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Contribution from the Departments of Chemistry, Martin Chemical Laboratory, Davidson College, Davidson, North Carolina 28036, and University of South Carolina, Columbia, South Carolina 29208

Reactions of Gallium Trichloride with Bis(dialkylamino)dimethylsilanes and Bis(alkylamino)dimethylsilanes

W. Rodger Nutt,*[,1a] Jeffery S. Blanton,[1a] Anthony M. Boccanfuso,[1b] Louis A. Silks III,[1b] Albert R. Garber,[1b] and Jerome D. Odom[1b]

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The Lewis acid–base adduct $Me_2Si(NMe_2)_2\cdot GaCl_3$ was isolated when $GaCl_3$ was allowed to react with $Me_2Si(NMe_2)_2$. The reaction of $Me_2Si(NEt_2)_2$ with $GaCl_3$ proceeded by dehalosilylation to give $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ and $Et_2NSi(Cl)Me_2$. The N-alkylated hexamethylcyclotrisilazane $(RNSiMe_2)_3$ and $RNH_2\cdot GaCl_3$ were obtained from the reaction of $GaCl_3$ with $[R(H)N]_2SiMe_2$, where R = Et and *n*-Bu. The molecular structures of $Me_2Si(NMe_2)_2\cdot GaCl_3$ and $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ were confirmed by X-ray crystallography. Crystal data for $Me_2Si(NMe_2)_2\cdot GaCl_3$: monoclinic space group *C*2/*c* (No. 15), $a = 26.146$ (7) Å, $b = 8.043$ (2) Å, $c = 16.164$ (6) Å, $\beta = 124.97$ (2)°, $V = 2785$ (1) Å^3, $Z = 8$, ρ(calcd) = 1.538 g cm^{-3}, and $R = 0.0489$. Crystal data for $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$: orthorhombic space group $P2_12_12_1$ (No. 19), $a = 14.813$ (4) Å, $b = 15.768$ (4) Å, $c = 13.102$ (2) Å, $V = 3060$ (1) Å^3, $Z = 4$, ρ(calcd) = 1.665 g cm^{-3}, and $R = 0.0556$. The four-membered (Ga–N–Si–N) ring in $[Cl_2Ga(NEt_2)_2SiMe_2]^+$ is nonplanar with a fold angle of 165.5 (5)° on the Ga···Si diagonal. The ^1H, ^{13}C, and ^{29}Si NMR spectra are reported and discussed.

Introduction

Dehalosilylation reactions of bis(trimethylsilyl)amines with gallium trihalides and alkylgallium dichlorides have been studied extensively. Reactions of bis(trimethylsilyl)amine with $GaCl_3$[2,3b] or $GaBr_3$[3a] have been found to proceed with the elimination of halotrimethylsilane and the formation of (trimethylsilylamido)gallium dihalide, and [methyl(trimethylsilyl)amido]gallium dichloride has been isolated from the reaction of $GaCl_3$ with $(Me_3Si)_2NMe$ (eq 1).[2b] Both $[Me(Cl)GaN(H)SiMe_3]_2$ and $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ have been obtained from the reactions of bis(trimethylsilyl)amine with $MeGaCl_2$ and $n\text{-}BuGaCl_2$.[3c]

$$(Me_3Si)_2NR + GaX_3 \rightarrow 1/n\,[X_2GaN(R)SiMe_3]_n + Me_3SiX \qquad (1)$$

$$X = Cl,\ R = H,\ n = 2, 3;\ X = Cl,\ R = Me,\ n = 2;\ X = Br,\ R = H,\ n = 2$$

On the other hand, the facility of substituted bis(amino)dimethylsilanes to undergo dehalosilylation in the presence of $GaCl_3$ and form substituted amidogallium dichlorides has not been investigated. As an extension of our studies, the reactions of $GaCl_3$ with $(Me_2N)_2SiMe_2$, $(Et_2N)_2SiMe_2$, $[Et(H)N]_2SiMe_2$, and $[n\text{-}Bu(H)N]_2SiMe_2$ in diethyl ether were examined.

Experimental Section

Materials and General Procedures. Gallium trichloride was purchased from Johnson Matthey, Alfa Products, and sublimed prior to use. The compounds $(Me_2N)_2SiMe_2$, $(Et_2N)_2SiMe_2$, $[Et(H)N]_2SiMe_2$, and $[n\text{-}Bu(H)N]_2SiMe_2$ (Huls America, Petrarch Systems) were purified by distillation. The solvents diethyl ether, benzene, methylene chloride, and pentane were refluxed over sodium/benzophenone ketyl, calcium hydride, phosphorus pentoxide, and sodium, respectively, and distilled into storage flasks. Toluene-d_8 (Aldrich Chemical Co.) was refluxed over calcium hydride and distilled into a storage flask. All experiments were performed under an oxygen-free, dry-nitrogen or argon atmosphere by using Schlenk and glovebox techniques.[4]

The ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained from either toluene-d_8 or methylene-d_2 chloride solutions with a Bruker AM-500, WH-400, or AM-300 or IBM NR-80B spectrometer. Standard broadband proton noise-modulated decoupling or composite pulse decoupling was used where appropriate. Standard variable-temperature accessories that were calibrated with methanol were employed with an estimated accuracy of ±0.5 °C. Field-frequency stabilization was provided by locking the field to the CD_2Cl_2 or $-CD_3$ of toluene-d_8 deuterium resonance of the solvent. All NMR sample tubes (5 mm) were sealed under vacuum.

The ^1H, ^{13}C, and ^{29}Si chemical shifts are reported in parts per million (ppm) with respect to Me_4Si at 0.0 ppm. A positive chemical shift denotes a resonance to lower shielding (higher frequency). The ^1H chemical shifts were referenced to the ^1H resonance of the residual $CHD_2C_6D_5$ (δ 5.32) solvent impurity, and the chemical shifts in the ^{13}C spectra were referenced to the methyl ^{13}C resonance of the toluene-d_8 (δ 20.4) or carbon resonance for $CHDCl_2$ (δ 53.8). The ^{29}Si chemical shift was measured with respect to an external 10% Me_4Si solution in $CDCl_3$. Appropriate frequency corrections were applied to compensate for the deuterium field/frequency lock on toluene-d_8 ($-CD_3$) or methylene-d_2 chloride. The ^{29}Si spectra were obtained by using a pulse angle of 50° and a recycle time of 2.2 s. Digital resolution (Hz/pt) of 0.96 Hz was obtained by using a 128K data table and a sweep width of 600 ppm at 99.363 MHz. Typically, 10000–15000 scans were required for adequate signal-to-noise.

