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Synthesis and Thermolysis of Alkyl- and Phenylamido Diphenylgallium, $[Ph_2GaN(H)R]_2$. Isolation and Structural Characterization of $(PhGaNMe)_7$ and $(PhGaNPh)_4$

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Alkyl- and phenylamido diphenylgallium compounds, $[Ph_2GaN(H)R]_2$ (R = Me, **1**; Et, **2**; ^{n}Pr, **3**; ^{i}Bu, **4**; Ph, **5**), were prepared from the reactions of Ph_3Ga with the corresponding primary amines and aniline at elevated temperatures and were characterized by elemental analysis, mass spectroscopy, and ^{1}H NMR and IR spectroscopy. These dimeric compounds contained bridging amido groups and exhibited both trans and cis isomers in solution. Thermolysis of compounds **1** and **5** was carried out either without solvent or in dodecane solutions, and two clusters, $(PhGaNMe)_7$ **6** and $(PhGaNPh)_4$ **7**, were isolated in 24% and 55% yields and characterized. The structure of **6** consisted of a heptameric Ga_7N_7 core constructed with Ga_2N_2 and Ga_3N_3 rings, and the structure of **7** possessed a Ga_4N_4 cubane core.

Introduction

Polyimidogallane, $(HGaNH)_n$, was reported to form as an intermediate in the ammonothermal conversion of cyclotrigallazane, $(H_2GaNH_2)_3$, into nanocrystalline gallium nitride.[1,2] While a two-dimensional network structure was consistent with the powder diffraction data and physical properties, no single crystals that would allow an unambiguous structural determination could be isolated. The formula, $(HGaNH)_n$, is related to a few structurally characterized clusters in which the hydride on gallium and proton on nitrogen are both replaced with hydrocarbyl ligands. The first reported structure of an imidogallane, $(MeGaNC_6F_5)_4$, exhibited a cubane Ga−N core,[3] and several cubane analogues have subsequently appeared.[4,5] When the substituent on nitrogen is 4-fluorophenyl or isobutyl, the hexameric compounds, $[MeGaN(4\text{-}C_6H_4F)]_6$[6] and $(MeGaN^iBu)_6$,[7] form with hexagonal prismatic Ga−N cores. Gallium nitrogen clusters having both amido and imido ligands are also known, and $(Me_2GaNHMe)_2(MeGaNMe)_6$[8] exhibits a structure related to the hexagonal prisms found in $[MeGaN(4\text{-}C_6H_4F)]_6$ and $(MeGaN^iBu)_6$. In a more complex reaction, trimesitylgallium ($2,4,6\text{-}Me_3C_6H_2$ = Mes), reacted with pentafluoroaniline to form $[(C_6F_5NH)Ga](MesGa)_3(\mu_3\text{-}NC_6F_5)_4$ that has a cubane core.[9] A more diverse family of rings and clusters comprises the frameworks of related aluminum−nitrogen compounds.[10−21]

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We sought to prepare hydrocarbyl derivatives of $(HGaNH)_n$ that might produce a soluble species and perhaps bridge the gap between the small molecular clusters noted previously and the proposed polymeric structure. Ideally, we hoped to use the size of Ga- and N-bound substituents to control the nuclearity of the final product. In this paper, we describe the synthesis and structural characterization of $(PhGaNMe)_7$ and $(PhGaNPh)_4$. These clusters were isolated in reasonable yields by the thermolysis of the new amidogallanes, $[Ph_2GaN(H)Me]_2$ and $[Ph_2GaN(H)Ph]_2$, respectively. The synthesis of these and several related amido complexes is also described.

Experimental Section

Materials and General Procedures. Diphenyl mercury and gallium metal were purchased from Strem, and all other chemicals were obtained from Aldrich. Anhydrous methylamine, ethylamine, diphenyl mercury, and gallium metal were used as received. Propylamine, isobutylamine, and aniline were distilled over calcium hydride under nitrogen. Diethyl ether, pentane, hexanes, benzene, and toluene were predried over calcium hydride and freshly distilled over sodium/benzophenone under nitrogen. Benzene-d_6 was distilled over calcium hydride under nitrogen. Except those indicated otherwise, all experiments were conducted under an oxygen-free, dry-nitrogen atmosphere using standard Schlenk and glovebox techniques.

Proton NMR spectra were obtained in benzene-d_6 solutions at room temperature on a Varian INOVA 300 spectrometer, and the residual proton (7.15 ppm) in C_6D_6 was used as the internal standard. In the cases for which the resonance of the residual proton was not distinguishable from the aromatic hydrogen atoms of the samples, the sharp singlet (0.29 ppm) from silicone grease was used as the internal standard. The IR spectra of KBr pellets were recorded on a Nicolet MAGNA-IR 560 spectrometer. Chemical ionization mass spectra were acquired on a Finnigan Mat 95 spectrometer using a direct insertion probe. The samples were evaporated at temperatures ranging from 25 to 340 °C, and the ionization gas mixture was methane with 4% ammonia. Melting points were obtained in sealed, nitrogen-filled capillaries and were uncorrected. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Desert Analytics, Tucson, AZ.

Synthesis of Ph_3Ga. The procedure was modified from that reported in the literature[22] using higher reaction temperatures and a much shorter reaction time. Gallium metal (8.10 g, 116 mmol) and diphenyl mercury (60.2 g, 170 mmol) were mixed in a flask in air. After an inert atmosphere was obtained from several cycles of pumping and refilling with nitrogen, the mixture was stirred at 170 °C for 5 h. A slightly yellow liquid mixed with metal drops was obtained, which solidified to afford a pale yellow solid at the ambient temperature. Toluene (200 mL) was used to dissolve the product and filtered to obtain a clear filtrate. After the filtrate was stored at −20 °C, a colorless crystalline solid was isolated. The remaining solution was further concentrated and stored at −20 °C to crystallize more Ph_3Ga. This process was repeated several times to yield 28.8 g of Ph_3Ga (85% yield). Mp: 164−166 °C (lit.[22] 165−166 °C). ^1H NMR: δ 7.29 (9H, m) and 7.74 (6H, m).

