Syntheses and Crystal Structures of Intramolecularly Stabilized Organogallium Compounds Containing an *o*-Carboranyl C,N-Chelating Ligand System

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Received December 23, 1998

The reaction of $HCab^N$ (**1**; $HCab^N$ = *closo*-1-[(dimethylamino)methyl]-*o*-carborane) with $GaCl_3$ yielded the simple Lewis acid−base adduct complex $HCab^N\cdot GaCl_3$ (**3**). The reaction of $LiCab^N$ (**2**; $LiCab^N$ = *closo*-1-[(dimethylamino)methyl]-2-lithio-*o*-carborane) with $GaCl_3$ in a 1:1 ratio produced the four-coordinated metallacyclic organogallium compound Cab^NGaCl_2 (**4**), in which the gallium atom was stabilized via intramolecular C,N-coordination. A similar intramolecularly base-stabilized four-coordinated gallane, Cab^NGaMe_2 (**5**), was synthesized from the reaction of **2** with Me_2GaCl. Complex **5** was also formed upon reaction of the complex **4** with 2 equiv of LiMe. The X-ray structural studies of complexes **4** and **5** indicate that the gallium atom is located in the center of a distorted tetrahedron. The Lewis acid **4** added the base pyridine to yield the adduct $Cab^NGaCl_2\cdot NC_5H_5$ (**6**). The trigonal-bipyramidal coordination of the metal center was proven by the single-crystal X-ray determination of the complex **6**. The reaction of $LiCab^N$ (**2**) with $GaCl_3$ in a 2:1 ratio afforded the bis[((dimethylamino)methyl)-*o*-carboranyl]gallium compound $(Cab^N)_2GaCl$ (**7**). The NMR spectra revealed that intramolecular Ga−N coordination occurs in solution, resulting in a pentacoordinate $(Cab^N)_2GaCl$ structure. Crystals of $(Cab^N)_2GaCl(H_2O)$ **(8)** were obtained while recrystallizing **7** in toluene over a period of several days. X-ray analysis of this complex **8** provides support for the assignment of the water-coordinated bis[((dimethylamino)methyl)-*o*-carboranyl]gallane structure.

Introduction

In recent years, the coordination behavior of organometallic compounds containing the potentially bidentate ligand 2-[(dimethylamino)methyl]phenyl (HAr^N) has been the focus of extensive studies.[1] The corresponding lithium compound, $LiAr^N$,[2] first reported in 1963, is the common starting material for the preparation of new complexes. Although the HAr^N ligand system has been used extensively during the past decade as an intramolecular coordinating ligand for many different metals,[3] many subclasses of these interesting compounds remain virtually unexplored. One such subclass, namely $HCab^N$ (**1**; $HCab^N$ = *closo*-1-[(dimethylamino)methyl]-*o*-carborane) metal complexes, has received little attention.

o-Carborane has attracted some interest due to its ease of preparation and derivatization, thermal stability, and steric bulk.[4] It was therefore of interest to investigate the possibility of synthesizing such intramolecularly coordinated complexes using the $HCab^N$ (**1**) system. In this respect, we have started investigating the synthesis of intramolecularly coordinated group 13 metal complexes bearing a bulky *o*-carborane unit that

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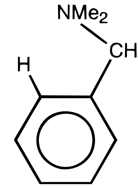
10.1021/om981041v CCC: $18.00

Table 1. NMR Spectroscopic Data for Compounds 1 and 3−8

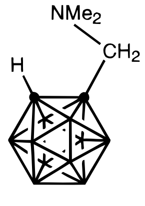
compd	NMR (δ)[a]		
	^{1}H	^{13}C	^{11}B
1	1.663 (s, 6H, N−CH_3)	46.731 (s, 2C, N−CH_3)	−13.43 (d, 4B, J_{BH} = 120 Hz)
	2.263 (s, 2H, N−CH_2)	58.774 (s, 1C, $CHCB_{10}H_{10}$)	−11.87 (d, 2B, J_{BH} = 110 Hz)
	3.256 (s, 1H, H−C_{cab})	63.233 (s, 1C, N−CH_2)	−9.27 (d, 2B, J_{BH} = 160 Hz)
		75.753 (s, 1C, $CHCB_{10}H_{10}$)	−5.48 (d, 1B, J_{BH} = 150 Hz)
			−3.33 (d, 1B, J_{BH} = 140 Hz)
3	2.196 (N(CH_3)$_2$)	61.729 (N(CH_3)$_2$)	−13.04 (d, 6B, J_{BH} = 115 Hz)
	3.191 (NCH_2)	62.770 (NCH_2)	−9.40 (d, 2B, J_{BH} = 155 Hz)
	6.098 (H−C_{cab})		−3.96 (d, 1B, J_{BH} = 115 Hz)
			−2.52 (d, 1B, J_{BH} = 150 Hz)
4	1.623 (N(CH_3)$_2$)	52.061 (N(CH_3)$_2$)	−12.96 (d, 2B, J_{BH} = 130 Hz)
	2.210 (NCH_2)	66.530 (NCH_2)	−11.75 (d, 2B, J_{BH} = 140 Hz)
		72.672 (C_2B_{10} unit)	−11.14 (d, 1B, J_{BH} = 125 Hz)
			−9.70 (d, 1B, J_{BH} = 180 Hz)
			−5.79 (d, 2B, J_{BH} = 150 Hz)
			−4.08 (d, 1B, J_{BH} = 175 Hz)
			−2.32 (d, 1B, J_{BH} = 150 Hz)
5	0.539 (Ga(CH_3)$_2$)	10.876 (Ga(CH_3)$_2$)	−12.98 (d, 6B, J_{BH} = 135 Hz)
	1.529 (N(CH_3)$_2$)	50.033 (N(CH_3)$_2$)	−10.02 (d, 2B, J_{BH} = 170 Hz)
	2.101 (NCH_2)	63.299 (NCH_2)	−4.47 (d, 1B, J_{BH} = 140 Hz)
		73.843 (C_2B_{10} unit)	−3.20 (d, 1B, J_{BH} = 155 Hz)
6	1.931 (N(CH_3)$_2$)	50.870 (N(CH_3)$_2$)	−11.62 (d, 4B, J_{BH} = 150 Hz)
	2.528 (NCH_2)	64.835 (NCH_2)	−10.46 (d, 2B, J_{BH} = 135 Hz)
	6.354 (t, NC_5H_5)	124.282 (NC_5H_5)	−7.46 (d, 2B, J_{BH} = 150 Hz)
	6.656 (t, NC_5H_5)	139.324 (NC_5H_5)	−4.56 (d, 1B, J_{BH} = 160 Hz)
	8.584 (d, NC_5H_5)	148.389 (NC_5H_5)	−2.01 (d, 1B, J_{BH} = 160 Hz)
7	1.920 (N(CH_3)$_2$)	50.210 (N(CH_3)$_2$)	−11.30 (d, 1B, J_{BH} = 145 Hz)
	2.200 (N(CH_3)$_2$)	62.196 (NCH_2)	−9.43 (d, 1B, J_{BH} = 140 Hz)
	2.275 (NCH_2, J_{gem} = 10 Hz)		−7.87 (d, 2B, J_{BH} = 145 Hz)
	3.520 (NCH_2, J_{gem} = 10 Hz)		−5.39 (d, 2B, J_{BH} = 140 Hz)
			−4.23 (d, 2B, J_{BH} = 110 Hz)
			−2.29 (d, 1B, J_{BH} = 160 Hz)
			−1.02 (d, 1B, J_{BH} = 130 Hz)
8	1.862 (N(CH_3)$_2$)	46.606 (N(CH_3)$_2$)	−7.48 (d, 4B, J_{BH} = 110 Hz)
	2.061 (NCH_2)	63.264 (NCH_2)	−6.68 (d, 4B, J_{BH} = 135 Hz)
	2.665 (NCH_2)	65.173 (NCH_2)	−5.01 (d, 1B, J_{BH} = 145 Hz)
	6.862 (H_2O)	77.057 (C_2B_{10} unit)	−1.84 (d, 1B, J_{BH} = 140 Hz)

