Organometallics **1996,** *15,* 5641−5644

Synthesis and Molecular Structure of an Orthometalated Aminogallane, $[Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)]_2$

Steven J. Schauer, Charles H. Lake, Charles L. Watkins,* and
Larry K. Krannich*

*Department of Chemistry, University of Alabama at Birmingham,
Birmingham, Alabama 35294*

Received June 4, 1996[⊗]

Monitoring the thermolysis reaction of Me_3Ga with $HN(CH_2Ph)_2$ in toluene with multinuclear NMR spectroscopy indicates the initial formation of $[Me_2GaN(CH_2Ph)_2]_2$ *via* 1,2-elimination of CH_4 followed by additional 1,2-elimination steps that give the orthometalated gallium dimer $[Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)]_2$ in 65% yield. This is the first reported example of orthometalation of an aromatic ring carbon by gallium. Because $[Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)]_2$ forms prior to the complete conversion of $(PhCH_2)_2NH{\cdot}GaMe_3$ to $[Me_2GaN(CH_2Ph)_2]_2$, thermolysis of a $Me_3Ga/HN(CH_2Ph)_2$ mixture is not a viable route to $[Me_2GaN(CH_2Ph)_2]_2$. Instead it was prepared by a salt elimination reaction. The single-crystal X-ray diffraction analysis establishes the dimeric nature of the orthometalated compound and indicates a structure that is consistent with the NMR chemical shift assignements obtained using both 1-D and 2-D NMR techniques.

Introduction

The synthesis and reactivity of aminogallanes has been of interest because of their use as precursors to gallium nitrides.[1] Traditionally, dimeric aminogallanes have been synthesized either by alkane elimination from the thermolysis of R_3Ga[2−9] with primary or secondary amines or by salt elimination reactions from the reactions of R_2GaCl[10−12] with LiNR′R″. Recently, methods have been described using the reactions of $Me_2GaC_5H_5$[13,14] with primary or secondary amines and of R_3Ga[15] (R = Me, Et) with $Me_3SnNR'R''$ as routes to aminogallanes.

As an extension of our work on the thermolysis of Me_3Al with a homologous series of secondary amines,[16] the thermolysis of Me_3Ga with these amines was investigated to determine the efficacy of this method for the formation of dimeric aminogallanes.[17] Although peaks associated with the formation of $[Me_2GaN(CH_2Ph)_2]_2$ are initially observed in the NMR spectra of the thermolyzed $Me_3Ga/HN(CH_2Ph)_2$ reaction mixture, peaks assignable to three intermediates that ultimately lead to $[Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)]_2$ **(1)** are also observed. Herein we report the synthesis of **1** from the thermolysis of an equimolar mixture of Me_3Ga and $HN(CH_2Ph)_2$ and of $[Me_2GaN(CH_2Ph)_2]_2$ from a salt elimination reaction. The X-ray structure and complete ^1H and ^{13}C NMR chemical shift assignments for this unique orthometallated gallium compound are reported.

Results and Discussion

The $Me_3Ga/NH(CH_2Ph)_2$ reaction system was studied in order to monitor the ease of 1,2-CH_4 elimination and of possible formation of the dimeric aminogallane $[Me_2GaN(CH_2Ph)_2]_2$. This was part of a systematic study of the influence of secondary amine steric bulk on the viability of using thermolysis to prepare a series of aminogallanes. Monitoring the reaction as a function of temperature and time by ^1H and ^{13}C NMR spectroscopy revealed the initial formation of $(PhCH_2)_2NH{\cdot}GaMe_3$ at room temperature. After heating of the mixture for 1 day at 120 °C, the ^1H NMR spectrum indicated the partial conversion to $[Me_2GaN(CH_2Ph)_2]_2$ as a result of 1,2-elimination of CH_4. After continued heating of the mixture over a period of 5 days, spectral data showed further conversion to the dimer and appearance of peaks in the CH_2 and Me_3Ga spectral regions assignable to $Me_2GaN(CH_2Ph)_2Ga(Me_2)N(CH_2Ph)_2{\cdot}GaMe_3$. When the temperature was increased to 135 °C, additional peaks appeared and were assigned to the partially orthometallated species $Me\overline{Ga(C}_6H_4$-

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Neumayer, D. A.; Ekerdt, J. G. *Chem. Mater.* **1996**, *8*, 9.