Infrared spectra of Nujol mulls or thin films were recorded on a Perkin-Elmer Model 283 spectrophotometer. Absorption intensities are reported with the abbreviations vw (very weak), w (weak), m (medium), s (strong), and vs (very strong).[5] The molecular weights were determined cryoscopically in benzene with an apparatus similar to that described by Dilts and Shriver.[6] Melting points were obtained in sealed tubes on an Electrothermal IA 6304 melting point apparatus and were uncorrected. All elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of $(Me_2N)_2SiMe_2$ with $GaCl_3$. Gallium trichloride (4.77 g, 27.1 mmol) was dissolved in 20 mL of diethyl ether, and the stirred solution was cooled with an ice bath prior to the addition of bis(dimethylamino)dimethylsilane (4.28 g, 29.2 mmol). Initially, a white solid precipitated but redissolved when the mixture was heated to reflux. After the solution was allowed to reflux for 5 h, the liquid portion was removed by vacuum distillation, leaving a crystalline solid. Recrystallization of the solid from methylene chloride gave $Me_2Si(NMe_2)_2\cdot GaCl_3$ (6.65 g, 76.1% yield): mp 94–95 °C; ^1H NMR (500.135 MHz, toluene-d_8, 0.12 M) δ 2.10 (s, CH_3N, 2), 0.10 (s, CH_3Si, 1); ^1H NMR (500.135 MHz, methylene-d_2 chloride, 0.15 M) δ 2.50 (s, CH_3N, 2), 0.47 (s, CH_3Si, 1); ^{13}C NMR (100.61 MHz, toluene-d_8, 0.12 M) δ 39.5 (CH_3N), −3.9 (CH_3Si); ^{29}Si NMR (99.363 MHz, toluene-d_8, 0.12 M) δ 15.8 (s, CH_3Si); ^{29}Si NMR (99.363 MHz, methylene-d_2 chloride, 0.15 M) δ 16.7 (s, CH_3Si); IR (cm^{-1}) 1298 (vs), 1274 (vs), 1220 (m), 1182 (sh, m), 1166 (vs), 1150 (sh, m), 1111 (m), 1073 (s), 996 (vs), 874 (s), 843 (s), 822 (sh, s), 811 (vs), 781 (m), 711 (m), 631 (s), 602 (m), 500 (m), 402 (s), 377 (s), 346 (s), 275 (w). Anal. Calcd for $C_6H_{18}Cl_3GaN_2Si$: C, 22.35; H, 5.63; Cl, 32.99; Ga, 21.63; N, 8.69; Si, 8.71. Found: C, 21.87; H, 5.51; Cl, 33.10; Ga, 21.55; N, 8.40; Si, 8.01. Molecular weight for $C_6H_{18}Cl_3GaN_2Si$: calcd, 322.4; found, 328 (calcd molality 0.0405).

Reaction of $(Et_2N)_2SiMe_2$ with $GaCl_3$. Gallium trichloride (8.39 g, 47.7 mmol) was dissolved in 35 mL of diethyl ether, and the stirred solution was cooled with an ice bath prior to the addition of bis(diethylamino)dimethylsilane (10.26 g, 50.7 mmol). Initially, a white solid

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(1) (a) Davidson College. (b) University of South Carolina.

(2) Wiberg, N.; Schmid, K. H. *Z. Anorg. Allg. Chem.* **1966**, *345*, 93.

(3) (a) Nutt, W. R.; Blanton, J. S.; Kroh, F. O.; Odom, J. D. *Inorg. Chem.* **1989**, *28*, 2224. (b) Nutt, W. R.; Anderson, J. A.; Odom, J. D.; Williamson, M. M.; Rubin, B. H. *Inorg. Chem.* **1985**, *24*, 159. (c) Nutt, W. R.; Stimson, R. E.; Leopold, M. F.; Rubin, B. H. *Inorg. Chem.* **1982**, *21*, 1909.

(4) Shriver, D. R.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(5) Durkin, T.; DeHayes, L.; Glore, J. *J. Chem. Educ.* **1971**, *48*, 452.

(6) Dilts, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 5769.

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precipitated but redissolved when the mixture was warmed to room temperature. The solution was heated to reflux and a solid precipitated within 10 min. After the mixture was allowed to reflux for 7 h, the liquid portion was removed from the solid by vacuum distillation. The diethyl ether was distilled from the distillate at atmospheric pressure. Vacuum distillation of the remaining liquid afforded $(Et_2N)_2SiMe_2$ (2.77 g, 33.0% recovered) and $Et_2NSi(Cl)Me_2$ (1.44 g, 54.8% yield): bp 53–55 °C/18 Torr, lit. bp 52 °C/18 Torr;[7a] ^1H NMR (500.135 MHz, toluene-d_8, 0.38 M) δ 2.71 (q, CH_2N, 2), 0.91 (t, $\mathit{CH_3}CH_2$, 3), 0.30 (s, CH_3Si, 3); ^{13}C NMR (125.767 MHz, toluene-d_8, 0.38 M) δ 40.2 (CH_2N), 15.4 ($\mathit{CH_3}CH_2$), 1.9 (CH_3Si); ^{29}Si NMR (99.363 MHz, toluene-d_8, 0.38 M) δ 11.1 (s, CH_3Si); IR (cm^{-1}) 2970 (vs), 2930 (s), 2870 (s), 2490 (vw), 1470 (m), 1453 (m), 1415 (m), 1381 (vs), 1370 (m), 1356 (m), 1347 (m), 1295 (m), 1262 (vs), 1211 (vs), 1173 (vs), 1104 (m), 1080 (m), 1064 (m), 1035 (vs), 939 (vs), 915 (m), 838 (vs), 817 (vs), 796 (vs), 699 (m), 622 (m). Anal. Calcd for $C_6H_{16}ClNSi$: C, 43.48; H, 9.73; Cl, 21.39; N, 8.45; Si, 16.95. Found: C, 43.97; H, 10.00; Cl, 19.67; N, 8.58; Si, 16.26.

Recrystallization of the solid from methylene chloride gave $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ (8.03 g, 65.9% yield): mp 129–130 °C; ^1H NMR (500.135 MHz, methylene-d_2 chloride, 0.13 M) δ 3.41 (q, CH_2N, 4), 3.37 (q, CH_2N, 4), 3.35 (q, CH_2N, 4), 1.35 (t, $\mathit{CH_3}CH_2$, 6), 1.31 (t, $\mathit{CH_3}CH_2$, 12), 1.07 (s, CH_3Si, 6); ^{13}C NMR (125.767 MHz, methylene-d_2 chloride, 0.13 M) δ 44.3 (CH_2N, 2), 44.1 (CH_2N, 4), 12.1 ($\mathit{CH_3}CH_2$, 2), 12.0 ($\mathit{CH_3}CH_2$, 4), −1.5 (CH_3Si, 2); ^{29}Si NMR (99.363 MHz, methylene-d_2 chloride, 0.13 M) δ 47.5 (s, CH_3Si); IR (cm^{-1}) 1302 (s), 1294 (m), 1283 (s), 1279 (s), 1175 (m), 1136 (s), 1101 (s), 1050 (m), 1037 (s), 1008 (sh, m), 998 (s), 908 (m), 889 (m), 882 (m), 864 (s), 850 (vs), 823 (sh, s), 818 (vs), 807 (s), 783 (s), 772 (s), 750 (m), 647 (s), 620 (m), 574 (m), 551 (w), 443 (m), 421 (m), 392 (vs), 374 (vs), 343 (s), 289 (w). Anal. Calcd for $C_{14}H_{36}Cl_8Ga_3N_3Si$: C, 21.91; H, 4.73; Cl, 36.96; Ga, 27.26; N, 5.48; Si, 3.66. Found: C, 21.69; H, 4.79; Cl, 36.76; Ga, 27.48; N, 5.27; Si, 3.71.

