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Reactivity of Organogallium−Amine Adducts and Gallium Amides toward Some Nonhydrolytic Gel Precursor Mixtures

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The synthesis and spectroscopic and structural characterization of some new amine−gallane adducts as well as gallium amides are described. This work was carried out in order to test their reactivity as gallium nitride precursors toward nonhydrolytic gel precursor mixtures. These mixtures usually consist of $M(OR)_n/M'Cl_n$ (M or M′ = B, Al, Si, or Ti) species combined in various proportions. It was found that the adduct $Me_3GaNH(i\text{-}Pr)_2$ reacts with $SiCl_4$ to form compounds with gallium−chlorine bonds and up to three chlorines may be substituted at gallium. The gallium amide $(Me_2GaNPh_2)_2$ also reacts with $SiCl_4$ to give a chlorinated species. The only amide precursor species that proved inert to $SiCl_4$ was the sterically encumbered derivative $Ga\{N(SiMe_3)_2\}_3$ which could be isolated unchanged after several days reaction time. In addition, the compound $\{TiCl_3OEt\}_n$ was isolated from a $Ti(OEt)_4/SiCl_4$ reaction system and structurally characterized.

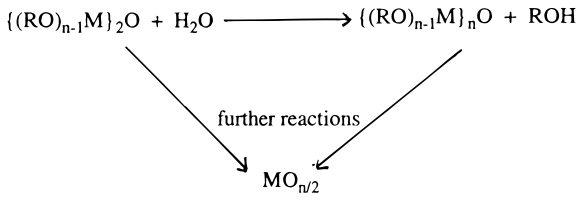
Introduction

The wide direct bandgap of GaN (3.4 eV) suggests the promise of short-wavelength optoelectronic devices in the near ultraviolet and has created a resurgence of interest in various aspects of III−V mononitride semiconductors as comprehensively summarized in current status reviews.[1] The choice of a broad range of bandgaps (from 3.4 to 6.2 eV) and the predicted large electron drift velocity has led to a special focus on alloys based on the GaN−AlN system. Recently revitalized research enthusiasm for these materials stems from the observations of Akasaki et al. and Nakamura et al.,[2−5] who investigated AlGaN/GaN multiheterostructures and reported a p−n junction type LED with blue-to-UV light emission. A significant fraction of experimental work reported in the literature is devoted to growth of crystalline GaN films by CVD, MBE, and related techniques. Some of the important issues that emerge from these studies are the crystal structure of films (wurtzite or cubic), substrate compatibility with GaN and the use of buffer layers, attempts to lower growth temperatures, the search for precursors for CVD reactions, study of native defects responsible for the natural n-type films normally obtained, and the important question, how can one grow p-type films? In answer to this last question, Amano et al.[6] reported success in growing p-type GaN and p-type AlGaN doped with Mg. The proceedings of a recent MRS symposium,[7] published in late 1992, gives a good window on recent research on the preparation and properties of III−V nitrides and other wide bandgap materials.

The motivation for the work described here is based on photoluminescence (PL) evidence[3,7] for "quantum size effects" in AlGaN/GaN quantum wells in which carriers are confined in only two spatial dimensions. These PL measurements show shifts in the emission energy with the width of the GaN quantum wells. Since this is judged to be fairly convincing support of quantum confinement in these thin-film quantum wells, it raises the exciting possibility of starting the quest for synthesizing quantum dots of direct wide-bandgap GaN−AlN alloys in which confinement occurs in all three spatial dimensions.

The use of organometallic or inorganic precursors for the preparation of oxide materials via conventional sol−gel processing routes generally involves hydrolysis/condensation reactions of a variety of precursors. In the case of alkoxysilanes, silica gels can be obtained by processes that have been intensively studied.[8] The hydrolysis of such compounds inevitably involves the use of species that have the reactive −OH moiety, whether as part of an organometallic species, an alcohol, or water itself, as illustrated by the sequence

$$2M(OR)_n + 2H_2O \longrightarrow 2(RO)_{n-1}MOH + 2ROH$$



Unfortunately, the presence of the −OH moiety is in many instances undesirable since it is reactive toward

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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many other organometallic precursors.[9] For example, if it is desired to use the silica gel as a matrix for the transformation of organometallic species into materials such as GaN, GaAs, or InP, etc., the reactivity of the −OH moiety toward these binary compounds and their precursors (e.g., amine adducts or amides) renders the hydrolytic sol−gel method wholly unsuitable as the formation of metal oxide (i.e., GaO or InO) formation would be the major result.

The hydrolytic sensitivity of many organometallic precursors has led to the proposal of nonhydrolytic sol−gel routes.[10] The essential feature of such routes is to form oxygen bridges from halides and a variety alkoxides as shown by eq 1.

$$\equiv\mathrm{MOR} + \mathrm{XM'}\equiv \rightarrow \equiv\mathrm{MOM'}\equiv + \mathrm{R{-}X} \qquad (1)$$
$$\mathrm{M} = \mathrm{Si, Ti, Al}$$

In the case of silicon similar reactions were reported as long ago as 1956 and were shown to require the use of R groups that can stabilize positive charges.[11] To test the compatibility of these and mixtures composed of silicon halides and a variety of metal alkoxides with gallium amine adducts or gallium adducts, a variety of compounds have been synthesized and tested. The main conclusion from these results is that sterically crowding groups are required to protect the Ga−N precursor prior to formation of the SiO_2 gel.