Synthesis of $[Ph_2GaN(H)Me]_2$ (1). Excess methylamine was condensed into a flask containing Ph_3Ga (8.00 g, 26.6 mmol) at −196 °C. The mixture was allowed to warm, and a colorless solution (~10 mL) formed at low temperatures. A white crystalline solid was obtained after the excess amine was evaporated at room temperature. The solid was then heated in an oil bath and melted at around 150 °C accompanied by benzene elimination. Benzene was collected and identified by ^1H NMR spectroscopy. The reaction was allowed to proceed at 160 °C for 2 h, and finally, a white solid was obtained. After the solid was recrystallized from toluene (30 mL), small colorless blocks were obtained (4.90 g, 73% yield). Mp: 163.5−165.0 °C. ^1H NMR for the trans isomer: δ 1.72 (2H, q, NH), 2.10 (6H, d, CH_3). ^1H NMR for the cis isomer: δ 1.44 (2H, q, NH), 2.28 (6H, d, CH_3). The multiplets of the aromatic hydrogens at δ 7.29, 7.47, 7.58, and 7.75 were not distinguished between the two isomers. The trans/cis isomer molar ratio was 2:1. IR (cm^{-1}): ν_{NH}, 3302. CI MS [assignment, % relative intensity]: 526 [$(M + NH_4)^+$, 5.0], 509 [$(M + H)^+$, 32.2], 495 [$(M - N(H)Me + H)^+$, 6.5], 478 [$\{M - N(H)Me\}^+$, 6.8], 462 [$(M - Ph + H_2NMe)^+$, 2.7], 448 [$(M - Ph + NH_3)^+$, 100], 431 [$(M - Ph)^+$, 49.4], 417 [$\{Ph_3Ga_2(NHMe)(NH_2)\}^+$, 2.6], 370 [$\{Ph_2Ga_2(NHMe)_2(NH_2)\}^+$, 4.5], 271 [$\{Ph_2Ga(NH_2Me)(NH_3)\}^+$, 0.9], 257 [$\{Ph_2Ga(NH_3)_2\}^+$, 5.1], 240 [$\{Ph_2Ga(NH_3)\}^+$, 5.0], 223 [$(Ph_2Ga)^+$, 2.6], 78 [$(C_6H_6)^+$, 23], 69 [$Ga^+$, 5.4]. Anal. Calcd for $C_{26}H_{28}GaN_2$: C, 61.48; H, 5.56; N, 5.51. Found: C, 60.71; H, 5.57; N, 5.12.

Synthesis of $[Ph_2GaN(H)Et]_2$ (2). Ethylamine (3 mL) was condensed at −78 °C and added to a slurry of Ph_3Ga (6.00 g, 19.9 mmol) in pentane (20 mL) at 0 °C. A colorless solution was obtained immediately. After it was stirred at room temperature for 0.5 h, volatiles were removed under vacuum leaving a colorless, glassy solid. The solid was heated in an oil bath and melted at approximately 85 °C. Benzene elimination was observed at 160 °C, and the reaction was allowed to proceed for 1 h to afford a white solid. Recrystallization from toluene (20 mL) at −20 °C yielded a colorless crystalline solid (4.41 g, 83% yield). Mp: 199−201 °C. ^1H NMR for the trans isomer: δ 0.57 (6H, t, CH_3), 1.85 (2H, t, NH), 2.59 (4H, m, CH_2). ^1H NMR for the cis isomer: 0.59 (6H, t, CH_3), 1.63 (2H, t, NH), 2.80 (4H, m, CH_2). The multiplets at δ 7.33, 7.63, 7.73, and 7.86 for the aromatic hydrogens were not distinguished between the two isomers. The trans/cis isomer molar ratio was 2:1. IR (cm^{-1}): ν_{NH}, 3291, 3269, and 3249. CI MS [assignment, % relative intensity]: 997 [$\{[Ph_2GaN(H)Et]_3PhGa(NH_2Et)\}^+$, 3.9], 605 [$(M + Ga)^+$, 12.6], 553 [$(M + NH_3)^+$, 2.9], 537 [$(M + H)^+$, 7.5], 509 [$(M - NHEt + NH_3)^+$, 5.0], 492 [$(M - NHEt)^+$, 5.5], 476 [$(M - Ph + NH_3)^+$, 100], 459 [$(M - Ph)^+$, 30.4], 431 [$\{Ph_3Ga_2(NHEt)(NH_2)\}^+$, 0.9], 398 [$\{Ph_2Ga_2(NHEt)_2(NH_2)\}^+$, 2.1], 311 [$\{[PhGa(NHEt)_2](C_6H_5)\}^+$, 7.7], 268 [$(0.5M + H)^+$, 1.7], 257 [$\{Ph_2Ga(NH_3)_2\}^+$, 0.5], 223 [$(Ph_2Ga)^+$, 1.2], 69 [$Ga^+$, 0.8]. Anal. Calcd for $C_{28}H_{32}Ga_2N_2$: C, 62.74; H, 6.02; N, 5.23. Found: C, 62.97; H, 6.17; N, 5.15.

Synthesis of $[Ph_2GaN(H)^nPr]_2$ (3) To a slurry of Ph_3Ga (5.00 g, 16.6 mmol) in Et_2O (20 mL) at room temperature was added 1.37 mL of $^nPrNH_2$ (0.980 g, 16.6 mmol). A colorless solution was obtained immediately. After it was stirred for 0.5 h, volatiles were removed under vacuum leaving a colorless crystalline solid. The solid was then heated in an oil bath and melted at around 120 °C. Benzene elimination occurred at 150 °C, and the reaction was allowed to proceed for 2 h. The product was a liquid at 150 °C and solidified at room temperature. After it was recrystallized from ether (100 mL) at −20 °C, a colorless crystalline solid was isolated (4.10 g, 88% yield). Mp: 136−138 °C. ^1H NMR for the trans isomer: δ 0.34 (6H, t, CH_3), 1.02 (4H, m, $CH_2CH_2CH_3$), 2.10 (2H, t, NH), 2.59 (4H, m, $CH_2CH_2CH_3$). ^1H NMR for the cis isomer:

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0.37 (6H, t, CH_3), 1.02 (4H, m, $CH_2C\mathit{H}_2CH_3$), 1.86 (2H, t, NH), 2.80 (4H, m, $C\mathit{H}_2CH_2CH_3$). The multiplets at δ 7.35, 7.70, 7.79, and 7.93 for the aromatic hydrogens and at δ 1.02 for $CH_2C\mathit{H}_2CH_3$ were not distinguished between the two isomers. The trans/cis isomer molar ratio was 2:1. IR (cm^{-1}): ν_{NH}, 3300, 3294, and 3275. CI MS [assignment, % relative intensity]: 582 [$(M + NH_3 + H)^+$, 1.4], 565 [$(M + H)^+$, 17.1], 523 [$(M - NH^nPr + NH_3)^+$, 2.1], 504 [$(M - Ph + NH_3)^+$, 100], 487 [$(M - Ph)^+$, 20.6], 462 [$\{Ph_3Ga_2(NH^nPr)(NH_2)(NH_3)\}^+$, 1.6], 426 [$\{Ph_2Ga_2(NH^nPr)_2(NH_2)\}^+$, 1.5], 299 [$\{Ph_2Ga(NH_2{}^nPr)(NH_3)\}^+$, 0.6], 257 [$\{Ph_2Ga(NH_3)_2\}^+$, 2.0], 240 [$\{Ph_2Ga(NH_3)\}^+$, 1.1], 223 [$(Ph_2Ga)^+$, 0.7], 69 [$Ga^+$, 0.7]. Anal. Calcd for $C_{30}H_{36}Ga_2N_2$: C, 63.88; H, 6.43; N, 4.97. Found: C, 63.76; H, 6.72; N, 4.99.