[a] All NMR spectra were recorded in C_6D_6 at room temperature.

might potentially stabilize the desired Lewis acidic metal moiety. Thus, we now report the detailed synthesis and complete characterization of intramolecularly coordinated gallium complexes. Methods for preparing this type of compound are generally based on the addition of [(aminomethyl)-*o*-carboranyl]lithium to a suitable gallium halide complex. The synthesis, properties, and structural studies of novel intramolecularly coordinated gallium complexes are reported in this paper. The appropriate synthetic and spectroscopic characteristics of the corresponding gallium derivatives will be included. Moreover, the reactivity of these compounds toward a Lewis base will be discussed.



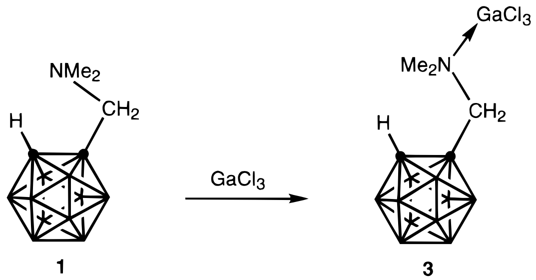
HAr^{N}



HCab^{N} **1**

Results and Discussion

Preparation of HCab^{N}·$GaCl_3$ (3). The amine moiety of HCab^{N} (**1**) is a strong Lewis base which rapidly reacts at room temperature with simple electron-deficient gallium chloride, $GaCl_3$, in a 1:1 stoichiometry to form the corresponding adduct HCab^{N}·$GaCl_3$ (**3**).



(1)

Compound **3** has been isolated as white, transparent crystals. The complex is both air- and moisture-sensitive in the solid state, decomposing over a period of seconds upon exposure to air. They are moderately soluble in pentane, benzene, and toluene. The ^{1}H, ^{11}B, and ^{13}C NMR spectral data for the adduct **3** are presented in the Experimental Section and in Table 1. The proton resonance for the NMe_2 group is a singlet and is shifted downfield with respect to that of the free ligand. The CH_2 protons also resonate as a singlet and are shifted downfield in comparison to that of the free ligand with a pronounced Δδ 0.93 ppm observed for **3**.

The ORTEP diagram of HCab^{N}·$GaCl_3$ (**3**) is presented in Figure 1. Crystallographic data and processing parameters are given in Table 2, and selected bond

Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 3−6 and 8·$C_6H_5CH_3$

	3	**4**	**5**	**6**	**8**·$C_6H_5CH_3$
formula	$B_{10}C_5H_{19}Cl_3NGa$	$B_{10}C_5H_{18}Cl_2NGa$	$B_{10}C_7H_{24}NGa$	$B_{10}C_{10}H_{23}Cl_2N_2Ga$	$B_{20}C_{17}H_{46}ClN_2GaO$
fw	377.38	340.92	300.09	420.02	615.93
cryst class	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$Pca2_1$ (No. 29)	*Pnma* (No. 62)	$Cmc2_1$ (No. 36)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	4	4	4	4	4
cell constants					
a, Å	11.1330(3)	18.5119(13)	11.9226(7)	9.8879(4)	14.6650(1)
b, Å	11.6650(3)	11.7106(6)	8.9597(5)	7.8913(4)	16.0320(1)
c, Å	13.1140(3)	7.1343(9)	14.6973(8)	26.3511(11)	14.8320(2)
V, Å^3	1703.07(7)	1546.6(2)	1570.01(15)	2031.80(16)	3282.42(7)
α, deg					
β, deg				98.823(3)	109.73(6)
γ, deg					
μ, cm^{-1}	2.064	4.195	3.455	1.612	0.939
cryst size, mm	0.30 × 0.30 × 0.45	0.10 × 0.10 × 0.15	0.10 × 0.20 × 0.25	0.15 × 0.15 × 0.20	0.10 × 0.10 × 0.10
D_{calcd}, g/cm^3	1.472	1.464	1.270	1.373	1.246
F(000)	752	1360	1232	848	1272
radiation	Mo Kα (λ = 0.7170 Å)	Mo Kα (λ = 0.7170 Å)	Mo Kα (λ = 0.7170 Å)	Mo Kα (λ = 0.7170 Å)	Mo Kα (λ = 0.7170 Å)
θ range, deg	1.75−24.80	2.20−25.96	2.77−24.93	1.56−25.97	1.95−24.76
h,*k*,*l* collected	±13, +13, ±15	+22, +14, +8	+14, +10, +17	+12, +9, ±32	+17, ±18, +16
no. of rflns measd	1704	1629	829	4297	5569
no. of unique rflns	1538	1593	755	3982	5512
no. of rflns used in refinement ($I > 2\sigma(I)$)	1538	1593	755	3982	5512
no. of params	254	124	105	243	564
data/param ratio	6.06	12.85	7.19	16.39	9.77
R1[a]	0.0436	0.0543	0.0414	0.0735	0.0679
wR2[b]	0.1061	0.1250	0.1046	0.1611	0.1563
GOF	1.164	0.886	0.954	0.943	1.154

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma F_o^2$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F_o^2$).

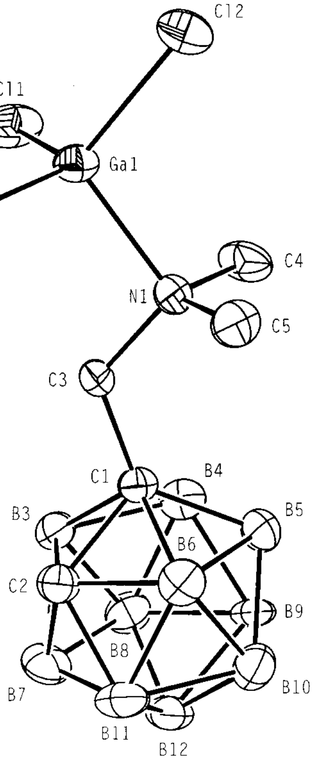
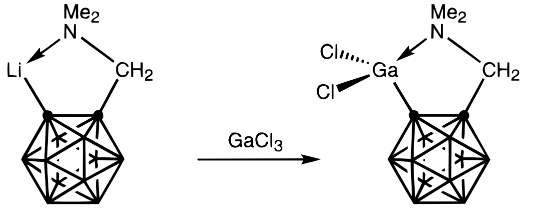


Figure 1. Molecular structure of HCab^N·$GaCl_3$ (**3**). The thermal ellipsoids are drawn at the 30% probability level.

distances and bond angles are presented in Table 3. The molecular geometry is C_s, in which the Cl_3Ga group is staggered with respect to the two methyl groups on the N(1) atom. The coordination geometry around the gallium is approximately tetrahedral; however, there is a wide scatter of angles: N(1)−Ga(1)−Cl(3) = 105.49(16)°, N(1)−Ga(1)−Cl(1) = 105.24(18)°, Cl(3)−Ga(1)−Cl(1) = 114.40(10)°, N(1)−Ga(1)−Cl(2) = 105.73(17)°, Cl(3)−Ga(1)−Cl(2) = 113.88(8)°, Cl(1)−Ga(1)−Cl(2) = 111.15(9)°. The Ga(1)−N(1) distance of 2.050(7) Å is similar to that of other nitrogen adducts[5] and greater than the Ga−N distance observed in amido complexes.[6]

