Solution Chemistry of Cyclotrigallazane: Supercritical Ammonia and Lewis Base Catalyzed Dehydrogenation To Produce Poly(imidogallane)

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The polymeric hydrido gallium imide $[HGaNH]_n$, or poly(imidogallane), was isolated as an intermediate in the conversion of cyclotrigallazane, $[H_2GaNH_2]_3$, to gallium nitride in supercritical ammonia. Poly(imidogallane) can be converted to nanocrystalline GaN via solid-state pyrolysis or by extended thermolysis in supercritical ammonia. Characterization by IR spectroscopy, elemental analysis, and X-ray and electron diffraction suggests that the structure of poly(imidogallane) is a layered solid with a coherent length of approximately 15 nm. The interaction of $[H_2GaNH_2]_3$ and various Lewis bases leads to the isolation of $[HGaNH]_n$ and gallane−Lewis base adducts, $H_3Ga{\cdot}base$, rather than the expected gallazane adducts, $H_2GaNH_2{\cdot}base$. Experiments involving the use of ND_3 resulted in the isolation of $[H_2GaND_2]_3$ and suggest that the donor−acceptor complex $H_2Ga(NH_2)(ND_3)$ was present in solution. It was proposed that these gallazane−base adducts equilibrate via a ligand redistribution reaction and that the formation of $[HGaNH]_n$ results from NH_3 elimination from a diamidogallium hydride. The proposed mechanism is used to explain the catalytic role of ammonia in the conversion of $[H_2GaNH_2]_3$ to $[HGaNH]_n$.

Introduction

Due to their unique electronic properties, there has been increased interest in the syntheses of nanocrystalline 13−15 semiconducting materials.[1] Unfortunately, the current synthetic methods offer little control over particle size and dispersion, especially for the nitrides. Cyclotrigallazane ($[H_2GaNH_2]_3$, **1**) is one of the known precursors to nanocrystalline GaN.[2] Its dehydrogenation to GaN involved a topochemical conversion of **1**[3] resulting from a network of unconventional hydrogen bonds in the crystal structure of **1**.[4] We became interested in developing a more controlled, solution-based route to GaN utilizing cyclotrigallazane. The solvent of choice was supercritical NH_3, which has been found to be useful in the syntheses of solid-state compounds, especially metal amides, imides, and nitrides.[5−7] During the course of our investigations, we have isolated poly(imidogallane) (**2**), a polymeric intermediate in the conversion of $[H_2GaNH_2]_3$ to GaN in ammonia solution.[8] This paper describes the full synthesis and characterization of **2** and delves more deeply into the reactions of **1** with a variety of Lewis bases in solution. These studies have indicated that cyclotrigallazane possesses an unusual reactivity in solution and have led to an explanation for the formation of **2**.

Experimental Section

General. All manipulations were carried out with the rigorous exclusion of oxygen and moisture using standard Schlenk and drybox techniques (Vacuum Atmospheres Company, Dri-Train Model 40-1). Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous NH_3, ND_3, and NMe_3 were dried over a sodium mirror before being vacuum transferred to reaction vessels. Cyclotrigallazane, $[H_2GaNH_2]_3$,[4] and the gallane adducts $H_3Ga{\cdot}quinuclidine$,[9] $H_3Ga{\cdot}NMe_3$,[10] and $H_3Ga{\cdot}PCy_3$[11] were prepared by literature methods.

Infrared spectra were acquired as KBr pellets or in solution using a Nicolet Magna-IR 560 spectrometer and are reported in cm^{-1}. Proton NMR spectra were recorded on a Varian Inova 300 spectrometer in C_6D_6 solvent and are referenced to the residual protons in the solvent (7.15 ppm). Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

High-Pressure Experiments. Reactions involving the use of NH_3 at elevated temperatures were conducted in a steel autoclave (Parr Instrument Corporation, Model A1120HC, 50 mL capacity) equipped with a Pyrex sleeve and ethylene/propylene O-rings. The autoclave was heated using an aluminum block, and the temperature was controlled by means of an Omega temperature controller. Pressure was monitored with an Omega electronic pressure transducer.

Synthesis of $[HGaNH]_n$ (2). In the drybox, the autoclave was charged with **1** (2.15 mmol, 565 mg). The autoclave was sealed, removed from the drybox, and attached to a vacuum line, where ammonia (approximately 15 mL) was condensed into the autoclave at −78 °C. The autoclave was then sealed and placed in the heating block where it was heated to 150 °C over a period of 30 min. The reactor was held at this temperature for 30 min, with a sustained pressure of 63 atm, and then cooled to 25 °C. The NH_3 was vented, and the

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autoclave was flushed with a stream of dry N_2. The product recovered from the autoclave was placed under vacuum for 24 h, resulting in the isolation of **2** as a slightly off-white solid (507 mg, 92%). Mp: >270 °C. IR (KBr): ν_{N-H} 3280 (m); ν_{Ga-H} 1883 (s), 1817 (m); ω,τ_{N-H} 962 (s), 906 (s). Anal. Calcd for $[GaH_2N]_n$: C, 0.0; H, 2.35; N, 16.34; Ga, 81.31. Found: C, <0.10; H, 2.34; N, 16.59; Ga, 81.25.

Conversion of $[H_2GaNH_2]_3$ to GaN in Liquid Ammonia. The procedure described above for the preparation of **2** was followed using **1** (1.14 mmol, 300 mg) and NH_3 (approximately 30 mL). The autoclave was maintained at 150 °C and 65 atm for 5 h. The product was isolated as an off-white solid (211 mg, 74%) and was shown by XRD to be GaN. Conducting the reaction at slightly lower pressures (52 atm) had no visible effect on the XRD of the product. XRD (2θ): 35.1°, 57.8°, 69.0°.

Attempted Synthesis of $[HGaNH]_n$ (2) in the Solid State. In the drybox, a quartz boat was loaded with **1** (0.569 mmol, 150 mg). The boat was placed in a pyrolysis tube and sealed. The tube was placed in a furnace and connected to a nitrogen line and heated to 150 °C under a flow of N_2 (approximately 30 mL/min). The tube was kept at this temperature for 30 min and then cooled to 25 °C. The product was isolated as a gray black powder (133 mg) which was shown to be amorphous by XRD. IR (KBr): 3242 (w), 1875 (w), 956 (w).

