# Gallane Complexes with Amido−Amine Ligands

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Gallane complexes bearing amido−amine ligands −N(R)CH$_2$CMe$_2$CH$_2$NMe$_2$ [R = H or SiMe$_3$ (TMS)], {H$_2$Ga-[N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$]}$_2$, **1**, H$_2$Ga[N(TMS)CH$_2$CMe$_2$CH$_2$NMe$_2$], **2**, {H(Cl)Ga[N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$]}$_2$, **3**, {[(TMS)$_2$N](H)Ga[N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$]}$_2$, **4**, and HGa[N(TMS)CH$_2$CMe$_2$CH$_2$NMe$_2$]$_2$, **5**, were synthesized from the reactions of the quinuclidine adducts of mono- and dichlorogallane with the corresponding lithium amides. Structural determinations of compounds **1**, **3**, and **4** showed all were dimeric with bridging amido groups. Rather than bond to gallium the tertiary amine groups in **1** and **4** were hydrogen-bonded to the amido N−H. In the structure of compound **3** the amine group occupied an axial position in the trigonal bipyramidal geometry of the five-coordinate gallium. The results were rationalized in terms of the steric and electronic properties of gallium ligands.

## Introduction

Gallium hydride derivatives are attractive precursors to produce carbon-free group III−V materials at lower temperatures.[1−7] Because pure gallane, which exists as a dimer (Ga$_2$H$_6$), decomposes at temperatures above −30 °C,[8] stable gallium hydride compounds are usually obtained in the form of Lewis acid−base adducts, H$_3$Ga(base).[9−12] If the base is a primary or secondary amine, 1 mol of hydrogen can be eliminated to afford the corresponding amidogallane.[13−16] An alternative approach to gallium hydride derivatives with direct gallium−nitrogen bonds can be achieved using chlorogallanes as reactants. For example, azidogallane, (H$_2$GaN$_3$)$_n$, was obtained from the reaction of H$_2$GaCl with LiN$_3$.[4] Recently, we reported the synthesis of several monomeric quinuclidine adducts of amido- and azidogallanes[17] from quinuclidine-stabilized mono- and dichlorogallanes.[18] We present in this paper the synthesis of gallane derivatives with chelating amido−amine ligands, −N(R)-CH$_2$CMe$_2$CH$_2$NMe$_2$ (R = H or SiMe$_3$).

Although several aluminum dihydrides stabilized by chelating amido−amine ligands, −N(R)CH$_2$CH$_2$NMe$_2$ (R = Me or Et), have been structurally characterized by Barron and co-workers,[19] no gallane analogue has been published. Previously reported reaction of H$_3$Ga(NMe$_3$) with a symmetric diamine, Me(H)-NCH$_2$CH$_2$N(H)Me, afforded a gallane-rich compound, H$_5$Ga$_3$-{[N(Me)CH$_2$]$_2$}$_2$, due to elimination of all the protons of the amine groups.[20] Tertiary diamines, Me$_2$NCH$_2$CH$_2$NMe$_2$ or Me$_2$NCH$_2$CH$_2$CH$_2$NMe$_2$, reacted with H$_3$Ga(NMe$_3$) to give gallane adducts, H$_3$GaNMe$_2$CH$_2$CH$_2$N(Me$_2$)GaH$_3$[11,21] and H$_3$GaNMe$_2$CH$_2$CH$_2$CH$_2$NMe$_2$.[22] Another group of gallane derivatives containing symmetric diamido ligands are those derived from 1,4-dialkyl-1,4-diazabutadiene (RN=CHCH=NR).[20,23,24] Compounds with oxygen−nitrogen or sulfur−nitrogen ligands, including [MeN(CH$_2$CH$_2$O)$_2$GaH]$_2$,[25] (Me$_2$NCH$_2$CH$_2$OGaH$_2$)$_2$,[26] and HGa(SCH$_2$CH$_2$NEt$_2$)$_2$[27] are known.

## Experimental Section

**Materials and General Procedures.** Lithium bis(trimethylsilyl)-amide (Aldrich) was recrystallized from hexanes. *N,N*-2,2-Tetramethyl-

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1,3-propanediamine (Aldrich), $H_2NCH_2CMe_2CH_2NMe_2$, was distilled over KOH under nitrogen. Chlorotrimethylsilane (Aldrich) was used as received. The hexanes solution of *n*-butyllithium (Aldrich) was titrated using $(1R,2S,5R)$-(−)-menthol. Diethyl ether, pentane, hexanes, and toluene were predried over calcium hydride and freshly distilled from sodium/benzophenone under nitrogen. Benzene-$d_6$ and toluene-$d_8$ were distilled over calcium hydride under nitrogen. All experiments were conducted under an oxygen-free, dry-nitrogen atmosphere using Schlenk and glovebox techniques.