Synthesis of Cab^{N}GaCl$_2$ (4). The intramolecularly stabilized tetracoordinated (*o*-carboranyl)gallium compound Cab^{N}GaCl$_2$ (**4**) was synthesized in toluene from the gallium trichloride and the [(aminomethyl)-*o*-carboranyl]lithium compound LiCab^N (**2**). The stabilization



2 **4** (2)

in compound **4** is due to the formation of a five-membered chelate ring. Compound **4** is moderately

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Table 3. Selected Interatomic Distances and Angles in 3−6 and 8·$C_6H_5CH_3$

		Bond Distances (Å)			
		Compound **3**			
Ga(1)−N(1)	2.050(7)	Ga(1)−Cl(3)	2.140(2)	Ga(1)−Cl(1)	2.151(2)
Ga(1)−Cl(2)	2.161(2)	N(1)−C(3)	1.488(8)	N(1)−C(4)	1.491(9)
N(1)−C(5)	1.497(8)	C(1)−C(3)	1.543(8)	C(1)−C(2)	1.645(9)
		Compound **4**			
Ga(1)−C(1)	1.96(1)	Ga(1)−N(1)	2.071(9)	Ga(1)−Cl(1)*	2.143(2)
Ga(1)−Cl(1)	2.143(2)	N(1)−C(4)*	1.487(8)	N(1)−C(4)	1.487(8)
N(1)−C(3)	1.50(1)	C(1)−C(2)	1.65(1)	C(2)−C(3)	1.54(1)
		Compound **5**			
Ga(1)−C(5)*	1.956(9)	Ga(1)−C(5)	1.956(9)	Ga(1)−C(1)	2.020(8)
Ga(1)−N(1)	2.168(7)	N(1)−C(4)*	1.483(8)	N(1)−C(4)	1.483(8)
N(1)−C(3)	1.50(1)	C(1)−C(2)	1.66(1)	C(2)−C(3)	1.48(1)
		Compound **6**			
Ga(1)−C(1)	2.003(9)	Ga(1)−N(2)	2.083(9)	Ga(1)−Cl(2)	2.162(3)
Ga(1)−Cl(1)	2.168(3)	N(1)−C(3)	1.41(1)	N(1)−C(5)	1.43(1)
N(1)−C(4)	1.46(2)	N(2)−C(20)	1.33(1)	N(2)−C(16)	1.34(1)
C(1)−C(2)	1.66(1)				
		Compound **8**·$C_6H_5CH_3$			
Ga(1)−O(1)	1.840(4)	Ga(1)−C(1)	2.012(5)	Ga(1)−C(1′)	2.019(5)
N(1′)−C(3′)	1.476(7)	Ga(1)−Cl(1)	2.212(1)	N(1′)−C(4′)	1.489(8)
N(1)−C(3)	1.473(7)	N(1′)−C(5′)	1.492(7)	N(1)−C(4)	1.485(8)
C(1′)−C(2′)	1.690(7)	N(1)−C(5)	1.483(7)	C(1)−C(2)	1.692(7)
C(2′)−C(3′)	1.540(7)	C(2)−C(3)	1.532(7)	O(1)−H(1a)	1.12
O(1)−H(1b)	1.04	N(1)−H(1a)	1.75	N(1′)−H(1b)	1.64
		Bond Angles (deg)			
		Compound **3**			
N(1)−Ga(1)−Cl(3)	105.5(2)	N(1)−Ga(1)−Cl(1)	105.2(2)	Cl(3)−Ga(1)−Cl(1)	114.4(1)
N(1)−Ga(1)−Cl(2)	105.7(2)	Cl(3)−Ga(1)−Cl(2)	113.88(8)	Cl(1)−Ga(1)−Cl(2)	111.15(9)
C(3)−N(1)−C(4)	113.4(6)	C(3)−N(1)−C(5)	113.6(5)	C(4)−N(1)−C(5)	110.8(6)
C(3)−N(1)−Ga(1)	104.1(4)	C(4)−N(1)−Ga(1)	107.1(4)	C(5)−N(1)−Ga(1)	107.2(5)
C(3)−C(1)−C(2)	113.1(5)				
		Compound **4**			
C(1)−Ga(1)−N(1)	91.9(4)	C(1)−Ga(1)−Cl(1)*	115.1(1)	N(1)−Ga(1)−Cl(1)*	110.4(1)
C(1)−Ga(1)−Cl(1)	115.1(1)	N(1)−Ga(1)−Cl(1)	110.4(1)	Cl(1)*−Ga(1)−Cl(1)	112.1(1)
C(4)*−N(1)−C(4)	108.2(8)	C(4)*−N(1)−C(3)	109.8(6)	C(4)−N(1)−C(3)	109.8(6)
C(4)*−N(1)−Ga(1)	109.3(5)	C(4)−N(1)−Ga(1)	109.3(5)	C(3)−N(1)−Ga(1)	110.4(6)
C(2)−C(1)−Ga(1)	107.1(6)	C(3)−C(2)−C(1)	116.2(8)	N(1)−C(3)−C(2)	114.5(9)
		Compound **5**			
C(5)*−Ga(1)−C(5)	122.4(6)	C(5)*−Ga(1)−C(1)	113.5(3)	C(5)−Ga(1)−C(1)	113.5(3)
C(5)*−Ga(1)−N(1)	107.1(3)	C(5)−Ga(1)−N(1)	107.1(3)	C(1)−Ga(1)−N(1)	86.4(3)
C(4)*−N(1)−C(4)	109.0(9)	C(4)*−N(1)−C(3)	108.9(5)	C(4)−N(1)−C(3)	108.9(5)
C(4)*−N(1)−Ga(1)	109.1(4)	C(4)−N(1)−Ga(1)	109.1(4)	C(3)−N(1)−Ga(1)	111.7(5)
C(2)−C(1)−Ga(1)	109.8(5)	C(3)−C(2)−C(1)	116.7(7)		
		Compound **6**			
C(1)−Ga(1)−N(2)	97.9(4)	C(1)−Ga(1)−Cl(2)	119.0(3)	N(2)−Ga(1)−Cl(2)	96.1(3)
C(1)−Ga(1)−Cl(1)	121.3(3)	N(2)−Ga(1)−Cl(1)	95.4(3)	Cl(2)−Ga(1)−Cl(1)	115.9(2)
C(3)−N(1)−C(5)	111(1)	C(3)−N(1)−C(4)	108(1)	C(5)−N(1)−C(4)	106(1)
C(20)−N(2)−C(16)	115(1)	C(2)−C(1)−Ga(1)	117.3(6)	C(3)−C(2)−C(1)	117.9(9)
N(1)−C(3)−C(2)	117.8(9)				
		Compound **8**·$C_6H_5CH_3$			
O(1)−Ga(1)−C(1)	105.2(2)	O(1)−Ga(1)−C(1′)	106.2(2)	C(3′)−N(1′)−C(4′)	112.9(5)
C(1)−Ga(1)−C(1′)	122.3(2)	C(3′)−N(1′)−C(5′)	107.9(4)	O(1)−Ga(1)−Cl(1)	106.9(2)
C(4′)−N(1′)−C(5′)	109.3(5)	C(1)−Ga(1)−Cl(1)	109.3(1)	C(2′)−C(1′)−B(5′)	108.6(4)
C(1′)−Ga(1)−Cl(1)	106.2(1)	C(3)−N(1)−C(4)	112.0(5)	C(3)−N(1)−C(5)	108.2(5)
C(4)−N(1)−C(5)	109.8(5)	C(2′)−C(1′)−Ga(1)	118.1(3)	C(2)−C(1)−Ga(1)	118.0(3)
C(3′)−C(2′)−C(1′)	119.0(4)	C(3)−C(2)−C(1)	119.5(4)	N(1′)−C(3′)−C(2′)	118.2(4)
N(1)−C(3)−C(2)	116.8(4)				

stable in air and shows only a slow decomposition when in contact with moisture. Compound **4** was purified by low-temperature recrystallization in toluene (colorless crystals, mp 220−222 °C). A satisfactory elemental analysis was obtained for compound **4**, and the ^{1}H, ^{11}B, and ^{13}C NMR spectral data were consistent with the presence of the bidentate (aminomethyl)-*o*-carboranyl ligand **1** (see Experimental Section).