Synthesis of $[Ph_2GaN(H)^iBu]_2$ (4). To a slurry of Ph_3Ga (3.42 g, 11.4 mmol) in Et_2O (30 mL) at room temperature was added 1.20 mL of $^iBuNH_2$ (0.871 g, 11.9 mmol). A colorless solution was obtained immediately. After it was stirred for 0.5 h, volatiles were removed under vacuum leaving a colorless crystalline solid. The solid was heated in an oil bath and melted at around 115 °C. Benzene elimination was observed at the temperatures above 130 °C, and the reaction was allowed to proceed at 150 °C for 1 h to afford a white solid. After it was recrystallized from ether (20 mL) at −20 °C, a colorless crystalline solid was isolated (2.64 g, 79% yield). Mp: 162.5−164.5 °C. ^1H NMR for the trans isomer: δ 0.44 (12H, d, CH_3), 1.34 (2H, m, CH), 2.48 (2H, t, NH), 2.60 (4H, t, CH_2). ^1H NMR for the cis isomer: 0.45 (12H, d, CH_3), 1.34 (2H, m, CH), 2.19 (2H, t, NH), 2.82 (4H, t, CH_2). The multiplets at δ 7.26, 7.35, 7.78, 7.85, and 7.98 for the aromatic hydrogens and at δ 1.34 for C*H* were not distinguished between the two isomers. The trans/cis isomer molar ratio was 2:1. IR (cm^{-1}): ν_{NH}, 3302, and 3280. CI MS (assignment, % relative intensity): 593 [$(M + H)^+$, 15.2], 537 [$(M - NH^iBu + NH_3)^+$, 4.1], 532 [$(M - Ph + NH_3)^+$, 100], 515 [$(M - Ph)^+$, 18.7], 476 [$\{Ph_3Ga_2(NH^iBu)(NH_2)(NH_3)\}^+$, 1.0], 454 [$\{Ph_2Ga_2(NH^iBu)_2(NH_2)\}^+$, 1.1], 313 [$\{Ph_2Ga(NH_2{}^iBu)(NH_3)\}^+$, 0.6], 257 [$\{Ph_2Ga(NH_3)_2\}^+$, 1.6], 240 [$\{Ph_2Ga(NH_3)\}^+$, 0.7], 223 [$(Ph_2Ga)^+$, 0.6], 69 [$Ga^+$, 0.4]. Anal. Calcd for $C_{32}H_{40}Ga_2N_2$: C, 64.91; H, 6.81; N, 4.73. Found: C, 64.54; H, 6.82; N, 4.69.

Synthesis of $Ph_3Ga(NH_2Ph)$. To a solution of Ph_3Ga (3.00 g, 9.97 mmol) in toluene (10 mL) at room temperature was added 0.91 mL of $PhNH_2$ (0.93 g, 10 mmol). The colorless solution was stirred for 0.5 h. The solution was stored at −20 °C overnight to afford colorless blocks (3.3 g, 83% yield). Mp: 100 °C, decomp without melting. ^1H NMR: δ 3.34 (2H, s, NH_2), 6.02 and 6.67 (5H, m, NPh), 7.31 and 7.67 (15H, m, $GaPh_3$). IR (cm^{-1}): ν_{NH}, 3309 and 3254. CI MS [assignment, % relative intensity]: 371 [$(Ph_3Ga_2)^+$, 100], 316 [$(Ph_2GaNHPh + H)^+$, 15.7], 223 [$(Ph_2Ga)^+$, 80.5], 93 [$(C_6H_5NH_2)^+$, 77.2].

Synthesis of $[Ph_2GaN(H)Ph]_2$ (5). Neat $Ph_3Ga(NH_2Ph)$ (1.30 g, 3.30 mmol) was heated in an oil bath at 110 °C for 2 h. Benzene was eliminated and removed under vacuum affording a white solid. After it was recrystallized in toluene (5 mL) at −20 °C, small colorless blocks were collected (0.93 g, 89% yield). Mp: 152 °C, decomp. ^1H NMR for the trans isomer: δ 4.91 (2H, s, NH). ^1H NMR for the cis isomer: 4.58 (2H, s, NH). The multiplets at δ 6.83, 7.16, and 7.50 for the aromatic hydrogens were not distinguished between the two isomers. The trans/cis isomer molar ratio was 2:1. IR (cm^{-1}): ν_{NH}, 3284. CI MS [assignment, % relative intensity]: 633 [$(M + H)^+$, 0.2], 572 [$(M - Ph + NH_3)^+$, 2.7], 557 [$(M - NHPh + NH_3)^+$, 1.8], 540 [$(M - NHPh)^+$, 0.5], 496 [$\{Ph_3Ga_2(NHPh)(NH_2)(NH_3)\}^+$, 1.0], 333 [$\{Ph_2Ga(NH_2Ph)(NH_3)\}^+$, 4.0], 316 [$(0.5M + H)^+$, 1.0], 257 [$\{Ph_2Ga(NH_3)_2\}^+$, 100], 240 [$\{Ph_2Ga(NH_3)\}^+$, 10.9], 223 [$(Ph_2Ga)^+$, 2.3], 195 [$PhGa(NH_2)_2(NH_3)$, 2.6], 69 [$Ga^+$, 0.2]. Anal. Calcd for $C_{36}H_{32}Ga_2N_2$: C, 45.48; H, 9.69; N, 8.16. Found: C, 43.40; H, 9.61; N, 7.70.

Synthesis of $(PhGaNMe)_7$ (6). Method 1. A slurry of compound **1** (1.80 g, 3.54 mmol) in 10 mL of dodecane (bp, 216 °C) was heated in an oil bath. A colorless solution formed at approximately 130 °C, and heating was continued to reflux (220 °C) for 6 h. When the solution was cooled to room temperature, a white solid precipitated. The slurry was stored at 0 °C overnight to induce additional precipitation. The precipitate was separated by a filtration and dissolved in toluene (10 mL). After the toluene solution was stored at −20 °C for 5 days, small blocks formed and were isolated. These crystals consisted of compound **6** and toluene molecules and were suitable for the single-crystal X-ray diffraction analysis. The solvent-free sample of compound **6** (0.30 g, 24% yield) was obtained as a white powder after the crystals were heated at 100 °C for 0.5 h under vacuum. Mp: 288−290 °C; a glassy solid was obtained when the melted sample was cooled, which remelted at 260−270 °C. ^1H NMR: δ 2.96 (9H, s, CH_3), 3.18 (9H, s, CH_3), 3.60 (3H, s, CH_3), 7.24, 7.68 and 7.83 (35H, m, Ph). IR (cm^{-1}; s, strong; m, medium; w, weak): 3063 m, 3047 m, 3010 w, 3001 w, 2990 w, 2929 m, 2900 m, 2871 s, 2800 s, 1483 w, 1459 m, 1426 s, 1254 w, 1098 m, 1086 s, 1080 s, 1031 s, 998 w, 964 s, 728 s, 701 s, 679 s, 664 s. CI MS [assignment, % relative intensity]: 1232 [$(M + H)^+$, 14], 1171 [$(M - Ph + NH_3)^+$, 1.5], 1154 [$(M - Ph)^+$, 7.4], 78 [$C_6H_6{}^+$, 100]. Anal. Calcd for $C_{49}H_{56}Ga_7N_7$: C, 47.81; H, 4.58; N, 7.96. Found: C, 48.06; H, 4.68; N, 7.59.

Method 2. Neat compound **1** (2.00 g, 3.94 mmol) was heated in an oil bath at 220 °C for 4 h. Benzene elimination was observed at temperatures above 200 °C. After benzene was removed under vacuum, a white, glassy solid remained. ^1H NMR spectrum of the solid indicated that it contained ∼20% compound **6** by comparing the −NMe resonances. Pure, solvent-free compound **6** (0.12 g, 8.7% yield) was isolated after the crude products were recrystallized twice in toluene and solvent was removed from the crystals upon heating under vacuum.