Reaction of $[Et(H)N]_2SiMe_2$ with $GaCl_3$. Gallium trichloride (10.14 g, 57.6 mmol) was dissolved in 40 mL of diethyl ether, and the stirred solution was cooled with an ice bath prior to the addition of bis(ethylamino)dimethylsilane (7.70 g, 52.6 mmol). After the solution was allowed to reflux for 9 h, the diethyl ether was removed by vacuum distillation, leaving two immiscible liquids. Pentane (15 mL) was added to the flask that contained the liquids and a solid precipitated. The solid was filtered and washed with pentane. The pentane was distilled from the filtrate at atmospheric pressure and a vacuum distillation of the remaining liquid afforded $(EtNSiMe_2)_3$ (3.56 g, 66.8% yield): bp 100–101 °C/1 Torr, lit. bp 103° C/2 Torr;[8a] n_D^{20} 1.4646, lit. n_D^{20} 1.4642;[8a] ^1H NMR (300.135 MHz, toluene-d_8, 0.11 M) δ 2.78 (q, CH_2N, 2), 1.00 (t, $\mathit{CH_3}CH_2$, 3), 0.20 (s, CH_3Si, 6); ^{13}C NMR (75.469 MHz, toluene-d_8, 0.11 M) δ 38.0 (CH_2N), 20.5 ($\mathit{CH_3}CH_2$), 1.4 (CH_3Si); ^{29}Si NMR (99.363 MHz, toluene-d_8, 0.11 M) δ 0.7 (s, CH_3Si). The IR spectrum was identical with the spectrum of $(EtNSiMe_2)_3$ reported by Abel and Bush[8a] with the exception that the weak bands at 1615, 1561, 1543, and 1510 cm^{-1} were absent. Molecular weight for $C_{12}H_{33}N_3Si_3$: calcd, 303.7; found, 298 (calcd molality 0.0287).

Recrystallization of the solid from methylene chloride gave $EtNH_2\cdot GaCl_3$ (7.18 g, 61.7% yield): mp 63–64 °C; ^1H NMR (300.135 MHz, toluene-d_8, 0.26 M) δ 2.08 (q, CH_2N, 2), 1.55 (broad singlet, NH_2, 2), 0.35 (t, $\mathit{CH_3}CH_2$, 3); ^{13}C NMR (20.13 MHz, toluene-d_8, 0.29 M) δ 37.7 (CH_2N), 14.5 ($\mathit{CH_3}CH_2$); IR (cm^{-1}) 3265 (vs), 3220 (s), 3115 (s), 2465 (m), 2414 (m), 2285 (m), 2250 (m), 2098 (w), 2045 (w), 1858 (w), 1737 (w), 1568 (s), 1560 (sh, s), 1253 (sh, s), 1238 (vs), 1165 (m), 1070 (vs), 1051 (s), 1025 (s), 975 (m) 939 (m), 920 (m), 885 (sh, m), 871 (m), 810 (w), 785 (w), 682 (s), 583 (m), 404 (sh, vs), 386 (vs), 360 (vs), 293 (m). Anal. Calcd for $C_2H_7Cl_3GaN$: C, 10.86; H, 3.19; Cl, 48.09; Ga, 31.52; N, 6.33. Found: C, 11.02; H, 3.23; Cl, 48.00; Ga, 31.29; N, 6.06. Molecular weight for $C_2H_7Cl_3GaN$: calcd, 221.2; found, 223 (calcd molality 0.0325).

Table I. Experimental Data from the X-ray Diffraction Study

	$Me_2Si(NMe_2)_2\cdot GaCl_3$	$[Cl_2Ga(NEt_2)_2SiMe_2]-[(Cl_3Ga)_2NEt_2]$
cryst syst	monoclinic	orthorhombic
space group	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)
cell dimens[a]		
a, Å	26.146 (7)	14.813 (4)
b, Å	8.043 (2)	15.768 (4)
c, Å	16.164 (6)	13.102 (2)
β, deg	124.97 (2)	
V, Å^3	2785 (1)	3060 (1)
Z	8	4
mol wt	322.4	767.3
ρ(calcd), g cm^{-3}	1.538	1.665
radiation	Mo K$\bar{\alpha}$ (0.710 69 Å)	
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2095	4926
R^b	0.0489	0.0556
R_w^c	0.0450	0.0484
weighting scheme, w	$1.3960/\sigma^2(F_o)$	$1.9595/\sigma^2(F_o)$

[a] Unit cell parameters were derived from a least-squares refinement of 15 reflections (19.94° ≤ θ ≤ 25.92°, 14.13° ≤ θ ≤ 22.22°). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}]$.