The molecular structure (Figure 2) of **4** has been determined by X-ray diffraction. Selected interatomic distances and angles are listed in Table 3. The molecule lies on a crystallographic reflection plane and thus contains a rigorously imposed reflection symmetry. The atoms Ga(1), N(1), and C(3) and the cage atoms C(1), C(2), B(7), and B(8) lie on the symmetry plane. The amine group of the *o*-carboranyl ligand is coordinated to the gallium metal in complex **4**, and the resulting five-membered chelate ring N(1)−Ga(1)−C(1)−C(2)−C(3) is formed. The Ga(1)Cl(1)Cl(1)*C(1) moiety is close to planarity, with gallium 0.509(5) Å above the Cl(1)-Cl(1)*C(1) plane. The angles around gallium do not deviate much from tetrahedral, with the exception of

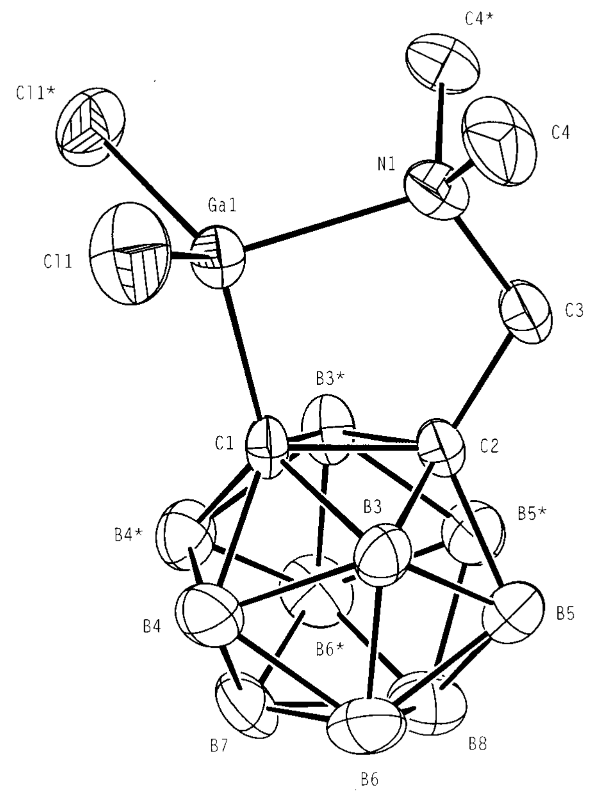
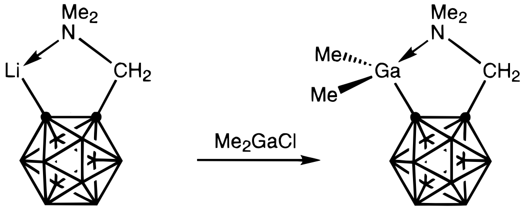


Figure 2. Molecular structure of Cab^{N}GaCl$_2$ (**4**). The thermal ellipsoids are drawn at the 30% probability level.

the C(1)–Ga(1)–N(1) angle within the five-membered ring, which is 91.9(4)°. This also influences the geometry around the *o*-carborane cage; the C(2)–C(1)–Ga(1) angle within the five-membered ring is smaller (107.1(6)°) than the expected 120°. The Ga(1)–N(1) distance in **4** (2.071(9) Å) is similar to that in the corresponding amine-ligated aryl system [*o*-(Me_2NCH_2)C_6H_4]$GaCl_2$ (2.071(2) Å).[7] The Ga(1)–N(1) distance of 2.071(9) Å is in agreement with the corresponding values observed in adducts formed between X_3Ga and NR_3;[5] all are longer than the sum of the covalent radii for gallium and nitrogen (1.95 Å).[8] The Ga(1)–C(1) distance (1.96(1) Å) is similar to that in **3** and also lies within the range reported for other organogallium compounds.[7] The Ga–Cl distance of 2.1434(19) Å is in the range of typical covalent Ga–Cl bond distances (2.10–2.20 Å).[7]

Synthesis of Cab^{N}GaMe$_2$ (5). The dimethylated compound Cab^{N}GaMe$_2$ (**5**) was obtained as a pure product from the reaction of dimethylgallium chloride with the [(aminomethyl)-*o*-carboranyl]lithium compound LiCab^N (**2**). This compound is also formed as colorless crystals, but they have a significant vapor pressure at room temperature. Complex **5** is stable in an inert-gas environment and shows slow decomposition when in contact with air. It is readily soluble in organic solvents, such as ether, hydrocarbons, and aromatic solvents. The ^{1}H, ^{11}B, and ^{13}C NMR spectra show the expected pattern and shifts.



2 **5** (3)

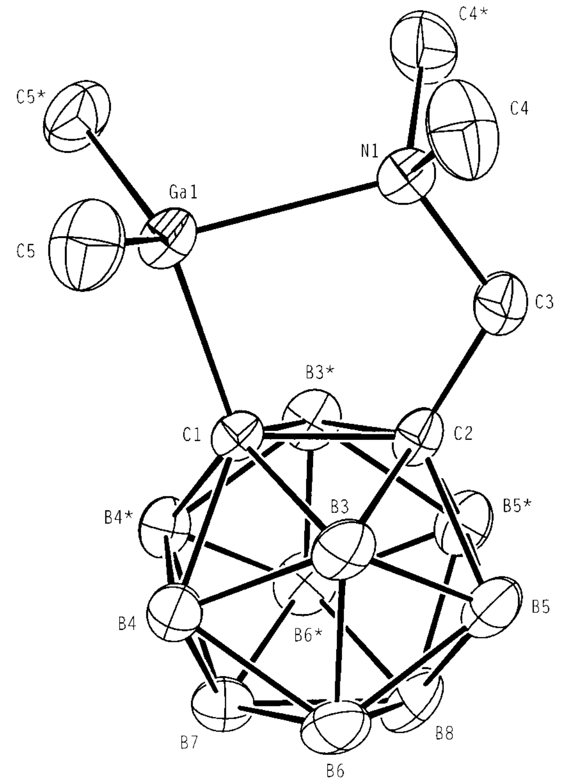


Figure 3. Molecular structure of Cab^{N}GaMe$_2$ (**5**). The thermal ellipsoids are drawn at the 30% probability level.

