Inorg. Chem. **2000,** *39,* 1705−1709

Syntheses and Structures of Quinuclidine-Stabilized Amido- and Azidogallanes

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Received August 23, 1999

Quinuclidine-stabilized amido- and azidogallanes, $HGa[N(TMS)_2]_2$(quin) (**1**), $H_2Ga[N(TMS)_2]$(quin) (**2**), HGa-$[N(H)(2,6\text{-}^iPr_2C_6H_3)]_2$(quin) (**3**), and H_2GaN_3(quin) (**4**), were synthesized from the quinuclidine adducts of mono- and dichlorogallane. Structural determinations revealed that all compounds were monomeric with four-coordinate gallium centers. Reactions of the five-coordinate compound, $HGaCl_2(quin)_2$, with 2 equiv of $Li[N(TMS)_2]$ or $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$ resulted in the isolation of compound **1** or **3**. A ligand redistribution during the reaction of H_2GaCl(quin) with $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$ produced compound **3** and H_3Ga(quin) in a 1:1 molar ratio.

Introduction

Much recent interest in gallium chemistry focuses on the syntheses of novel compounds that are precursors to solid-state materials such as gallium nitride.[1−8] Gallane and its derivatives are of particular interest because the absence of direct Ga−C bonds minimizes the potential carbon contamination. The high thermal reactivity of many of the hydrides allows depositions to be conducted at lower temperatures. For example, GaN films were prepared at a temperature as low as 200 °C using $(H_2GaN_3)_n$ as the precursor in chemical vapor deposition processes,[8,9] and GaN nanocrystals were synthesized from $[H_2GaNH_2]_3$ either by direct pyrolysis or dehydrogenation in a liquid-ammonia medium.[1,6] As problems associated with either the stability of the precursors or the quality of the GaN products still exist, syntheses of new gallane compounds are needed.

All structurally characterized amidogallane compounds including $[H_2GaN(CH_2)_2]_3$,[10] $[H_2GaNMe_2]_2$,[11] and $[H_2GaNH_2]_3$[12] exist as di- or trimeric species. Even in the presence of Lewis bases, monomeric amidogallane derivatives are unknown, although monomeric Lewis base adducts of other gallium compounds are common.[13,14] Most of the reported gallane derivatives were synthesized from $H_3Ga(NMe_3)$ by elimination of one or two of the hydrides.[15−19] Recently, we reported the syntheses of thermally robust quinuclidine-stabilized, mono- and dichlorogallane,[20] which offer an alternative route to novel gallane derivatives. In this paper, we report the syntheses and structures of a monomeric monoamidogallane, $H_2GaN(TMS)_2$(quin), and monomeric diamidogallanes, $HGa[N(TMS)_2]_2$(quin) and $H[GaN(H)(2,6\text{-}^iPr_2C_6H_3]_2$(quin), where TMS is trimethylsilyl and quin is quinuclidine. In addition, we report the synthesis and structure of a quinuclidine-stabilized azidogallane, H_2GaN_3(quin). The compound $(H_2GaN_3)_n$ was proposed to be trimeric in the gas-phase based on vibrational data and ab initio calculations.[8]

Experimental Section

Materials and General Procedures. The quinuclidine adducts of mono- and dichlorogallane were synthesized as previously reported.[20] Lithium bis(trimethylsilyl)amide (Aldrich) was recrystallized from hexanes. Sodium azide (Aldrich) was dried under vacuum (∼0.01 Torr) at room temperature for 24 h. The hexanes solution of *n*-butyllithium (Aldrich) was titrated using (1*R*,2*S*,5*R*)-(−)-menthol. 2, 6-Diisopropylaniline (Fluka) was distilled over calcium hydride (75 °C/0.01 Torr). Lithium 2,6-diisopropylanilide was prepared as an off-white powder from the reaction of the corresponding amine and *n*-butyllithium in a 1:1 molar ratio and was characterized by ^1H NMR and IR spectra. Diethyl ether, pentane, hexanes, and benzene were predried over calcium hydride and freshly distilled over sodium/benzophenone under nitrogen. Benzene-d_6 was distilled over calcium hydride under nitrogen. All experiments were conducted under an oxygen-free, dry-nitrogen atmosphere using Schlenk and glovebox techniques.