Reaction of $[n\text{-}Bu(H)N]_2SiMe_2$ with $GaCl_3$. Gallium trichloride (4.87 g, 27.7 mmol) was dissolved in 20 mL of diethyl ether, and the stirred solution was cooled with an ice bath prior to the addition of bis(n-butylamino)dimethylsilane (5.98 g, 29.5 mmol). After the solution was allowed to reflux for 8 h, the diethyl ether was removed by vacuum distillation, leaving two immiscible liquids. Pentane (7 mL) was added to the flask that contained the liquids and a solid precipitated. The solid was filtered and washed with pentane. The pentane was distilled from the filtrate at atmospheric pressure and vacuum distillation of the remaining liquid afforded $(n\text{-}BuNSiMe_2)_3$ (3.20 g, 89.3% yield): bp 102 °C/0.01 Torr; ^1H NMR (500.135 MHz, toluene-d_8, 0.13 M) δ 2.77 (t, CH_2N, 2), 1.43 (m, $\mathit{CH_2}CH_2$, 2), 1.22 (sextet, $CH_2\mathit{CH_2}$, 2), 0.89 (t, $\mathit{CH_3}CH_2$, 3), 0.26 (s, CH_3Si, 6); ^{13}C NMR (125.767 MHz, toluene-d_8, 0.13 M) δ 44.2 (CH_2N), 38.0 ($\mathit{CH_2}CH_2$), 20.9 ($CH_2\mathit{CH_2}$), 14.3 ($\mathit{CH_3}CH_2$), 1.6 (CH_3Si, $J(^{13}C-^{29}Si)$ = 63 Hz); ^{29}Si NMR (99.363 MHz, toluene-d_8, 0.13 M) δ 1.2 (s, CH_3Si); IR (cm^{-1}) 2962 (vs), 2935 (s), 2900 (m), 2875 (m), 2865 (s), 1478 (w), 1467 (m), 1408 (w), 1383 (w), 1371 (m), 1342 (w), 1313 (w), 1254 (vs), 1238 (m), 1165 (m), 1151 (m), 1126 (sh, m), 1113 (sh, m), 1088 (vs), 1060 (m), 1039 (m), 995 (m), 978 (s), 963 (s), 903 (vs), 880 (sh, m), 849 (m), 814 (s), 783 (s), 743 (w), 729 (w), 672 (sh, w), 667 (m), 608 (w). Anal. Calcd for $C_{18}H_{45}N_3Si_3$: C, 55.75; H, 11.70; N, 10.83; Si, 21.72. Found: C, 55.76; H, 10.95; N, 10.70; Si, 22.01. Molecular weight for $C_{18}H_{45}N_3Si_3$: calcd, 387.8; found 386 (calcd molality 0.0540).

Recrystallization of the solid from methylene chloride gave $n\text{-}BuNH_2\cdot GaCl_3$ (5.40 g, 78.3% yield): mp 46–47 °C; ^1H NMR (500.135 MHz, toluene-d_8, 0.16 M) δ 2.19 (t, CH_2N, 2), 1.84 (broad singlet, NH_2, 2), 0.68 (m, CH_2CH_2, 4), 0.61 (t, $\mathit{CH_3}CH_2$, 3); ^{13}C NMR (125.767 MHz, toluene-d_8, 0.16 M) δ 42.3 (CH_2N), 31.6 ($\mathit{CH_2}CH_2$), 19.4 ($CH_2\mathit{CH_2}$), 13.4 ($\mathit{CH_3}CH_2$); IR (cm^{-1}) 3268 (s), 3225 (vs), 3115 (s), 2420 (w), 2250 (w), 1573 (sh, s), 1568 (s), 1338 (s), 1290 (s), 1270 (s), 1250 (m), 1209 (vs), 1184 (sh, s), 1173 (sh, m), 1106 (s), 1081 (s), 1064 (m), 1023 (m), 1000 (m), 968 (sh, s), 957 (s), 945 (sh, s), 902 (m), 884 (sh, w), 843 (m), 828 (w), 803 (w), 795 (w), 752 (m), 738 (m), 682 (s), 588 (m), 485 (w), 402 (sh, vs), 390 (vs), 362 (vs), 233 (w). Anal. Calcd for $C_4H_{11}Cl_3GaN$: C, 19.28; H, 4.45; Cl, 42.68; Ga, 27.98; N, 5.62. Found: C, 19.35; H, 4.06; Cl, 42.40; Ga, 27.96; N, 5.37.

Collection of Crystallographic Data. Colorless crystals of $Me_2Si(NMe_2)_2\cdot GaCl_3$ and $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ were grown by slowly cooling saturated methylene chloride solutions, and suitable crystals were mounted in capillary tubes under a nitrogen atmosphere. The determination of the unit cell parameters and the orientation matrix as well as the collection of the intensity data were made on a Syntex P2$_1$ four-circle diffractometer.[9] The diffractometer was equipped with a graphite monochromator (Bragg 2θ angle 12.2°). Unit cell parameters and details of the data collection are given in Table I. Absorption corrections were applied to the intensity data by using λ scans for five reflections with 2θ values between 7 and 42° (former compound) and for seven reflections with 2θ values between 6 and 45° (latter compound).[10]

Structure Determination and Refinement. The positions of the gallium atoms were obtained from a Patterson map, and the positions of the Cl, C, N, and Si atoms were taken from various Fourier maps. After several cycles of a full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, the methyl and methylene hydrogen atoms were generated at calculated positions (C–H = 1.08 Å; H–C–H = 109.5°) with rigid geometry. Additional cycles of refinement led to convergence.

All calculations were performed on a DEC VAX 8530 computer using SHELX-76,[11a] SHELXS-86,[11b] and ORFFE4.[12] Scattering factors for all atoms

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(7) (a) Rühlmann, K.; Mansfield, M. *J. Prakt. Chem.* **1964**, *24*, 226. (b) Wannagat, U.; Schriener, G. *Monatsh. Chem.* **1965**, *96*, 1889.

(8) (a) Abel, E. W.; Bush, R. P. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1685. (b) Breed, L. W.; Elliott, R. L. *Inorg. Chem.* **1964**, *3*, 1622. (c) Andrianov, K. A.; Vasil'eva, T. V.; Minaeva, A. A. *Izv. Akad. Nauk. SSR, Ser. Khim.* **1963**, *12*, 2227.

(9) Crystallographic data were collected at Georgia Institute of Technology, Atlanta, GA, by Dr. Donald VanDerveer.

(10) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

Table II. Final Positional Parameters for $Me_2Si(NMe_2)_2{\cdot}GaCl_3$

atom	*x/a*	*y/b*	*z/c*
Cl(1)	0.3683 (1)	−0.1467 (2)	−0.1329 (2)
Cl(2)	0.2941 (1)	0.1482 (3)	−0.0731 (2)
Cl(3)	0.4573 (1)	0.1765 (3)	0.0478 (1)
Ga	0.3702 (1)	0.1074 (1)	−0.0893 (1)
N(1)	0.3525 (2)	0.2573 (6)	−0.2018 (4)
Si	0.4080 (1)	0.2633 (2)	−0.2398 (1)
N(2)	0.3816 (3)	0.4068 (7)	−0.3325 (4)
C(1)	0.2894 (3)	0.2106 (10)	−0.2916 (5)
C(2)	0.3465 (4)	0.4306 (8)	−0.1721 (6)
C(3)	0.4076 (4)	0.0553 (9)	−0.2873 (7)
C(4)	0.4853 (3)	0.3206 (11)	−0.1270 (6)
C(5)	0.3982 (6)	0.5806 (10)	−0.3146 (8)
C(6)	0.3413 (4)	0.3704 (12)	−0.4365 (5)