Synthesis of $(PhGaNPh)_4$ (7). Compound **5** (0.930 g, 1.47 mmol) was heated at 180 °C for 2 h. During this process, benzene formed and was removed under vacuum to afford a white solid. Colorless plates were isolated when the solid was recrystallized in benzene (30 mL) at 0 °C, and a solvent-free sample of compound **7** (0.39 g, 55% yield) was obtained as a white powder after benzene was removed under vacuum. Mp: 230 °C, decomp without melting. ^1H NMR: δ 6.71, 6.89, 7.02, 7.15, 7.29 and 7.37 (all m, Ph). IR (cm^{-1}; s, strong; m, medium; w, weak): 3067 m, 3048 w, 3017 m, 2993 w, 1588 s, 1485 s, 1447 w, 1429 m, 1224 s, 1177 w, 1154 w, 1088 m, 1077 m, 1028 m, 998 m, 892 w, 859 m, 822 w, 769 s, 733 m, 695 s, 673 m. CI MS [assignment, % relative intensity]: 970 [$(M + NH_4)^+$, 0.7], 953 [$(M + H)^+$, 2.4], 875 [$(M - Ph)^+$, trace], 94 [$C_6H_5NH_3{}^+$, 100]. Anal. Calcd for $C_{48}H_{40}Ga_4N_4$: C, 60.57; H, 4.24; N, 5.89. Found: C, 59.67; H, 4.77; N, 5.56.

X-ray Data Collection, Structure Solution, and Refinement. Suitable crystals of compounds **6** and **7** were mounted on top of glass fibers under a cooled nitrogen flow. Both 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. 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. The data collection technique was generally known as a hemisphere collection. However, in the experiment for compound **6**, around 20% of the reflections were not indexed. Twinning was investigated but not found. We believe that these reflections belonged to several small satellite crystals that were picked up during the low-temperature mounting. The integration was carried out on a matrix based on reflections harvested from the actual data collection. Those not indexed were neglected, and it was assumed that their intensities did not interfere with those of the primary crystal. The final cell constants were calculated from a set of strong reflections that were 4851 for compound **6** and 5494 for **7**.

The space groups of $P\bar{1}$ for compound **6** and $P2_1/c$ for **7** were determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution was applied to both structures that 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. Except those indicated below, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The asymmetric unit of the structure of **6** consisted of one molecule of **6** and 1.5 toluene molecules. One of the toluene molecules, C(50) to C(56), was disordered over two positions with a 66:34 occupancy ratio. The anisotropic displacement parameters of the corresponding carbon atoms [e.g., C(50) and C(50D), etc.] of this disordered molecule were set to be equal, and the molecule was constrained to be planar. The second disordered toluene molecule was located on a crystallographic inversion center. Satisfactory refinement for this molecule was achieved by constraining all atoms in the same plane.

The structure of compound **7** contained a cubane Ga_4N_4 core. The asymmetric unit comprised half a molecule of **7** and 3.5 benzene molecules. Molecules of **7** were disordered over two orientations in such a manner that one orientation was the inversion image of the other. Each orientation had a 50% occupancy probability; thus, the fact that each molecule of **7** was located on a crystallographic inversion center was not contradictory to the nonexistence of an inversion symmetry in each molecule of **7**. Some restraints were used in the refinement. All the Ga$-$C and N$-$C bonds were set equal with the standard deviation of 0.001 Å. The anisotropic displacement parameters of each gallium and nitrogen atom on the same site were set to be the same. All the phenyl groups were restrained to have the ideal geometry. Three of the solvent molecules were located on crystallographic inversion centers, one of which [containing C(67), C(68), and C(69)] was disordered over two positions with a 63:37 occupancy ratio. The carbon atoms of this disordered benzene molecule were refined isotropically. All benzene molecules were refined as rigid bodies or using idealized geometries. For those on the inversion centers, satisfactory results were achieved by constraining all atoms of each molecule in the same plane.

All calculations were performed using SGI INDY R4400-SC or Pentium computers and the SHELXTL V5.0 suite of programs.

Results and Discussion

Synthesis and Characterization of $[Ph_2GaN(H)R]_2$ (1$-$5). Triphenylgallium, Ph_3Ga, was first synthesized by Gilman and Jones[22] in 1940 from the reaction of gallium metal and diphenyl mercury at 130 °C for 50$-$75 h. These reaction conditions were generally used in later studies.[23,24] We prepared Ph_3Ga in 85% yield from the same reaction within a much shorter time (5 h) at 170 °C.

The reactions for synthesizing compounds **1**$-$**5** are summarized in eq 1. Ph_3Ga reacted with the amines and aniline at temperatures up to room temperature leading to colorless, crystalline Lewis acid$-$base adducts, $Ph_3Ga(NH_2R)$. One of these adducts, $Ph_3Ga(NH_2Ph)$, was isolated and characterized by ^1H NMR and IR spectroscopy. Two strong absorptions at 3309 and 3254 cm^{-1} were characteristic of the asymmetric and symmetric N$-$H vibrations of the NH_2 group. The ^1H NMR spectrum indicated one phenyl group on nitrogen and three on gallium. The base peak at 371 in the mass spectrum, however, was assigned to $(Ph_3Ga_2)^+$, indicating that the compound reacted when heated in the mass spectrometer.

$$Ph_3Ga + RNH_2 \rightarrow Ph_3Ga(NH_2R) \xrightarrow[-C_6H_6]{\text{heat}} 0.5\,[Ph_2GaN(H)R]_2 \quad (1)$$

$$R = Me, \mathbf{1};\ Et, \mathbf{2};\ {}^{n}Pr, \mathbf{3};\ {}^{i}Bu, \mathbf{4};\ Ph, \mathbf{5}.$$

Heating these adducts as neat solids to 100$-$160 °C for 1$-$2 h followed by extraction and recrystallization using toluene resulted in the isolation of colorless, crystalline compounds **1**$-$**5** in high yields (73$-$88%). Compounds **1**$-$**5** were characterized by elemental analysis and spectroscopic methods. The CI mass spectra of compounds **1**$-$**4** exhibited base peaks of $(M - Ph + NH_3)^+$. The presence of NH_3 in these species was derived from the NH_3 in the ionization gas, and the relative intensities of the molecular ion peaks (plus 1) of compounds **1**$-$**4** were 8$-$32%. Except for compound **2**, no mass peaks higher than those for $(M + NH_4)^+$ were found. In the spectrum of **2**, species containing 3 and 4 gallium atoms were found with intensities of 4 and 13% of the base peak, respectively. These species probably resulted from the reactions that occurred upon heating in the evaporation step. For compound **5**, the base peak was attributed to $[Ph_2Ga(NH_3)_2]^+$, and the $(M + 1)^+$ ion was only 0.2% of the base peak, indicating that the Ga$-$N bond cleavage was dominant.