Experimental Section

General Procedures. All syntheses were carried out under anaerobic and anhydrous conditions by using Schlenk techniques or a Vacuum Atmospheres HE43-2 drybox. Hydrocarbon solvents were distilled from a sodium/potassium alloy and degassed twice prior to use. CCl_4 was dried over P_2O_5 and distilled. Amines were dried by distillation from CaH_2. $GaMe_3$, $B(OMe)_3$, Al{O(*i*-Pr)}$_3$, $SiCl_4$, $Si(OR)_4$ (R = Et, *n*-Pr, $SiMe_2H$), and $Ti(OEt)_4$ were purchased commercially and used as received. Ga{N(SiMe$_3$)$_2$}$_3$ was synthesized by a literature procedure.[12]

$SiCl_4$ + $M(OR)_n$ Reactions. The following mixtures were tested for gel formation: silicon tetrachloride as a neat liquid together with an equivalent of one of the compounds $Si(OEt)_4$, Si{O(*n*-Pr)}$_4$, $Si(OSiMe_2H)_4$, $B(OMe)_3$ (1.33 equiv), Al{O(*i*-Pr)}$_3$ (1.33 equiv), or $Ti(OEt)_4$, were heated to reflux (ca. 60 °C) for periods of 4−6 days. The reaction between $SiCl_4$ and Al{O(*i*-Pr)}$_3$ was also tested at 60 °C for 4 days in CCl_4 or *n*-hexane at ca. 2 M concentration. No gel formation was observed except in the case of $SiCl_4$ and $Ti(OEt)_4$ where the formation of both a pale yellow gel and the heteroleptic alkoxide $(TiCl_3OEt)_n$ was observed after stirring for 1 day at 25 °C and 1 h at 60 °C. This reaction is now described in more detail.

$Ti(OEt)_4$ + $SiCl_4$. $SiCl_4$ (9.2 g, 54.1 mmol) was added via a syringe to 12.4 g (54.1 mmol) $Ti(OEt)_4$. The resultant pale yellow solution was stirred overnight (16 h). Heating to ca. 90 °C for 4 h resulted in the formation of a clear gel and a supernatant yellow oil. This oil solidified upon cooling to room temperature to afford $\{TiCl_3OEt\}_n$ (**1**) as pale yellow crystals: mp 76−78 °C; ^1H NMR (C_6D_6) δ 0.80 (t, 3H ($^3J_{H-H}$ = 6.9 Hz), OCH$_2$C*H*$_3$), 3.83 (q, 2H ($^3J_{H-H}$ = 6.9 Hz), −OC*H*$_2$CH$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6), δ 17.7 (−OCH$_2$*C*H$_3$), 87.9 (−O*C*H$_2$CH$_3$); IR (Nujol, cm^{-1}) 1345 m, 1258 w, 1090 vs br, 1060 vs br, 939 s, 865 m, 796 w, 615 ms, 525 w, 473 s, 439 s, 400 s br, 330 s br.

Synthesis of Precursors. *Me$_3$GaNH(i-Pr)$_2$.* With rapid stirring a solution of HN(*i*-Pr)$_2$ (1.44 g, 14.3 mmol) in toluene (30 mL) was added to a solution of $GaMe_3$ (1.64 g, 14.3 mol) in toluene (10 mL). The solution was then refluxed for 16 h. Removal of the solvent under reduced pressure afforded a colorless oil in almost quantitative yield. Upon storage in a −20 °C freezer the oil solidified to afford essentially pure Me$_3$GaNH(*i*-Pr)$_2$ as colorless crystals: mp = ca. −15 °C; ^1H NMR (C_6D_6) δ 0.33 (s, 9H, GaMe), 0.92 (d, 12H ($^3J_{H-H}$ = 6.6 Hz), -CH(C*H*$_3$)$_2$), 1.34 (br, s, 1H, N*H*), 2.95 (sept, 2H ($^3J_{H-H}$ = 6.6 Hz), -C*H*(CH$_3$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6), δ = −2.1 (Ga*C*H$_3$), 22.0 (*C*H$_3$), 47.2 (*C*H).

*(Me$_2$GaNPh$_2$)$_2$ (**2**).* A solution of $HNPh_2$ (2.09 g, 12 mmol) and $GaMe_3$ (1.38 g, 12 mmol) in toluene (30 mL) was heated in a 100 °C oil bath for 3 days. The temperature was then raised to 130 °C for 1 h. The solvent was then pumped off to give a pale yellow solid which was recrystallized from a hexane/toluene (2:1) mixture: yield 2.15 g (67%); mp 148 °C; ^1H NMR (C_6D_6) δ 0.03 (s, 6H, −Ga(C*H*$_3$)$_2$), δ 6.90−7.17 (m, 10H, −N(C$_6$*H*$_5$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −0.9 (Ga(*C*H$_3$)$_2$), 124.5 (*p*-C$_6$H$_5$), 127.8 (*m*-C$_6$H$_5$), 128.9 (*o*-C$_6$H$_5$), 152.7 (*i*-C$_6$H$_5$); IR (Nujol, cm^{-1}) 1963 w, 1942 m, 1925 w, 1590 vs, 1494 vs, 1486 vs, 1414 w, 1338 m, 1312 m, 1282 vw, 1216 vs, 1178 vs, 1081 s, 1031 s, 1003 m, 981 vw, 971 w, 959 vv, 928 sh, 920 s, 896 m, 865, 841 vs, 752 vs, 700 vs, 643 ms, 575 s, 535 ms, 502 s, 580 ms, 315 w.

*(MeGa-μ-NPh$_2$)$_2$(μ-NPhC$_6$H$_4$)·0.5 PhMe (**3**).* A solution of $HNPh_2$ (2.50 g, 14.4 mmol) and $GaMe_3$ (1.65 g, 14.4 mmol) in toluene (ca. 30 mL) was refluxed for 3 days. Removal of the solvent afforded a pale yellow solid which was recrystallized from *n*-hexane/toluene (2:1) at 0 °C to give $(Me_2GaNPh_2)_2$ in ca. 60% yield. All volatile materials were removed from the mother liquid under reduced pressure and the residue was taken up in *n*-hexane/diethyl ether (2:1). Cooling for 3 days at −30 °C gave large, colorless crystals of (MeGa-μ-NPh$_2$)$_2$(μ-NPhC$_6$H$_4$)·0.5 PhMe: yield 0.65 g (12%); mp 164−166 °C (decomp); ^1H NMR (C_6D_6) δ 0.28 (s, 3H, MeGa), 0.63 (s, 3H, MeGa), 6.19−7.39 (m, 29H, Ph); ^{13}C NMR (C_6D_6) δ −7.1 (MeGa), −5.3 (MeGa), 157.5−113.8 (Ph); IR (Nujol, cm^{-1}) 1579 s, 1566 vs, 1548 sh, 1480 vs, 1420 vs, 1282 vs, 1273 sh, 1230 vw, 1202 sh, 1191 vs, 1183 sh, 1158 s, 1102 w, 1071 ms, 1047 w, 1021 ms, 993, w, 973 vw, 952 vw, 928 m, 913 s, 895 m, 870 m, 846 vs, 816 w, 741 vs, 692 vs, 643 m, 579 w, 554 m, 493 s, 412 w, 384 m, 306 m.