^1H NMR spectra were obtained in benzene-d_6 solutions at room temperature on a Varian INOVA 300 spectrometer, and the residual proton (δ 7.15) in C_6D_6 was used as the internal standard. In the cases where the compounds contained aromatic hydrogens, the sharp singlet (δ 0.288) from silicone grease was used as the internal standard. The

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10.1021/ic9910110 CCC: $19.00

IR spectra of KBr pellets 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 $HGa[N(TMS)_2]_2(quin)$ (1). To a stirred solution of $HGaCl_2(quin)$ (0.600 g, 2.37 mmol) in 30 mL of Et_2O at room temperature was added a solution of $Li[N(TMS)_2]$ (0.794 g, 4.75 mmol) in 10 mL of Et_2O over a period of 10 min. The mixture was stirred for 4 h and filtered. Ether was removed under vacuum from the colorless filtrate. Hexanes (10 mL) were then added, and the solution was filtered. Upon storage at −15 °C overnight, colorless plates were collected (0.64 g, 54% yield). Mp: 90−93 °C. ^{1}H NMR: δ 0.29 (36H, s, $SiCH_3$), 1.22 (6H, m, CH_2), 1.43 (1H, m, CH), 2.76 (6H, t, NCH_2), 6.35 (1H, br s, GaH). IR: ν_{GaH}, 1893 cm^{-1}. Anal. Calcd for $C_{19}H_{50}GaN_3Si_4$: C, 45.40; H, 10.03; N, 8.36. Found: C, 44.71; H, 9.92; N, 8.22.

Synthesis of $H_2Ga[N(TMS)_2](quin)$ (2). To a stirred solution of $H_2GaCl(quin)$ (1.00 g, 4.58 mmol) in 60 mL of Et_2O at room temperature was added a solution of $Li[N(TMS)_2]$ (0.766 g, 4.58 mmol) in 20 mL of Et_2O over a period of 10 min. The mixture was stirred for 17 h and filtered. The colorless filtrate was concentrated and cooled in a 2-propanol/dry ice bath for a short time. After the crystal seeds formed, the filtrate was stored in a freezer (−15 °C), and colorless plates were eventually collected (1.278 g, 81% yield). Mp: 74−75 °C. ^{1}H NMR: δ 0.45 (18H, s, $SiCH_3$), 0.97 (6H, m, CH_2), 1.18 (1H, m, CH), 2.61 (6H, m, NCH_2), 4.94 (2H, br s, GaH_2). IR: ν_{GaH}, 1855 and 1872 cm^{-1}. Anal. Calcd for $C_{13}H_{33}GaN_2Si_2$: C, 45.48; H, 9.69; N, 8.16. Found: C, 43.40; H, 9.61; N, 7.70.

Synthesis of $HGa[N(H)(2,6\text{-}^iPr_2C_6H_3)]_2(quin)$ (3). To a stirred solution of $HGaCl_2(quin)$ (0.600 g, 2.37 mmol) in 30 mL of Et_2O at room temperature was added a solution of $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$ (0.870 g, 4.75 mmol) in 30 mL of Et_2O over a period of 5 min. The mixture was stirred for 17 h and filtered. The yellow filtrate was concentrated and stored at −15 °C. Colorless plates were collected (0.828 g, 65% yield). Mp: 129 °C (dec). ^{1}H NMR: δ 0.89 (6H, m, CH_2), 1.13 (1H, m, CH), 1.36 (24H, d, CH_3), 2.60 (6H, t, NCH_2), 3.02 (2H, s, NH), 3.56 (4H, m, C*H*Me$_2$), 5.25 (1H, br s, GaH), 6.96 (2H, m, aromatic), 7.19 (4H, m, aromatic). IR: ν_{GaH}, 1909 cm^{-1}; ν_{NH}, 3384 and 3375 cm^{-1}. Anal. Calcd for $C_{31}H_{50}GaN_3$: C, 69.66; H, 9.43; N, 7.86. Found: C, 69.11; H, 9.73; N, 7.75.