The molecular structure of **5** has been determined by X-ray diffraction. The structure is given in Figure 3, and selected bond lengths and angles are compiled in Table 3. The molecule lies on a crystallographic reflection plane and thus contains a rigorously imposed reflection symmetry. The atoms Ga(1), N(1), and C(3) and the cage atoms C(1), C(2), B(7), and B(8) lie on the symmetry plane. The geometry of **5** is similarly distorted like that of **4** by intramolecular Ga–N coordination. The GaC_3 moiety is close to planarity with the gallium atom pulled out of the C(1), C(5), and C(5)* plane by 0.397(4) Å. This tetrahedral distortion showing nearly "normal" angles C(5)–Ga(1)–N(1) (107.1(3)°) and C(5)–Ga(1)–C(1) (113.5(3)°), and also a significantly different angle C(1)–Ga(1)–N(1) (86.4(3)°), is caused by the transannular Ga–N interaction. The Ga(1)–N(1) distance (2.168(7) Å) is in agreement with the corresponding values observed in $C_9H_{18}NGa$ (2.095(2) Å),[5b] $Me_2Ga(N_4C_6H_{12})$ (2.14(2) Å),[5c] and Me_3GaNMe_3 (2.20(3) Å)[5d] but is longer than the sum of the covalent radii for Ga and N (1.95 Å).[8] The Ga(1)–C(1) distance (2.020(8) Å) is slightly longer than the other two Ga–C distances (Ga(1)–C(5) and Ga(1)–C(5)*, 1.956(9) Å). The Ga–C distances of the Me_2Ga group are similar to those found in Me_3Ga in the gas phase.[9]

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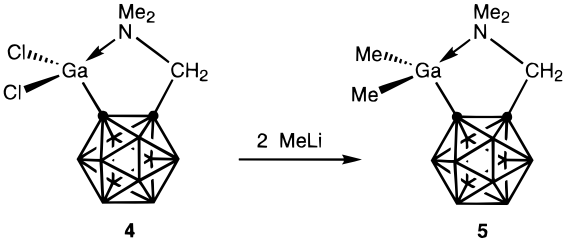
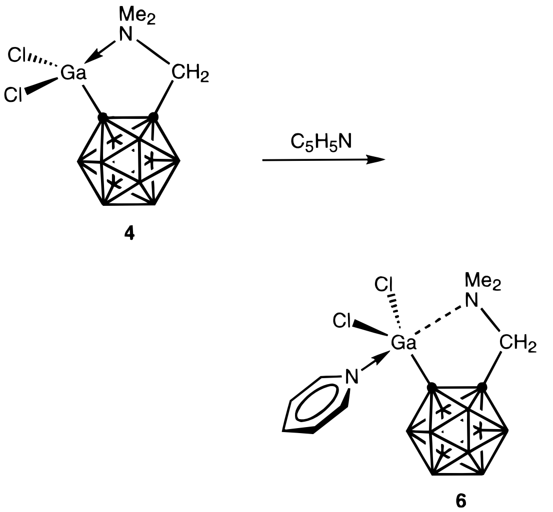
Reaction of Cab^{N}GaCl$_2$ (4) with LiMe. **5** can be synthesized using a second route. When compound **4** (reaction 4) was reacted with 2 equiv of MeLi reagent, the dimethylated compound Cab^{N}GaMe$_2$ **(5)** was obtained. According to reaction 4, the two chlorine atoms of compound **4** can be selectively replaced by organic ligands to give the crystalline compound **5**. The NMR spectra of this product were identical with those of **5**. Thus, the ^{1}H and ^{13}C NMR data, which confirm the proposed stoichiometry, are presented in Table 1.



(4)

Reaction of Cab^{N}GaCl$_2$ (4) with Pyridine. To determine whether this four-coordinate gallium compound **4** would exhibit Lewis acidity, the reaction of **4** with pyridine was investigated. Consequently, complex **4** added the base pyridine to yield the adduct Cab^{N}GaCl$_2$·NC$_5$H$_5$ (**6**). The adduct **6** was stable to dissociation at room temperature and thus was fully characterized by elemental analysis, high-resolution mass spectral analysis, and multinuclear NMR spectroscopic studies. The C_s symmetry of **6** in solution is derived from the ^{1}H, ^{11}B, and ^{13}C NMR spectra. The ^{1}H NMR spectra have signals for compound **6**: one for the unique N(CH$_3$)$_2$ proton, one for the NCH$_2$ group, and one set of signals attributable to the pyridine. The signals for both N(CH$_3$)$_2$ and NCH$_2$ in adduct **6** are at lower field than for compound **4**. This can be explained by a trigonal-bipyramidal geometry with two donor atoms in the axial positions and a fast envelope inversion.



(5)

The site of coordination of pyridine to **4** in the solid state was elucidated by an X-ray structural study of **6**. The molecular structure and labeling of the atoms are shown in Figure 4. Interatomic distances and angles are listed in Table 3. The gallium atom of compound **6** has a distorted-trigonal-bipyramidal coordination geometry in which the N donors occupy the axial coordination sites. The central gallium atom has an unusual stereochemistry, as it is essentially a distorted trigonal bipyramid with one very long (and presumably very weak) bond to the nitrogen and four more normal bonds: one to the nitrogen, one to the carbon, and two to the chlorine atoms. The Ga(1)−C(1) distance in **6** lies within the range (1.924(4)−2.080(4) Å) reported for other five-coordinate organogallium compounds.[10] In contrast, the two Ga−N distances in **6** differ significantly, with the longer Ga(1)−N(1) distance (2.497(9) Å) exceeding the range of previously reported Ga−N bond lengths (2.024(5)−2.471(4) Å).[10] It may also be noted that the shorter Ga(1)−N(2) bond length (2.083(9) Å) in **6** is slightly shorter than the Ga−N bond lengths found for Ga(N$_3$)$_3$·3py[11] (2.131(4) Å (av)) and Me$_2$Ga(hfac)·py (2.128 (9) Å).[12] The Ga−Cl bond lengths (Ga(1)−Cl(1) = 2.168(3) Å, Ga(1)−Cl(2) = 2.162(3) Å) are comparable to those of [*o*-(Me$_2$NCH$_2$)C$_6$H$_4$]GaCl$_2$ (2.178 Å (av)).[7] The N donor atoms occupy the axial sites (N(1)−Ga(1)−N(2) = 175.93°), and the gallium atom is in a trigonal-planar environment formed by two chloro ligands and the C(1) atom. In the base-coordinated gallium chloride containing a C,N-chelating ligand, normally the gallium atom has a trigonal-bipyramidal coordination geometry, as a result of intramolecular coordination. It is anticipated that the *o*-carboranyl carbon atom and two chloride ligands are at the equatorial sites, while the more electronegative nitrogen atom of *o*-carboranylamine and the coordinating pyridine reside at axial positions. The angle between the equatorial plane and the least-squares plane defined by N(1), Ga(1), N(2), and C(1) is

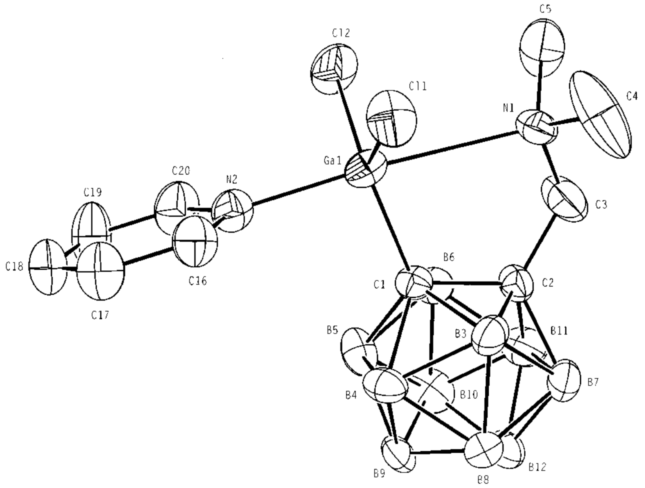


Figure 4. Molecular structure of Cab^{N}GaCl$_2$·NC$_5$H$_5$ (**6**). The thermal ellipsoids are drawn at the 30% probability level.