Stability of GaN Precursors toward Neat $SiCl_4$ or $Si(OEt)_4$ Mixtures. *ClMe$_2$GaNHPh$_2$ (**4**).* An excess of $SiCl_4$ (2.0 mL, 17.5 mmol) was added to a stirred solution of Me_2GaNPh_2 (0.35 g, 1.31 mmol) in ca. 15 mL of *n*-hexane. The resulting solution was stirred overnight at ambient temperature. A ^1H NMR sample showed the formation of a new compound (ca. 15%) with a chemical shift of 0.28 ppm in the MeGa range as well as unchanged starting material. After refluxing for 20 h, two ^1H NMR signals at 0.28 and 0.12 ppm were observed which had a 1:2 intensity ratio. The volume of the solution was reduced to ca. 5 mL under reduced pressure. Cooling in a −30 °C freezer overnight afforded colorless crystals of $ClMe_2GaNHPh_2$: yield 0.12 (30%); mp 91−92 °C; ^1H NMR (C_6D_6) δ 0.12 (s, 6H, Ga(C*H*$_3$)$_2$), 6.02 (s, 1H, NH), 6.82−7.00 (m, 10H, N(C$_6$*H*$_5$)$_2$); ^{13}C NMR (C_6D_6) δ 0.2 (Ga(*C*H$_3$)$_2$), 120.6 (*o*-C$_6$H$_5$), 123.9 (*p*-C$_6$H$_5$), 129.6 (*m*-C$_6$H$_5$), 142.8 (*i*-C$_6$H$_5$); IR (Nujol, cm^{-1}) 3150 m, 1491 s, 1412 m, 1362 s, 1307 m, 1260 w, 1227 m, 1195 w, 1070 w, 1020 m, 913 w, 813 m, 741 s, 687 ms, 577 m, 530 w, 468 m, 320 m br.

*ClMe$_2$GaNH(i-Pr)$_2$ (**5**).* $SiCl_4$ (0.67 g, 3.94 mmol) was added via a syringe to a stirred solution of Me$_3$GaNH(*i*-Pr$_2$)$_2$ (0.79 g,

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[7] See papers in part V on III−V nitrides and especially an overview by: Akasaki, I.; Amano, H. In *Wide Band Gap Semiconductors, Materials Research Society Symposia Proceedings*; **1992**, *242*, 383.

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Table 1. Selected Crystallographic Data

	$(TiCl_3OEt)_n$ (**1**)	$(Me_2GaNPh_2)_2$ (**2**)	$(MeGaNPh_2)_2(\mu\text{-}NPhC_6H_4)\cdot 0.5PhMe$ (**3**)	$ClMe_2GaNHPh_2$ (**4**)	$(ClMe_2GaNH\text{-}i\text{-}Pr_2)_2$ (**5**)	$[NH_2\text{-}i\text{-}Pr_2][MeGaCl_3]$ (**6**)
formula	$C_2H_5Cl_3OTi$	$C_{28}H_{32}Ga_2N_2$	$C_{38}H_{35}Ga_2N_3\cdot 0.5C_7H_8$	$C_{14}H_{17}ClGaN$	$C_{16}H_{42}Cl_2Ga_2N_2$	$C_7H_{19}Cl_3GaN$
fw	199.3	536.0	719.2	304.5	472.8	293.3
color, habit	pale yellow, plate	colorless, block	colorless, block	colorless, block	colorless, block	colorless, plate
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P2_1/c$	$Pbca$
a/Å	5.971(2)	8.637(2)	16.079(6)	14.909(6)	7.718(2)	13.285(3)
b/Å	7.221(3)	14.245(3)	13.073(4)	13.712(4)	14.214(3)	13.380(3)
c/Å	8.729(3)	20.564(4)	16.560(5)	14.398(5)	21.803(4)	14.530(3)
α/deg	94.01(1)					
β/deg	98.24(1)		97.06(3)	102.43(3)	96.48(3)	
γ/deg	110.89(2)					
V/Å^3	345.0(2)	2530.1(9)	3454(1)	2874(1)	2376.6(8)	2582.8(9)
Z	2	4	4	8	4	8
d/g cm^{-3}	1.919	1.407	1.391	1.407	1.322	1.509
cryst dimens/mm	0.04 × 0.04 × 0.01	0.75 × 0.30 × 0.30	0.76 × 0.64 × 0.58	0.56 × 0.38 × 0.26	0.80 × 0.25 × 0.15	0.50 × 0.35 × 0.08
temp/K	130	130	130	130	130	130
radiation	Cu Kα (λ = 1.541 78 Å)	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 78 Å)	Cu Kα (λ = 1.541 78 Å)
μ/cm^{-1}	203.52	27.29	15.94	20.79	48.26	82.78
unique data	905	2350	6782	2822	3219	1719
data with $I > 2\sigma(I)$	669	2325	5017	2163	2849	1301
no. of parameters	69	283	441	176	363	120
R_1 ($I > 2\sigma(I)$)	0.0674	0.0377	0.0492	0.0545	0.0457	0.0519
wR_2 (all data)	0.1779	0.1070	0.1321	0.1489	0.1228	0.1364

3.65 mmol) in n-hexane (15 mL). Stirring was continued at ambient temperature for 3 days, whereupon the volatile materials were removed under reduced pressure. The residue was taken up in *n*-hexane and cooled overnight at −30 °C to give colorless crystals of $\{ClMe_2GaNH(i\text{-}Pr)_2\}_2$: yield 0.46 g (53%); mp 79 °C; ^1H NMR (C_6D_6) δ 0.15 (s, 6H, $Ga(CH_3)_2$), 0.80 (d, 12H ($^3J_{H-H}$ = 6.9 Hz), $CH(CH_3)_2)_1$, 2.48 (s, 1H, NH), 3.09 (sept, 2H ($^3J_{H-H}$ = 6.9 Hz), $CH(CH_3)_2$); ^{13}C NMR (C_6D_6) δ −0.3 ($Ga(CH_3)_2$), 21.5 ($CH(CH_3)_2$), 47.3 ($CH(CH_3)_2$); IR (Nujol, cm^{-1}) 3195 vs, 1590 w, 1395 vs, 1342 ms, 1306 ms, 1261 w, 1219 s, 1204 vs, 1185 s, 1162 s, 1144 vs, 1112 s, 1094 sh, 1077 vs, 972 s, 948 m, 934 ms, 912 ms, 838 ms, 778 sh, 742 vs, 685 s, 575 s, 536 ms, 462 w, 388 vs, 267 m.