Synthesis of $[H_2GaND_2]_3$ (3) and $[H_2GaN(H)D]_3$ (4). ND_3 (3 mL) was condensed onto **1** (0.855 mmol, 225 mg) at -196 °C. The flask was slowly warmed to -33 °C, resulting in a clear, colorless solution. The flask was allowed to warm to 25 °C over a period of several hours, and the solvent and byproducts were evaporated under a flow of dry N_2, resulting in the isolation of a white solid in essentially quantitative yield. This solid was found to be **3**, $[H_2GaND_2]_3$, containing small amounts ($<5\%$) of **1**, $[H_2GaNH_2]_3$, and **4**, $[H_2GaNHD]_3$. IR for **3** (KBr): ν_{N-D} 2470 (s), 2461 (s), 2391 (s), 2385 (s); ν_{Ga-H} 1890 (s), 1865 (s), 1834 (s); δ_{N-D} 1122 (m). IR for **1** (KBr): ν_{N-H} 3312 (w), 3299 (w), 3255 (w), 3246 (w); ν_{Ga-H} 1890 (s), 1865 (s), 1834 (s). IR for **4** (KBr): ν_{N-H} 3286 (w), 3272 (w); ν_{N-D} 2428 (w), 2420 (w), ν_{Ga-H} 1890 (s), 1865 (s), 1834 (s); δ_{N-H} 1339 (w).

Reaction of $[H_2GaNH_2]_3$ with Tetrahydrofuran. To a flask charged with **1** (0.950 mmol, 250 mg) was added THF (10 mL). The flask was sealed and the slightly turbid solution was allowed to stand undisturbed for 5 days at 25 °C, resulting in the deposition of a white film at the bottom of the flask. The solvent was decanted off, and the solid film was washed with THF (5 mL). The solid was dried under vacuum, resulting in the isolation of **2** in approximately 20% yield. IR (KBr): 3324 (w), 3277 (m), 1878 (s), 960 (s), 905 (s). In a separate experiment, **1** (0.569 mmol, 150 mg) was dissolved in THF (10 mL). After the solid had completely dissolved, an aliquot was removed and the IR spectrum was obtained (ν_{Ga-H} 1858 cm^{-1}). Over the course of several days the ν_{Ga-H} at 1858 cm^{-1} diminished and a new peak at 1817 cm^{-1} grew.

Reaction of $[H_2GaNH_2]_3$ with Quinuclidine. To a mixture of **1** (0.950 mmol, 250 mg) and quinuclidine (2.85 mmol, 317 mg) was added THF (20 mL). The resulting clear, colorless solution was stirred at 25 °C. After 1 h, an aliquot was removed (approximately 0.4 mL) and characterized by IR spectroscopy (ν_{Ga-H} 1821 cm^{-1}). After 2 h the solution became hazy. The mixture was stirred for 48 h, resulting in a colorless solution and a white solid. The mixture was filtered on a fine glass frit, and the white solid was washed with an additional 10 mL of THF. The solid was dried under reduced pressure, yielding 110 mg (90%) of **2**. IR (KBr): 3327 (w), 3278 (m), 1879 (s), 960 (s), 905 (s). The volatiles were removed from the filtrate under reduced pressure, yielding 214 mg (82%) of a white crystalline solid which was identified as H_3Ga(quinuclidine). IR (KBr): ν_{Ga-H} 1818 (independently prepared sample of H_3Ga(quinuclidine) 1818; lit.[9] 1810). ^1H NMR (C_6D_6): δ_{Ga-H} 4.85 (br s) (independently prepared sample of H_3Ga(quinuclidine) 4.87 (br s); lit.[9] 4.80 (br s)).

Reaction of $[H_2GaNH_2]_3$ with Trimethylamine. Trimethylamine (approximately 25 mL) was condensed onto **1** (1.52 mmol, 400 mg) at -196 °C. The flask was warmed to -10 °C and stirred for 1 h. The excess NMe_3 was allowed to evaporate at 0 °C under a stream of N_2, resulting in an opaque oil which solidified at 25 °C. The volatiles were sublimed into a cold trap, leaving a white, nonvolatile solid (294 mg), with the physical and spectroscopic properties of **2**. IR (KBr): 3316 (w), 3258 (m), 1880 (s), 956 (s). The crystalline solid collected in the cold trap (68 mg, 23%) was determined to be $H_3Ga(NMe_3)$. IR (benzene): ν_{Ga-H} 1831 (independently prepared sample of $H_3Ga(NMe_3)$ 1831; lit.[12] 1832, 1852).

Reaction of $[H_2GaNH_2]_3$ with Tricyclohexylphosphine. To a flask charged with **1** (1.52 mmol, 400 mg) and tricyclohexylphosphine (4.56 mmol, 1.278 g) was added THF (35 mL). The slightly hazy solution was stirred at 25 °C for 1 h and an aliquot (0.4 mL) was removed and its IR spectrum recorded (ν_{Ga-H} 1848, 1818 cm^{-1}). The mixture was stirred for 48 h, resulting in a colorless solution and white precipitate. The mixture was filtered through a fine frit, yielding a white solid and a clear filtrate. The filter cake was washed with an additional 10 mL of THF and dried under vacuum, yielding **2** as a white solid (145 mg, 75%). IR (KBr): 3327 (w), 3279 (m), 1880 (s), 958 (s), 905 (s). The volatiles were removed from the filtrate under reduced pressure, resulting in the isolation of a white crystalline solid which was identified as a mixture of PCy_3 and $H_3Ga(PCy_3)$ (1.334 g, 92% mass recovery). IR (KBr) ν_{Ga-H} 1844 (m), 1825 (s), 1801 (s) (independently prepared sample of $H_3Ga(PCy_3)$ 1846, 1824, 1801; lit.[11] 1800 (br) (no medium given). ^1H NMR (C_6D_6) δ_{Ga-H} 4.26 (br s) (independently prepared sample of $H_3Ga(PCy_3)$ 4.26 (br s); lit.[11] 4.32 (br s)).