(2) Coates, G. E. *J. Chem. Soc.* **1951**, 2003.

(3) Sen, B.; White, G. L. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2207.

(4) Storr, A.; Thomas, B. S. *J. Chem. Soc.* **1971**, 3850.

(5) Beachley, O. T., Jr.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* **1981**, *20*, 2423.

(6) Beachley, O. T., Jr.; Noble, M. J.; Churchill, M. R.; Lake, C. H. *Organometallics* **1992**, *11*, 1051.

(7) Hoffmann, G. G.; Fischer, R. *Z. Anorg. Allg. Chem.* **1990**, *590*, 181.

(8) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(9) Park, J. T.; Kim, Y.; Kim, J.; Kim, K.; Kim, Y. *Organometallics* **1992**, *11*, 3320.

(10) Bradley, D. C.; Dawes, H. M.; Hursthouse, M. B.; Smith, L. M.; Thornton-Pett, M. *Polyhedron* **1990**, *9*, 343.

(11) Atwood, D. A.; Jones, R. A.; Cowley, A. H.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1992**, *434*, 143.

(12) Barry, S. T.; Richeson, D. S. *J. Organomet. Chem.* **1996**, *510*, 103.

(13) Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1976.

(14) Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Toomey, L. M. *Organometallics* **1996**, *15*, 3653.

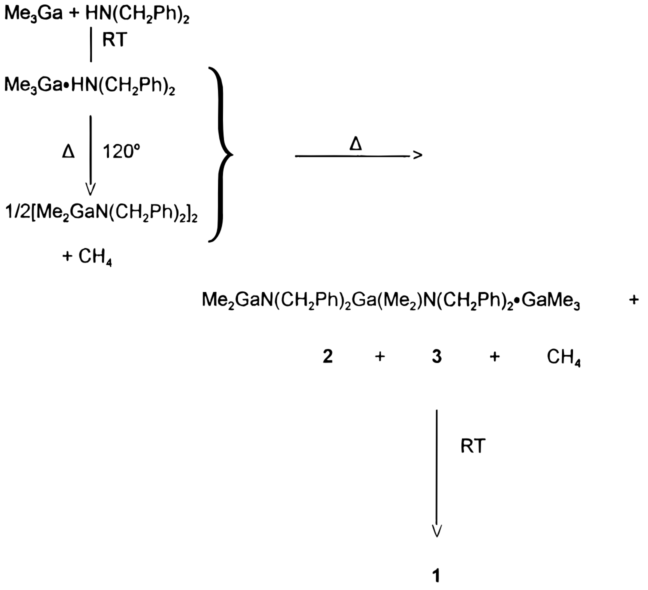
(15) Nutt, W. R.; Murray, K. J.; Gulick, J. M.; Odom, J. D.; Ding, Y.; Lebioda, L. *Organometallics* **1996**, *15*, 1728.

(16) Thomas, C. J.; Krannich, L. K.; Watkins, C. L. *Polyhedron* **1993**, *12*, 389.

(17) Unpublished results.

S0276-7333(96)00438-4 CCC: $12.00

Scheme 1



$CH_2)N(CH_2Ph)Ga(Me)_2N(CH_2Ph)_2•GaMe_3$, **2**. Continued heating at 135 °C results in further conversion of $[Me_2GaN(CH_2Ph)_2]_2$ to **2** and the transformation of **2** to $MeGa(C_6H_4CH_2)N(CH_2Ph)Ga(Me)N(CH_2C_6H_4)(CH_2Ph)•HN(CH_2Ph)_2$, **3**. Increasing the temperature to 140 °C and heating for 8 days resulted in an increase in the intensity of peaks associated with **2** and **3**, a downfield shift in the chemical shift of the original adduct as the Me_3Ga is in exchange with **2**, and the appearance with peaks associated with **1**. Upon cooling of the mixture to room temperature, crystals of **1** formed. Thus, the NMR data support a stepwise elimination of 2 equiv of CH_4 from $[Me_2GaN(CH_2Ph)_2]_2$ which results in the orthometalation of one benzyl moiety on each nitrogen (Scheme 1). $[MeGaN(CH_2C_6H_4)(CH_2Ph)]_2$ **(1)** is obtained in 65% yield after recrystallization. These results also suggest that the thermolysis is not a viable route to $[Me_2GaN(CH_2Ph)_2]_2$ because peaks assignable to **2** and **3** were observed in the NMR spectra before the $(PhCH_2)_2NH•GaMe_3$ adduct was converted to $[Me_2GaN(CH_2Ph)_2]_2$. Instead, it was synthesized in 78% yield by the reaction of Me_2GaCl with $LiN(CH_2Ph)_2$.