Synthesis of $H_2GaN_3(quin)$ (4). To a stirred slurry of NaN_3 (0.600 g, 9.14 mmol) in 35 mL of benzene at room temperature was added a solution of $H_2GaCl(quin)$ (1.000 g, 5.58 mmol) in 30 mL of benzene. The mixture was heated to 55 °C, stirred for 46 h, and then filtered. After the benzene was removed from the colorless filtrate, a white waxy solid remained. Hexanes (100 mL) were added to the waxy solid, and the solution was filtered. Upon storage at −15 °C overnight, colorless needles were collected (0.30 g, 29% yield). Mp: 47−50 °C. ^{1}H NMR: δ 0.76 (6H, s, CH_2), 1.00 (1H, m, CH), 2.33 (6H, t, NCH_2), 4.81 (2H, br s, GaH). IR: ν_{GaH}, 1915 and 1893 cm^{-1}; ν^{as}_{NNN}, 2091 cm^{-1}; ν^{s}_{NNN}, 1293 cm^{-1}. Anal. Calcd for $C_7H_{15}GaN_4$: C, 37.38; H, 6.72; N, 24.91. Found: C, 36.77; H, 6.73; N, 21.32.

Reaction of $HGaCl_2(quin)_2$ with 2 $Li[N(TMS)_2]$. To a stirred solution of $HGaCl_2(quin)_2$ (0.800 g, 2.20 mmol) in 50 mL of Et_2O at room temperature was added a solution of $LiN(TMS)_2$ (0.735 g, 4.40 mmol) in 20 mL of Et_2O over a period of 5 min. The mixture was stirred for 6 h and filtered. The colorless filtrate was concentrated and stored in a freezer (−15 °C). Colorless plates were collected and identified as $HGa[N(TMS)_2]_2(quin)$ (**1**) (0.935 g, 85% yield based on $HGaCl_2(quin)_2$).

Reaction of $HGaCl_2(quin)_2$ with 2 $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$. To a stirred solution of $HGaCl_2(quin)_2$ (0.800 g, 2.20 mmol) in 40 mL of Et_2O at room temperature was added a solution of $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$ (0.805 g, 4.40 mmol) in 30 mL of Et_2O over a period of 10 min. The mixture was stirred for 3 h and filtered. The yellow filtrate was concentrated and stored at −15 °C for crystallization. The colorless crystals were identified as $HGa[N(H)(2, 6\ \text{-}^iPr_2C_6H_3)]_2(quin)$ (**3**) (0.80 g, 68% yield based on $HGaCl_2(quin)_2$).

Reaction of $H_2GaCl(quin)$ with $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$. To a stirred solution of $H_2GaCl(quin)$ (0.500 g, 2.29 mmol) in 20 mL of Et_2O at room temperature was added a solution of $LiN[(H)(2,6\text{-}^iPr_2C_6H_3)]$ (0.419 g, 2.29 mmol) in 20 mL of Et_2O over a period of 10 min. The mixture was stirred for 2 h and filtered. After ether was removed under vacuum from the yellow filtrate, a slightly yellow, sticky oil remained. Pentane (8 mL) was added to dissolve it, and the solution was stored at −15 °C for crystallization. The colorless crystalline product was identified as a mixture of $HGa[N(H)(2,6\text{-}^iPr_2C_6H_3)]_2(quin)$ (**3**) and $H_3Ga(quin)$ (0.61 g, 74.1% yield for total). The ^{1}H NMR spectrum of the mixture indicated that the molar ratio of the two compounds was close to 1:1.

X-ray Data Collection, Structure Solution, and Refinement. Suitable crystals of compounds **1**−**4** were selected and mounted on top of glass fibers under a nitrogen atmosphere. All 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 or 25 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 ω. In the event the lattice was triclinic some additional sets of frames were collected to better model the absorption correction. The final cell constants were calculated from a set of strong reflections which were 8192 for **1**, 6232 for **2**, 7252 for **3**, and 4660 for **4**.

The space groups were determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution was applied to all the structures which provided most non-hydrogen atoms from the *E*-maps. Several full-matrix, least-squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except those listed below, were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydrides in all compounds and the hydrogens of the amido groups in compound **3** were refined isotropically. The hydrides, H1G and H2G, in compound **4** were refined with a fixed distance to the metal. The experimental conditions and unit cell information are summarized in Table 1.