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[10] (a) Lee, B.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1990**, *9*, 1709. (b) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Ruiz, J.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1150. (c) Kynast, U.; Skelton, B. W.; White, A. H.; Henderson, M. J.; Raston, C. L. *J. Organomet. Chem.* **1990**, *384*, C1. (d) Onyiriuka, E. C.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1987**, *65*, 782. (e) Rettig, S. J.; Storr, A.; Trotter, J.; Uhrich, K. *Can. J. Chem.* **1984**, *62*, 2783. (f) McPhail, A. T.; Miller, R. W.; Pitt, C. G.; Gupta, G.; Srivastava, S. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1657. (g) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1976**, *54*, 1278. (h) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1975**, *53*, 58.

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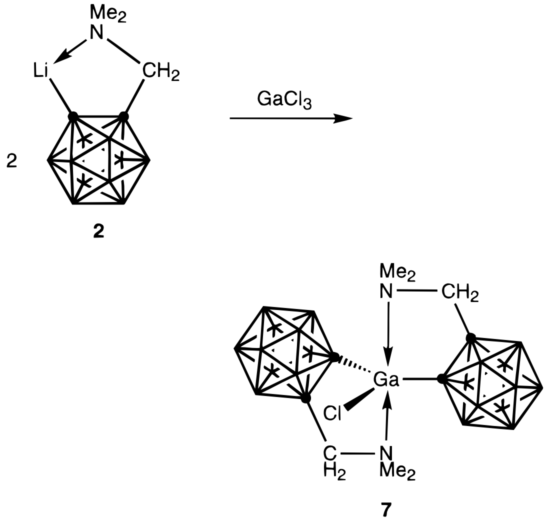
90°. The five-membered ring adopts an envelope conformation; the N(1) atom is situated 2.497(9) Å outside the Ga(1)−Cl(1)−Cl(2)−C(1) plane.

Synthesis of $(Cab^N)_2GaCl$ (7). The reaction of 2 equiv of $LiCab^N$ (**2**) with $GaCl_3$ afforded $(Cab^N)_2GaCl$ **7** in 40% yield (reaction 6). The driving force for this reaction is the formation of the intramolecular N→Ga coordination in **7**, as shown previously for the similar compound **6**. The composition of **7** was established by both elemental analysis and high-resolution mass spectral analysis. Furthermore, the spectroscopic data (^1H, ^{11}B, and ^{13}C NMR) associated with $(Cab^N)_2GaCl$ (**7**) are also consistent with its assigned structure. Indeed, the ^1H NMR spectrum consists of two singlets from the NMe_2 resonances (at 1.92 and 2.20 ppm) and an AB pattern for the NCH_2 protons (2.28 and 3.52 ppm (J_{gem} = 10 Hz)). This result demonstrates that, under these conditions, the NMe_2 and NCH_2 hydrogen atoms are diastereotopic, in agreement with the coordination of at least one NMe_2 ligand to the gallium atom. This points to coordination of the N atoms to Ga resulting in blocking of the inversion at the nitrogen on the NMR time scale, because only in this situation is the N atom in a stable trigonal-bipyramidal array, thereby producing diastereotopic Me groups. Furthermore, the appearance of the diastereotopic NMe_2 proton signals at lower field relative to the chemical shift of these protons in the free ligand $HCab^N$ also provides evidence of Ga−N coordination. This observation is consistent with similar findings for the general intramolecularly coordinated metal complexes of the HAr^N ligand system.[13] The ^1H NMR spectrum of the compound further suggests the presence of only molecules in the trans conformation in solution, as only one set of lines for the NMe_2 and NCH_2 protons for the two *o*-carboranylamine groups was observed. If the cis isomer had been present, two sets of lines of equal intensity, one for each type of proton, would have been expected. Since only one pattern is observed for the two *o*-carboranylamine groups, compound **7** must have the stereochemistry shown in reaction 6, which is similar to that found in complex **6**.



(6)

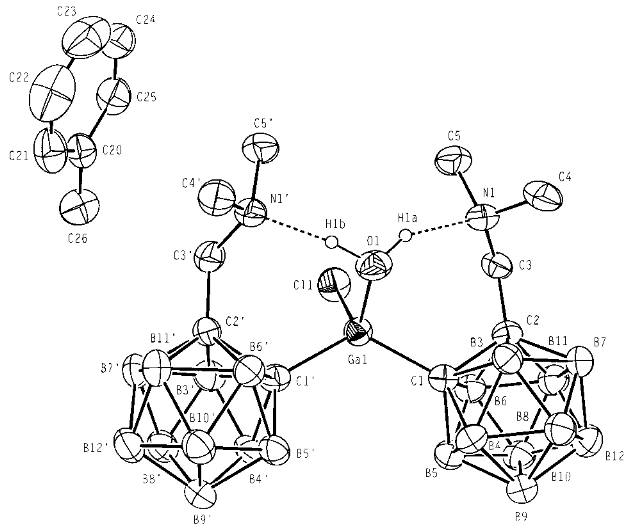


Figure 5. Molecular structure of $(Cab^N)_2GaCl{\cdot}H_2O$ (**8**). The thermal ellipsoids are drawn at the 30% probability level.

It is very likely that the coordination geometry of $(Cab^N)_2GaCl$ (**7**) parallels that of the pyridine adduct $Cab^NGaCl_2{\cdot}NC_5H_5$ (**6**). As in compound **6**, the preferred coordination geometry of the gallium atom in the bis(*o*-carboranylamine)chloride is trigonal bipyramidal with the two carboranyl carbon atoms and chlorine atom at equatorial positions and the more electronegative nitrogen atoms at axial sites. This type of structure has actually been observed for $(2\text{-}Me_2NCH_2C_6H_4)_2AlCl$[1a] and $(2\text{-}Me_2NCH_2C_6H_4)_2InCl$[14] in the solid state.

Isolation of $(Cab^N)_2GaCl(H_2O)$ (8). Crystals of **8** were obtained while recrystallizing compound **7** in toluene over a period of several days. The resulting white crystalline solid was recrystallized from toluene at −20 °C as clear colorless crystals which are not particularly air- or moisture-sensitive. The ^1H NMR spectrum of **8** confirms the presence of a NMe_2 group, showing a broad singlet of intensity 6 at about 1.86 ppm, two NCH_2 resonances at 2.06 and 2.67 ppm, and a less intense $Ga{\cdot}H_2O$ resonance at 6.86 ppm. Infrared spectroscopic data confirm the presence of the O−H group (ν_{O-H} = 3620 cm^{-1}). X-ray structural analysis of **8** reveals the presence of a single water molecule coordinated to the gallium center.