An X-ray crystallographic analysis of **1** was performed, and the molecular structure is given in Figures 1 and 2. Details of the data collection are listed in Table 1, and selected interatomic distances and angles are listed in Table 2. Each dimeric molecule **1** crystallized with a center of symmetry, indicating that the four-membered Ga_2N_2 core must possess a planar conformation. This fact coupled with the internal angles Ga(1)–N(2)–Ga(1A) = 89.3(1)° and N(2)–Ga(1)–N(2A) = 90.7(1)° reveals that the four-membered Ga_2N_2 core possesses a slightly distorted square geometry. The bond distances associated with this core are Ga(1)–N(2A) = Ga(1A)–N(2) = 2.018(3) Å and Ga(1)–N(2) = Ga(1A)–N(2A) = 2.045(3) Å (this pair is also associated with the five-membered orthometalated rings) and are within the range of other dimeric aminogallanes (2.01–2.08 Å).[6,8,9,11,12,15] The Ga–N bond pair associated with the orthometalated rings is longer than that of the other set of Ga–N bond distances. This feature may not necessarily be attributed to the presence of the orthometalated ring since other symmetric aminogallane dimers show similar variations.

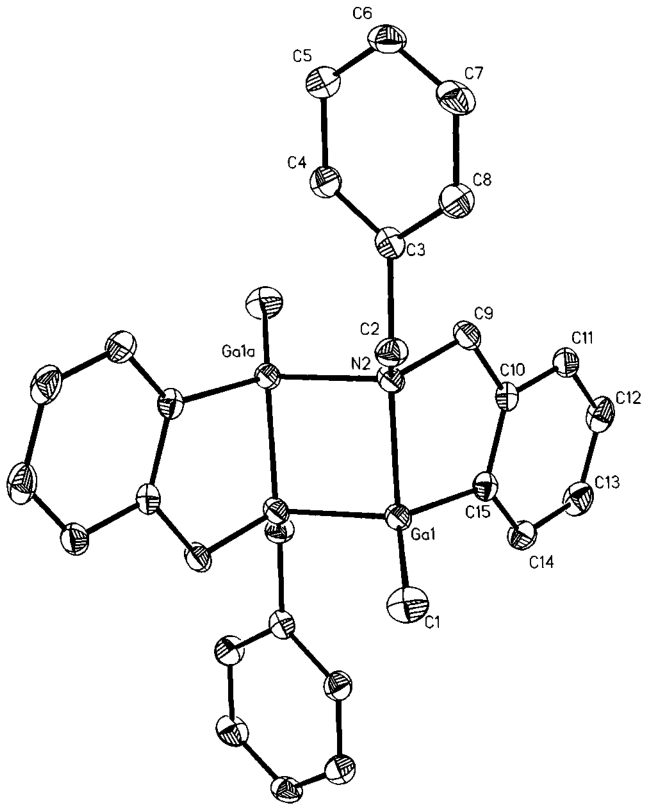


Figure 1. Molecular structure and atom-numbering scheme for $[MeGaN(CH_2C_6H_4)(CH_2Ph)]_2$.