The ^1H NMR spectrum of compound **1** exhibited two doublets at 2.10 and 2.28 ppm for the methyl resonances and two quartets at 1.44 and 1.72 ppm for the NH resonances, indicating the existence of both trans and cis isomers. Similarly, the ^1H NMR spectra of compounds **2**$-$**4** also contained two sets of alkyl and NH resonances, and for compound **5**, two singlets at 4.83 and 4.91 ppm for the NH resonances were found. We assigned the resonances with greater integrations to the trans isomers, and the trans/cis isomer ratios were 2:1 for all the five compounds. This assignment was consistent with the facts that most amidogallanes of the type of $[R_2GaN(H)R']_2$[14,25$-$30] adopted the

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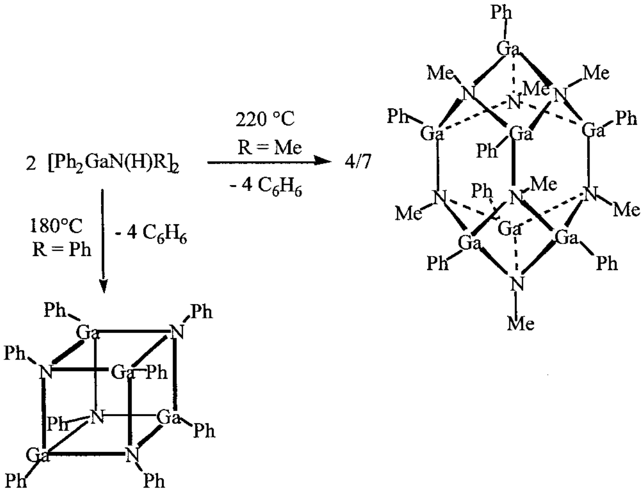
Scheme 1



trans geometry and that the trans/cis isomerization studies for [Me$_2$GaN(H)^{t}Bu]$_2$,[31] [Me$_2$GaN(H)SiEt$_3$]$_2$,[32] and [Et$_2$GaN(H)SiEt$_3$]$_2$[32] showed a higher trans molar percentages in solutions at room temperature. More than one ν_{NH} absorption was found in the IR spectra of compounds **2**−**4**, consistent with the existence of both trans and cis isomers in the solid state. For **1** and **5**, only one ν_{NH} absorption was observed.

Thermolyses of Compounds 1−5 and Synthesis of (PhGaNMe)$_7$ (6) and (PhGaNPh)$_4$ (7). It was anticipated that further elimination of benzene from compounds **1**−**5** would result in the formation of imidogallanes, (PhGaNR)$_n$, with varied degrees of association depending on the nitrogen substituents (Scheme 1). The thermolyses were carried out either without solvent or in dodecane solutions. For compounds **1**−**4**, benzene elimination was observed at temperatures above 200 °C, whereas for compound **5**, the reaction took place readily at 180 °C. From all of these reactions, however, only two products, compounds **6** and **7,** were isolated and characterized. The products from the thermolysis of **2** and **3** were mixtures of solids and sticky oils. The solids were not soluble in toluene. Gallium metal was found as one of the products when compound **4** was heated at 230 °C for 1 h.

Compared with the solvent-free reaction, compound **6** was synthesized in a higher yield when compound **1** was heated in a dodecane solution (24% yield). Colorless crystals containing solvent molecules were isolated from a toluene solution. The solvent-free sample was obtained as a white powder when the crystals were heated at 100 °C under vacuum. No N−H absorption was found in the IR spectrum. An initial formula (PhGaNMe)$_n$ was suggested by the C−H−N analysis of the solvent-free sample, and the heptameric formulation (PhGaNMe)$_7$ was established by the single-crystal XRD study. In the CI mass spectrum, the highest *m*/*e* peaks centered at 1232 (14% to the base peak) were attributed to (M + H)$^+$, indicating the existence of the heptamer in the gas phase. In the ^{1}H NMR spectrum, the three singlets at 2.96, 3.18, and 3.60 ppm with an integration ratio of 3:3:1 were assigned to the −NMe groups, consistent with the solid-state structure as shown below.

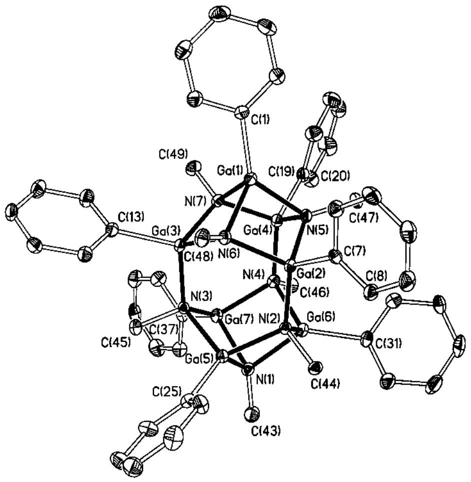


Figure 1. Molecular structure and atom labeling scheme for (PhGaNMe)$_7$ (**6**). Atoms are shown at the 30% probability level. All hydrogen atoms, the toluene solvent molecules, and the disorders are omitted for clarity. For carbon atoms, only those bonded to gallium and nitrogen atoms and relevant to the discussion were labeled.

Compound **7** was isolated as colorless plates containing benzene molecules. The benzene of solvation could be easily removed under vacuum at room temperature to afford a white powder. Only aromatic groups were found in the ^{1}H NMR spectrum, and no N−H absorption was observed in the IR spectrum. The C−H−N elemental analysis of the solvent-free sample suggested a formula (PhGaNPh)$_n$, and the structural determination established its tetrameric formulation (PhGaNPh)$_4$. In the CI mass spectrum collected in CH$_4$ with 4% NH$_3$, peaks centered at 970 and 953 were assigned to (M + NH$_4$)$^+$ and (M + H)$^+$, respectively.

By way of comparison to the alkane elimination observed for compounds **1**−**5**, thermolysis of the closely related hydrazido gallium compounds [Me$_2$GaN(H)N(H)R]$_2$ (R = Ph[33] and ^{t}Bu[34]) in refluxing toluene afforded [MeGaN(H)NR]$_4$ that have structures with both nitrogens bonded to galliums. It is interesting that the deprotonation occurs from −N(H)R rather than from the gallium-bonded nitrogen.

Structures of (PhGaNMe)$_7$ (6) and (PhGaNPh)$_4$ (7). The molecular structures of compounds **6** and **7** are shown in Figures 1 and 2, respectively, crystallographic data are provided in Table 1, and the selected bond lengths and angles are listed in Tables 2 and 3.

Compound **6** has the same cluster framework as that found in (MeAlNMe)$_7$[18] and (^{t}BuGaS)$_7$.[35] The core of the cluster was composed of four-coordinate gallium and nitrogen atoms with each gallium bonded to three nitrogen atoms and a phenyl group, and each nitrogen atom to three gallium atoms

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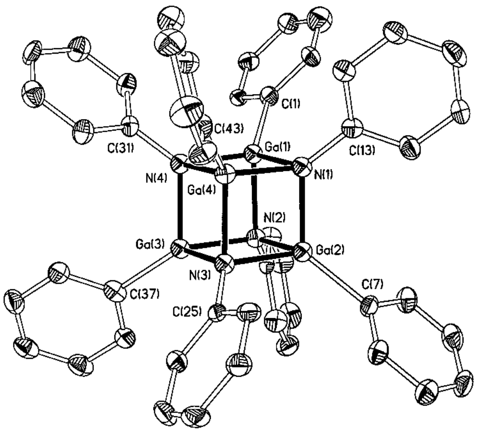


Figure 2. Molecular structure and atom labeling scheme for $(PhGaNPh)_4$ (**7**). Atoms are shown at the 30% probability level. Only one orientation of the disordered structure is shown. All hydrogen atoms and benzene solvent molecules are omitted for clarity. For carbon atoms, only those bonded to gallium and nitrogen atoms were labeled.