The quinuclidine adducts of mono- and dichlorogallane, $H_2GaCl$-(quin) and $HGaCl_2$(quin), were synthesized as previously reported.[18] $Li[N(H)CH_2CMe_2CH_2NMe_2]$ was prepared from the reaction of $H_2NCH_2CMe_2CH_2NMe_2$ with 1 equiv of *n*-butyllithium and crystallized as a colorless compound from pentane solution (90% yield). HN(TMS)-$CH_2CMe_2CH_2NMe_2$ was obtained as a colorless liquid from the reaction of chlorotrimethylsilane with $Li[N(H)CH_2CMe_2CH_2NMe_2]$ in a 1:1 molar ratio and distilled under a reduced pressure (50 °C/0.01 Torr, 71% yield). $Li[N(TMS)CH_2CMe_2CH_2NMe_2]$, prepared from the lithiation of HN(TMS)$CH_2CMe_2CH_2NMe_2$ with *n*-butyllithium in pentane, was initially a colorless liquid and solidified to afford a colorless crystalline solid upon storage. The above as-prepared lithium amides and HN(TMS)$CH_2CMe_2CH_2NMe_2$ were characterized by $^1H$ NMR and IR spectroscopy.

Except those indicated otherwise, $^1H$ NMR spectra were obtained in benzene-$d_6$ solutions at room temperature on either a Varian INOVA 300 or a Varian UNITY 300 spectrometer. The residual proton ($\delta$ 7.15) in benzene-$d_6$ was used as the internal standard. The IR spectra of KBr pellets or liquid films between NaCl windows were recorded on a Nicolet MAGNA-IR 560 spectrometer. Melting points were measured in sealed glass capillaries and were not corrected. All elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Synthesis of $\{H_2Ga[N(H)CH_2CMe_2CH_2NMe_2]\}_2$, 1.** To a stirred solution of $H_2GaCl$(quin) (1.500 g, 6.87 mmol) in 40 mL of $Et_2O$ at room temperature was added a solution of $Li[N(H)CH_2CMe_2CH_2NMe_2]$ (0.935 g, 6.87 mmol) in 40 mL of $Et_2O$ over a period of 10 min. The mixture was stirred for 2 h and filtered. After volatiles were removed under vacuum from the filtrate, a colorless, sticky oil remained. To facilitate crystallization of the oil, pentane (10 mL) was added and removed immediately under vacuum. Upon storage for a day at room temperature, the pentane-treated oil solidified to afford a colorless crystalline solid (1.37 g, 99% yield). Mp: 51−53 °C. $^1H$ NMR: $\delta$ 0.73 (12H, s, $CMe_2$), 1.87 (4H, s, $Me_2NCH_2$), 2.00 (12H, s, $NMe_2$), 2.92 (4H, d, $^3J_{HH}$ = 6.3 Hz, HN$CH_2$), 3.31 (2H, br s, NH), and 5.26 (4H, br s, Ga$H_2$). IR: $\nu_{GaH}$, 1875 cm$^{-1}$; $\nu_{NH}$, 3179 cm$^{-1}$. MS (CI, %, where fw equals the formula weight of one monomeric unit): 471.2 ([3fw − N(H)$CH_2CMe_2CH_2NMe_2$]$^+$, 14), 401.2 ([2fw + H]$^+$, 14), 215.1 ([fw + Me]$^+$, 19), 201.1 ([fw + H]$^+$, 100), 131.2 ([$Me_2NCH_2CMe_2$-$CH_2NH_3$]$^+$, 56). Anal. Calcd for $C_{14}H_{38}Ga_2N_4$: C, 41.84; H, 9.53; N, 13.94. Found: C, 38.74; H, 8.97; N, 11.75.

**Synthesis of $H_2Ga[N(TMS)CH_2CMe_2CH_2NMe_2]$, 2.** To a precooled (−78 °C) solution of $H_2GaCl$(quin) (0.800 g, 3.66 mmol) in 40 mL of $Et_2O$ was added a solution of $Li[N(TMS)CH_2CMe_2CH_2NMe_2]$ (0.763 g, 3.66 mmol) in 20 mL of $Et_2O$ over a period of 10 min. The mixture was stirred for 0.5 h at −78 °C and then for 3 h at room temperature. Upon filtration and removal of volatiles in the filtrate under vacuum, a slightly yellow liquid was collected (0.86 g, 86% yield). $^1H$ NMR: $\delta$ 0.33 (9 H, s, $SiMe_3$), 0.71 (6H, s, $CMe_2$), 1.87 (6H, s, $NMe_2$), 1.89 (2H, s, (TMS)N$CH_2$), 3.04 (2H, s, $Me_2NCH_2$), and 4.97 (2H, br s, Ga$H_2$). IR: $\nu_{GaH}$, 1825 and 1869 cm$^{-1}$. MS (CI, %, where fw equals the formula weight): 545.5 ([2fw + H]$^+$, 2.5), 343.2 ([fw + Ga$H_2$]$^+$, 4), 273.2 ([fw + H]$^+$, 100), 257.2 ([fw − Me]$^+$, 16), 203.3 ([HN-(TMS)$CH_2CMe_2CH_2NMe_2$ + H]$^+$, 72), 187.2 ([HN(TMS)$CH_2CMe_2$-$CH_2NMe_2$ − Me]$^+$, 34). Anal. Calcd for $C_{10}H_{27}GaN_2Si$: C, 43.97; H, 9.96; N, 10.26. Found: C, 46.18; H, 10.17; N, 10.28. To test for thermal stability, a small amount of the oil was sealed in a capillary under $N_2$ and slowly heated to 135 °C at which point the decomposition occurred as indicated by the formation of gray particles.