Results and Discussion

Syntheses of Quinuclidine-Stabilized Amido- and Azidogallanes. The syntheses of compounds **1** and **3** from $HGaCl_2(quin)$ and related reactions from $HGaCl_2(quin)_2$ are summarized in Scheme 1. Scheme 2 outlines the syntheses of compounds **2** and **4** from $H_2GaCl(quin)$ and the reaction of $H_2GaCl(quin)$ with $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$. All compounds were characterized by ^{1}H NMR and IR spectroscopy and single-crystal X-ray diffraction. Agreement between calculated and measured elemental analyses was acceptable for **1** and **3**, but **2** was low in carbon and **4** was low in nitrogen. In the latter case, the loss of N_2 from the azido ligand during analysis was probably responsible for the discrepancy.

Compounds **1**−**3** were isolated in moderate yields. In the preparation of compound **3** the use of isolated $Li[N(H)(2,6\text{-}^iPr_2C_6H_3)]$, rather than its solution prepared in situ, was to better control the stoichiometry of the starting materials. The IR and ^{1}H NMR spectra of these compounds were in accord with their formulas. The δ_{GaH} of compound **1** (6.35 ppm) appeared most downfield of all previously reported gallane derivatives. The ν_{GaH} at 1893 cm^{-1} was consistent with related compounds.[20] These compounds were stable for at least several months under an inert atmosphere at room temperature. In an attempt to synthesize $[H_2GaN(TMS)_2]_n$ by the elimination of volatile $HSiMe_3$,[19] Wells et al. reported that no reaction occurred between $H_3Ga(NMe_3)$ and $N(TMS)_3$. The route used here, involving LiCl elimination, facilitated the formation of Ga−N bonds in the syntheses of compounds **1** and **2**.

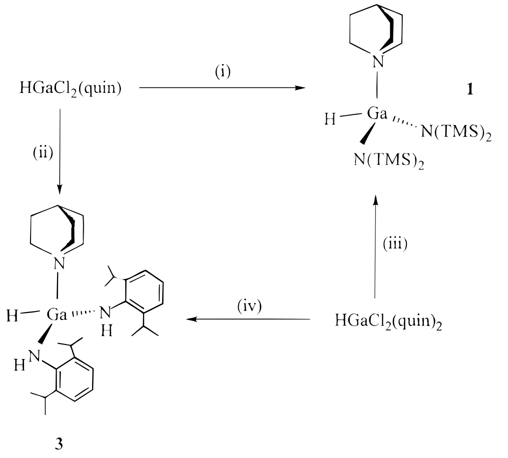
Compound **4**, synthesized in a 29% yield, was stable as colorless needles at −15 °C for several days and a much shorter

Table 1. Crystallographic Data for Compounds **1**−**4**

chem formula	$C_{19}H_{50}GaN_3Si_4$ (**1**)	$C_{13}H_{33}GaN_2Si_2$ (**2**)	$C_{31}H_{50}GaN_3$ (**3**)	$C_7H_{15}GaN_4$ (**4**)
fw	502.70	343.31	534.46	224.95
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	10.9550(2)	11.33920(1)	10.7610(1)	7.1580(2)
b, Å	11.3715(1)	14.78540(1)	19.4052(3)	22.7772(7)
c, Å	11.9400(2)	12.0588(2)	14.3919(2)	12.5316(3)
α, deg	79.681(1)			
β, deg	85.018(1)	112.3670(1)	97.650(1)	101.6470(1)
γ, deg	87.772(1)			
V, Å^3	1457.42(4)	1869.61(4)	2978.56(7)	2001.07(1)
Z	2	4	4	8
T, °C	−100			
λ, Å	0.710 73			
ρ_{calcd}, g cm^{-3}	1.146	1.220	1.192	1.493
μ, cm^{-1}	11.18	15.89	9.46	27.06
R1, wR$_2$[a] [$I > 2\sigma(I)$]	0.0235, 0.0639	0.0258, 0.0574	0.0281, 0.0630	0.0479, 0.0840

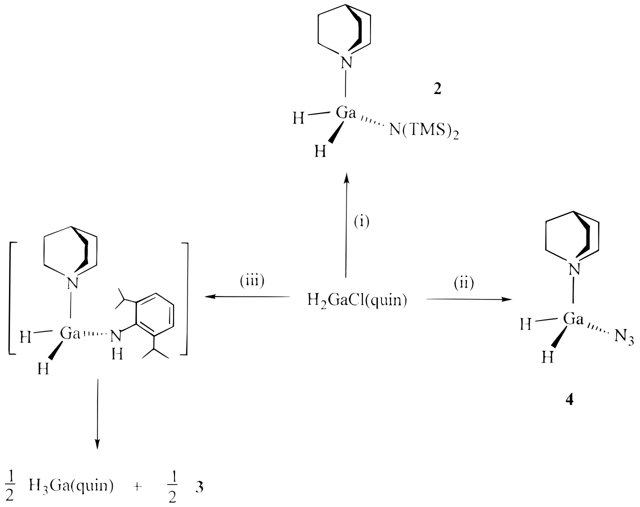
[a] $R_1 = \sum||F_o - F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] /\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, $P = (F_o^2 + 2F_c^2)/3$ and a, b are constants given in the Supporting Information.

