH$_2$ unit, which has its 4-fold coordination environment completed by a molecule of trimethylamine. Each of the aluminum centers is in distorted tetrahedral coordination environments. The molecule is devoid of symmetry.

Geometrical parameters worthy of note for the structure of **5** include the Al−N distances from the primary amide nitrogen to the chelated aluminum center (1.938(4) Å), the bridging AlH$_2$ group (1.924(4) Å), and the terminal AlH$_2$ group (1.859(4) Å); all are reduced relative to their counterparts found in the related secondary amides in this work and are consistent with the observations of compound **4**.

Conclusions

We have been able to identify and structurally characterize five products obtained from the reactions of *N*,*N*′-bis(trimethylsilyl)ethylenediamine with H$_3$Al·NMe$_3$ and H$_2$(Cl)-Al·NMe$_3$. The chemistry based on metalation of the amine has proven to be similar to the analogous *tert*-butyl-substituted system.[3,4] However, the relative instability of the intermediate [Me$_3$SiN(H)CH$_2$CH$_2$N(SiMe$_3$)AlH$_2$] means that the alane rich species [(CH$_2$-μ-NSiMe$_3$)$_2$(AlH$_2$)$_2$] could not be prepared in this

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(17) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. Unpublished results.

case. Furthermore, the alternative reactivity of the silylamine (allowing it to undergo cleavage of the trimethylsilyl substituent to give imino/dimetalated amido−aluminum species) was established and highlights the increased complexity of this system. We have structurally characterized two complexes bearing novel structural features and are pursuing this theme with the goal of preparing silylamido−aluminum hydride complexes suitably labile for the production of aluminum nitride films by chemical vapor deposition processes under mild conditions.

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Supporting Information Available: Lists of atomic coordinates, U_{ij} values, bond distances and angles, and summaries of the X-ray diffraction data for compounds **1**−**5** (23 pages). Ordering information is given on any current masthead page.

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