**Synthesis of $\{H(Cl)Ga[N(H)CH_2CMe_2CH_2NMe_2]\}_2$, 3.** To a stirred solution of $HGaCl_2$(quin) (2.000 g, 7.91 mmol) in 50 mL of $Et_2O$ at room temperature was added a solution of $Li[N(H)CH_2CMe_2CH_2NMe_2]$

(1.077 g, 3.91 mmol) in 80 mL of $Et_2O$ over a period of 20 min. The mixture was stirred for 2 h and filtered. Volatiles ($Et_2O$ and quinuclidine) were removed under vacuum from the colorless filtrate, and a white crystalline compound remained. $Et_2O$ (180 mL) was again added, and the solution was filtered. Upon concentration and storage at −15 °C overnight, small colorless blocks were collected (1.28 g, 69% yield). Mp: 105−108 °C. $^1H$ NMR (25 °C): $\delta$ 0.60 (12H, br s, $CMe_2$), 1.95 (16H, br s, $NMe_2$ and $CH_2NMe_2$), 2.94 (6H, br s, NH and $CH_2NH$), and 5.17 (2H, br s, GaH). $^1H$ NMR (60 °C): $\delta$ 0.68 (12H, br s, $CMe_2$), 2.02 (16H, br s, $NMe_2$ and $CH_2NMe_2$), 2.93 (6H, br s, NH and $CH_2$-NH), and 5.32 (2H, br s, GaH). $^1H$ NMR (21 °C, toluene-$d_8$): $\delta$ 0.64 (12H, br s, $CMe_2$), 1.97 (16H, br s, $NMe_2$ and $CH_2NMe_2$), 2.87 (6H, br s, NH and $CH_2NH$), and 5.14 (2H, br s, GaH). $^1H$ NMR (−60 °C, toluene-$d_8$): $\delta$ 0.45 (6H, s) and 0.52 (6H, s) for $CMe_2$, 1.58 (6H, s) and 1.99 (6H, s) for $NMe_2$, 2.03 (4H, s, $CH_2NMe_2$), 2.66 (4H, d, $^3J_{HH}$ = 13.2 Hz, $CH_2NH$), 3.38 (2H, t, $^3J_{HH}$ = 13.6 Hz, NH), and 4.93 (2H, s, GaH). The residual proton ($\delta$ 6.98) in toluene-$d_8$ was used as the internal standard. IR: $\nu_{GaH}$, 1870 cm$^{-1}$; $\nu_{NH}$, 3310 cm$^{-1}$. Anal. Calcd for $C_{18}H_{44}N_2Ga_2Cl_2$: C, 35.86; H, 7.31; N, 11.95. Found: C, 35.24; H, 7.74; N, 11.58.

**Synthesis of $\{[(TMS)_2N](H)Ga[N(H)CH_2CMe_2CH_2NMe_2]\}_2$, 4.** To a stirred solution of compound **3** (0.400 g, 0.849 mmol) in 40 mL of toluene at room temperature was added a solution of $Li[N(TMS)_2]$ (0.284 g, 1.70 mmol) in 20 mL of toluene over a period of 5 min. The mixture was stirred for 3 h and filtered. After the colorless filtrate was concentrated and stored at −15 °C, colorless plates were collected (0.41 g, 67% yield). Mp: 172−175 °C. $^1H$ NMR: $\delta$ 0.42 (36H, s, $SiMe_3$), 0.66 (6H, s) and 1.08 (6H, s) for $CMe_2$, 1.90 (2H, d, $J$ = 1.8 Hz) and 1.94 (2H, d, $J$ = 1.8 Hz) for $CH_2NMe_2$, 2.12 (12H, s, $NMe_2$), 2.84 (2H, t, $J$ = 11.1 Hz, NH), 3.18 (4H, d, $J$ = 12.6 Hz, $CH_2NH$), and 5.31 (2H, br s, GaH). IR: $\nu_{GaH}$, 1903 cm$^{-1}$; $\nu_{NH}$, 3201 cm$^{-1}$. Anal. Calcd for $C_{26}H_{72}N_6Si_4Ga_2$: C, 43.33; H, 10.07; N, 11.66. Found: C, 43.73; H, 10.42; N, 11.78.

**Synthesis of $HGa[N(TMS)(CH_2CMe_2CH_2NMe_2)]_2$, 5.** To a stirred solution of $HGaCl_2$(quin) (0.837 g, 3.31 mmol) in 30 mL of $Et_2O$ at room temperature was added a solution of $Li[N(TMS)(CH_2CMe_2CH_2$-$NMe_2)]$ (1.380 g, 6.62 mmol) in 20 mL of $Et_2O$ over a period of 10 min. The mixture was stirred for 3 h and filtered. After volatiles were removed from the colorless filtrate under vacuum, a colorless liquid was collected (1.29 g, 82% yield). $^1H$ NMR: $\delta$ 0.38 (18H, s, $SiMe_3$), 0.85 (6H, s), and 1.06 (6H, s) for $CMe_2$, 1.94 (2H, d, $^2J_{HH}$ = 13.0 Hz) and 2.23 (2H, d, $^2J_{HH}$ = 13.5 Hz) for (TMS)N$CH_2$, 2.13 (12H, s, $NMe_2$), 2.89 (2H, d, $^2J_{HH}$ = 13.5 Hz), and 3.14 (2H, d, $^2J_{HH}$ = 14.0 Hz) for $Me_2NCH_2$ and 4.94 (1H, br s, GaH). IR: $\nu_{GaH}$, 1884 cm$^{-1}$. Anal. Calcd for $C_{20}H_{51}GaN_4Si_2$: C, 50.73; H, 10.86; N, 11.83. Found: C, 50.51; H, 11.11; N, 11.37. To test for thermal stability, a small amount of the oil was sealed in a capillary under $N_2$ and slowly heated to 85 °C at which point the decomposition occurred as indicated by the formation of gray particles.