Scheme 1[a]



[a] Key: (i) 2 Li[N(TMS)$_2$], −2 LiCl; (ii) 2 Li[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)], −2 LiCl; (iii) 2 Li[N(TMS)$_2$], −2 LiCl, −quin; (iv) 2 Li[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)], −2 LiCl, −quin.

Scheme 2[a]



[a] Key: (i) Li[N(TMS)$_2$], −LiCl; (ii) NaN$_3$, −NaCl; (iii) Li[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)], −LiCl.

time at room temperature. It was difficult to optimize the reaction conditions because the limited solubility of NaN$_3$ requires a long reaction time and a relatively high reaction temperature. The actual reaction conditions (55 °C, ∼2 d) represented a compromise of the two competing factors. Unfortunately, the low thermal stability prohibited use of this compound as a precursor to GaN in a MOCVD process which utilizes standard vapor phase delivery methods. It may be feasible to use compound **4** in a direct liquid injection system.

The attempt to prepare H$_2$Ga[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)](quin) via the reaction of H$_2$GaCl(quin) with LiN[(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)] was unsuccessful. In addition to LiCl, a mixture of compound **3** and H$_3$Ga(quin) was isolated in a 1:1 molar ratio as determined by ^{1}H NMR spectroscopy. The attempt to further separate them was not totally successful, and only a small fraction of H$_3$Ga(quin) and an unidentified oil were obtained. This result implied that a ligand redistribution reaction had taken place via a possible intermediate, H$_2$Ga[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)](quin) (Scheme 2). Hydrido/amido ligand redistributions have been found in the reactions of [H$_2$GaNH$_2$]$_3$ with Lewis bases including tetrahydrofuran, quinuclidine, and tricyclohexylphosphine.[6]

The reactions of the five coordinate HGaCl$_2$(quin)$_2$ with LiN[(TMS)$_2$] or Li[N(H)(2,6-^{i}Pr$_2$C$_6$H$_3$)] in a 1:2 molar ratio resulted in the isolation of the four-coordinate compound **1** or **3**. The steric congestion produced by the bulky organoamido ligands undoubtedly limited the stoichiometry to one quinuclidine per gallium.

Structural Studies. Compounds **1**−**4** were all monomeric with the gallium atoms adopting distorted tetrahedral geometries. The Ga−N bond distances of the quinuclidine ligands ranged from 2.028(3) to 2.108(2) Å, comparable to those in H$_3$Ga(quin) (2.063(4) Å)[21] and HGaCl$_2$(quin) (2.017(3) Å)[20] and shorter than those in the five-coordinate compounds, H$_2$GaCl(quin)$_2$ (2.259(2) Å) and HGaCl$_2$(quin)$_2$ (2.254(8) and 2.232(8) Å).[20] Selected bond lengths and angles for **1** and **2** are listed in Table 2, and those for **3** and **4**, in Table 3.

Compound **1** crystallized in space group $P\bar{1}$ with one molecule in the asymmetric unit, and the molecular structure of **1** is shown in Figure 1. The largest angle around the Ga was found between the two amido nitrogens (119.41(6)°), and the smallest was between the hydride and the nitrogen of the quinuclidine (93.7(8)°). The geometries at both amido nitrogens, N2 and N3, were nearly planar with the sum of the angles around each being 357.82 and 359.14°, respectively. All angles around N3 were within 120 ± 2°, and the two N−Si bond lengths were identical (1.7387(14) and 1.7381(14) Å). For N2, the angle of Ga1−N2−Si2 (135.97(8)°) was about 20° larger