X-ray Diffraction Studies. XRD data were collected on a Siemens D5005 diffractometer or a Siemens Microdiffractometer equipped with a Hi-Star 2-D area detector using monochromatic (graphite) Cu Kα radiation. Samples of GaN were prepared as powders dispersed on glass slides (Siemens D5005), while powdered samples of **2** were sealed under nitrogen in glass capillaries (Siemens Micro-diffractometer). The coherent lengths of the samples were estimated using the Scherrer equation and the Jade 3.0 software package.

Transmission Electron Microscopy and Electron Diffraction Studies. TEM images and electron diffraction patterns were obtained on a Philips CM30 TEM operating at 300 kV. Samples were prepared by sprinkling the powder over lacy carbon films supported on Cu mesh grids. Particles overhanging the carbon support were used for analysis. Despite the use of a liquid nitrogen cooled sample stage, the electron beam degraded the samples of **2**, as evidenced by the rapid decay of the diffraction patterns.

Results

Synthesis and Characterization of Poly(imidogallane). Cyclotrigallazane ($[H_2GaNH_2]_3$, **1**) was found to be soluble in liquid ammonia. Heating an ammonia solution of $[H_2GaNH_2]_3$ at 150 °C for 30 min in an autoclave led to the isolation of a slightly off-white solid following removal of the ammonia. This solid was found to be involatile and insoluble in all solvents (including NH_3) except for strong mineral acids with which it reacted with gas evolution. The solid was also found to be relatively stable with regard to attack from atmospheric oxygen and moisture.

The IR spectrum of this solid (Figure 1) was simplified compared to that of **1** and suggested that the product was a hydrido gallium imide of the formula HGaNH (**2**). The single peak at 3280 cm^{-1} was assigned to an imide (NH) rather than an amide (NH_2) group. The Ga$-$H vibration appeared as a strong, broad peak at 1883 cm^{-1} and a sharper, less intense band at 1818 cm^{-1}. The peaks at 962 and 906 cm^{-1} were attributed to the wagging motion of the N$-$H. Notably absent was any peak in the region around 1510 cm^{-1} due to the scissoring vibration of NH_2 groups.

The formulation of this solid as a hydrido gallium imide was supported by elemental analysis. Drying a sample of **2** under dynamic vacuum for 24 h resulted in the isolation of a solid which gave satisfactory elemental analyses and H:N:Ga ratios of 1.99:1.02:1. Analysis of a sample prior to drying showed that it was rich in nitrogen (calcd 16.34% for pure $[HGaNH]_n$;

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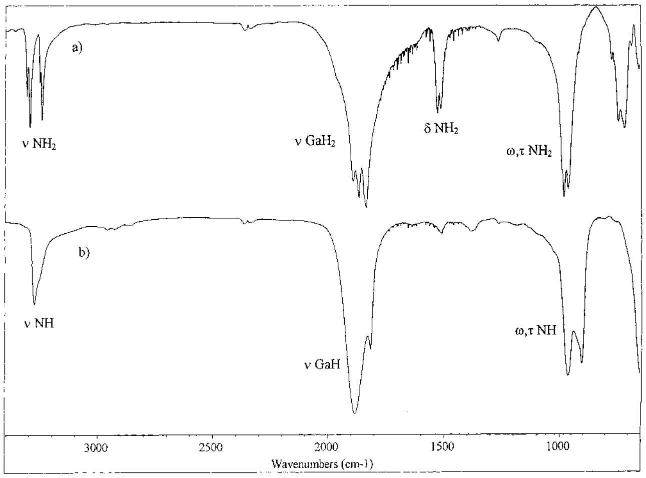

Figure 1. Infrared spectra (KBr pellet) of (a) $[H_2GaNH_2]_3$ (**1**) and (b) $[HGaNH]_n$ (**2**).

found 18.13%) and consequently gallium poor. This was attributed to the presence of approximately 10% residual NH_3 entrained in the solid, $HGaNH{\cdot}0.1NH_3$. Reports of the analogous aluminum compound, $[HAlNH]_n$, suggested that as-prepared samples “tenaciously” entrained solvent.[13]

These results were most consistent with the formulation of the product as HGaNH. The poor solubility and involatility of this solid led to the conclusion that **2** was most likely poly(imidogallane), $[HGaNH]_n$. Reports of the analogous aluminum compound suggested that $[HAlNH]_n$ was also polymeric.[13,14]

Conversion of $[H_2GaNH_2]_3$ to GaN in Ammonia. Reaction times as short as 10 min to as long as 1.5 h at 150 °C resulted in the isolation of **2** as the only product. Lower temperatures and times (i.e., 10 min at 100 °C) led to an incomplete reaction and gray powders indicative of the decomposition of **1**. Poly(imidogallane) was also the only product isolated at a variety of pressures ranging from 8.4 to 71 atm. The products isolated from higher reaction pressures ranging from 112 to 124 atm exhibited shifts in ν_{N-H} from 3279 to 3254 cm^{-1} and ν_{Ga-H} from 1883 to 1869 cm^{-1} as well as a coalescence of the peaks at 962 and 906 cm^{-1} to a single peak at 955 cm^{-1}. These shifts suggested that **2** underwent further reaction. Extended reaction (5 h) under these conditions resulted in GaN powders with an average coherent length of 3 nm.

Reaction of $[H_2GaNH_2]_3$ with ND_3. Dissolution of **1** in ND_3 followed by slow evaporation of the solvent resulted in the isolation of a white, crystalline powder which was identical in appearance to the starting material. However, the IR spectrum (Figure 4) of this solid indicated >95% conversion of **1** to $[H_2GaND_2]_3$ (**3**) and lesser amounts of **1** and $[H_2GaN(H)D]_3$ (**4**). The IR spectrum of **3** exhibited N−D vibrations at 2470, 2460, 2391, and 2385 cm^{-1}, while the spectrum of **4** consisted of N−H vibrations at 3286 and 3272 cm^{-1} and N−D vibrations at 2428 and 2420 cm^{-1}. The ν_{Ga-H} region of the spectrum remained unchanged. The assignment of these bands compared well those of the fully deuterated analogue $[D_2GaND_2]_3$[4] as well as with the vibrational energies predicted by theory.[4,15]

Interaction of $[H_2GaNH_2]_3$ with Various Lewis Bases. $[H_2GaNH_2]_3$ was found to exhibit moderate to good solubility in other polar solvents such as THF, trimethylamine, and diethylamine, but little or no solubility in diethyl ether. Cyclotrigallazane also reacted with neat THF and trimethylamine and with quinuclidine and tricyclohexylphosphine in THF solution. These reactions did not yield the expected $H_2GaNH_2{\cdot}$base complexes, but resulted in the isolation of poly(imidogallane) and Lewis base adducts of gallane, $H_3Ga{\cdot}$base. The poly(imidogallane) products were isolated in good yields (75 and 90%, respectively, for the reactions with PCy_3 and quinuclidine) based on the stoichiometry discussed below. A greater than theoretical yield of **2** was obtained for the reaction of **1** with NMe_3. This was believed to be due to the presence of excess NMe_3 entrained in the product. A low (approximately 20%) yield of **2** was obtained from the reaction of **1** with THF after 5 days.