Table III. Final Positional Parameters for $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$

atom	*x/a*	*y/b*	*z/c*
Ga(1)	0.5034 (1)	0.3038 (1)	−0.1567 (1)
Ga(2)	0.4849 (1)	0.4170 (1)	0.3222 (1)
Ga(3)	0.3300 (1)	0.2783 (1)	0.3914 (1)
Si	0.4437 (2)	0.4693 (2)	−0.1561 (2)
Cl(1)	0.4929 (2)	0.2461 (2)	−0.3028 (2)
Cl(2)	0.5453 (2)	0.2242 (2)	−0.0358 (2)
Cl(3)	0.3088 (2)	0.3730 (2)	0.5089 (2)
Cl(4)	0.3144 (2)	0.1544 (2)	0.4614 (3)
Cl(5)	0.2332 (2)	0.2888 (2)	0.2690 (3)
Cl(6)	0.5333 (2)	0.4709 (2)	0.4626 (2)
Cl(7)	0.5896 (2)	0.4300 (2)	0.2063 (2)
Cl(8)	0.3691 (2)	0.4835 (2)	0.2619 (3)
N(1)	0.3890 (4)	0.3691 (4)	−0.1213 (5)
N(2)	0.5572 (5)	0.4210 (5)	−0.1661 (6)
N(3)	0.4535 (4)	0.2947 (4)	0.3379 (6)
C(1)	0.3637 (7)	0.3603 (6)	−0.0112 (7)
C(2)	0.2765 (7)	0.4061 (8)	0.0187 (9)
C(3)	0.3124 (7)	0.3415 (6)	−0.1947 (9)
C(4)	0.2832 (8)	0.2486 (7)	−0.1665 (12)
C(5)	0.6152 (7)	0.4404 (7)	−0.0723 (8)
C(6)	0.7063 (7)	0.3955 (9)	−0.0736 (11)
C(7)	0.6059 (7)	0.4352 (7)	−0.2669 (8)
C(8)	0.6408 (8)	0.5269 (7)	−0.2785 (12)
C(9)	0.4402 (7)	0.5485 (6)	−0.0530 (8)
C(10)	0.4019 (7)	0.5073 (7)	−0.2837 (8)
C(11)	0.5136 (7)	0.2534 (7)	0.4193 (8)
C(12)	0.6152 (7)	0.2509 (10)	0.3887 (13)
C(13)	0.4628 (8)	0.2555 (6)	0.2336 (8)
C(14)	0.4420 (9)	0.1608 (7)	0.2286 (10)

included real and imaginary anomalous dispersion components.[13] In all least-squares refinements the quantity minimized was $\sum w(|F_0| - |F_c|)^2$. The final positional parameters are found in Tables II and III. Selected bond lengths and bond angles are given in Tables IV and V. Tables of observed and calculated structure factors, thermal parameters, and hydrogen coordinates as well as a complete listings of bond lengths, bond angles, and dihedral angles are available as supplementary material.

Results and Discussion

When $Me_2Si(NMe_2)_2$ was allowed to react with $GaCl_3$ in 1:1 mole ratio, the Lewis acid–base adduct $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ was isolated (eq 2). The adduct is a colorless, crystalline solid. The

$$Me_2Si(NMe_2)_2 + GaCl_3 \rightarrow Me_2Si(NMe_2)_2{\cdot}GaCl_3 \quad (2)$$

metal chlorides $ZrCl_4$, $HfCl_4$, and $SnCl_4$ also have been found to form 1:1 complexes with $Me_2Si(NMe_2)_2$, while dehalosilylation has been observed in the reaction of $TiCl_4$ with $Me_2Si(NMe_2)_2$.[14]

Table IV. Bond Distances (Å) and Bond Angles (deg) for $Me_2Si(NMe_2)_2{\cdot}GaCl_3$

Distances			
Cl(1)–Ga	2.154 (2)	Cl(2)–Ga	2.176 (2)
Cl(3)–Ga	2.149 (2)	Ga–N(1)	2.003 (5)
N(1)–Si	1.874 (5)	N(2)–Si	1.695 (6)
C(3)–Si	1.839 (7)	C(4)–Si	1.842 (7)
C(1)–N(1)	1.491 (7)	C(2)–N(1)	1.512 (7)
C(6)–N(2)	1.411 (8)	C(5)–N(2)	1.442 (9)
Angles			
C(5)–N(2)–Si	124.0 (6)	C(6)–N(2)–Si	124.0 (6)
C(5)–N(2)–C(6)	112.0 (7)	Cl(2)–Ga–Cl(1)	109.4 (1)
Cl(3)–Ga–Cl(1)	113.2 (1)	Cl(3)–Ga–Cl(2)	109.8 (1)
Cl(1)–Ga–N(1)	108.9 (1)	Cl(2)–Ga–N(1)	105.5 (2)
Cl(3)–Ga–N(1)	109.8 (1)	C(1)–N(1)–Ga	106.4 (4)
C(2)–N(1)–Ga	106.2 (4)	Si–N(1)–Ga	106.4 (4)
C(1)–N(1)–Si	108.8 (4)	C(2)–N(1)–Si	108.7 (4)
C(1)–N(1)–C(2)	106.5 (5)	N(2)–Si–N(1)	107.9 (3)
C(3)–Si–N(1)	107.0 (3)	C(4)–Si–N(1)	107.4 (3)
C(3)–Si–N(2)	110.4 (4)	C(4)–Si–N(2)	111.4 (3)
C(4)–Si–C(3)	112.5 (4)		

Table V. Selected Intramolecular Distances (Å) and Bond Angles (deg) for $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$

Distances			
Ga(1)···Si	2.755 (3)	N(1)···N(2)	2.687 (10)
Cl(1)–Ga(1)	2.125 (2)	Cl(2)–Ga(1)	2.114 (3)
Cl(3)–Ga(3)	2.167 (3)	Cl(4)–Ga(3)	2.169 (3)
Cl(5)–Ga(3)	2.157 (3)	Cl(6)–Ga(2)	2.149 (3)
Cl(7)–Ga(2)	2.180 (3)	Cl(8)–Ga(2)	2.160 (3)
Ga(1)–N(1)	2.036 (7)	Ga(1)–N(2)	2.016 (7)
Ga(2)–N(3)	1.995 (7)	Ga(3)–N(3)	1.977 (6)
Si–N(1)	1.833 (7)	Si–N(2)	1.849 (7)
Si–C(9)	1.840 (9)	Si–C(10)	1.881 (10)
Angles			
N(1)–Ga(1)–N(2)	83.1 (3)	N(1)–Si–N(2)	93.7 (3)
Ga(1)–N(1)–Si	90.6 (3)	Ga(1)–N(2)–Si	90.8 (3)
Cl(1)–Ga(1)–Cl(2)	116.3 (1)	Cl(1)–Ga(1)–N(1)	111.1 (2)
Cl(1)–Ga(1)–N(2)	111.5 (2)	Cl(2)–Ga(1)–N(1)	111.9 (2)
Cl(2)–Ga(1)–N(2)	118.3 (2)	Cl(1)–Ga(1)···Si	112.6 (1)
Cl(2)–Ga(1)···Si	130.9 (1)	C(9)–Si–C(10)	115.3 (5)
C(9)–Si···Ga(1)	130.8 (3)	C(10)–Si···Ga(1)	113.9 (4)
C(9)–Si–N(1)	112.9 (4)	C(9)–Si–N(2)	110.9 (4)
C(10)–Si–N(1)	110.5 (4)	C(10)–Si–N(2)	111.6 (4)
C(1)–N(1)–C(3)	112.9 (7)	C(1)–N(1)···N(2)	118.1 (5)
C(3)–N(1)···N(2)	129.0 (6)	C(1)–N(1)–Ga(1)	112.4 (6)
C(1)–N(1)–Si	115.5 (6)	C(3)–N(1)–Ga(1)	109.0 (5)
C(3)–N(1)–Si	114.3 (6)	C(5)–N(2)–C(7)	113.7 (7)
C(5)–N(2)···N(1)	114.0 (6)	C(7)–N(2)···N(1)	132.4 (6)
C(5)–N(2)–Ga(1)	110.8 (6)	C(5)–N(2)–Si	111.8 (6)
C(7)–N(2)–Ga(1)	112.0 (6)	C(7)–N(2)–Si	115.6 (6)
C(11)–N(3)–C(13)	113.8 (8)	Ga(2)–N(3)–Ga(3)	112.3 (3)
C(11)–N(3)–Ga(2)	110.2 (6)	C(11)–N(3)–Ga(3)	103.6 (5)
C(13)–N(3)–Ga(2)	106.4 (5)	C(13)–N(3)–Ga(3)	110.7 (6)