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

$C_{19}H_{50}GaN_3Si_4$ (**1**)		$C_{13}H_{33}GaN_2Si_2$ (**2**)	
Ga1−N1	2.1057(14)	Ga1−N1	2.108(2)
Ga1−N2	1.9315(13)	Ga1−N2	1.913(2)
Ga1−N3	1.9138(13)	Ga1−H1G	1.473(2)
Ga1−H1	1.49(2)	Ga1−H2G	1.462(2)
N2−Si1	1.7521(14)	N2−Si1	1.736(2)
N2−Si2	1.7277(14)	N2−Si2	1.723(2)
N3−Si3	1.7387(14)		
N3−Si4	1.7381(14)		
N1−Ga1−N2	113.04(6)	N1−Ga1−N2	106.26(7)
N1−Ga1−N3	105.48(5)	H1G-Ga1−H2G	117.6(2)
N2−Ga1−N3	119.41(6)	N1−Ga1−H1G	98.16(10)
N1−Ga1−H1	93.7(8)	N1−Ga1−H2G	102.36(10)
N2−Ga1−H1	107.3(7)	N2−Ga1−H1G	115.87(11)
N3−Ga1−H1	115.0(7)	N2−Ga1−H2G	113.42(11)
Ga1−N2−Si1	106.19(7)	Ga1−N2−Si1	114.85(9)
Ga1−N2−Si2	135.97(8)	Ga1−N2−Si2	121.32(10)
Si1−N2−Si2	116.98(7)	Si1−N2−Si2	122.42(10)
Ga1−N3−Si3	121.53(7)		
Ga1−N3−Si4	118.17(7)		
Si3−N3−Si4	118.12(8)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3** and **4**

$C_{31}H_{50}GaN_3$ (**3**)		$C_7H_{15}GaN_4$ (**4**)	
Ga1−N1	2.0831(14)	Ga1−N1	2.063(3)
Ga1−N2	1.902(2)	Ga1−N2	1.922(5)
Ga1−N3	1.899(2)	Ga1−H1G	1.43(2)
Ga1−H1	1.47(2)	Ga1−H2G	1.41(2)
N2−C8	1.407(2)	N2−N3	1.179(6)
N2−H2N	0.78(2)	N3−N4	1.123(7)
N3−C20	1.408(2)	Ga2−N5	2.028(3)
N3−H3N	0.79(2)	Ga2−N6	1.992(5)
		Ga2−H3G	1.38(6)
		Ga2−H4G	1.33(5)
		N6−N7	1.041(6)
		N7−N8	1.226(7)
N1−Ga1−N2	102.47(6)	N1−Ga1−N2	100.0(2)
N1−Ga1−N3	101.48(6)	H1G−Ga1−H2G	132(3)
N2−Ga1−N3	109.89(7)	N1−Ga1−H1G	104(2)
N1−Ga1−H1	103.6(8)	N1−Ga1−H2G	101(2)
N2−Ga1−H1	119.1(7)	N2−Ga1−H1G	103(2)
N3−Ga1−H1	117.2(7)	N2−Ga1−H2G	113(2)
Ga1−N2−H2N	105(2)	Ga1−N2−N3	121.6(4)
Ga1−N2−C8	127.38(12)	N2−N3−N4	168.4(6)
H2N−N2−C8	110(2)	N5−Ga2−N6	98.1(2)
Ga1−N3−H3N	116(2)	H3G-Ga2−H4G	128(3)
Ga1−N3−C20	122.61(12)	N5−Ga2−H3G	106(2)
H3N−N3−C20	111(2)	N5−Ga2−H4G	103(2)
		N6−Ga2−H3G	107(2)
		N6−Ga2−H4G	111(2)
		Ga2−N6−N7	124.0(4)
		N6−N7−N8	176.2(6)

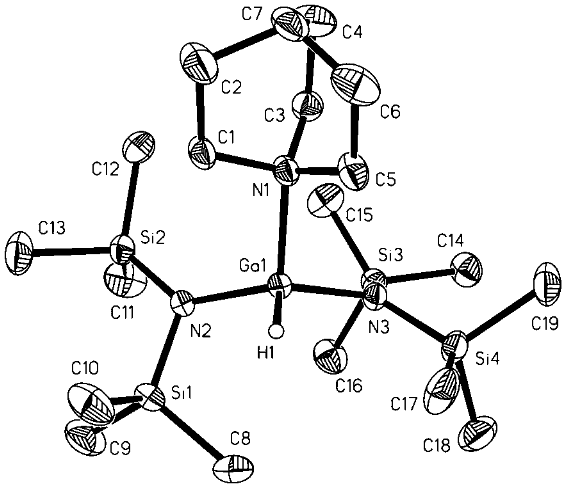

Figure 1. Structure of $HGa[N(TMS)_2]_2$(quin) (**1**). The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except the hydride are omitted for clarity.