**X-ray Data Collection, Structure Solution, and Refinement.** Suitable crystals of **1**, **3**, **4** were selected and mounted on glass fibers under a nitrogen atmosphere. The data collections were conducted on a Siemens SMART system. In each experiment, an initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection technique was generally known as a hemisphere collection. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in $\omega$.

The space groups were determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution was applied to the structures of compounds **3** and **4**, which provided most non-hydrogen atoms from the E-maps. Several full-matrix, least squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except those indicated below, were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydrides and the hydrogen atoms of the amido groups were refined isotropically. The structure of compound **1** was solved by Patterson

**Table 1.** Crystallographic Data of Compounds **1**, **3**, and **4**

|  | $C_{14}H_{38}Ga_2N_4$ **1** | $C_{14}H_{36}Cl_2Ga_2N_4$ **3** | $C_{26}H_{72}Ga_2N_6Si_4$ **4** |
|---|---|---|---|
| fw | 401.92 | 470.82 | 720.70 |
| space group | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 12.1974(7) | 9.7800(2) | 12.0948(2) |
| $b$, Å | 6.2638(3) | 8.3030(1) | 14.2229(1) |
| $c$, Å | 13.9611(8) | 13.0967(3) | 12.9553(1) |
| $\beta$, deg | 105.1550(1) | 91.545(1) | 114.883(1) |
| $V$, Å$^3$ | 1029.6(1) | 1063.11(4) | 2021.73(4 |
| $Z$ | 2 | 2 | 2 |
| temp, °C |  | −100 |  |
| $\lambda$, Å |  | 0.710 73 |  |
| $\rho_{cald}$, g cm$^{-3}$ | 1.296 | 1.471 | 1.184 |
| $\mu$, cm$^{-1}$ | 26.15 | 27.88 | 14.74 |
| R1, wR2$^a$ [$I > 2\sigma(I)$] | 0.0183, 0.0457 | 0.0308, 0.0586 | 0.0287, 0.0745 |

$^a$ R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, $P = (F_o^2 + 2F_c^2)/3$ and $a$ and $b$ are constants given in Supporting Information.
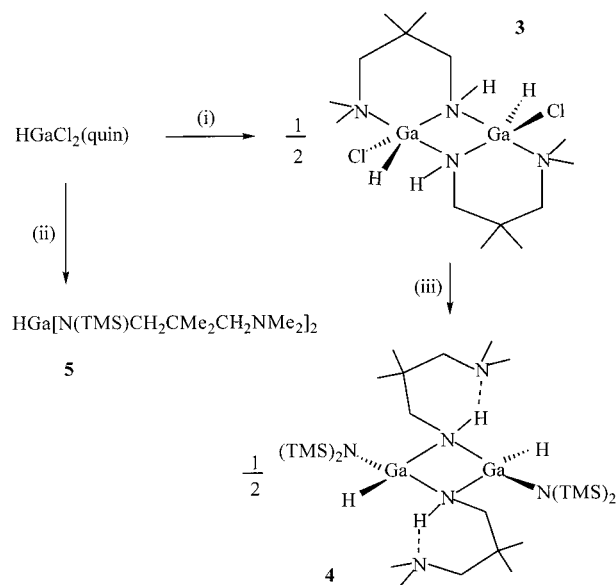
**Scheme 1**$^a$
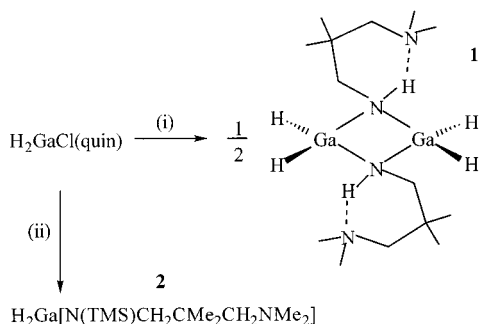


$^a$ (i) Li[N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$], −LiCl, −quin. (ii) Li[N(TMS)-CH$_2$CMe$_2$CH$_2$NMe$_2$], −LiCl, −quin.

synthesis. The refinement process was the same as that for compounds **3** and **4** except that all the hydrogen atoms were located from the E map and refined isotropically. The experimental conditions and unit cell information are summarized in Table 1.