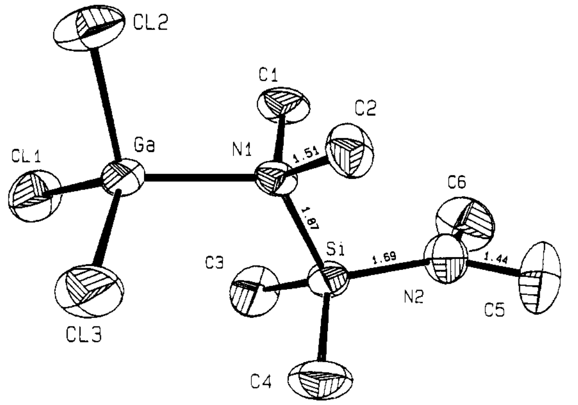

Figure 1. ORTEP diagram of $Me_2Si(NMe_2)_2{\cdot}GaCl_3$.

The crystal and molecular structure of $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ was determined by X-ray crystallography. The ORTEP diagram of the adduct is shown in Figure 1. The gallium atom is bonded

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(11) (a) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; Cambridge University Press: New York, 1975. (b) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Ed.; Oxford University Press: London, 1985; pp 175–189.

(12) Busing, W. R.; Martin, K. O.; Levy, H. A. *ORFFE*; revised by F. M. Brown, C. K. Johnson, and W. E. Thiessen; Oak Ridge National Laboratory: Oak Ridge, TN, 1985.

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(14) Wade, S. R.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1981**, 1264.

to one of the two nitrogen atoms in bis(dimethylamino)dimethylsilane and three chlorine atoms. The coordination environment around nitrogen atom N(2) is trigonal planar. The displacement of nitrogen atom N(2) from the plane that is formed by the Si, C(5), and C(6) atoms is 0.004 (11) Å. The C(5)–N(2)–Si, C(6)–N(2)–Si, and C(5)–N(2)–C(6) bond angles are 124.0 (6), 124.0 (6), and 112.0 (7)°, and the N(2)–Si bond length (1.695 (6) Å) is significantly shorter than the N(1)–Si bond length (1.874 (5) Å). These structural features are consistent with the hypothesis of ($p \rightarrow d$) π-bonding from nitrogen atom N(2) to the silicon atom.[15]

The ^1H and ^{13}C NMR spectra of $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ in toluene-d_8 (100% D) are found to be temperature dependent. At room temperature the proton spectrum exhibits two singlets at 2.10 and 0.10 ppm with the integrations in a ratio of 2:1. The two singlets have been assigned to the protons of the dimethylamino and dimethylsilyl groups, respectively. As the temperature is lowered, the deshielded singlet broadens and eventually splits at −81.5 °C. The singlet at 2.1 ppm sharpens and the singlet at 1.9 ppm broadens as the sample is cooled further to −107 °C. A similar temperature dependency is observed in the proton-decoupled ^{13}C NMR spectrum. However, the ^1H NMR spectrum of $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ in methylene-d_2 chloride is found to contain two singlets at 2.50 and 0.47 ppm and to be temperature independent as the sample is cooled to −103 °C.[16]

Rapid exchange of the $GaCl_3$ moiety between the two nitrogen atoms may be responsible for the apparent equivalence of the two Me_2N environments in $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ at room temperature. If the rate of this exchange is slow on the NMR time scale at temperatures below −81.5 °C, then two resonances associated with the two magnetically different Me_2N groups should be observed at those temperatures. Only a single O–Si–Me and Al–Me environment has been observed in the ^1H, ^{13}C, ^{17}O, and ^{29}Si NMR spectra of $Me_3Al[(OSiMe_2)_3]$ from room temperature to −80 °C and has been attributed to the rapid exchange of the Me_3Al group between the three oxygen atoms in $Me_3Al[(OSiMe_2)_3]$.[17] Additional NMR studies of the $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ system as well as others are planned in order to characterize the exchange process and the role of the solvent in the process.

In contrast to the preceding reaction (eq 2) in which adduct formation occurred, the reaction of $Me_2Si(NEt_2)_2$ with $GaCl_3$ proceeded with dehalosilylation. The ionic compound $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ and the compounds $Et_2NSi(Cl)Me_2$ and $Me_2Si(NEt_2)_2$ were isolated from the reaction mixture (eq 3). A similar cation in the compound $[Me_2Ga(N{=}PMe_2)_2SiMe_2][Me_4Ga]$ has been reported,[18] and anions of the form $Et_3GaXGaEt_3^-$ (X = F, Cl, Br) and $Cl_3GaClGaCl_3^-$ are known.[19]

$$3Me_2Si(NEt_2)_2 + 3GaCl_3 \rightarrow [Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2] + Et_2NSi(Cl)Me_2 + Me_2Si(NEt_2)_2 \quad (3)$$

The ionic nature of $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ suggests that the dehalosilylation reaction in eq 3 proceeded by a S_N2-Si rather than a S_Ni-Si pathway.[20] The reaction pathway may be similar to the one that has been proposed for the dehalosilylation reaction of BCl_3 with isobutyl(methylnaphthylphenylsilyl)amine, (methylnaphthylphenylsilyl)amine, or methylnaphthylphenyl(1-pyrrolidinyl)silane.[20c] Initially, $GaCl_3$ and $(Et_2N)_2SiMe_2$ may have formed an adduct. An unidentified solid precipitated when the reactants were mixed at 0 °C and redissolved when the mixture was warmed to room temperature. Nucleophilic attack at the silicon atom in one adduct by a chlorine atom in a second adduct with heterolytic cleavage of Si–N and Ga–Cl bonds would result in the formation of $Cl_3GaNEt_2^-$, $Et_2NSi(Cl)Me_2$, and $Cl_2GaN(Et_2)SiNEt_2^+$. The formation of a second Ga–N bond and hence a four-membered (Ga–N–Si–N) ring would stabilize the cation, and an exchange of $GaCl_3$ from an adduct to the stronger Lewis base $Cl_3GaNEt_2^-$ would yield the anion $(Cl_3Ga)_2NEt_2^-$ and $(Et_2N)_2SiMe_2$.