*$[NH_2(i\text{-}Pr)_2][MeGaCl_3]$ (**6**).* $Me_3GaNH(i\text{-}Pr)_2$ (2.42 g, 11.2 mmol) was added via a syringe to a mixture of $SiCl_4$ (19.0 g, 112 mmol) and $Si(OEt)_4$ (23.3 g, 112 mmol). The resulting solution was stirred overnight at ambient temperature and then refluxed (oil bath 95 °C) for 6 days. Cooling to room temperature over several hours afforded large crystals which were washed twice with a small amount of *n*-hexane. Yield 1.24 g (38%), mp 95 °C (decomp); ^1H NMR (CD_3CN) δ 3.48 (sept, 2H ($^3J_{H-H}$ = 6.3 Hz), $CH(CH_3)_2$), −0.01 (s, 3H, $GaCH_3$), 1.28 (d, 12H ($^3J_{HH}$ = 6.3 Hz), $CH(CH_3)_2$), 6.28 (t, 2H ($^1J_{NH}$ = 52 Hz), $-NH_2$); ^{13}C NMR (CD_3CN) δ 19.3 ($CH(CH_3)_2$), 49.6 ($CH(CH_3)_2$), MeGa not observed; IR (Nujol, cm^{-1}) 3160 s, 3130 sh, 3080 sh, 2420 w, 2375 w, 1554 s, 1390 s, 1313 m, 1298 w, 1208 w, 1192 m, 1180 m, 1166 sh, 1139 s, 1096 ms, 1080 w, 970 w, 942 m, 869 w, 825 m, 794 vw, 737 s, 582 m, 471 m, 315 vs, 243 vw.

$Ga\{N(SiMe_3)_2\}_3$ and $SiCl_4$. A solution of 0.55 g (1.0 mmol) $Ga\{N(SiMe_3)_2\}_3$ and 3 mL (26.2 mmol) of $SiCl_4$ in ca. 15 mL of *n*-hexane was first stirred at room temperature for 2 days and then refluxed (oil bath 85 °C) for another day. NMR samples taken after 1, 2, and 3 days showed no visible reaction.

Crystallographic Studies. X-ray-quality crystals were obtained as described in the Experimental Section. Crystals were removed from Schlenk tubes and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature N_2 stream, as previously described. All data were collected at 130 K using either a Siemens P4/RA (**1**), a Siemens R3 (**3**, **4**) or a Syntex $P2_1$ (**2**, **5**, **6**) diffractometer. Crystal data are given in Table 1. Calculations were carried out with the SHELXTL-PLUS and SHELXL-93 program system installed on a UNIX workstation or PC's. Scattering factors and the correction for anomalous scattering were taken from common sources.[13a] The structures were solved by direct methods and refined by blocked-diagonal least-squares refinement. An absorption correction was applied by using the program XABS2.[13b] Anisotropic thermal parameters were included for all non-hydrogen atoms, excluding C18 and C23 in **2**. The interstitial toluene in **3** is disordered over two positions. Positions for all H atoms in **5** and for H atoms attached to N1 in **4** and **6** were allowed to refine. All other H atoms were included by use of a riding model with fixed C−H distances only the rotation of methyl groups was refined. Isotropic thermal parameters for H atoms were refined or otherwise fixed equal to 1.2 or 1.5 times that of the bonded carbon.

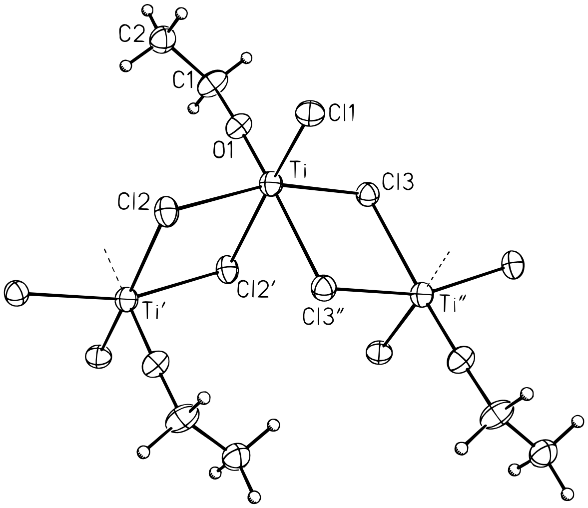

Figure 1. Thermal ellipsoidal plot (40% occupancy) of $(TiCl_3OEt)_n$.

Structures. The structure of $(TiCl_3OEt)_n$ features edge-sharing octahedra arranged in a chainlike structure as illustrated in Figure 1. Each titanium has distorted octahedral coordination being bound to five chlorides and one ethoxide. These octahedral units are edge-bridged through two pairs of chlorides to two neighboring octahedra and so on along the chain. The bridging Ti−Cl distances are not symmetric, how-

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(13) (a) *International Tables for X-Ray Crystallography*; Kynoch Press, Birmingham, England, 1974; (b) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

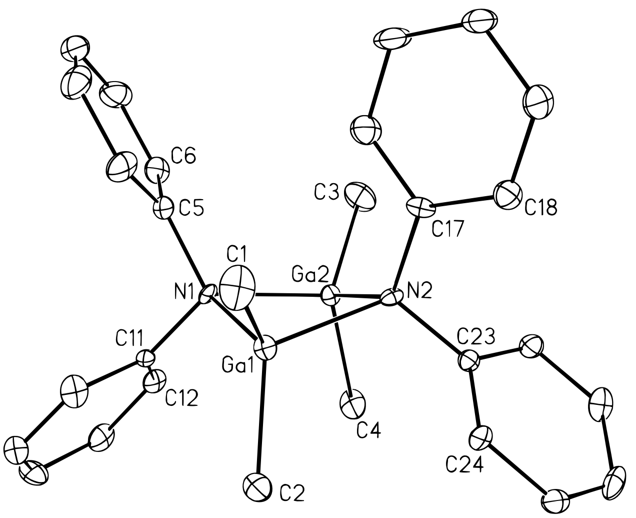

Figure 2. Thermal ellipsoidal plot (50% occupancy) of ($(Me_2GaNPh_2)_2$). Hydrogen atoms are omitted for clarity.