## Results and Discussion

**Syntheses and Structures of Compounds 1, 3, and 4.** Compounds **1**, **3**, and **4**, which all contained a −N(H)CH$_2$CMe$_2$-CH$_2$NMe$_2$ ligand, were synthesized according to the reactions described in Schemes 1 and 2. In each reaction the quinuclidine ligand in the starting material was replaced by the amido−amine ligand in the products and was removed under vacuum.

Compound **1** was initially obtained as a colorless oil that was not further purified by distillation because of decomposition at elevated temperatures. Small amounts of impurities were detected by $^1$H NMR spectroscopy. After a small amount of pentane was added and removed, the oil solidified to form a colorless crystalline solid upon storage at room temperature for a day. Without use of pentane the oil did not solidify even if stored for 2 weeks under the same conditions. The $^1$H NMR spectra in benzene-$d_6$ of the liquid and the solid were identical, but their IR spectra differed. The spectrum of the solid sample gave a sharp absorption at 1875 cm$^{-1}$ for $\nu_{GaH}$ and a broad peak at 3179 cm$^{-1}$ for $\nu_{NH}$, whereas the corresponding peaks of the liquid sample shifted to lower frequencies (1865 cm$^{-1}$ for $\nu_{GaH}$ and 3137 cm$^{-1}$ for $\nu_{NH}$) and were broader. These differences were in part due to matrix effects (KBr pellet vs neat liquid). The elemental analysis of compound **1** was unsatisfactory possibly because of its sensitivity to air and moisture, but the chemical ionization mass spectrum exhibited a molecular ion

**Scheme 2**$^a$



$^a$ (i) Li[N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$], −LiCl, −quin. (ii) Li[N(TMS)-CH$_2$CMe$_2$CH$_2$NMe$_2$], −LiCl, −quin. (iii) LiN(TMS)$_2$, −LiCl, −quin.

**Scheme 3**
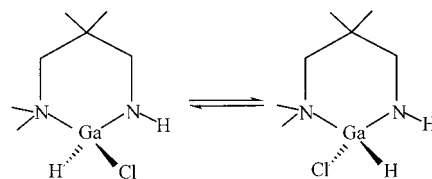


peak (plus 1) at 401.2 (14%) and a monomer peak (plus 1) at 201.1 (100%). A higher ion peak at 471.2 (14%) was also observed, which can be assigned to a trimer losing a N(H)CH$_2$-CMe$_2$CH$_2$NMe$_2$ ligand. Reactions in the evaporation process of the MS experiment possibly accounted for the presence of the trimer.

Compounds **3** and **4** were isolated as colorless crystalline solids in moderate yields. The room temperature $^1$H NMR spectrum of **3** was broadened, indicative of an exchange process. Variable temperature measurements from −60 to +60 °C using benzene-$d_6$ and toluene-$d_8$ were obtained, and below −40 °C the spectra were consistent with the solid-state structure. At low temperature the two halves of the molecule were equivalent to each another by an inversion operation, but the two sides of each ring comprised of the gallium and chelating amido−amine ligand were not equivalent. This was most readily evidenced in the pair of methyl resonances due to both the CMe$_2$ (0.45 and 0.52 ppm) and NMe$_2$ (1.58 and 1.99 ppm) moieties. As the temperature was raised, these resonances coalesced and eventually became equivalent. Similar changes in the resonances for the remaining hydrogen atoms were also attributed to an exchange process that caused the two sides of the rings to become equivalent at higher temperatures.

The exchange process can best be considered by recalling that the molecule is a dimer. The monomer (Scheme 3), which was the original target molecule in this study, is chiral; thus, dimerization would lead to diastereomers. This further implies that the only method by which the two sides of the chelating ring can become equivalent involves a racemization. Racemization by dissociating the amido, chloro, or hydrido ligand in nonpolar, noncoordinating solvents is unlikely at these temperatures. Inversion can be achieved by dissociation of the weakest
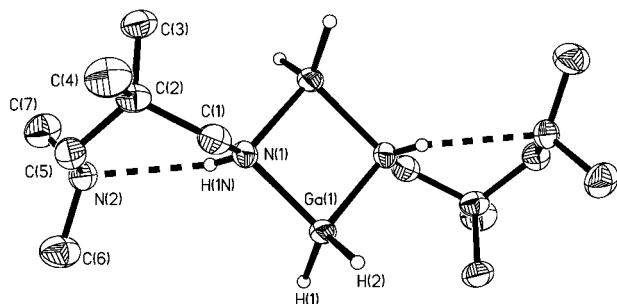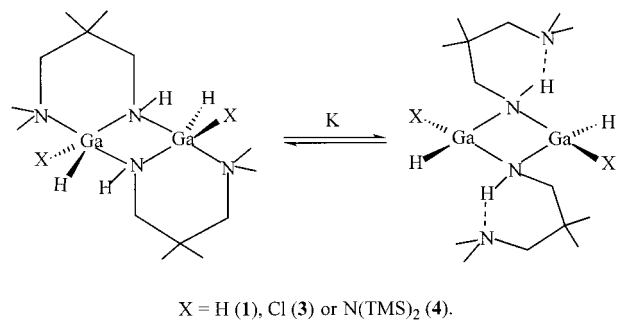
**Figure 1.** Structure of {H₂Ga[N(H)CH₂CMe₂CH₂NMe₂]}₂, **1**. The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except those on gallium and nitrogen atoms are omitted for clarity.