Table 1. Crystallographic Data of Compounds **6** and **7**.

	$\mathbf{6}\cdot1.5C_7H_8$	$\mathbf{7}\cdot7C_6H_6$
fw	1369.25	1498.48
space group	$P\bar{1}$	$P2_1/c$
a, Å	12.4038(7)	11.8216(7)
b, Å	13.3356(7)	18.3642(10)
c, Å	18.8316(10)	17.2032(10)
α, deg	105.1880(10)	90
β, deg	99.3070(10)	91.6750(10)
γ, deg	100.3330(10)	90
V, Å^3	2885.1(3)	3733.1(4)
Z	2	2
T, °C	−100	
λ, Å	0.710 73	
ρ_{calcd}, g cm^{-3}	1.576	1.333
μ, cm^{-1}	32.63	14.77
R1, wR2^a [$I > 2\sigma(I)$]	0.0372, 0.0810	0.0491, 0.1188

[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, b are constants given in Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**

	$\mathbf{6}\cdot1.5C_7H_8$		
Ga(1)−C(1)	1.961(6)	Ga(4)−N(5)	1.987(3)
Ga(1)−N(5)	1.982(3)	Ga(4)−N(7)	1.969(3)
Ga(1)−N(6)	1.995(2)	Ga(5)−C(25)	1.963(4)
Ga(1)−N(7)	1.985(3)	Ga(5)−N(1)	1.995(3)
Ga(2)−C(7)	1.988(4)	Ga(5)−N(2)	1.974(3)
Ga(2)−N(2)	1.934(3)	Ga(5)−N(3)	1.970(3)
Ga(2)−N(5)	1.999(3)	Ga(6)−C(31)	1.956(4)
Ga(2)−N(6)	1.968(3)	Ga(6)−N(1)	1.985(3)
Ga(3)−C(13)	1.986(4)	Ga(6)−N(2)	1.986(4)
Ga(3)−N(3)	1.956(3)	Ga(6)−N(4)	1.975(3)
Ga(3)−N(6)	1.987(3)	Ga(7)−C(37)	1.960(4)
Ga(3)−N(7)	1.980(3)	Ga(7)−N(1)	1.986(3)
Ga(4)−C(19)	1.985(4)	Ga(7)−N(3)	1.968(3)
Ga(4)−N(4)	1.932(3)	Ga(7)−N(4)	1.975(3)
C(1)−Ga(1)−N(5)	133.93(16)	N(4)−Ga(4)−N(5)	111.99(13)
C(1)−Ga(1)−N(7)	120.12(15)	N(4)−Ga(4)−N(7)	111.94(14)
C(1)−Ga(1)−N(6)	123.68(15)	N(5)−Ga(4)−N(7)	88.70(13)
N(5)−Ga(1)−N(6)	88.89(13)	C(25)−Ga(5)−N(1)	129.43(16)
N(5)−Ga(1)−N(7)	88.41(13)	C(25)−Ga(5)−N(2)	119.66(15)
N(6)−Ga(1)−N(7)	89.16(13)	C(25)−Ga(5)−N(3)	115.56(15)
C(7)−Ga(2)−N(2)	119.38(15)	N(1)−Ga(5)−N(2)	88.10(13)
C(7)−Ga(2)−N(5)	108.27(15)	N(1)−Ga(5)−N(3)	89.10(13)
C(7)−Ga(2)−N(6)	114.13(15)	N(2)−Ga(5)−N(3)	109.02(13)
N(2)−Ga(2)−N(5)	111.35(13)	C(31)−Ga(6)−N(1)	131.53(16)
N(2)−Ga(2)−N(6)	110.44(14)	C(31)−Ga(6)−N(2)	116.21(14)
N(5)−Ga(2)−N(6)	89.15(13)	C(31)−Ga(6)−N(4)	115.23(16)
C(13)−Ga(3)−N(3)	110.06(15)	N(1)−Ga(6)−N(2)	88.07(13)
C(13)−Ga(3)−N(6)	114.49(15)	N(1)−Ga(6)−N(4)	89.92(14)
C(13)−Ga(3)−N(7)	118.29(15)	N(2)−Ga(6)−N(4)	111.28(13)
N(3)−Ga(3)−N(6)	111.32(13)	C(37)−Ga(7)−N(1)	126.17(16)
N(3)−Ga(3)−N(7)	111.75(13)	C(37)−Ga(7)−N(3)	117.07(15)
N(6)−Ga(3)−N(7)	89.53(13)	C(37)−Ga(7)−N(4)	119.50(15)
C(19)−Ga(4)−N(4)	118.87(16)	N(1)−Ga(7)−N(3)	89.42(13)
C(19)−Ga(4)−N(5)	109.80(16)	N(1)−Ga(7)−N(4)	89.91(14)
C(19)−Ga(4)−N(7)	111.55(16)	N(3)−Ga(7)−N(4)	108.70(13)
C(43)−N(1)−Ga(5)	126.8(3)	Ga(4)−N(4)−Ga(6)	117.31(16)
C(43)−N(1)−Ga(6)	121.7(3)	Ga(4)−N(4)−Ga(7)	121.15(16)
C(43)−N(1)−Ga(7)	128.0(3)	Ga(6)−N(4)−Ga(7)	89.49(14)
Ga(5)−N(1)−Ga(6)	90.38(13)	C(47)−N(5)−Ga(1)	126.1(3)
Ga(5)−N(1)−Ga(7)	89.51(13)	C(47)−N(5)−Ga(2)	112.1(2)
Ga(6)−N(1)−Ga(7)	88.92(14)	C(47)−N(5)−Ga(4)	117.4(3)
C(44)−N(2)−Ga(2)	114.6(2)	Ga(1)−N(5)−Ga(2)	88.53(13)
C(44)−N(2)−Ga(5)	106.7(2)	Ga(1)−N(5)−Ga(4)	89.36(13)
C(44)−N(2)−Ga(6)	103.2(2)	Ga(2)−N(5)−Ga(4)	119.29(16)
Ga(2)−N(2)−Ga(5)	120.37(16)	C(48)−N(6)−Ga(1)	123.7(3)
Ga(2)−N(2)−Ga(6)	117.56(16)	C(48)−N(6)−Ga(2)	114.7(2)
Ga(5)−N(2)−Ga(6)	90.98(13)	C(48)−N(6)−Ga(3)	116.6(3)
C(45)−N(3)−Ga(3)	110.3(2)	Ga(1)−N(6)−Ga(2)	89.02(13)
C(45)−N(3)−Ga(5)	108.9(2)	Ga(1)−N(6)−Ga(3)	88.41(13)
C(45)−N(3)−Ga(7)	106.0(2)	Ga(2)−N(6)−Ga(3)	119.25(16)
Ga(3)−N(3)−Ga(5)	118.48(16)	C(49)−N(7)−Ga(1)	120.4(3)
Ga(3)−N(3)−Ga(7)	120.48(16)	C(49)−N(7)−Ga(3)	118.1(3)
Ga(5)−N(3)−Ga(7)	90.75(13)	C(49)−N(7)−Ga(4)	115.0(3)
C(46)−N(4)−Ga(4)	114.0(3)	Ga(1)−N(7)−Ga(3)	88.91(13)
C(46)−N(4)−Ga(6)	106.4(2)	Ga(1)−N(7)−Ga(4)	89.78(13)
C(46)−N(4)−Ga(7)	105.2(2)	Ga(3)−N(7)−Ga(4)	118.54(16)