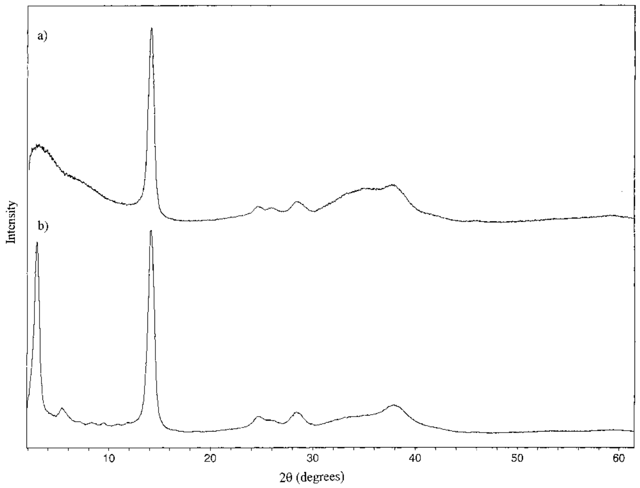

Figure 2. X-ray powder diffraction pattern for $[HGaNH]_n$ (**2**) produced from (a) the thermolysis of **1** in NH_3 and (b) the reaction of **1** and PCy_3 in THF.

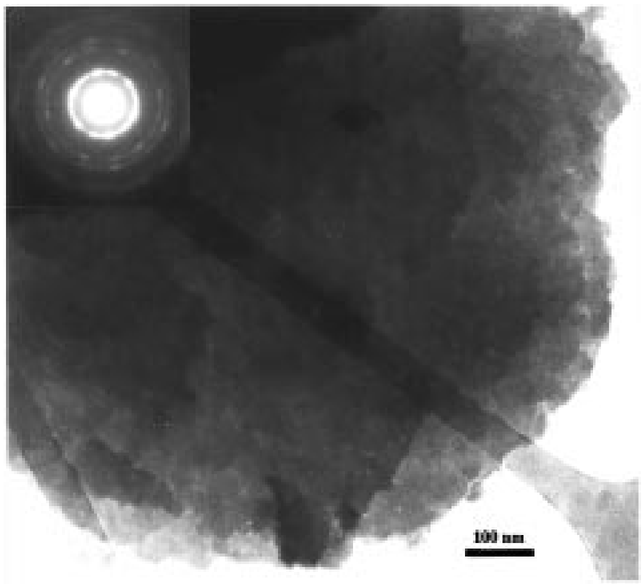

Figure 3. TEM and electron diffraction (insert) of poly(imidogallane) (**2**). The tabular morphology is evident by the characteristic image density present over large regions of the particle, which is comprised of many small crystallites (not individually visible.)

The gallane−Lewis base adducts were also isolated in high yield (82% for $H_3Ga{\cdot}$quinuclidine). Due to difficulties encountered in separating PCy_3 and $H_3Ga{\cdot}PCy_3$, no yield could be determined for this reaction. However, the total mass recovered was 92% of that expected for the mixture of the two compounds. The low isolated yield of $H_3Ga{\cdot}NMe_3$ was due to its high volatility, resulting in the substantial loss of product during

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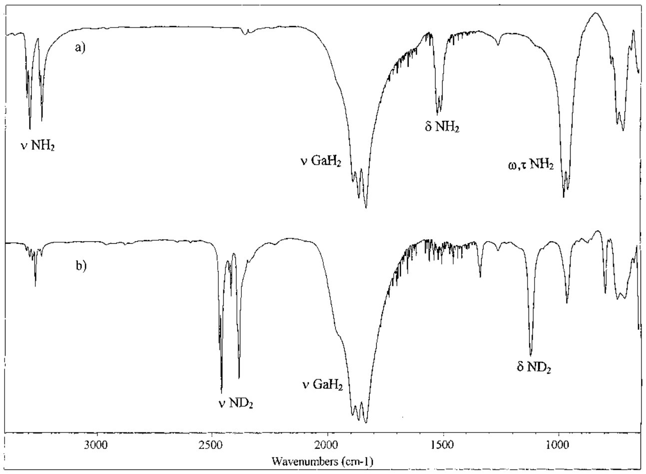


Figure 4. Infrared spectra of (a) $[H_2GaNH_2]_3$ (**1**) and (b) $[H_2GaND_2]_3$ (**3**). Spectrum b indicates the presence of small amounts (approximately 5%) of **1** and $[H_2GaN(H)D]_3$ (**4**).

evaporation of the excess NMe_3. No attempt was made to isolate the presumed $H_3Ga{\cdot}THF$.

Spectroscopic characterization of the gallane−base adducts compared well with independently prepared samples and with literature values (see Experimental Section).[9−12] The IR spectra of the poly(imidogallane) prepared by these reactions were essentially identical to those of samples prepared in NH_3. However, there was a weak band at approximately 3325 cm^{-1} which was not present in samples of **2** prepared from ammonia solution. The strong Ga−H vibration was generally shifted from 1883 to 1880 cm^{-1} and the weak band at 1818 cm^{-1} was absent. The greatest deviation was seen in the sample prepared from NMe_3. The N−H vibration was shifted by approximately 20 cm^{-1} to 3258 cm^{-1}. The Ga−H vibration was shifted to 1869 cm^{-1} in the as-prepared sample. This was believed to be due to the presence of excess NMe_3 entrained in the product, resulting in the isolation of a greater than theoretical yield of poly(imidogallane). Drying a small sample of this solid under dynamic vacuum for 24 h led to a shift in ν_{Ga-H} from 1869 to 1879 cm^{-1}, but no change in ν_{N-H}.