**Scheme 4**



X = H (**1**), Cl (**3**) or N(TMS)₂ (**4**).

bond in the structure (i.e., the bond between gallium and the tertiary amine) followed by rearrangement and Ga–N bond reformation (Scheme 3). The structure of the dimer found in the solid state, which is consistent with the low-temperature solution NMR spectrum, contains a center of symmetry, making it a meso stereoisomer. It is hard to imagine a process that would lead to racemization of the intact dimeric compound. Even the conversion of **3** to an isomer analogous to **1** (Scheme 4), which involves cleavage of the weak donor–acceptor Ga–N bond and formation of the intramolecular hydrogen bond, cannot lead to racemization. We propose that the changes in the NMR spectrum involve dissociation of the dimer into monomers, racemization, and dimer re-formation.

The IR spectrum of compound **4** showed a broad N–H absorption at 3201 cm$^{-1}$, which is evidence for the presence of hydrogen bonding (see below). Compound **4** was not sensitive to air and moisture; a sample of **4** exposed in air for 2 weeks gave the same ¹H NMR and IR spectra as the freshly isolated samples.

The molecular structures of **1**, **3**, and **4** are shown in Figures 1−3 and the selected bond lengths and angles are listed in Tables 2−4, respectively. The three structures were dimeric with bridging amido groups, and each possessed a centrosymmetric Ga₂N₂ ring with the substituents on the gallium and nitrogen atoms adopting a trans conformation.

The molecular structures of compounds **1** and **4** were very similar. The planar Ga₂N₂ rings with a Ga–N–Ga bond angle of 91.54(6)° and bond lengths of 1.9948(13) and 2.0088(14) Å for compound **1**, and 92.13(8)° and 1.994(2) and 2.011(2) Å for compound **4** were comparable to those in a number of other structures with nearly perfect square Ga₂N₂ rings. Known examples include (H₂GaNMe₂)₂ [Ga–N–Ga, 90.6(8)°; Ga–N, 2.027(4) Å],[28] [(Me)(Cl)GaN(H)(TMS)]₂ [91.0(5)°; 2.012-
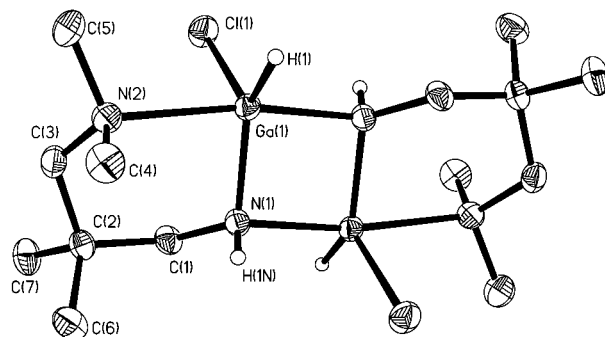
(28) Baxter, P. L.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1985**, 807−814.



**Figure 2.** Structure of {[(TMS)₂N](H)Ga[N(H)CH₂CMe₂CH₂NMe₂]}₂, **4**. The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except those on gallium and nitrogen atoms are omitted for clarity.



**Figure 3.** Structure of {H(Cl)Ga[N(H)CH₂CMe₂CH₂NMe₂]}₂, **3**. The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except those on gallium and nitrogen atoms are omitted for clarity.
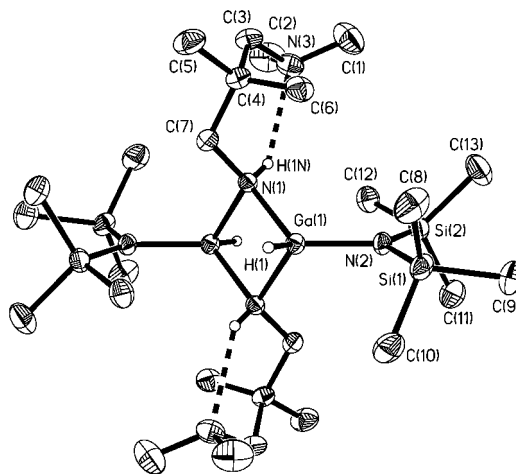
**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**

| C₁₄H₃₈Ga₂N₄, 1 | | | |
|---|---|---|---|
| Ga(1)−N(1) | 1.9948(13) | N(1)−H(1N) | 0.80(2) |
| Ga(1)−N(1A) | 2.0088(14) | N(1)−C(1) | 1.483(2) |
| Ga(1)−H(1) | 1.50(2) | N(2)···H(1N) | 2.30(2) |
| Ga(1)−H(2) | 1.50(2) | N(1)···N(2) | 2.989(2) |
| N(1)−Ga(1)−N(1A) | 88.45(6) | C(1)−N(1)−Ga(1A) | 117.77(10) |
| N(1)−Ga(1)−H(1) | 113.7(8) | Ga(1)−N(1)−Ga(1A) | 91.54(6) |
| N(1)−Ga(1)−H(2) | 112.2(7) | H(1N)−N(1)−Ga(1) | 109.0(12) |
| N(1A)-Ga(1)−H(1) | 105.8(7) | H(1N)−N(1)−Ga(1A) | 113.2(14) |
| N(1A)-Ga(1)−H(2) | 111.6(8) | H(1N)−N(1)−C(1) | 107.0(13) |
| H(1)−Ga(1)−H(2) | 120.3(10) | N(1)−H(1N)···N(2) | 144.3(16) |
| C(1)−N(1)−Ga(1) | 117.75(10) | | |