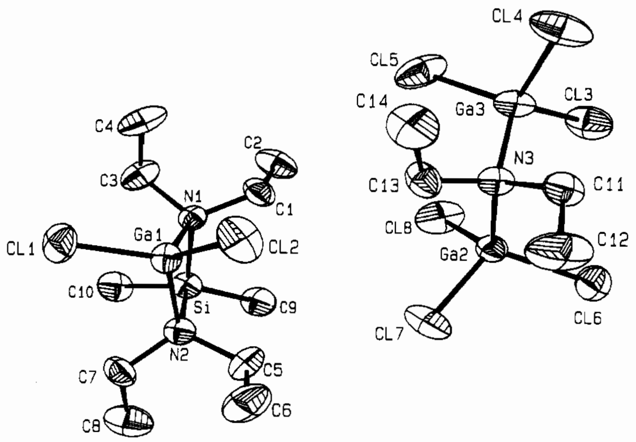

Figure 2. ORTEP diagram of $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$.

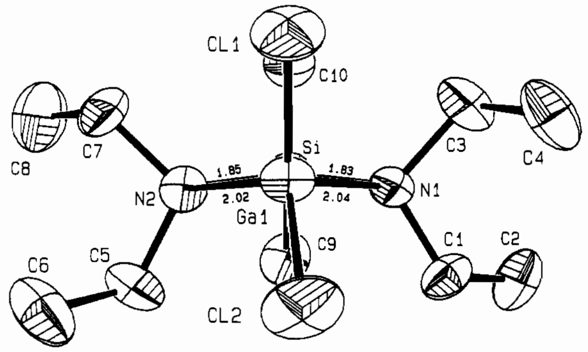

Figure 3. ORTEP diagram of $[Cl_2Ga(NEt_2)_2SiMe_2]^+$.

The X-ray crystallographic study of $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ revealed that the four-membered ring in the cation is nonplanar (Figures 2 and 3). The dihedral angles Ga(1)–N(1)–N(2)–Si and N(1)–Ga(1)–Si–N(2) are 165.8 (4) and 165.6 (5)°. Presumably, the steric overcrowding that would occur if the ring were planar is relieved by the distortion of the ring away from C_2 symmetry. The N(1)–Ga(1)–N(2) bond angle (83.1 (3)°) is significantly smaller than the corresponding angles (range: 89.1 (1)–90.1 (2)°) in the compounds $[Me(Cl)GaN(H)SiMe_3]_2$, $[Cl_2GaN(H)SiMe_3]_2$, $[Cl_2GaN(Me)SiMe_3]_2$, and $[Br_2GaN(H)SiMe_3]_2$ with a planar $(Ga–N)_2$ ring[3] but is similar to the N–Ga–N bond angle (82.1°) in the compound $[Me_2GaN{=}CMe_2]_2$ that also contains a planar $(Ga–N)_2$ ring.[21] The N(1)–Si–N(2) (93.7 (3)°) and C(9)–Si–C(10) (115.3 (5)°) bond angles in the cation are larger than the corresponding bond angles (90.0 (1) and 107.3 (2)°) in the compound $Cl_2Al(t\text{-}BuN)(t\text{-}BuNH)SiMe_2$ with a planar (Al–N–Si–N) ring.[22] On the other hand the endocyclic bond angles subtended at the nitrogen atoms (average: 90.7 (3)°) are similar to the Ga–N–Ga bond angles (range: 89.9 (2)–91.0 (1)°) in the planar compounds.[3] The Cl(1)–Ga(1)–Cl(2) bond angle (116.3 (1)°) is larger than the comparable bond angles in $[Cl_2GaN(H)SiMe_3]_2$ (111.9 (1)°) and $[Cl_2GaN(Me)SiMe_3]_2$ (108.1 (1)°), and the Ga–Cl bond lengths (2.125 (2) and 2.114 (3) Å) lie at the lower end of the range of values (2.136 (2)–2.155 (2) Å) found in these compounds. The Ga–N bond lengths in compounds with a planar $(Ga–N)_2$ ring[3,21]

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(15) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastave, R. C. *Metal and Metalloid Amides*; Ellis Horwood Limited: Chichester, England, 1980; p 245.

(16) Boccanfuso, A. M. Ph.D. Dissertation, University of South Carolina, 1988.

(17) Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137.

(18) Schmidbaur, H.; Wolfsberger, W.; Schwirten, K. *Chem. Ber.* **1969**, *102*, 556.

(19) (a) Wilson, I. L.; Dehnicke, K. *J. Organomet. Chem.* **1974**, *67*, 229. (b) Taylor, M. J. *J. Chem. Soc. A* **1970**, 2812.

(20) (a) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (b) Sommer, L. H. *Intra-Sci. Chem. Rep.* **1973**, *7*, 1. (c) Sommer, L. H.; Citron, J. D.; Parker, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 4729.

(21) Zettler, R.; Hess, H. *Chem. Ber.* **1977**, *110*, 3943.

(22) Veith, M.; Lange, H.; Recktenwald, O.; Frank, W. *J. Organomet. Chem.* **1985**, *294*, 273.

vary from 1.964 (4) to 2.012 (8) Å, and the Ga–N bond lengths (2.036 (7) and 2.016 (7) Å) in the cation fall at the upper end of this range. The Si–N bond lengths (1.833 (7) and 1.849 (7) Å) are within the range of values (1.744 (8)–1.874 (5) Å) observed in compounds where the silicon atom is bonded to a nitrogen atom with a tetrahedral coordination environment in this and other studies.[3,22]

The Ga–Cl (range: 2.149 (3)–2.180 (3) Å), Ga–N (1.995 (7) and 1.977 (6) Å), and C–N (average: 1.520 (12) Å) bond lengths in the anion $[(Cl_3Ga)_2NEt_2]^-$ (Figure 2) are similar to the corresponding bond lengths (range 2.149 (2)–2.176 (2) Å, 2.003 (5) Å, average 1.502 (7) Å) in $Me_2Si(NMe_2)_2{\cdot}GaCl_3$. The larger steric requirements of the ethyl groups versus the methyl groups on a nitrogen atom are reflected in the larger C(11)–N(3)–C(13) bond angle (113.8 (8)°) in the anion and the mean C–N–C bond angle (113.3 (7)°) in the cation in comparison to the C(1)–N(1)–C(2) bond angle (106.5 (5)°) in $Me_2Si(NMe_2)_2{\cdot}GaCl_3$. There are no abnormally close contacts between the ionic species in the unit cell.