In the reactions of **1** with THF, quinuclidine, and PCy_3, aliquots were removed from the reaction mixtures and the progress of the reactions was monitored by IR spectroscopy. In THF solution, **1** exhibited ν_{Ga-H} at 1858 cm^{-1}. Aliquots were taken over a period of several days. The initially clear solution grew turbid and a white solid began to precipitate as the peak at 1858 cm^{-1} diminished and a new peak at 1817 cm^{-1} appeared. When three equivalents of quinuclidine were added to a THF solution of **1**, the IR spectrum consisted of a single absorption at 1821 cm^{-1} before the onset of precipitation. The reaction of **1** with PCy_3 in THF appeared to be the intermediate case. The IR spectrum of an aliquot of the slightly hazy reaction mixture after 1 h displayed vibrations at 1848 and 1818 cm^{-1}. The ν_{N-H} region of all of these spectra were similar and exhibited broad bands at 3238 cm^{-1} with less intense shoulders ranging from 3300 to 3312 cm^{-1}.

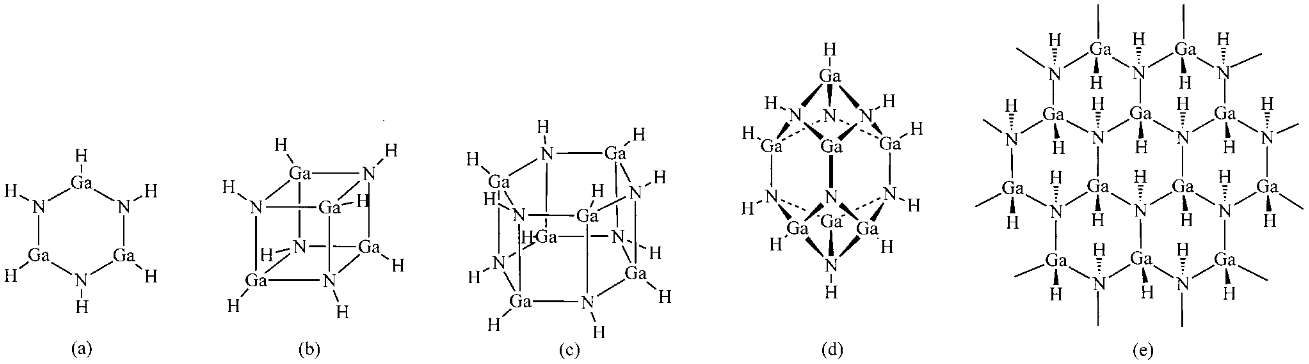
X-ray and Electron Diffraction Studies on 2. Figure 2 shows the X-ray powder diffraction patterns of samples of **2** prepared by the reaction of $[H_2GaNH_2]_3$ in supercritical ammonia (**2a**) and by the reaction of $[H_2GaNH_2]_3$ with PCy_3 in THF (**2b**). Measurement of the pattern of an empty glass capillary tube verified that the intensity of background reflections was insignificant. The XRD obtained from a sample of **2** prepared from the reaction of **1** with quinuclidine was identical to that seen in Figure 2b. This eliminated the possibility that any of the reflections were due to residual PCy_3 or $H_3Ga{\cdot}PCy_3$. On the basis of the line broadening, the coherent length of the crystallites was 150 Å. Several of the reflections exactly coincided in both position and relative intensity for both samples; however, there were striking differences below 2θ values of 14°. In Figure 2a a broad maximum is centered at 3°, while an intense, well-defined reflection is observed in Figure 2b at 2.8°. Table 1 summarizes the results shown in Figure 2b. Due to the small number and breadth of the reflections, it was not possible to assign a crystal system and unit cell unambiguously. Analysis of the *d* spacings suggested that the four, well-defined reflections above 14° fit a pattern consistent with a hexagonal cell. Unfortunately, none of these reflections contained a component along the *c*-axis, so the only unit cell dimension obtained was limited to the crystallographic *a*-axis (7.27 Å). If the intense reflection at 2.8° was assigned to 001, most of the additional reflections below 14° could be assigned as 002 through 004. These values were consistent with a *c*-axis of 32.6 Å. Using these two cell constants, the reflection located at 25.7° was assigned to 113. In Figure 2a the breadth of the low-angle reflections may be attributed to increased disorder along the *c*-axis caused by incorporation of trace quantities of NH_3 between the layers.

Table 1. X-ray Diffraction Data for $[HGaNH]_n$ Prepared from $[H_2GaNH_2]_3$ and PCy_3

expl 2θ (deg)	d (Å)	I/I_o	tentative *hkl*	calcd 2θ	difference
2.893	30.52	88.2	001	2.710	−0.1861
5.369	16.45	4.9	002	5.415	0.0464
7.103	12.44	0.7			
8.285	10.66	1.3	003	8.127	−0.1581
9.523	9.280	1.4			
10.846	8.150	0.8	004	10.843	−0.0030
11.838	7.469	0.6			
14.046	6.265	100	100	14.050	0.0041
24.504	3.630	3.1	110	24.460	−0.0441
25.721	3.445	0.5	113	25.814	0.0935
28.400	3.140	4.9	200	28.317	−0.0828
37.919	2.371	3.1	210	37.760	−0.1594

This assignment was supported by TEM analysis of **2**. Detailed analyses of the particles was not possible because the sample rapidly degraded in the electron beam, as evidenced by the rapid decay of the diffraction patterns. However, bright field images of the particles showed a broadly tabular morphology (Figure 3). The sharp diffraction rings frequently showed strong intensity only over small arcs, rather than being uniformly intense around the whole ring. A few samples did show complete rings, with intensity strongly peaked every 60° around the rings. Within the rings there was a streaking of the diffraction spots around the ring, which suggested that within the platelets there were areas which were rotationally misaligned. There was also an appreciable intensity peak corresponding to a rotation of 90° within the plane. These observations suggested that the particles were planar agglomerations, with most of the particles oriented with the basal plane normal to the electron beam (to give complete rings) or slightly off normal (to give the arc patterns). The particles were aligned reasonably well within the layer, with a small fraction aligned 90° out of phase. The intense peaks were indexed as a hexagonal (or pseudohexagonal) lattice with a plane spacing of 6.4 Å and a unit cell dimension within the plane of 7.5 Å, which was entirely consistent with the X-ray data. No data could be determined for the unit cell dimensions normal to the plane.