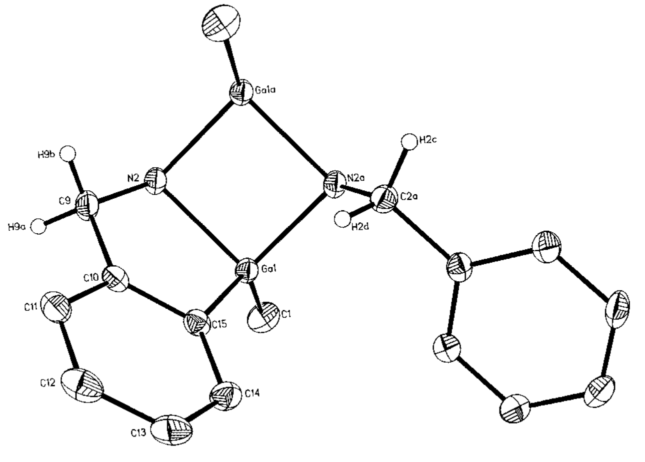


Figure 2. Molecular structure of $[MeGaN(CH_2C_6H_4)(CH_2Ph)]_2$ showing only the ligands on one side of the Ga_2N_2 plane. Calculated hydrogen atoms for the methylenes are included.

The geometry around the gallium atoms is best described as a distorted tetrahedron, with the largest distortions being the interligand angles C(1)–Ga(1)–C(15) = 130.5(2)° and N(2)–Ga(1)–C(15) = 88.4(1)°. These distortions can be attributed to the orthometalation of the benzyl group. The geometry around the bridging nitrogen atom can also be described as a distorted tetrahedron, with angles varying from 89.3(1) to 117.4(2)°. This range in variation is similar to that observed in other aminogallane dimers.[6,8,9,11,12,15] The five-membered orthometalated ring is slightly puckered along the Ga(1)–C(9) axis with an angle of 13.5°

Table 1. Crystallographic Data for $[\mathrm{MeGaN(CH_2C_6H_4)(CH_2Ph)}]_2$

empirical formula	$C_{30}H_{32}Ga_2N_2$
fw	560.0
cryst system	monoclinic
space group	$P2_1/c$
a (Å)	9.0502(15)
b (Å)	19.5400(29)
c (Å)	7.5642(6)
β (deg)	99.548(10)
V (Å)	1319.1(7)
Z	2
D_{calcd} (g cm^{-3})	1.410
abs coeff (mm^{-1})	2.063
F(000)	576
2θ range (deg)	5.0−45.0
scan type	ω-2θ
index ranges	$\pm h, -k, +l$
reflcns collcd	1776
indepdt reflcns	1625 ($R_{\mathrm{int}} = 1.70\%$)
obsd reflcns	1253 ($\lvert F_o\rvert > 6.0\sigma(\lvert F_o\rvert)$)
min/max transm	0.4713/0.5739
largest diff peak e A^{-3}	0.49
largest diff hole, e A^{-3}	−0.32
no. of params refined	155
data-to-parm ratio	10.5:1
final R indices (6σ data)	$R = 3.29$, $R_w = 3.87$
R indices (all data)	$R = 4.21$, $R_w = 5.61$
goodness-of-fit	0.83

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{MeGaN(CH_2C_6H_4)(CH_2Ph)}]_2$

Ga(1)−N(2)	2.045 (3)	Ga(1)−N(2A)	2.018 (3)
N(2)−Ga(1A)	2.018 (3)	Ga(1)−Ga(1A)	2.854 (1)
Ga(1)−C(1)	1.947 (5)	Ga(1)−C(15)	1.971 (4)
N(2)−C(2)	1.468 (5)	N(2)−C(9)	1.487 (5)
C(2)−C(3)	1.519 (5)	C(3)−C(4)	1.382 (5)
C(9)−C(10)	1.503 (6)	C(10)−C(15)	1.398 (5)

N(2)−Ga(1)−C(1)	115.0(2)	N(2)−Ga(1)−C(15)	88.4(1)
C(1)−Ga(1)−C(15)	130.5(2)	N(2)−Ga(1)−N(2A)	90.7(1)
C(1)−Ga(1)−N(2A)	115.1(2)	C(15)−Ga(1)−N(2A)	107.0(1)
Ga(1)−N(2)−C(2)	115.4(2)	Ga(1)−N(2)−C(9)	107.2(2)
C(2)−N(2)−C(9)	110.8(3)	Ga(1)−N(2)−Ga(1A)	89.3(1)
C(2)−N(2)−Ga(1A)	115.1(2)	C(9)−N(2)−Ga(1A)	117.4(2)
N(2)−C(2)−C(3)	116.2(3)	N(2)−C(9)−C(10)	113.1(3)
C(9)−C(10)−C(15)	120.1(4)	Ga(1)−C(15)−C(10)	109.4(3)
Ga(1)−C(15)−C(14)	132.4(3)	C(10)−C(15)−C(14)	118.1(4)