An X-ray structure analysis revealed a distorted-tetrahedral coordination at gallium with a donor set comprised of two carbon atoms and a chlorine atom and a coordinating water molecule (see Figure 5). The electron deficiency of the metal is balanced by water coordination. The trigonal-bipyramidal environment of the metal atom in the complex $(Cab^N)_2GaCl$ (**7**) is considerably tetrahedralized by the addition of water to form the bis(*o*-carboranylamine)chlorogallium water adduct **8**. The short Ga(1)−O(1) distance (1.840(4) Å) is comparable with that observed for the gallium water adduct $[(Me_3Si)_3CGaMe(OH)(\mu\text{-}OH)MeGaC(SiMe_3)_3]{\cdot}H_2O{\cdot}2THF$ (1.895(4) Å)[15] and shorter than in other donor−acceptor complexes such as $(Mes)_3Ga{\cdot}OH_2{\cdot}2THF$

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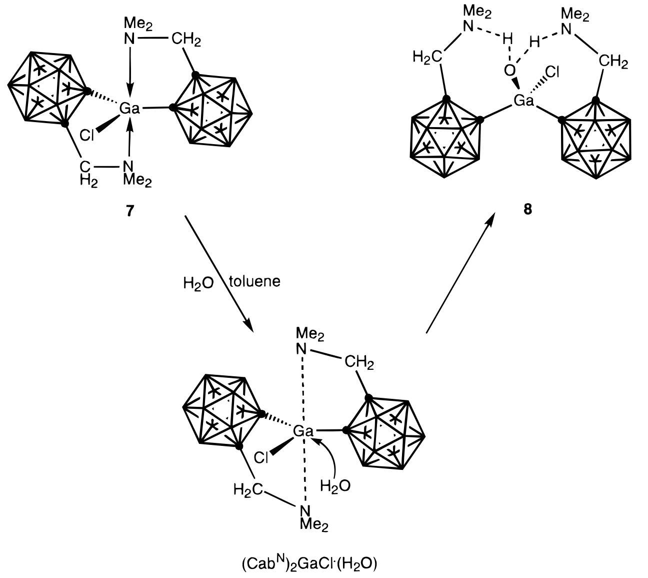
Scheme 1



(2.047 Å (av)),[16] (o-$MeC_6H_4)_3Ga·OEt_2$ (2.107(6) Å),[17] and $(C_6H_5CH_2)_3Ga·THF$ (2.069(7) Å).[18] The Ga−C bond distances (Ga(1)−C(1), 2.012(5) Å; Ga(1)−C(1)′, 2.019(5) Å) in **8** are virtually identical; they are similar to the Ga−C distances in **4**−**6** and lie within the range (1.924(4)−2.080(4) Å) reported for other organogallium compounds.[10] The Ga(1)−Cl(1) distance is not exceptional, having a value of 2.212(1) Å.[7] The geometry around the gallium atom is best described as a distorted tetrahedron, with the largest distortions being the interligand angles C(1)−Ga(1)−C(1)′ = 122.3(2)° and O(1)−Ga(1)−C(1) = 105.2(2)°. Despite the presence of a sterically unprotected site of the distorted tetrahedron, the compound is rather stable against moisture and air. Both hydrogen atoms of the water molecule are involved in hydrogen bonds, each to a single *o*-carboranylamine unit. The (HO)H···N(*o*-carboranylamine) distances of 1.75 Å (H(1a)) and 1.64 Å (H(1b)) and the H_2O···N(*o*-carboranylamine) distances of 2.80 Å (N(1)) and 2.64 Å (N(1′)) indicate medium-strong hydrogen bonding.[19] A reasonable reaction sequence for the formation of **8** involves the initial nucleophilic addition of the water molecule to the gallium center of **7**, leading to the hexacoordinate intermediate $(Cab^N)_2GaCl·H_2O$, followed by the rearrangement to **8** (Scheme 1). Thus, in **8**, the span of the amine units is not sufficient to allow for chelating coordination at a hexacoordinate gallium center. In coordinating the water molecule, the Ga−N bond in **7** weakens. The weakening of the $Ga−NMe_2$ bond is ascribed to the coordination of a water molecule to the gallium atom. The two Ga−N bonds can dissociate when the water coordination process, pointed out for **8**, takes place. The water coordination prevents the nitrogens from moving closer to the metal center.

Conclusions

This report provides the first report of the intramolecularly coordinated gallium complexes containing an *o*-carboranyl C,N-chelating ligand system. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The X-ray crystallographic study of complexes **3**−**6** and **8**, as described above, provides the first structural data for the [((dimethylamino)methyl)-*o*-carborane]gallium complexes. In such gallium chloride complexes, the gallium atom may be either tetracoordinate or pentacoordinate, depending on the number (one or two) of C,N-chelating ligands present in the molecule. Moreover, *o*-carboranyl C,N-chelating ligands can stabilize gallium compounds to such an extent that these compounds can be isolated as well-defined monomeric species. Additionally, it has been shown that internal coordination of the nitrogen atom of the *o*-carboranyl ligand to the gallium metal center has a significant influence not only on the stability of the starting compounds but also on the products of the base addition reaction for the gallium compounds. This may be the result of the stabilization of the gallium−carbon bond by the chelate effect, the electronic properties of the gallium center, and the strength of the gallium−nitrogen bond. Thus, application of the C,N-chelating *o*-carboranylamine ligand allowed the synthesis of stable gallium(III) compounds. In this paper we describe (1) the synthesis of some new (*o*-carboranyl)gallium compounds containing one or two [(dimethylamino)methyl]-*o*-carborane ligands and (2) the behavior of intramolecularly coordinated gallium complexes toward a Lewis base such as pyridine.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. THF was freshly distilled over potassium benzophenone. Ether and toluene were dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200.1, 64.2, and 50.3 MHz, respectively. All boron-11 chemical shifts were referenced to $BF_3·O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). IR spectra were recorded on a Biorad FTS-165 spectrophotometer. High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. The following starting materials were prepared according to literature procedures. Decaborane and (dimethylamino)-2-propyne were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without purification. $HCab^N$ (**1**; $HCab^N$ = *closo*-1-[(dimethylamino)methyl]-*o*-carborane)[20] was prepared by the literature method. The starting material $GaCl_3$ was purchased from Strem Chemical and sublimed under dynamic vacuum prior to each use. Dimethylgallium chloride[21] was prepared by stoichiometric ligand redistribution reactions in pentane at room temperature and was purified by vacuum sublimation at room temperature.

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Preparation of $HCab^N \cdot GaCl_3$ (3). $HCab^N$ (**1**; 0.604 g, 3.0 mmol) was stirred in toluene (60 mL), and $GaCl_3$ (0.528 g, 3.0 mmol) was added over a period of 10 min. The reaction appeared to be instantaneous, but to ensure complete reaction the solution was stirred for 2 h. The volume of the reaction mixture was reduced to half under vacuum, resulting in the precipitation of a colorless transparent solid. The precipitate was isolated, washed with 10−15 mL of cold pentane, and dried under vacuum. The compound was recrystallized from a toluene solution at −20 °C, resulting in the colorless crystalline compound **3** (0.51 g, 1.35 mmol, 45% yield). Exact mass: calcd for $^{11}B_{10}{}^{12}C_5{}^{70}Ga^{14}N^1H_{19}{}^{35}Cl_3$ 377.0769, found 377.0762. Anal. Calcd: C, 15.91; H, 5.07; N, 3.71. Found: C, 15.94; H, 5.10; N, 3.73. Mp: 146−148 °C. IR spectrum (KBr pellet, cm^{-1}): 3054 (w), 2720 (w, sh), 2598 (s), 1635 (m), 1472 (m), 1454 (m), 1402 (m), 1370 (m), 1317 (w), 1171 (w), 1123 (w), 1071 (w), 1022 (w), 1002 (w), 971 (w), 930 (w), 724 (w), 612 (w), 473 (w), 435 (w), 414 (w).