than that of Ga1−N2−Si1 (106.19(7)°), and the corresponding Si−N bond lengths were 1.7521(14) and 1.7277(14) Å. This feature was not observed in compound **2** and other group 13 compounds containing one or more bis(trimethylsilyl)amido groups such as $ClGaN(TMS)_2$,[22] $Ga[N(TMS)_2]_3$,[22] $MesAl[N(TMS)_2]_2$,[22] $Al[N(TMS)_2]_3$,[23] $In[N(TMS)_2]_3$,[24] $ArGa(Cl)[N(TMS)_2]$,[25] $ArIn[N(TMS)_2]_2$,[25] and $Tl[N(TMS)_2]_3$.[26] No unusually short intermolecular distances were found in the crystal structure of compound **1**, suggesting that the distortion of this $N(TMS)_2$ group be attributed to the repulsion between the $N(TMS)_2$ group and other ligands. In particular, close contacts existed between C12 and two carbon atoms in the quinuclidine ligand, C1 (3.703(3) Å) and C3 (3.584(3) Å), and between C12 and one of the methyls, C15, in the other $N(TMS)_2$ group (3.740(3) Å). According to Pauling,[27] the average van der Waals radii of methyl and methylene groups are 2.00 Å. The action of these nonbonded repulsion forces on C12 was also reflected in the enlarged N2−Si2−C12 angle (118.00(8)°). The other N−Si−C angles in this compound were in the range from 111.38(9) to 114.67(8)°. The hydrogen atoms on these carbon atoms were assigned as riding atoms, and the accuracy of the distances between these hydrogen atoms is questionable. A comparison to the normal van der Waals H···H distance (2.4 Å),[27] the shortest distances between the hydrogen atoms on C12 and the hydrogen atoms on other groups were calculated as 2.088 Å for H12A···H1C, 2.185 Å for H12C···H3A, and 2.034 Å for H12C···H15B.

The molecular structure of compound **2**, which crystallized in space group $P2_1/n$ with one molecule in the asymmetric unit, is shown in Figure 2. The largest bond angle around Ga was found between the two hydrides (117.6(2)°), and the smallest was between one hydride (H1G) and the nitrogen of the quinuclidine (98.16(10)°). Large H−Ga−H angles have also been reported in the structures of **4** (see below), five-coordinate $H_2GaCl(quin)_2$ (127(2)°), and $H_5Ga_3[(NMeCH_2)_2]_2$ (127°).[18] In $H_2GaCl(PCy_3)$[28] and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaH_2$,[29] however, the H−Ga−H angles were 103.0(1) and 116(4)°, respectively. The geometry at the amido nitrogen (N2) was nearly planar with the sum of the angles at the nitrogen being 358.6°. The Ga−H bond lengths were 1.473(2) and 1.462(2) Å, and the bond length of the Ga−N to the amido group was 1.913(2) Å. Two methyls (C11 and C12) on one of the trimethylsilyl groups were disordered.

The molecular structure of compound **3**, which crystallized in space group $P2_1/n$ with one molecule in the asymmetric unit,

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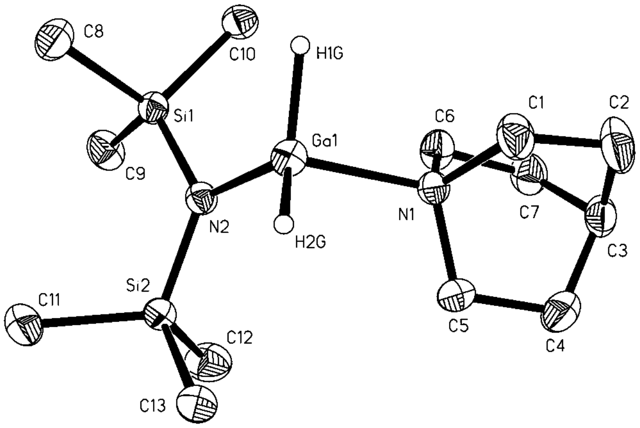

Figure 2. Structure of $H_2Ga[N(TMS)_2](quin)$ (**2**). The non-hydrogen atoms are shown at the 50% probability level. The disorders on C11 and C12 and the hydrogen atoms except the hydrides are omitted for clarity.