between the planes defined by Ga(1)−C(9)−C(10)−C(15) and Ga(1)−N(2)−C(9). This five-membered ring system intercepts the Ga_2N_2 core at approximately 70.2°.

The ^{1}H NMR spectrum of **1** consists of a single sharp resonances for the Me−Ga groups but two sets of AB quartets for the CH_2 groups indicating that the methylene protons are chemically nonequivalent. The aromatic region indicated two distinct subspectra, one for the metalated benzyl groups and one of the normal benzyl groups. The ^{1}H NMR chemical shift assignments were made using 1-D homonuclear decoupling, 2-D COSY, and 2-D NOESY experiments. The individual aromatic and methylene group subspectra were determined from the homonuclear decoupling and 2-D COSY spectra on the basis of $^3J_{\mathrm{HH}}$ coupling. The final chemical shift assignments were determined by combined use of the 2-D NOESY spectra and the calculated hydrogen positions from the X-ray structure (Figure 2). The ^{13}C NMR spectrum of **1** consisted of one resonance for the Me−Ga groups, two resonances for the methylene carbons, and ten resonances for the aromatic carbons as expected from the symmetry of the structure. The ^{13}C NMR chemical shift assignments were carried out using 2-D $^{13}C\{^1H\}$ heteronuclear correlated $^1J_{\mathrm{CH}}$ and $^{2,3}J_{\mathrm{CH}}$ spectroscopies for the protonated and quaternary carbons, respectively.

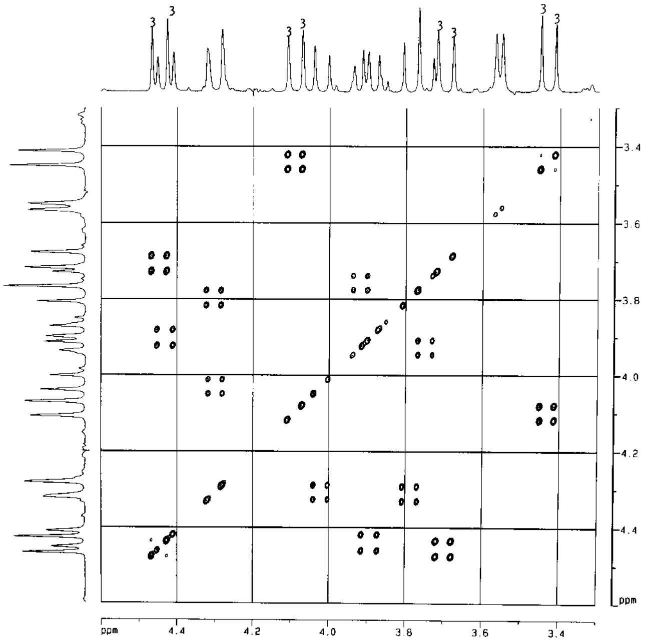


Figure 3. ^{1}H COSY NMR spectrum of the CH_2 region of the 140 °C reaction mixture. The eight marked resonances (3) are assigned to **3**. Overlapping resonances occur at 4.32, 4.28, and 3.77 ppm. The doublet at 3.55 ppm is assigned to the exchanged averaged adduct, $(PhCH_2)_2NH{\cdot}GaMe_3$.