Scheme 1



(a) (b) (c) (d) (e)

Discussion

Poly(imidogallane). An attempt to synthesize GaN in supercritical ammonia led to the isolation of hydridogallium imide. The spectroscopic and elemental analytical data and the physical characteristics of the solid are consistent with a polymeric species having the formula $[\mathrm{HGaNH}]_n$. The polymeric nature of **2** is consistent with other related group 13 imides and amide imides such as $[\mathrm{HAlNH}]_n$,[13,14] $[\mathrm{Ga(NH)_{3/2}}]_n$,[16] and $[\mathrm{Al(NH_2)(NH)}]_n$.[17,18]

Poly(imidogallane) was found to be crystalline by both X-ray and electron diffraction methods. There is precedent for forming crystalline polymeric precursors to solid-state materials. Poly(borazylene), which contains linked borazine rings, exhibits some long-range ordering and a diffraction pattern similar to those observed for turbostratic boron nitride.[19] Reports of $[\mathrm{HAlNH}]_n$ have not suggested any evidence of a crystalline nature.[13,14]

The simplicity of the spectroscopic and diffraction data suggests that **2** is composed of one discreet compound, and Scheme 1 depicts several possible molecular and solid-state structures. Structures a−d are based upon related, structurally characterized organoaluminum and organogallium imides.[20−27] Six-membered rings containing the heavier group 13 elements, such as the type depicted in structure 1a, have only been isolated when bulky substituents have been utilized.[26] While structures b−d cannot be eliminated from consideration, we suggest that a two-dimensional solid-state network such as shown in Scheme 1e is most consistent with the volatility and solubility of **2**.

The connection between the crystal and molecular structure of **2** is complicated by the uncertainty in the crystal structure, the assignment of the observed reflections, and, therefore, the true lattice constants. While the XRD and ED results are not inconsistent with a layered structure, as shown in Scheme 1e, it has not been possible to reconcile the lattice constants with the proposed molecular structure. Such an arrangement is related to the proposed structure of carbon monofluoride, $(\mathrm{CF})_n$, prepared by the direct fluorination of graphite.[28,29] Taking a 001 slice of hexagonal GaN as a model layer to compare with **2**, we would predict the centerpoint distance between adjacent six-membered rings of a hexagonal net would be 3.18 Å; a value somewhat less than half of the in-plane lattice constant (7.27 Å) found in **2**. Assuming that the crystal structure requires a doubling of this distance, the agreement between 6.36 and 7.27 Å is still unsatisfactory. Considering that the Ga−N bond distance in GaN is nearly identical to the corresponding distances in $[\mathrm{H_2GaNH_2}]_3$ and related compounds,[30−32] a 14% lengthening of the lattice constant seems unrealistic. It is also hard to rationalize the length of the *c*-axis based upon a structure with stacked layers, as shown in Scheme 1e; an estimated interlayer spacing would be approximately 5.2 Å. The observed lattice constant (32.6 Å) would require approximately six such layers within each unit cell. One possible explanation is that $[\mathrm{HGaNH}]_n$ formed from the $\mathrm{PCy_3}$-induced reaction crystallizes in a particular polytype that exhibits an elongated *c*-axis. This is observed in other layered structures including $\mathrm{CdI_2}$ and various micas.[33]

One of the attractive aspects about the planar model is that the long-range ordering can apparently be disrupted by the intercalation of small molecules such as $\mathrm{NH_3}$. It is believed that the additional peaks observed in the X-ray diffraction pattern for samples of **2** prepared from the reactions of **1** with $\mathrm{PCy_3}$ and quinuclidine are due to increased ordering in the alignment of the two-dimensional sheets (the crystallographic c direction). This ordering is disrupted in the samples of **2** prepared from ammonia, resulting in only a broad diffraction peak in this region. This is supported by the observation that samples of **2** prepared in ammonia were nitrogen rich and had to be subjected to vacuum before correct elemental analyses could be obtained.

What alternatives exist? A molecular cluster that is large enough to be insoluble or possibly a more complex (perhaps microporous) solid-state structure. In either case we can say little about the molecular structure. We conclude that despite the problems, the best candidate for the structure of poly(imidogallane) is the planar hexagonal network.

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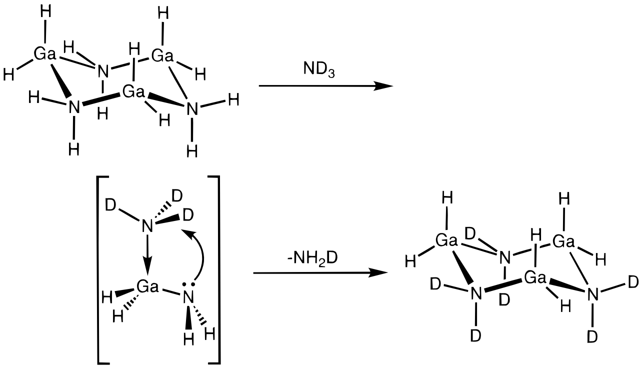
Scheme 2



The Nature of [H$_2$GaNH$_2$]$_3$ in Ammonia Solution. There was a large difference in the reactivity of cyclotrigallazane in the solid state and in ammonia solution. Whereas heating an ammonia solution of **1** at 150 °C for 30 min produced white, crystalline poly(imidogallane) **2**, heating **1** at 150 °C for the same duration in the solid state resulted in the isolation of an amorphous gray-black solid which contained only small peaks due to N−H and Ga−H vibrations in its IR spectrum. The gray color, presumably due to the formation of small amounts of Ga^0, and lack of crystallinity are typical of the solid-state conversion of **1** to GaN at low temperatures.[2,3] This difference in reactivity may be due to a difference in the degree of association between the two states.