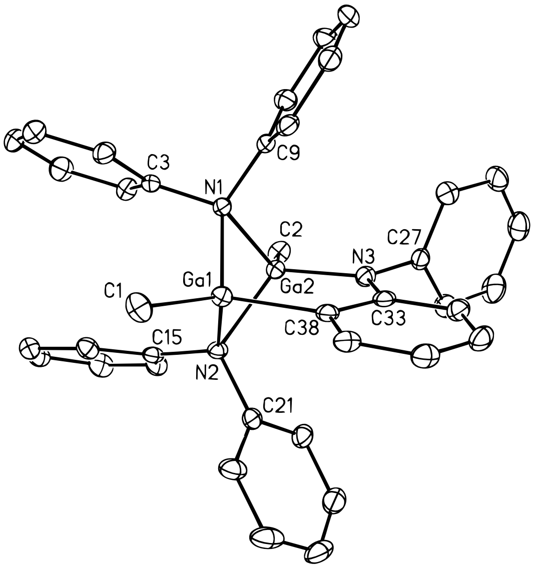

Figure 3. Thermal ellipsoidal plot (30% occupancy) of $(MeGaNPh_2)_2(\mu\text{-}NPhC_6H_4)\cdot 0.5PhMe$. Hydrogen atoms and toluene molecule are omitted for clarity.

ever, and vary from 2.363(3) to 2.600(3) Å. The terminal Ti–Cl and Ti–O distances are 2.234(3) and 1.705(7) Å. It is also notable that the Ti–O(1)–C(1) angle has an almost linear value of 176.3(7)°.

The compound $(Me_2GaNPh_2)_2$ has a bridged dimeric structure as shown in Figure 2. In the Ga_2N_2 core the average Ga–N distance is 2.088(4) Å. The Ga_2N_2 array is not planar but has a fold angle of 151° along the Ga- - -Ga vector. The Ga–C distances are in the range 1.953(6)–1.985(5) Å. The ring angles at the nitrogen and gallium are 88.2(2)°.

The compound $(MeGaNPh_2)_2(\mu\text{-}NPhC_6H_4)$ is composed of $(GaMeNPh_2)_2$ units with a Ga_2N_2 folded core structure in which the two galliums are bridged by an ortho-deprotonated and bidentade $-NPhC_6H_4$ ligand (Figure 3). Within the Ga_2N_2 ring the Ga–N distances average 2.053(11) Å. The terminal Ga(2)–N(3) distance is 1.892(3) Å. The fold angle in the Ga_2N_2 moiety is 132° and the Ga- - -Ga separation is 2.7686(6) Å. Further details are given in Table 2.

In the adduct $ClMe_2GaNHPh_2$ (Figure 4) a Ga–N distance of 2.101(4) Å is observed. The average Ga–C and the Ga–Cl bond lengths are 1.993(4) and 2.250(2) Å. Each molecule is associated with a neighboring molecule by a weak 2.52 Å Cl- - -H–N interaction. Additional structural data are given in Table 2.

The adduct $ClMe_2GaNH(i\text{-}Pr)_2$ (Figure 5) has two molecules in the asymmetric unit which can be viewed as being weakly associated by 2.71 Å (avg) interactions between the chlorines and amine hydrogens of adjacent molecules. The monomeric units involve a Ga–N distance of 2.079(4) and 2.081(4) Å. The Ga–C and Ga–Cl bond lengths average 1.959(4) and 2.279(1) Å. The angles surrounding Ga and N are given in Table 2.

The ionic compound $[NH_2(i\text{-}Pr)_2][MeGaCl_3]$ crystallizes in the orthorhombic space group Pbca as weakly interacting (Cl(2)- - -H(1) = 2.60 Å) cations and anions (Figure 6). Both gallium and nitrogen have distorted tetrahedral coordination. It is notable that the Ga(1)–Cl(2) distance, 2.239(2) Å, is marginally longer than that of either Ga(1)–Cl(1) 2.222(2) Å or Ga(1)–Cl(3) 2.210(2) Å. The Ga(1)–C(1) distance is 1.951(6) Å. Further data are provided in Table 2.

Discussion

The gel-formation reactions tested here yielded only a gel in the case of the reaction between $SiCl_4$ and $Ti(OEt)_4$.[14] The observation of the latter reaction is in agreement with the recently described results[10b] for the similar system $SiCl_4/Ti\{O(n\text{-}Pr)\}_4$ although in our case the reaction period was significantly shorter and the formation of the heteroleptic species $TiCl_n\{O(n\text{-}Pr)\}_{4-n}$ ($n = 1$, 2, or 3) was not mentioned. In contrast to the previous results,[10b] in our hands no gel formation was observed for the reaction between $SiCl_4$ and $Al\{O(i\text{-}Pr)\}_3$ despite several experiments conducted under similar conditions at 60 °C for 3–5 days. However, the lack of formation of any gel in $SiCl_4/Si(OR)_4$ (R = alkyl) systems is in agreement with similar investigations that have been known since the 1950s.[11] In fact, it is only when the R group in the $SiCl_4/Si(OR)_4$ system is stabilized by charge-delocalizing substituents, such as the Ph group at an α-carbon atom, that gel formation is observed under relatively mild conditions according to the simplified reaction stochiometry

$$SiCl_4 + Si(OR)_4 \rightarrow 2SiO_2 + 4RCl \qquad (2)$$

The mechanistic aspects of these reactions which occur with the generation of HCl are currently under investigation by this group and our results will be reported in the near future.