The CH_2 portion of the ^{1}H NMR spectrum of the reaction mixture, after being heated to 140 °C, shows 16 resonances for **2** and 8 resonances for **3**. Analysis of an ^{1}H COSY NMR spectrum of the mixture (Figure 3) for this region leads to an assignment of four nonequivalent CH_2 groups for **2** [4.43 and 3.89 ppm, $\Delta\delta = 0.54$ ppm; 4.30 and 3.79 ppm, $\Delta\delta = 0.51$ ppm; 4.30 and 4.02 ppm, $\Delta\delta = 0.28$ ppm; 3.92 and 3.75 ppm, $\Delta\delta = 0.17$ ppm]. The ^{1}H NMR spectrum of the Me−Ga region also supports the proposed structure of **2** in that there are three resonances of 1:1:1 intensity assignable to **2**. The eight resonances for **3** in the CH_2 region of the ^{1}H NMR spectrum are assigned to two nonequivalent CH_2 groups [4.45 and 3.70 ppm, $\Delta\delta = 0.75$ ppm; 4.09 and 3.43 ppm, $\Delta\delta = 0.66$ ppm]. The observed spectral pattern is very similar to that for **1**, with the $\Delta\delta$ values being the same and the eight resonances in **3** being displaced upfield, about 0.13 ppm. The Me−Ga region shows only one resonance each for **1** (0.18 ppm) and **3** (0.054 ppm).

Compound **1** represents, to our knowledge, the first reported example of orthometalation of an aromatic ring carbon by gallium. Similar orthometalation reactions have been reported for organoaluminum compounds,[18−20] as well as for aminoalanes.[21−23] Of related interest are the cyclometalation reactions that involve the metalation of alkyl groups at the *ortho*-position on an aromatic ring. These have been reported for several aminoalanes[24,25] and aminogallanes.[8]

---

[18] Schmidbaur, H.; Wolfsberger, W. *J. Organomet. Chem.* **1969**, *16*, 188.

[19] Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 1501.

[20] Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2976.

[21] Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257.

[22] Lee, B.; Pennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1991**, *190*, 173.

[23] Hoberg, H. *Liebigs Ann. Chem.* **1971**, *746*, 86.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for the synthesis and manipulation of all compounds using a high-vacuum line in conjunction with an inert-atmosphere drybox (Vacuum Atmospheres HE-43 DriLab). Toluene was distilled under an atmosphere of nitrogen over calcium hydride. $HN(CH_2Ph)_2$ (Aldrich) was dried over KOH and distilled under vacuum prior to use. Me_3Ga was obtained as a gift from Morton Advanced Materials, Danvers, MA. Benzene-d_6 (Isotec) was stored over molecular sieves.

^{1}H and ^{13}C NMR spectral data were collected on a Bruker DRX 400 NMR spectrometer using a 0.2 M C_6D_6 solution of the compound and were referenced with respect to the solvent. Hydrogen and carbon atoms are labeled according to Figure 1. 2-D ^{1}H−^{1}H COSY, ^{1}H−^{1}H NOESY, ^{13}C{^{1}H} HETCOR, and long-range HETCOR NMR spectra were obtained using standard Bruker programs. The NOESY spectra were obtained as a function of mixing time to eliminate any transferred NOE effects. FTIR data were collected using a Bruker Vector 22 FT spectrometer using samples prepared as Kel-F (halocarbon) and Nujol mulls on KBr plates. Elemental analysis was performed by E+R Microanalytical laboratory, Inc., Corona, NY.

Synthesis of $[\mathrm{Me}\overline{\mathrm{GaN(CH_2C}}\mathrm{_6H_4)(CH_2Ph)}]_2$. A 2.004 g (17.5 mmol) amount of Me_3Ga, 3.444 g (17.5 mmol) of $HN(CH_2Ph)_2$, and 30 mL of toluene were mixed at room temperature. The mixture was heated to reflux, and the progress of the reaction was monitored on aliquots over a 5 day period using ^{1}H and ^{13}C NMR spectroscopy. **1** was isolated from the reaction solution in 65% yield by recrystallization at −15 °C. Mp: 193−195 °C. ^{1}H NMR: δ 0.18 (s, 3 H, H1), 3.56 (d, 1 H, J = 15.2 Hz, H2c), 3.83 (d, 1 H, J = 16.2 Hz, H9a), 4.22 (d, 1 H, J = 15.2 Hz, H2d), 4.58 (d, 1 H, J = 16.2 Hz, H9b), 7.07 (d, 1 H, H11), 7.16 (t, 1 H, H13), 7.25 (m, 1 H, H6), 7.26 (m, 1 H, H12), 7.32 (m, 2 H, H4 and H8), 7.35 (m, 2 H, H5 and H7), 7.66 (d, 1 H, H14). ^{13}C NMR: δ −10.8 (C1), 58.2 (C2), 59.6 (C9), 124.2 (C11), 126.6 (C13), 127.5 (C6), 127.8 (C4 and C8), 128.6 (C12), 128.8 (C5 and C7), 135.5 (C14), 140.6 (C3), 143.9 (C15), 149.2 (C10). IR (cm^{-1}): 3040 (m), 2919 (vs), 2840 (s), 1485 (w), 1443 (m), 1428 (m), 1352 (m), 1299 (w), 1251 (w), 1231 (w), 1195 (m), 1150 (w), 1089 (s), 1069 (s), 1045 (m), 1020 (m), 956 (w), 931 (m), 886 (w), 822 (w), 726 (s), 682 (s), 660 (m). Anal. Calcd (found) for $C_{30}H_{32}Ga_2N_2$: C, 64.34 (64.68); H, 5.76 (5.92); N, 5.00 (4.98).