To gain insight into the degree of association of cyclotrigallazane in ammonia solution, [H$_2$GaNH$_2$]$_3$ was dissolved in ND$_3$, resulting in a nearly quantitative conversion to [H$_2$GaND$_2$]$_3$. The H/D exchange in this transamination reaction most likely occurred directly on the donor−acceptor complex H$_2$GaNH$_2$·ND$_3$ (Scheme 2). Similar transamination reactions are common for the group 13 metals.[16,34,35] This result suggests that in ammonia solution, [H$_2$GaNH$_2$]$_3$ exists as (or is in equilibrium with) the monomeric ammonia adduct of gallazane, H$_2$GaNH$_2$·NH$_3$.

The Interaction of [H$_2$GaNH$_2$]$_3$ with Other Lewis Bases. While the ammonia adduct of gallazane, H$_2$GaNH$_2$·NH$_3$, was not isolable, an attempt was made to isolate various other donor−acceptor complexes of the general formula H$_2$GaNH$_2$·base. A summary of these reactions and their products can be seen in Scheme 3. In all cases, the reaction of **1** with a Lewis base led to the isolation of poly(imidogallane) (**2**) and Lewis base adducts of gallane (H$_3$Ga·base) rather than to H$_2$GaNH$_2$·base. It is interesting to note that H$_3$Ga·NMe$_3$ is isolated from the reaction of cyclotrigallazane and NMe$_3$. This is the reverse of the reaction used to synthesize [H$_2$GaNH$_2$]$_3$, where H$_3$Ga·NMe$_3$ is reacted with ammonia.[4] The inability to isolate the species H$_2$GaNH$_2$·base is surprising in light of the isolation and stability of the related chlorogallane adducts, H$_n$GaCl$_{3-n}$·base (where $n = 1$, 2 and base = quinuclidine, PCy$_3$).[36,37]

We propose a possible mechanism to account for the isolation of these products (Scheme 4), beginning with cleavage of the cyclotrigallazane ring to form the desired gallazane adduct H$_2$GaNH$_2$·base. This adduct could participate in a Schlenk-type equilibrium with the gallane base adduct H$_3$Ga·base and a proposed diamidogallane adduct, HGa(NH$_2$)$_2$·base. The latter compound appears to be unstable with regard to the loss of ammonia and Lewis base, yielding poly(imidogallane). This last step is related to the transamination mechanism proposed for the isotope exchange experiment described above. The loss of NH$_3$ from complexes containing multiple NH$_2$ groups to form metal amide imides such as [M(NH$_2$)(NH)]$_n$ (M = B, Al)[14,17,34,35] and metal imides such as [Ga(NH)$_{3/2}$]$_n$[16] is well-documented. The decomposition of the diamidogallane adduct, HGa(NH$_2$)$_2$·base, would shift the equilibrium to the right, resulting in the isolation of H$_3$Ga·base and poly(imidogallane) as the only products. Thus the overall reaction for this process can be written as

$$2\,[\mathrm{H_2GaNH_2}]_3 + 3\ \mathrm{Base} \longrightarrow 3\ \mathrm{H_3Ga{\cdot}Base} + 3/n\,[\mathrm{HGaNH}]_n + 3\ \mathrm{NH_3} \qquad (1)$$

In an attempt to observe one or more of the proposed intermediates, the progress of several of the above reactions was monitored by IR spectroscopy. In the reaction of [H$_2$GaNH$_2$]$_3$ with THF, the $\nu_{\mathrm{Ga-H}}$ region of the spectrum exhibits a single peak at 1858 cm^{-1}. This peak could be due to H$_2$GaNH$_2$·THF or intact [H$_2$GaNH$_2$]$_3$. Over the course of several days, the peak at 1858 cm^{-1} slowly disappeared and was replaced by a new peak at 1818 cm^{-1} as the solid began to precipitate.

The addition of 3 equiv of quinuclidine to a solution of [H$_2$GaNH$_2$]$_3$ in THF resulted in a single $\nu_{\mathrm{Ga-H}}$ at 1821 cm^{-1}. This represents a shift of nearly 40 cm^{-1} from that of [H$_2$GaNH$_2$]$_3$ in THF. While it is tempting to assign this peak as H$_2$GaNH$_2$·quinuclidine, its similarity to the peak eventually observed for the reaction of [H$_2$GaNH$_2$]$_3$ with THF, as well as the peak observed at 1818 cm^{-1} for the reaction of [H$_2$GaNH$_2$]$_3$ with PCy$_3$ in THF, would suggest it is due to a common as yet unidentified species. This assertion is supported by the nearly identical N−H vibrations observed for all three reactions. Further studies are aimed at identifying this unknown.

There was no evidence for the presence of a species such as Ga(NH$_2$)$_3$·base or [Ga(NH$_2$)$_3$]$_n$ in these reactions. Wells and Janik attempted to synthesize [Ga(NH$_2$)$_3$]$_n$ from [Ga(NMe$_2$)$_3$]$_2$ and NH$_3$. However, this reaction produced the imide [Ga(NH)$_{3/2}$]$_n$, which possessed a strong $\nu_{\mathrm{N-H}}$ at 3150 cm^{-1}.[16] This vibration is not present in any of the spectra of our samples, and is not the source of the N−H vibration at approximately 3325 cm^{-1}, which is seen in the spectra of poly(imidogallane).

The above results suggest that the formation of **2** in ammonia occurs via the elimination of H$_2$ and NH$_3$. The mechanism of this ammonia-assisted dehydrogenation can be seen in Scheme 5. The first step involves cleavage of the cyclotrigallazane ring to yield the transient ammonia adduct of gallazane, H$_2$GaNH$_2$·NH$_3$. This species equilibrates with H$_3$Ga·NH$_3$ and HGa(NH$_2$)$_2$·NH$_3$, and the diamidogallane−ammonia adduct eventually eliminates two molecules of NH$_3$ to yield poly(imidogallane). The gallane−ammonia adduct, H$_3$Ga·NH$_3$, which is presumed to be present in the initial synthesis of cyclotrigallazane, eliminates H$_2$ to form H$_2$GaNH$_2$·NH$_3$. This cycle continues until all of the gallazane is consumed. The overall equation for this process is shown in eq 2, which emphasizes the catalytic role of NH$_3$.

$$[\mathrm{H_2GaNH_2}]_3 \xrightarrow[\mathrm{NH_3}]{} 3/n\,[\mathrm{HGaNH}]_n + 3\ \mathrm{H_2} \qquad (2)$$

Poly(imidogallane) appears to be an intermediate in the conversion of cyclotrigallazane to GaN in ammonia solution.