The isolation of the product $(TiCl_3OEt)_n$ (in addition to the gel) from the reaction of $SiCl_4$ and $Ti(OEt)_4$ demonstrates that the reaction to give a bicomponent Si/TiO_2 oxide gel is incomplete under the conditions described. Despite the widespread interest in metal alkoxides there are relatively few structures of compounds of the type $TiCl_n(OR)_{4-n}$[15,16] ($n = 1$, 2, or 3, R = simple alkyl or aryl ligand). The polymeric structure of $(TiCl_3OEt)_n$ appears to be unique, and this type of structure has not been reported for any other heteroleptic titanium chloride alkoxide compound. However, the structural form, involving connection of octahedra by "skew" edges to form planar zig-zag chains (i.e., the $TeCl_4$ type of structure[17]) is well-known in solid-state chemistry. It is further notable that the bridging occurs through chloride and not the alkoxide groups. Previous

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Table 2. Some Important Bond Distances (Å) and Angles (deg) for Compounds 1−6

1

Ti−O(1)	1.705(7)	Cl(1)−Ti−Cl(2)	92.34(10)
Ti−Cl(1)	2.234(3)	Cl(1)−Ti−Cl(3)	98.25(10)
Ti−Cl(3)	2.363(3)	Cl(2)−Ti−Cl(3)	161.79(12)
Ti−Cl(2)	2.406(3)	Cl(1)−Ti−Cl(2)′	169.66(12)
Ti−Cl(2)′	2.523(3)	Cl(3)−Ti−Cl(2)′	86.48(9)
Ti−Cl(3)″	2.600(3)	Cl(2)−Ti−Cl(2)′	80.84(10)
O(1)−C(1)	1.428(12)	Cl(1)−Ti−Cl(3)″	88.13(10)
		Cl(3)−Ti−Cl(3)″	81.23(10)
C(1)−C(2)	1.507(14)	Cl(2)−Ti−Cl(3)″	84.38(10)
O(1)−Ti−Cl(1)	98.6(2)	Cl(2)′−Ti−Cl(3)″	83.48(10)
O(1)−Ti−Cl(2)	97.7(2)	Ti−Cl(2)−Ti′	99.16(10)
O(1)−Ti−Cl(3)	95.3(2)	Ti−Cl(3)−Ti″	98.77(10)
O(1)−Ti−Cl(2)′	90.1(2)	C(1)−O(1)−Ti	176.3(7)
O(1)−Ti−Cl(3)″	172.8(2)	O(1)−C(1)−C(2)	109.4(8)

2

Ga(1)−C(1)	1.953(6)	C(2)−Ga(1)−N(2)	111.1(2)
Ga(1)−C(2)	1.985(5)	N(2)−Ga(1)−N(1)	88.2(2)
Ga(2)−C(3)	1.964(6)	C(5)−N(1)−C(11)	106.9(4)
Ga(2)−C(4)	1.971(5)	C(5)−N(1)−Ga(2)	115.0(3)
Ga(1)−N(1)	2.093(5)	C(11)−N(1)−Ga(2)	116.0(3)
Ga(1)−N(2)	2.084(4)	C(5)−N(1)−Ga(1)	121.2(4)
Ga(2)−N(1)	2.077(4)	C(11)−N(1)−Ga(1)	109.2(3)
Ga(2)−N(2)	2.098(5)	Ga(2)−N(1)−Ga(1)	88.2(2)
Ga(1)···Ga(2)	2.9008(10)	C(3)−Ga(2)−C(4)	117.9(3)
N(1)−C(5)	1.471(7)	C(3)−Ga(2)−N(1)	116.5(2)
N(1)−C(11)	1.488(7)	C(4)−Ga(2)−N(1)	111.1(2)
N(2)−C(17)	1.448(7)	C(3)−Ga(2)−N(2)	112.3(2)
N(2)−C(23)	1.460(7)	C(4)−Ga(2)−N(2)	106.6(3)
		N(1)−Ga(2)−N(2)	88.2(2)
C(1)−Ga(1)−C(2)	119.4(3)	C(17)−N(2)−C(23)	110.8(4)
C(1)−Ga(1)−N(1)	120.1(2)	C(17)−N(2)−Ga(1)	113.9(3)
C(2)−Ga(1)−N(1)	105.7(2)	C(23)−N(2)−Ga(1)	117.5(3)
C(1)−Ga(1)−N(2)	107.9(2)	C(17)−N(2)−Ga(2)	116.6(3)
		C(23)−N(2)−Ga(2)	108.5(3)
		Ga(1)−N(2)−Ga(2)	87.8(2)

3

Ga(1)−C(1)	1.965(4)	N(1)−Ga(1)−N(2)	84.22(12)
Ga(1)−C(38)	1.968(4)	N(1)−Ga(2)−N(2)	85.73(12)
Ga(2)−C(2)	1.953(4)	N(1)−Ga(2)−N(3)	102.43(13)
Ga(1)−N(1)	2.069(3)	N(2)−Ga(2)−N(3)	106.26(13)
Ga(1)−N(2)	2.066(3)	N(3)−Ga(2)−C(2)	112.9(2)
Ga(2)−N(1)	2.035(3)	C(2)−Ga(2)−N(1)	123.6(2)
Ga(2)−N(2)	2.041(3)	C(2)−Ga(2)−N(2)	121.7(2)
Ga(2)−N(3)	1.892(3)	C(3)−N(1)−C(9)	109.0(3)
Ga(1)···Ga(2)	2.7686(8)	C(3)−N(1)−Ga(1)	112.1(2)
N(1)−C(3)	1.463(5)	C(9)−N(1)−Ga(1)	118.5(2)
N(1)−C(9)	1.465(5)	C(3)−N(1)−Ga(2)	120.8(2)
N(2)−C(15)	1.465(5)	C(9)−N(1)−Ga(2)	110.5(2)
N(2)−C(21)	1.461(5)	Ga(1)−N(1)−Ga(2)	84.85(11)
N(3)−C(27)	1.437(5)	Ga(1)−N(2)−Ga(2)	84.76(12)
N(3)−C(33)	1.406(5)	C(15)−N(2)−C(21)	111.1(3)
		C(21)−N(2)−Ga(2)	117.1(2)
C(1)−Ga(1)−C(38)	120.8(2)	C(15)−N(2)−Ga(2)	110.9(2)
C(1)−Ga(1)−N(1)	118.2(2)	C(21)−N(2)−Ga(1)	110.5(2)
C(1)−Ga(1)−N(2)	120.7(2)	C(15)−N(2)−Ga(1)	120.5(2)
C(38)−Ga(1)−N(1)	105.58(14)	C(27)−N(3)−C(33)	117.6(3)
C(38)−Ga(1)−N(2)	100.55(14)	C(33)−N(3)−Ga(2)	126.1(3)
		C(27)−N(3)−Ga(2)	116.2(2)