Synthesis of $[Me_2GaN(CH_2Ph)_2]_2$. A solution of Me_2GaCl (2.00 g, 14.8 mmol) in hexane (20 mL) was slowly added to a 50 mL hexane solution of $LiN(CH_2Ph)_2$ (14.8 mmol, previously prepared from the reaction of $H(NCH_2Ph)_2$ and LiBu^n) at −40 °C. LiCl precipitated from the solution upon warming the mixture to room temperature. After the mixture was stirred overnight at room temperature, the solution was decanted and the remaining solids were washed with hexane. The hexane was then removed *in vacuo*, leaving a white solid, which was purified by recrystallization from toluene at −15 °C. A 78% yield was obtained. Mp: 135−137 °C. ^{1}H NMR (δ): 0.21 (s, 12 H, $GaCH_3$); 4.15 (s, 8 H, NCH_2); 6.94 (m, 8H, H-2), 7.01 (m, 4H, H-4), 7.03 (m, 8H, H-3) ($NCH_2C_6H_5$). ^{13}C NMR (δ): −5.91 ($GaCH_3$), 54.35 (NCH_2), 127.03, C-4; 128.06, C-3; 129.14, C-2; 137.64, C-1 ($NCH_2C_6H_5$). IR (cm^{-1}): 3086 (m), 3060 (m), 3028 (s), 2958 (s), 2912 (s), 2861 (m), 1306 (w), 1209 (m), 1153 (w), 1086 (w), 1064 (m), 1032 (w), 1018 (w), 964 (w), 952 (w), 907 (m), 882 (m), 738 (vs), 697 (s), 665 (w), 813 (m), 571 (m), 530 (w), 512 (w), 492 (w), 474 (m). Cryoscopic molecular weight: calcd, M_r 592.11; obsd M_r (molality), 563 (0.095). Anal. Calcd (found) for $C_{32}H_{40}Ga_2N_2$: C, 64.91 (63.74); H, 6.81 (6.77); N, 4.73 (4.78).

X-ray Data Collection and Structure Refinement. A crystal of **1** (0.30 × 0.25 × 0.25 mm) was sealed into a thin-walled capillary under anerobic conditions. Data were collected at 296 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Details of the data collection are listed in Table 1. The structure was solved by a Patterson Synthesis. All crystallographic calculations were accomplished with the Siemens SHELXTL-PC program package.[26] All positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with the appropriate geometry. Hydrogen atoms were placed in calculated positions with the appropriate geometry. The U_{eq} of each hydrogen atom was set equal to that of the carbon atom to which it was bound.

Supporting Information Available: Tables listing positional and thermal parameters and complete bond distances and angles and ^{1}H and ^{13}C 1-D and 2-D NMR spectra (11 pages). Ordering information is given on any current masthead page.

OM9604381

---

(24) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 245.

(25) Dillingham, M. D. B.; Hill, J. B.; Lee, B.; Schauer, S. J.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1993**, *28*, 337.

(26) *Siemens SHELXTL-PC Manual*, Release 4.1; Siemens Analytical Instruments: Madison, WI, 1990.