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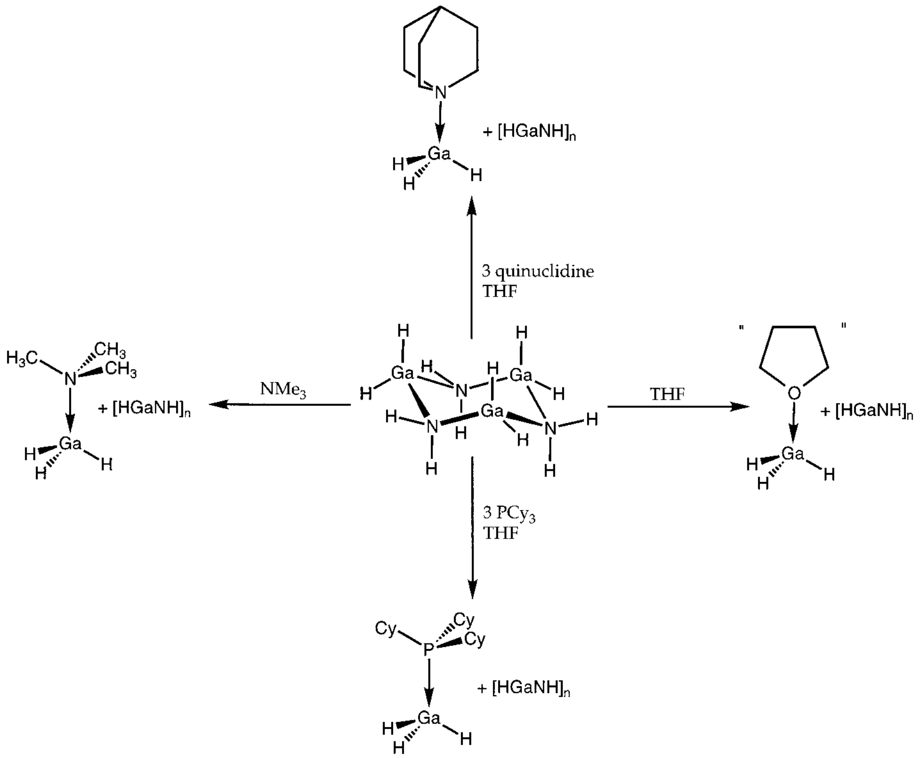
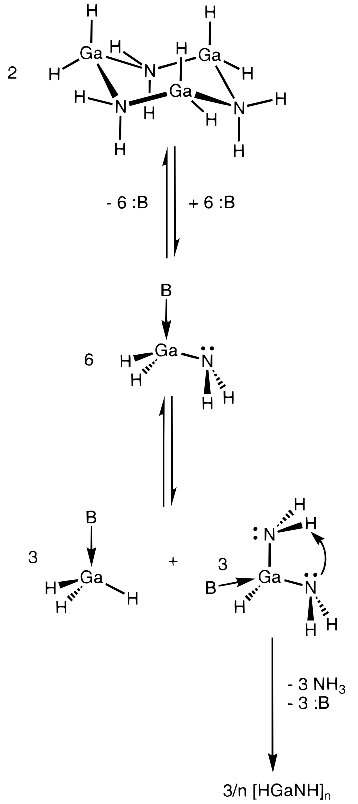
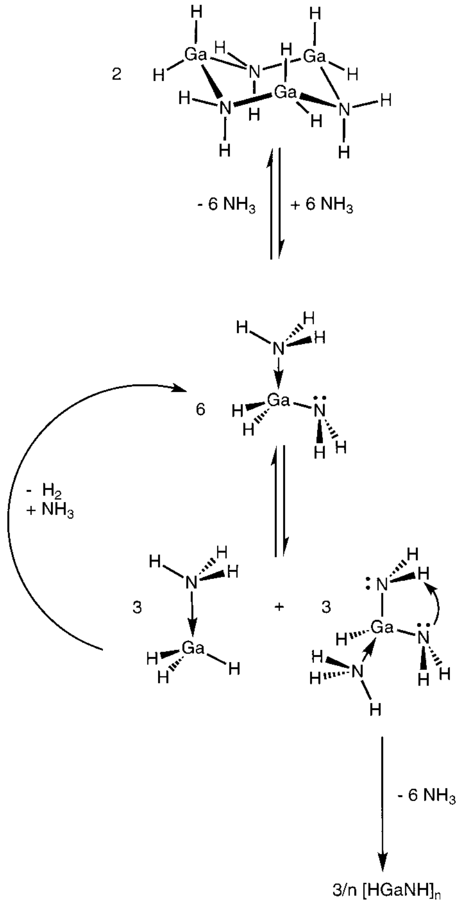
Scheme 3



Scheme 4



Scheme 5



In various syntheses of **2**, increasing the reactor pressure leads to changes in the IR spectra of the isolated solids, indicative of **2** undergoing further reaction. Increases in reaction time (5 h) and reactor pressure result in the complete conversion to nanocrystalline GaN powders (coherent length = 3 nm). Increasing the reaction time to 24 h resulted in larger (4 nm) coherent lengths. While the above results suggest that **1** dissociates into monomers in liquid NH_3, it is unlikely that such a reaction would be important for the conversion of **2** to GaN. This is supported by the lack of solubility of **2** in NH_3 and the observation that **2** precipitates from solution when **1** is reacted with quinuclidine in liquid NH_3. Details of the syntheses of GaN powders from the thermolysis of cyclotrigallazane in supercritical ammonia and a study of the effect of temperature and pressure on this conversion will be described in future publications.

Conclusions

The reaction of $[H_2GaNH_2]_3$ with a variety of Lewis bases results in the isolation of gallane–Lewis base adducts and the novel hydrido gallium imide poly(imidogallane). Isolation of these products is due to the presence of the NH_2 group, which undergoes ligand redistribution reactions and the eventual elimination of NH_3. This chemistry has been exploited to synthesize poly(imidogallane) in high yield in liquid NH_3, where the NH_3 acts as both solvent and catalyst. Poly(imidogallane) is an intermediate in the conversion of cyclotrigallazane to GaN in supercritical NH_3. This new, low-temperature route to nanocrystalline GaN will be discussed in future publications.

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