4

Ga(1)−C(1)	1.989(4)	C(2)−Ga(1)−N(1)	109.7(2)
Ga(1)−C(2)	1.996(3)	C(1)−Ga(1)−Cl(1)	111.0(2)
Ga(1)−N(1)	2.101(4)	C(2)−Ga(1)−Cl(1)	107.21(12)
Ga(1)−Cl(1)	2.250(2)	N(1)−Ga(1)−Cl(1)	95.64(12)
N(1)−C(3)	1.460(6)	C(3)−N(1)−C(9)	111.4(3)
N(1)−C(9)	1.476(6)	C(3)−N(1)−Ga(1)	115.8(3)
N(1)−H(1)	0.86(5)	C(9)−N(1)−Ga(1)	114.6(3)
Cl(1)···H(1)′	2.50(6)	C(3)−N(1)−H(1)	109(4)
		C(9)−N(1)−H(1)	105(4)
C(1)−Ga(1)−C(2)	124.3(2)	Ga(1)−N(1)−H(1)	99(4)
C(1)−Ga(1)−N(1)	105.2(2)		

5

Ga(1)−C(1)	1.957(5)	C(2)−Ga(1)−Cl(1)	107.6(2)
Ga(1)−C(2)	1.965(5)	N(1)−Ga(1)−Cl(1)	96.23(11)
Ga(2)−C(9)	1.959(5)	C(3)−N(1)−C(6)	114.1(4)
Ga(2)−C(10)	1.953(6)	C(3)−N(1)−Ga(1)	117.3(3)
Ga(1)−N(1)	2.079(4)	C(6)−N(1)−Ga(1)	114.2(3)
Ga(2)−N(2)	2.081(4)	C(3)−N(1)−H(1)	107(4)
Ga(1)−Cl(1)	2.2777(13)	C(6)−N(1)−H(1)	104(3)
Ga(2)−Cl(2)	2.2794(14)	Ga(1)−N(1)−H(1)	97(4)
N(1)−C(3)	1.511(6)	C(10)−Ga(2)−C(9)	123.6(3)
N(1)−C(6)	1.521(6)	C(10)−Ga(2)−N(2)	113.9(2)
N(2)−C(11)	1.514(6)	C(9)−Ga(2)−N(2)	107.1(2)
N(2)−C(14)	1.513(6)	C(10)−Ga(2)−Cl(2)	105.6(2)
N(1)−H(1)	0.82(5)	C(9)−Ga(2)−Cl(2)	106.7(2)
N(2)−H(2)	0.78(5)	N(2)−Ga(2)−Cl(2)	96.13(11)
Cl(1)···H(2)	2.72(5)	C(14)−N(2)−C(11)	114.3(3)
Cl(2)···H(1)	2.69(6)	C(14)−N(2)−Ga(2)	117.2(3)
		C(11)−N(2)−Ga(2)	114.8(3)
C(1)−Ga(1)−C(2)	122.9(3)	C(14)−N(2)−H(2)	107(4)
C(1)−Ga(1)−N(1)	113.2(2)	C(11)−N(2)−H(2)	107(4)
C(2)−Ga(1)−N(1)	107.4(2)	Ga(2)−N(2)−H(2)	94(4)
C(1)−Ga(1)−Cl(1)	106.0(2)		

6

Ga(1)−C(1)	1.951(6)	Cl(3)−Ga(1)−Cl(1)	105.99(7)
Ga(1)−Cl(1)	2.222(2)	C(1)−Ga(1)−Cl(2)	113.4(2)
Ga(1)−Cl(2)	2.239(2)	Cl(3)−Ga(1)−Cl(2)	101.99(7)
Ga(1)−Cl(3)	2.210(2)	Cl(1)−Ga(1)−Cl(2)	104.90(7)
N(1)−C(2)	1.510(9)	C(2)−N(1)−C(5)	118.7(5)
N(1)−C(5)	1.513(7)	C(2)−N(1)−H(1)	106(6)
N(1)−H(1)	0.71(7)	C(5)−N(1)−H(1)	104(6)
N(1)−H(2)	1.00(7)	C(2)−N(1)−H(2)	111(4)
C(2)−C(3)	1.513(9)	C(5)−N(1)−H(2)	104(4)
C(2)−C(4)	1.516(9)	H(1)−N(1)−H(2)	113(7)
C(5)−C(6)	1.514(10)	N(1)−C(2)−C(3)	110.5(5)
C(5)−C(7)	1.514(9)	N(1)−C(2)−C(4)	107.3(5)
Cl(2)···H(1)	2.60(7)	C(3)−C(2)−C(4)	112.5(6)
Cl(1)′···H(2)	2.43(7)	N(1)−C(5)−C(6)	106.9(5)
		N(1)−C(5)−C(7)	111.0(5)
C(1)−Ga(1)−Cl(1)	113.7(2)	C(6)−C(5)−C(7)	112.5(6)
C(1)−Ga(1)−Cl(3)	115.7(2)		

related structures, e.g., the dimers $\{TiCl_2(OPh)_2\}_2$[16a] or $\{TiCl_2(OEt)_2\}_2$[16b] have indicated that alkoxide ligands, especially those that are not sterically encumbered, have a strong tendency to bridge through oxygen in preference to halide.

The remaining structures under consideration here all involve gallium nitrogen systems and they were all obtained as part of the investigation of the sensitivity of various gallium nitrogen amine adduct or amide precursors to the $SiCl_4/Si(OEt)_4$ environment.