(8) Å],[29] [Cl₂GaN(H)(TMS)]₂ [91.0(1)°; 1.974(4) and 1.964(4) Å],[30] [Cl₂GaN(Me)(TMS)]₂ [90.0(2)° and 89.9(2)°; 1.983(5), 1.985(5), 1.987(5), and 1.989(5) Å],[30] [Br₂GaN(H)(TMS)]₂ [90.4(7)°; 1.993(16) and 2.000(18) Å],[31] [(Me₂N)₂Ga(μ-NMe₂)]₂ [92.3(1)°; 2.005(2) and 2.021(3) Å],[32] and [Me₂GaN(H)(SiEt₃)]₂ (91.9(2)°; 2.025(4) and 2.033(4) Å].[33] The terminal Ga(1)−

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**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **3**

| | | | |
|---|---|---|---|
| $C_{14}H_{36}Cl_2Ga_2N_4$, **3** | | | |
| Ga(1)−N(1) | 1.962(2) | Ga(1)−Cl(1) | 2.2478(8) |
| Ga(1)−N(1A) | 2.116(2) | N(1)−H(1N) | 0.84(3) |
| Ga(1)−N(2) | 2.310(2) | N(1)−C(1) | 1.475(3) |
| Ga(1)−H(1) | 1.69(2) | | |
| | | | |
| N(1)−Ga(1)−N(2) | 86.95(9) | H(1)−Ga(1)−N(2) | 87.1(8) |
| N(1)−Ga(1)−N(1A) | 83.49(10) | H(1)−Ga(1)−N(1A) | 110.2(8) |
| N(1)−Ga(1)−H(1) | 131.9(7) | Cl(1)−Ga(1)−N(2) | 90.14(6) |
| N(1)−Ga(1)−Cl(1) | 109.35(8) | Cl(1)−Ga(1)−N(1A) | 91.86(7) |
| H(1)−Ga(1)−Cl(1) | 118.4(7) | C(1)−N(1)−Ga(1) | 116.2(2) |
| Ga(1)−N(1)−H(1N) | 112(2) | C(1)−N(1)−Ga(1A) | 116.6(2) |
| Ga(1A)−N(1)−H(1N) | 106(2) | C(1)−N(1)−H(1N) | 109(2) |
| Ga(1)−N(1)−Ga(1A) | 96.51(10) | Ga(1)−N(2)−C(3) | 112.9(2) |
| Ga(1)−N(2)−C(4) | 107.2(2) | Ga(1)−N(2)−C(5) | 109.6(2) |

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for **4**

| | | | |
|---|---|---|---|
| $C_{26}H_{72}Ga_2N_6Si_4$, **4** | | | |
| Ga(1)−N(1) | 1.994(2) | N(1)−H(1N) | 0.77(3) |
| Ga(1)−N(1A) | 2.011(2) | N(1)−C(7) | 1.489(3) |
| Ga(1)−N(2) | 1.893(2) | N(2)−Si(1) | 1.738(2) |
| Ga(1)−H(1) | 1.51(3) | N(2)−Si(2) | 1.721(2) |
| N(3)···H(1N) | 2.38(3) | N(2)···N(3) | 3.019(3) |
| | | | |
| N(1)−Ga(1)−N(2) | 119.90(8) | N(2)−Ga(1)−N(1A) | 114.02(8) |
| N(1)−Ga(1)−N(1A) | 87.87(8) | N(2)−Ga(1)−H(1) | 115.2(11) |
| N(1)−Ga(1)−H(1) | 106.9(11) | N(1A)−Ga(1)−H(1) | 109.6(11) |
| Ga(1)−N(1)−Ga(1A) | 92.13(8) | Ga(1)−N(1)−C(7) | 116.65(14) |
| Ga(1)−N(1)−H(1N) | 113(2) | Ga(1A)−N(1)−C(7) | 119.08(14) |
| Ga(1A)−N(1)−H(1N) | 108(2) | H(1N)−N(1)−C(7) | 108(2) |
| Si(1)−N(2)−Si(2) | 123.55(11) | Si(1)−N(2)−Ga(1) | 111.19(10) |
| Si(2)−N(2)−Ga(1) | 125.18(11) | N(1)−H(1N)···N(3) | 141(2) |