and a methyl group. The faces of the cluster consisted of six Ga_2N_2 rings and three boat-shaped Ga_3N_3 rings. The internal angles of the Ga_2N_2 rings on gallium varied from 88.07(13) to 89.92(14)°, and those on nitrogen, from 88.41(13) to 90.98(13)°. All the Ga_2N_2 rings were nonplanar with sums of the internal angles ranging from 355.59 to 358.78°. The Ga−N−Ga bond angles of Ga_3N_3 rings ranged from 117.31(16) to 120.48(16)°, and the N−Ga−N bond angles from 108.70(13) to 111.99(13)°.

The 21 Ga−N bonds in the structure of **6** could be placed into three groups: those that were only part of Ga_3N_3 rings (group 1), those that were only part of Ga_2N_2 rings (group 2), and those on both rings (groups 3). The bonds in group 1, Ga(2)−N(2) [1.934(3) Å], Ga(3)−N(3) [1.956(3) Å], and Ga(4)−N(4) [1.932(3) Å], were systematically (0.01−0.07 Å) shorter than those in groups 2 and 3. The bonds in groups 2 and 3 varied from 1.982(3) to 1.995(3) and 1.968(3) to 1.999(3) Å, respectively. Except for Ga(2)−N(5) [1.999(3) Å], the bonds in group 3 were shorter or equal to those in group 2. The hexamers, $[MeGaN(4\text{-}C_6H_4F)]_6$[6] (**8**) and $(MeGaN^iBu)_6$[7] (**9**), and the amido-imidogallane,[8] $(Me_2GaNHMe)_2(MeGaNMe)_6$ (**10**), were the only gallium−nitrogen clusters in the literature containing both Ga_2N_2 and Ga_3N_3 rings. Each of the structures of **8** and **9** contained a hexagonal prism core with six planar Ga_2N_2 rings bridging two planar Ga_3N_3 rings (Figure 3a). The bonds [1.967(3) and 1.971(3) for **8** and 1.937(2) and 1.955(2) Å for **9**] on the Ga_3N_3 rings (also on the Ga_2N_2 rings) were shorter than the transverse bonds [2.033(4) for **8** and 2.067(7) Å for **9**] that were only on the Ga_2N_2 rings. Similar structural features as in **8** and **9** were found for aluminum analogues such as $(ClAlN^iPr)_6$[17] and $(HAlN^nPr)_6$[19] and were explained by the involvement of more p character in the longer, transverse bonds.[19] The structure of compound **10** possessed some common features compared to those of **6**: two types of bonds, as those in

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **7**

7·7C$_6$H$_6$			
Ga(1)−C(1)	1.963(3)	Ga(3)−C(37)	1.963(3)
Ga(1)−N(1)	2.041(16)	Ga(3)−N(2)	2.018(17)
Ga(1)−N(2)	2.023(14)	Ga(3)−N(3)	1.952(14)
Ga(1)−N(4)	1.984(18)	Ga(3)−N(4)	1.991(16)
Ga(2)−C(7)	1.962(3)	Ga(4)−C(43)	1.962(3)
Ga(2)−N(1)	1.961(15)	Ga(4)−N(1)	2.014(17)
Ga(2)−N(2)	1.954(18)	Ga(4)−N(3)	2.032(16)
Ga(2)−N(3)	2.020(18)	Ga(4)−N(4)	2.04(2)
C(1)−Ga(1)−N(1)	124.3(4)	C(13)−N(1)−Ga(1)	121.3(9)
C(1)−Ga(1)−N(2)	128.8(5)	C(13)−N(1)−Ga(2)	127.9(11)
C(1)−Ga(1)−N(4)	126.8(5)	C(13)−N(1)−Ga(4)	123.5(11)
N(1)−Ga(1)−N(2)	85.9(7)	Ga(1)−N(1)−Ga(2)	91.6(6)
N(1)−Ga(1)−N(4)	89.3(8)	Ga(1)−N(1)−Ga(4)	90.6(6)
N(2)−Ga(1)−N(4)	88.9(7)	Ga(2)−N(1)−Ga(4)	91.7(5)
C(7)−Ga(2)−N(1)	129.0(5)	C(19)−N(2)−Ga(1)	126.8(9)
C(7)−Ga(2)−N(2)	122.2(5)	C(19)−N(2)−Ga(2)	122.9(12)
C(7)−Ga(2)−N(3)	125.6(5)	C(19)−N(2)−Ga(3)	122.8(11)
N(1)−Ga(2)−N(2)	90.1(7)	Ga(1)−N(2)−Ga(2)	92.4(6)
N(1)−Ga(2)−N(3)	90.3(7)	Ga(1)−N(2)−Ga(3)	90.1(6)
N(2)−Ga(2)−N(3)	87.9(7)	Ga(2)−N(2)−Ga(3)	92.0(6)
C(37)−Ga(3)−N(2)	124.9(4)	C(25)−N(3)−Ga(2)	120.6(12)
C(37)−Ga(3)−N(3)	128.1(4)	C(25)−N(3)−Ga(3)	130.2(10)
C(37)−Ga(3)−N(4)	124.5(5)	C(25)−N(3)−Ga(4)	122.0(11)
N(2)−Ga(3)−N(3)	88.0(8)	Ga(2)−N(3)−Ga(3)	92.0(6)
N(2)−Ga(3)−N(4)	88.8(7)	Ga(2)−N(3)−Ga(4)	89.5(5)
N(3)−Ga(3)−N(4)	90.6(8)	Ga(3)−N(3)−Ga(4)	91.9(6)
C(43)−Ga(4)−N(1)	127.0(5)	C(31)−N(4)−Ga(1)	127.3(12)
C(43)−Ga(4)−N(3)	131.2(5)	C(31)−N(4)−Ga(3)	126.8(11)
C(43)−Ga(4)−N(4)	121.5(5)	C(31)−N(4)−Ga(4)	118.3(13)
N(1)−Ga(4)−N(3)	88.4(7)	Ga(1)−N(4)−Ga(3)	92.1(6)
N(1)−Ga(4)−N(4)	88.5(7)	Ga(1)−N(4)−Ga(4)	91.5(6)
N(3)−Ga(4)−N(4)	87.0(6)	Ga(3)−N(4)−Ga(4)	90.6(7)