Synthesis of Cab^NGaCl_2 (4). To a stirred solution of $HCab^N$ (**1**; 0.604 g, 3.0 mmol) in 30 mL of hexane, which was cooled to −20 °C, was added 1.6 M *n*-BuLi (2 mL, 3.2 mmol) via a syringe. The resulting white suspension was stirred at −20 °C for 2 h and then transferred through a cannula to a suspension of $GaCl_3$ (0.528 g, 3.0 mmol) in 80 mL of diethyl ether at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After being stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling it to −20 °C. Cab^NGaCl_2 (**4**) was isolated from the reaction solution in 40% yield (0.41 g, 1.2 mmol). Exact mass: calcd for $^{11}B_{10}{}^{12}C_5{}^{70}Ga^{14}N^1H_{18}{}^{35}Cl_2$ 341.1003, found 341.1012. Anal. Calcd: C, 17.62; H, 5.32; N, 4.11. Found: C, 17.58; H, 5.22; N, 4.04. Mp: 220−222 °C. IR spectrum (KBr pellet, cm^{-1}): 3100 (w), 2990 (w), 2590 (vs), 1499 (w), 1460 (vs), 1455 (vs), 1440 (s, sh), 1430 (m), 1390 (w), 1300 (w), 1250 (w), 1220 (w), 1200 (w), 1155 (m), 1151 (m), 1105 (w), 1095 (s), 1050 (w, sh), 1010 (m), 998 (w), 959 (s), 940 (m), 910 (w), 860 (m), 850 (w, sh), 800 (s), 710 (s), 699 (m), 690 (m), 620 (w), 600 (w), 551 (w), 549 (w), 490 (m).

Synthesis of Cab^NGaMe_2 (5). A solution of Me_2GaCl (0.406 g, 3.0 mmol) in hexane (20 mL) was slowly added to a 50 mL hexane solution of $LiCab^N$ (**2**; 3.0 mmol, previously prepared from the reaction of $HCab^N$ (**1**) and $LiBu^n$) at −78 °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 53% yield (0.48 g, 1.6 mmol) was obtained. Exact mass: calcd for $^{11}B_{10}{}^{12}C_7{}^{70}Ga^{14}N^1H_{24}$ 301.2095, found 301.2100. Anal. Calcd: C, 28.02; H, 8.06; N, 4.67. Found: C, 28.07; H, 8.10; N, 4.72. Mp: 126−128 °C. IR spectrum (KBr pellet, cm^{-1}): 3100 (w), 2990 (w), 2590 (vs), 1499 (w), 1460 (vs), 1455 (vs), 1440 (s, sh), 1430 (m), 1390 (w), 1300 (w), 1250 (w), 1220 (w), 1200 (w), 1155 (m), 1151 (m), 1105 (w), 1095 (s), 1050 (w, sh), 1010 (m), 998 (w), 959 (s), 940 (m), 910 (w), 860 (m), 850 (w, sh), 800 (s), 710 (s), 699 (m), 690 (m), 620 (w), 600 (w), 551 (w), 549 (w), 490 (m).

Reaction of Cab^NGaCl_2 (4) with LiMe. A 1.4 M solution of LiMe in diethyl ether (1.6 mL, 2.2 mmol) was added to a solution of **4** (0.68 g, 2.0 mmol) in diethyl ether (30 mL) at −78 °C. The dry ice bath was removed, and the solution was stirred for 3 h. Subsequently, all volatile components were distilled off in vacuo at room temperature. The crude product was dissolved in toluene (40 mL) and the solution separated by filtration. The volume was then reduced to 20 mL, and crystallization at −20 °C gave pure **5** (0.15 g, 0.50 mmol, 25% yield).

Reaction of Cab^NGaCl_2 (4) with Pyridine. A solution of **4** (0.34 g, 1.0 mmol) and pyridine (0.32 mL, 4.0 mmol) in toluene (30 mL) was stirred for 10 min at room temperature and subsequently evaporated to dryness, which left the crude yellow product. Crystallization from toluene (20 mL) at −20 °C gave the pure crystalline form of complex **6** (0.37 g, 0.88 mmol, 88%). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{10}{}^{70}Ga^{14}N_2{}^1H_{23}{}^{35}Cl_2$ 420.1425, found 420.1428. Anal. Calcd: C, 28.6; H, 5.52; N, 6.67. Found: C, 28.57; H, 5.48; N, 6.70. Mp: 248−249 °C. IR spectrum (KBr pellet, cm^{-1}): 3390 (w, br), 3380 (w, br), 2950 (w), 2587 (vs), 2363 (m), 2360 (w, br), 1717 (w), 1620 (w), 1717 (w), 1620 (m), 1558 (w), 1541 (w), 1475 (m), 1457 (m), 1410 (w), 1100 (m, sh), 1073 (vs), 1000 (m, sh), 750 (w), 745 (w), 728 (w), 728 (w), 780 (m), 760 (m), 614 (s), 458 (vs).

Synthesis of $(Cab^N)_2GaCl$ (7). A suspension of freshly prepared $LiCab^N$ (**2**; 3.0 mmol) in toluene (30 mL) was added over 1 h to a suspension of $GaCl_3$ (0.264 g, 1.5 mmol) in toluene solvent (20 mL) at −78 °C. The reaction mixture was stirred for 12 h at room temperature, after which the suspended solid was collected by filtration. The volume of the filtrate was reduced, and when this was allowed to stand at −20 °C for several days, colorless crystals of **7** were formed in 40% yield (0.61 g, 1.2 mmol). Exact mass: calcd for $^{11}B_{20}{}^{12}C_{10}{}^{70}Ga^{14}N_2{}^1H_{36}{}^{35}Cl$ 508.3684, found 508.3690. Anal. Calcd: C, 23.75; H, 7.17; N, 5.54. Found: C, 23.78; H, 7.23; N, 5.60. Mp: 165−167 °C. IR spectrum (KBr pellet, cm^{-1}): 2923 (s), 2853 (s), 2600 (w, br), 2591 (s), 2360 (w), 2348 (w), 1631 (w), 1458 (m), 1384 (m), 1077 (w), 985 (w), 775 (w), 731 (w), 614 (w), 441 (w).

Recrystallization of $(Cab^N)_2GaCl(H_2O)$ (8). Compound **8** was obtained while recrystallizing **7** in toluene over a period of several days. Anal. Calcd: C, 22.93; H, 7.31; N, 5.35. Found: C, 22.98; H, 7.38; N, 5.40. Mp: 276 °C. IR spectrum (KBr pellet, cm^{-1}): 3620 (br), 2990 (w), 2880 (w), 2610 (m, sh), 2595 (vs), 2390 (m), 1710 (w), 1690 (w), 1560 (w), 1505 (w), 1409 (w), 1495 (m, sh), 1490 (m), 1450 (w), 1345 (w), 1250 (w), 1180 (w), 1160 (w), 1150 (w), 1078 (m), 1020 (w), 996 (w), 948 (w), 855 (w), 850 (w), 795 (w), 748 (m), 700 (w), 660 (w). 580 (w), 535 (w), 515 (w), 470 (w), 420 (m).

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **3**−**6** and **8** are given in Table 1. Crystals of **3**−**6** and **8** were grown from toluene solutions stored at −20 °C. Crystals of **3**−**6** and **8** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **3** and **8** were collected on a Rigaku diffractometer with an area detector at a temperature of 195 K, and an Enraf CAD4 automated diffractometer was used for the collection of data for compounds **4**−**6**. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[22a] and least-squares refinement using SHELXL-97.[22b] All non-hydrogen atoms in compounds **3**−**6** and $\mathbf{8}\cdot C_6H_5CH_3$ were refined anisotropically. The coordinates of hydroxyl hydrogens of $\mathbf{8}\cdot C_6H_5CH_3$ were refined free, with the OH distance being restrained to a standard value. All other hydrogen atoms were included in calculated positions.

Acknowledgment. We are grateful to the Korea Science and Engineering Foundation (Grant No. 971-0306-048-2 and 98-0300-08-01-3) for financial support.

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and thermal parameters for compounds **3**−**6** and $\mathbf{8}\cdot C_6H_5CH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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