N(2) bond length in compound **4** [1.870(3) Å] was typical for covalent Ga−N bonds (1.82−1.94 Å) as summarized by Brothers and Power.[34] The Ga−H bond lengths in the two structures were equal [1.50(2) Å in **1**, 1.51(3) Å in **4**]. The six-membered ring, constructed by a −N(H)CH$_2$CMe$_2$CH$_2$NMe$_2$ ligand and an intramolecular hydrogen bond between the amido hydrogen and the amine nitrogen, adopted a distorted chair conformation in each of the two compounds. The N···N distance 2.9891(18) Å and N−H···N angle 144.3(16)° of the hydrogen bond in compound **1** were close to those in compound **4** [3.019-(3) Å, 141(2)°]. Intramolecular hydrogen bonds between the secondary amine and the tertiary amine groups were previously found in the structures of $^t$Bu$_3$Al adducts, $^t$Bu$_3$Al[N(H)(Me)-CH$_2$CH$_2$CH$_2$NMe$_2$] [N···N, 2.96 Å; N−H···N, 127°] and $^t$Bu$_3$-Al[N(H)(Me)CH$_2$CH$_2$NMe$_2$] [N···N, 2.98 Å; N−H···N,101°].[35]

In **3**, the gallium atom was five-coordinate, adopting a distorted trigonal bipyramidal geometry with Cl(1), H(1), and N(1) atoms in the equatorial plane. Constrained by two rings, the N(2)−Ga(1)−N(1A) angle was only 170.36(8)°. The internal angles of the Ga$_2$N$_2$ ring were 83.49(10)° at gallium and 96.51-(10)° at nitrogen. The six-membered ring formed from a −N(H)-CH$_2$CMe$_2$CH$_2$NMe$_2$ group, and a gallium atom adopted a chair conformation. It was interesting to notice that there were three different Ga−N bonds in this structure, Ga(1)−N(1) [1.962(2) Å], Ga(1)−N(1A) [2.116(2) Å], and Ga(1)−N(2) [2.310(2) Å]. The axial, dative Ga(1)−N(2) bond was the longest of the three and was in the range of the corresponding Ga−N bond lengths in other gallium compounds with a trigonal bipyramidal geometry, such as (Me$_2$NCH$_2$CH$_2$OGaMe$_2$)$_2$ [2.471(4) Å],[26] (Me$_2$NCH$_2$CH$_2$OGaH$_2$)$_2$ [2.279(3) Å],[26] [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]-GaH$_2$ [2.380(6) and 2.398(6) Å],[36] HGa(SCH$_2$CH$_2$NEt$_2$)$_2$ [2.252-

(9) and 2.28(1) Å],[27] H$_2$GaCl(quin)$_2$ [2.259(2) Å], and HGaCl$_2$-(quin)$_2$ [2.232(8) and 2.254(8) Å].[18] The Ga(1)−N(1) bond length was in good agreement with those in planar Ga$_2$N$_2$ rings as described above. The longer Ga(1)−N(1A) bond length than Ga(1)−N(1) reflected its axial position in this five-coordinate gallium compound.

Compounds **1**, **3**, and **4** differed only by the substituent X in the generic formula [HGaXL], where L = the amido−amine ligand. The two observed structures were related by the equilibrium shown in Scheme 4, in which the loss of the fifth ligand on gallium is balanced by the formation of the intramolecular hydrogen bond. We emphasize that for the particular substituents studied here, only one compound was identified and NMR spectroscopy did not exhibit resonances attributable to the other. Thus, for the three X ligands, −H, −Cl, and −N(TMS)$_2$, we suggest that the equilibrium value of $K_{eq}$ is greater than ∼100 for X = H and N(TMS)$_2$ and less than ∼0.01 for X = Cl. The trend can be understood by considering the steric and electronic properties of the ligand. The steric bulk of the −N(TMS)$_2$ will favor a lower coordination number for gallium. The electronegative −Cl ligand will enhance the Lewis acidity of the metal, thus strengthening the extra Ga−N bond. It has been noted that in the structures of the alane derivatives, {H$_2$Al[N(R)CH$_2$CH$_2$NMe$_2$]}$_2$ (R = Me or Et),[19] the amine group coordinated to aluminum because of the greater Lewis acidity of aluminum over gallium and no available proton for forming hydrogen bond in these compounds.

Gallium metal was observed as one of the products when compounds **1**, **3**, and **4** were heated at 110, 130, and 200 °C, respectively. The other products were viscous oils and were not characterized.

**Syntheses of Compounds 2 and 5.** Compounds **2** and **5** were obtained as liquid products at room temperature (Schemes 1 and 2), and prolonged storage did not induce solidification. Attempts to distill them under reduced pressures resulted in decomposition; however, the $^1$H NMR spectra of **2** and **5** showed that both were pure and only trace quinuclidine was found in the spectrum of compound **2**. Elemental analyses of **2** and **5** were satisfactory except for the high carbon percentage for compound **2** (2% greater than the calculated value). This was probably due to the presence of the quinuclidine impurity. The base peak in the chemical ionization mass spectrum of compound **2** appeared at 273 corresponding to the formula weight (plus 1) of H$_2$Ga[N(TMS)CH$_2$CMe$_2$CH$_2$NMe$_2$]. A small (2.5% of base peak) peak at 545 corresponded to a dimer (2FW + H)$^+$, which may be present in the liquid.

Replacing one amido hydrogen with a TMS group increased the steric congestion and reduced the Lewis basicity of the amido nitrogen. Given the trends discussed above, we anticipated that **2** and **5** would have a greater chance of being monomeric. The liquid nature of the products precluded single-crystal X-ray diffraction studies.

**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of compounds **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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