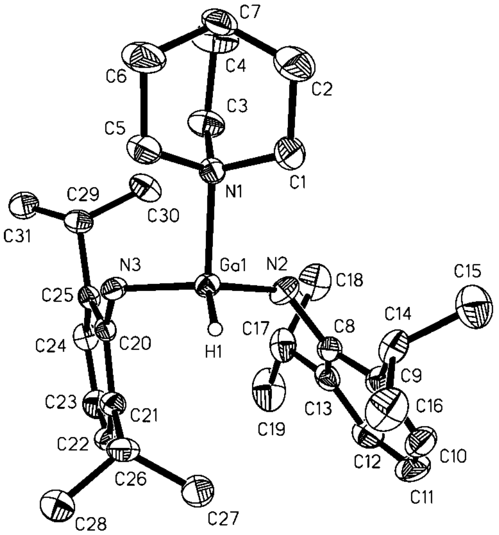

Figure 3. Structure of $H[GaN(H)(2,6\text{-}^{i}Pr_2C_6H_3)]_2(quin)$ (**3**). The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except the hydride are omitted for clarity.

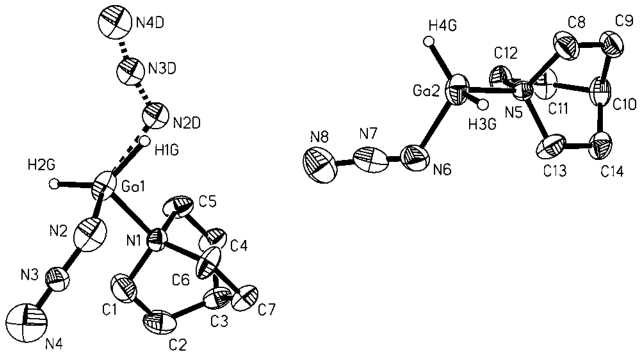

Figure 4. Structures of the two independent molecules of H_2GaN_3-(quin) (**4**). The non-hydrogen atoms are shown at the 50% probability level. The hydrogen atoms except the hydrides are omitted for clarity. The atoms labeled N2D−N3D−N4D represent the disordered azide location.

is shown in Figure 3. The two diisopropylphenyl groups were oriented away from the quinuclidine ligand in such a manner as to put the planes approximately parallel to one another. The geometry for the amido nitrogens was more pyramidal with the sum of the angles being 343 and 350°. The Ga−H bond length was 1.47(2) Å.

Compound **4** crystallized in the space group $P2_1/n$ with two independent molecules in the asymmetric unit (Figure 4). Both exhibited the same tetrahedral geometry about the Ga but differed with respect to some of the bond lengths and angles. The hydrido and azido ligands around Ga1 were disordered over two orientations as shown in Figure 4. The position denoted by N2D, N3D, and N4D represented 10% of the electron density attributable to the azido ligand. The hydrides corresponding to this orientation were not located. Within experimental error, the angles of H1G−Ga1−H2G and H3G−Ga2−H4G were equal (132(3) and 128(3)°). The angles at N2 and N6 were 121.6(4) and 124.0(4)°, respectively. The geometry of the azido group (N2−N3−N4) was somewhat bent (168.4(6)°), whereas N6−N7−N8 was close to linear (176.2(6)°). In the azido group attached to Ga1 the distance of N2−N3 (1.179(6) Å) was longer than N3−N4 (1.123(7) Å) while in the azido group attached to Ga2 the distance of N6−N7 (1.041(6) Å) was shorter than that of N7−N8 (1.226(7) Å). Only the former case has been observed in the previously published azidogallium compounds including Me_2GaN_3,[30] $[(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2$,[2] $[HClGaN_3]_4$,[7] $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$,[31] $Ga(N_3)_3(py)_3$,[32] $Na[Ga(N_3)_4]$[5], and $Ga(N_3)_3(NEt_3)$.[5] We suspect that these small derivations from the typical azide geometry are caused by the effect of crystal disorder in the structural analysis.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-9616501). We also thank Dr. Maren Pink for her work on solving the crystal structure of H_2GaN_3(quin).

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

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