The ^1H NMR spectrum of $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga)_2NEt_2]$ in methylene-d_2 chloride exhibited three overlapping quartets at 3.41, 3.37, and 3.35 ppm; a triplet at 1.35 ppm; a triplet at 1.31 ppm; and a singlet at 1.07 ppm in the ratios of 12:6:12:6. The quartet at 3.41 ppm and the triplet at 1.35 ppm were assigned to the methylene and methyl protons of the ethyl groups in the anion, and the two upfield quartets (3.37 and 3.35 ppm) and the upfield triplet (1.31 ppm) were assigned to the methylene and methyl protons of the ethyl groups in the cation on the basis of decoupling experiments. When the triplet at 1.35 ppm was irradiated, the quartet at 3.41 ppm collapsed into a singlet, while irradiation of the triplet at 1.31 ppm resulted in the collapse of the two upfield quartets (3.37 and 3.35 ppm) into singlets. The singlet at 1.07 ppm was assigned to the protons in the methyl groups bonded to the silicon atom.

The reaction of $[Et(H)N]_2SiMe_2$ or $[n\text{-}Bu(H)N]_2SiMe_2$ with $GaCl_3$ gave the N-alkylated hexamethylcyclotrisilazane and an alkylamine–gallium trichloride adduct (eq 4). The cyclotrisilazane

$$[R(H)N]_2SiMe_2 + GaCl_3 \rightarrow {}^1\!/_3(RNSiMe_2)_3 + RNH_2{\cdot}GaCl_3 \qquad (4)$$

$$R = Et,\ n\text{-}Bu$$

$(EtNSiMe_2)_3$ has been prepared previously by refluxing $[Et(H)N]_2SiMe_2$ for 120 h in the presence of a catalytic amount of ammonium sulfate.[8a,b] Interestingly, no cyclosilazanes were isolated when $[n\text{-}Bu(H)N]_2SiMe_2$ was heated to 170–190 °C for 28 h in the presence of ammonium sulfate.[8b] The reaction pathway that leads to the formation of the N-alkylated hexamethylcyclotrisilazane and alkylamine–gallium trichloride in eq 4 is not known. However, the pathway probably does not involve a dehalosilylation reaction, in which $[Cl_2GaN(H)R]_n$ and $R(H)NSi(Cl)Me_2$ are formed, and subsequently the elimination of HCl by $R(H)NSi(Cl)Me_2$ with condensation to give $(RNSiMe_2)_3$. Autocondensation of $n\text{-}Bu(H)NSi(Cl)Me_2$ at 70 °C for a period of 330 h was found to yield $n\text{-}BuNH_3Cl$, $n\text{-}BuN[Si(Cl)Me_2]_2$, and $n\text{-}BuN[Si(Cl)Me_2][Si(N(H)(n\text{-}Bu))Me_2]$. Similar N-ethylated disilazanes along with $EtNH_3Cl$ were obtained when a petroleum ether solution of $EtNH_2$ and Me_2SiCl_2 in a 2:1 mole ratio was allowed to reflux for 320 h.[23]

While dehalosilylation has been observed in the reactions of $(Me_3Si)_2NH$ and $(Me_3Si)_2NMe$ with $GaCl_3$,[2,3b] only the reaction of $(Et_2N)_2SiMe_2$ with $GaCl_3$ resulted in the metathetical elimination of $Et_2NSi(Cl)Me_2$. Of the other substituted bis(amino)dimethylsilanes studied, $(Me_2N)_2SiMe_2$ formed a Lewis acid–base adduct with $GaCl_3$ and $[Et(H)N]_2SiMe_2$ or $[n\text{-}Bu(H)N]_2SiMe_2$ reacted with $GaCl_3$ to give the N-alkylated hexamethylcyclotrisilazane and alkylamine–gallium trichloride.

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Supplementary Material Available: Listings of crystallographic data, bond lengths, bond angles, selected dihedral angles, hydrogen coordinates, and anisotropic temperature factors and ORTEP diagrams illustrating the contents of the unit cells for $Me_2Si(NMe_2)_2{\cdot}GaCl_3$ and $[Cl_2Ga(NEt_2)_2SiMe_2][(Cl_3Ga_2NEt_2]$ (13 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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(23) Wannagat, U.; Schreiner, G. *Monatsh. Chem.* **1965**, *96*, 1895.

Contribution from the Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7 Canada,
and Merck Sharp and Dohme Research Laboratories, Rahway, New Jersey 07065

Multidentate Lewis Acids. Synthesis and Structure of Complex Aluminum Chloride Alkoxides

Francine Bélanger-Gariépy,[1a] Karst Hoogsteen,[1b] Vijay Sharma,[1a] and James D. Wuest*,[1a]

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Complexes of simple aluminum chloride alkoxides with THF can be prepared by treating the corresponding alcohols or trimethylsilyl ethers with aluminum chloride and THF. Low-temperature ^1H, ^{13}C, and ^{27}Al NMR spectra suggest that the products of these reactions are inhomogeneous and exist in solution as mixtures resulting from redistribution. More complex aluminum chloride alkoxides and their adducts can be prepared from the bis(trimethylsilyl) ethers of cyclic 1,2-diols. These chloride alkoxides also appear to undergo redistribution in solution, but some adopt well-defined structures in the solid state. An X-ray crystallographic study of representative chloride alkoxide **8b**, derived from a *trans*-1,2-cyclohexanediol, reveals a characteristic pentacyclic structure organized around a central Al_2O_2 ring containing approximately trigonal oxygens and trigonal-bipyramidal aluminums. Compound **8b** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.710\ (3)$ Å, $b = 9.309\ (5)$ Å, $c = 9.600\ (3)$ Å, $\alpha = 88.82\ (3)°$, $\beta = 82.02\ (3)°$, $\gamma = 75.31\ (4)°$, $V = 745.6$ Å^3, $\rho_{calcd} = 1.333$ g cm^{-3}, and $Z = 1$ (dimer). Full-matrix least-squares refinement of 1425 reflections ($I \geq 3.00\sigma(I)$) converged at $R = 0.054$ and $R_w = 0.050$.

Host molecules with suitably oriented sites of Lewis acidity can recognize, bind, transport, and chemically activate complementary basic guests.[2] We have recently shown that potential multidentate hosts with sites of strong Lewis acidity can be created conveniently

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