The compound $(Me_2GaNPh_2)_2$ was synthesized by the reaction of $GaMe_3$ with $HNPh_2$. The observed dimeric structure with amide bridges and terminal alkyl groups is typical of a range of dimeric aminogallanes[18] although the folding in the Ga_2N_2 core is suggestive of some steric crowding. Prolonged heating of reaction mixtures of $GaMe_3$ and $HNPh_2$ affords the ortho-metalated product $(MeGaNPh_2)_2(\mu\text{-}NPhC_6H_4)$. The structure is very similar to the corresponding aluminum compound.[19] The Ga(2)−N(3) distance 1.892(3) Å is much shorter than the other Ga−N bond lengths owing to the fact that it is nonbridging. It is, however, at the longer end of the

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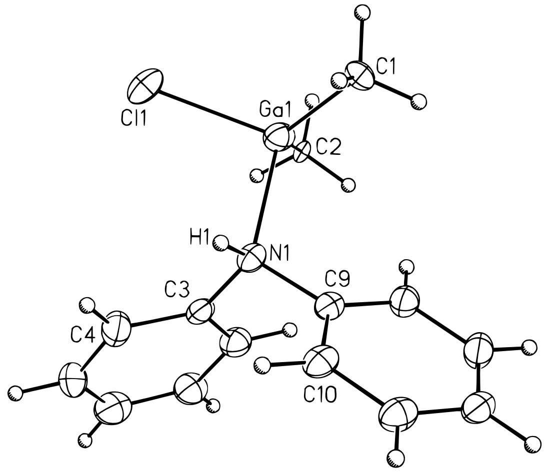

Figure 4. Thermal ellipsoidal plot (40% occupancy) of $ClMe_2GaNHPh_2$.

scale for bonds between three-coordinate nitrogen and gallium[20] owing to the fact that the gallium in this case is four-coordinate.

The adducts $ClMe_2GaNHPh_2$ and $ClMe_2GaNH(i\text{-}Pr)_2$ were isolated from mixtures involving the precursors $(Me_2GaNPh_2)_2$ or $Me_3GaNH(i\text{-}Pr)_2$ in $SiCl_4$. The isolation of the precursor $Me_3GaNH(i\text{-}Pr)_2$ from the reaction of Me_3Ga with $HN(i\text{-}Pr)_2$ may be contrasted with the reaction between Me_3Ga and $HNPh_2$ which eliminates methane to form $(Me_2GaNPh_2)_2$. The adduct $Me_3GaNH(i\text{-}Pr)_2$ does not eliminate methane readily, however. One possible explanation of this difference involves the different acidities of the N−H bond which is significantly greater for $HNPh_2$ in comparison to $HN(i\text{-}Pr)_2$.[21] The higher acidity of the arylamine facilitates methane elimination and the amide $(Me_2GaNPh_2)_2$ is more readily formed.

The structures of $ClMe_2GaNHPh_2$ and $ClMe_2GaNH(i\text{-}Pr)_2$ clearly demonstrate that ligand exchange takes place between $SiCl_4$ and $GaMe_3$. Further exchange is observed when more drastic reaction conditions (95 °C, 6 days) are used and formation of the salt $[NH_2(i\text{-}Pr)_2][MeGaCl_3]$ is observed. The structural parameters of these two compounds have no unusual features. The Ga−N distances 2.101(4) in $ClMe_2GaNHPh_2$ and 2.080(4) Å (avg) in $ClMe_2GaNH(i\text{-}Pr)_2$ are quite long owing to the four-coordinate nature of gallium and nitrogen and lie in the same range observed for other R_3GaNR_3 adducts.[22] The Ga−C and Ga−Cl distances in all three compounds are comparable owing to the similar coordination numbers of the galliums. The structural data of the anion in **6** are very similar to the corresponding anion in $[Me_4As][MeGaCl_3]$.[23]

The behavior of $(Me_2GaNPh_2)_2$ and the adduct $Me_3GaNH(i\text{-}Pr)_2$ in the presence of $SiCl_4/Si(OEt)_4$ may be contrasted with a similar experiment involving the more crowded amido derivative $Ga\{N(SiMe_3)_2\}_3$ which could be recovered unchanged after stirring for 3 days at 85 °C. The greater steric crowding in this compound presumably hinders exchange reactions between silicon and gallium centers.

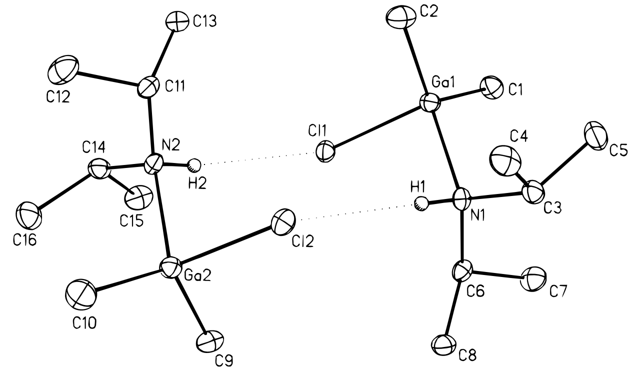

Figure 5. Thermal ellipsoidal plot (30% occupancy) of $(ClMe_2GaNH\text{-}i\text{-}Pr_2)_2$. Hydrogen atoms are omitted for clarity, excluding H1 and H2.

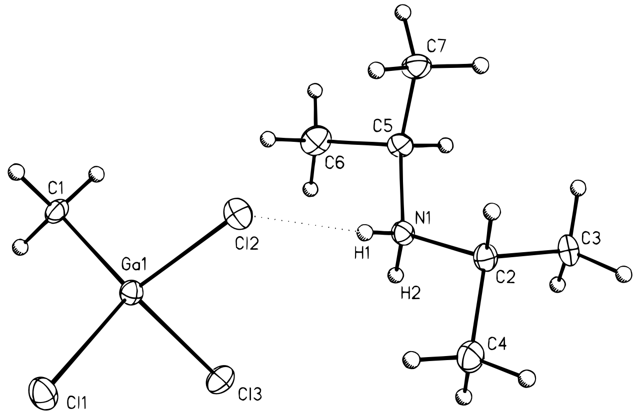

Figure 6. Thermal ellipsoidal plot (30% occupancy) of $[NH_2\text{-}i\text{-}Pr_2][MeGaCl_3]$.

The major implication of these studies is that the use of alkylgallium−amine adducts or gallium amides as precursors to gallium nitrides under the chemical conditions for nonhydrolytic gel synthesis require the use of sterically encumbered ligands if undesirable side reactions are to be avoided. Investigations of the use of other bulky amide compounds as Ga−N precursors in nonhydrolytic sol−gel environments are in hand.

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Supporting Information Available: Crystallographic data (43 pages). Ordering information is given on any current masthead page.

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