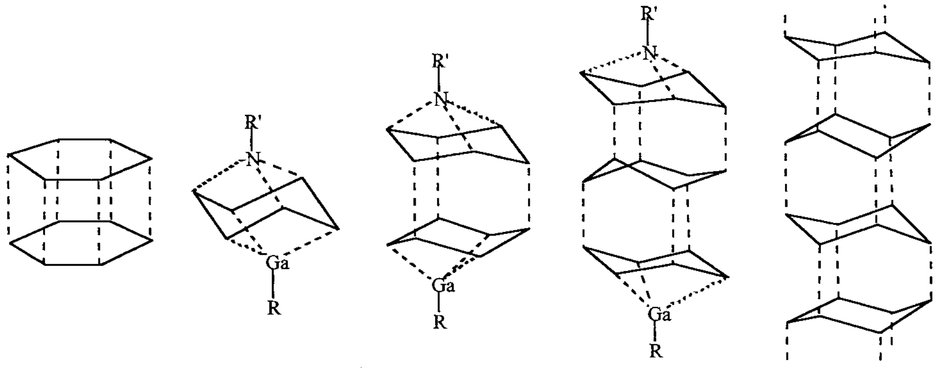
groups 1 and 3 for **6**, were present, and the Ga$_3$N$_3$ rings were boat-shaped. In the structure of **10**, the bonds in group 1 [1.940(7), 1.940(9), 1.953(7), and 1.961(10) Å] were also systematically shorter than those in group 3 [1.969(10), 1.973(11), 1.979(80), and 1.987(8) Å]. The disordered parts in the structure of **10** involving NHMe or Me$_2$Ga species were not solved, and the relevant Ga−N bond lengths are not cited here.

The bond-angle strain and steric effect involving the substituents on Ga and N in six-membered rings are different from those in four-membered rings. If the bond-angle strain was the factor dominating the Ga−N bond length difference in the structure of **6**, one might expect a similar pattern of bond length differences in the aluminum compound, (MeAlNMe)$_7$ (**11**). In the structure of **11**, however, the Al−N bond lengths of the Al$_3$N$_3$ rings were not shorter than other Al−N bonds, and the geometric parameters [Al$_2$N$_2$ rings, N−Al−N, 88.0(11)−93.0(14)°, Al−N−Al, 85.9(16)−91.7(10)°; Al$_3$N$_3$ rings, N−Al−N, 108.7(12)−111.1(12)°, Al−N−Al, 117.7(10)−123.5(11)°] were close to those in the structure of **6**. Thus, the difference in Ga−N bond lengths in the structure of **6** was largely attributed to the steric differences between substituents on the metal. Some C···C contacts between adjacent ligands in the structure of **6** such as C(7)···C(47) (3.322 Å), C(8)···C(44) (3.392 Å), C(13)···C(45) (3.194 Å), C(19)···C(49) (3.446 Å), and C(20)···C(46) (3.411 Å) were shorter than 3.5 Å.

As mentioned, the gallium−sulfur cluster, (^{t}BuGaS)$_7$ (**12**),[35] has the same type of structure as for **6** and **11**. From the comparison of the sizes of S^{2-} versus NR^{2-} and Ga versus Al atoms and the bond angles on Ga and S versus on Al and N atoms in the structures of **11** and **12**, Barron and coworkers suggested that the formation of this type of structure was dominated by the atom-packing schemes as in ionic crystal lattices.[35] The relevant structural features of **6** were consistent with this suggestion.

Despite the variations, the Ga−N bond lengths in the structure of **6** were typical compared to those in other amido and imidogallanes such as (MeGaNC$_6$F$_5$)$_4$ (1.972−2.039 Å),[3] (MeGaN^{t}Bu)$_4$ [1.984(6)−1.999(4) Å)],[4] (MeGaNSiMe$_5$)$_4$ [1.953(4)−1.997(3) Å],[5] and [(C$_6$F$_5$NH)Ga](MesGa)$_3$(μ_3-NC$_6$F$_5$)$_4$ (1.96−2.06 Å).[9] Although no crystallographically imposed symmetry was present in the solid-state structure of **6**, the room-temperature ^{1}H NMR spectroscopy data indicated that in solution a C_{3v} symmetry with the C_3 axis passing through Ga(1) and N(1) exists.

The structure of compound **7** was composed of a cubic Ga$_4$N$_4$ core, and all of the Ga$_2$N$_2$ rings in the cube were planar. The Ga−N bond lengths varied from 1.952(14) to 2.041(16) Å, and the N−Ga−N and Ga−N−Ga bond angles varied from 85.9(7) to 90.6(8)° and from 89.5(5) to 92.4(6)°, respectively. These bond lengths and angles were comparable to those found in other cubic structures as described previously. The 50% disorder as described in the Experimental Section was attributed to the energetic similarity of the two orientations in the crystal packing. This type of disorder was also found in the structure of (PhAlNPh)$_4$.[12]



(a) (RGaNR')$_6$ (b) (RGaNR')$_4$ (c) (RGaNR')$_7$ (d) (RGaNR')$_{10}$ (e) (GaN)$_n$

Figure 3. Relationship among the known organogallium imides, the proposed oligo- and polyimidogallanes, and (GaN)$_n$. Each six-membered ring represents a Ga$_3$N$_3$ unit, and except for those relevant to the discussion, the labelings for Ga and N atoms and the ligands R and R′ are omitted for clarity.

Relationship among the Known Organogallium Imides. Close inspection of the three known organogallium imides (the hexagonal prism, the cubane, and the heptamer) reveals a common structural unit, the six-membered, neutral, cyclic gallazine ring $(RGaNR')_3$. This is easiest to see in Figure 3a which involves face-to-face dimerization of two planar, gallazine rings through formation of six new Ga−N bonds. This dimerization motif allows saturation of the coordination spheres of all of the gallium and nitrogen atoms and should, except for the strain from the four-membered rings, be relatively stable. The cubane clusters can each be viewed as being constructed of one $(RGaNR')_3$ ring that is in a chair geometry (Figure 3b). The unsaturation of the galliums, which all lie above the molecular plane, is satisfied by coordinating the metals to the three electron pairs of one imido ($R'N^{2-}$) ligand. To achieve electroneutrality, this negative charge can be compensated by coordinating a dicationic unit, RGa^{2+}, to the three nitrogens that lie below the molecular plane. This completes the cubane geometry, conveniently saturates the coordination sphere of all the nitrogens, and leads to a stable structure.

Finally, we can see that construction of the core of the cluster, $(RGaNR')_7$, can be viewed as the coupling of two $(RGaNR')_3$ rings, both of which are in the chair conformation (Figure 3c). Note that this coupling produces three new six-membered rings around the circumference of the cylinder instead of the six four-membered rings in compounds **8** and **9**. As in the cubane case, capping the core structure with an $R'N^{2-}$ on one end and an RGa^{2+} on the other saturates the coordination spheres of all the framework atoms. Unlike the cubanes, the lower symmetry of the cluster that is now elongated in one direction produces a polar structure. Figure 3d,e further illustrate how this structural motif can be repeated to produce oligo- or polymeric rods which all have the formula $(RGaNR')_n$. The possible existence of $(RAlNR')_{10}$, the next higher oligomer in the organoaluminum imido series, was discussed by Smith and co-workers.[18] It is noteworthy that this is the identical structural pattern observed for $(GaN)_3$ rings along the crystallographic *c*-axis of the wurtzite form of gallium nitride.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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