Gallium Complexes of Potentially Tridentate Poly(pyrazolyl)borate Ligands. Crystal and Molecular Structures of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, and $[B(pz)_4]_2GaCH_3$ (pz = Pyrazolyl Ring)

Daniel L. Reger* and Yan Ding

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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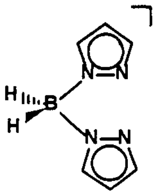
The potentially tridentate ligands $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ react with $GaCl_3$ to yield the respective salts $[(ligand)_2Ga]GaCl_4$. These compounds are stable and do not react with nucleophiles. The six coordinate cations are also formed in the reactions of 1 equiv of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCH_3Cl_2$. The reaction of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $GaCH_3Cl_2$ yields $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$. The solid state structure of this complex shows that it is four coordinate with a bidentate hydrotris(pyrazolyl)borate ligand. This complex is fluxional in solution, showing equivalent pyrazolyl rings in the ^1H NMR spectra even at −90 °C. The reaction of $[HB(pz)_3]^-$, $[B(pz)_4]^-$, or $[HB(3,5\text{-}Me_2pz)_3]^-$ with $Ga(CH_3)_2Cl$ yields the respective $(ligand)Ga(CH_3)_2$ complexes. The solid state structure of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ shows that it is also four coordinate. Both $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ and $[HB(pz)_3]Ga(CH_3)_2$ are fluxional in solution, showing equivalent pyrazolyl rings and methyl ligands at ambient temperature. At low temperatures a 2/1 pattern for each resonance type in the pyrazolyl rings and a 1/1 ratio for the methyl groups is observed. The reaction of 2 equiv of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCH_3Cl_2$ yields the respective $(ligand)_2GaCH_3$ complexes. The solid state structure of $[B(pz)_4]_2GaCH_3$ shows that it is six coordinate containing both a tridentate and bidentate tetrakis(pyrazolyl)borate ligand. The low temperature ^1H NMR spectrum of $[HB(pz)_3]_2GaCH_3$ shows a 1/1/2/2 pattern for each pyrazolyl ring resonance type, indicating a similar structure for $[HB(pz)_3]_2GaCH_3$. Crystal data: $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, monoclinic, $P2_1/c$, $a = 13.705(7)$ Å, $b = 7.780(3)$ Å, $c = 18.684(8)$ Å, $\beta = 93.71(4)°$, $V = 1988$ Å^3, $Z = 4$, $R(F) = 6.1\%$; $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, triclinic, $P\bar{1}$, $a = 7.976(3)$ Å, $b = 18.520(11)$ Å, $c = 7.942(3)$ Å, $\alpha = 97.01(4)°$, $\beta = 116.28(3)°$, $\gamma = 93.54(4)°$, $V = 1035$ Å^3, $Z = 2$, $R(F) = 6.8\%$; $[B(pz)_4]_2GaCH_3$, triclinic, $P\bar{1}$, $a = 12.316(6)$ Å, $b = 15.945(4)$ Å, $c = 8.622(4)$ Å, $\alpha = 101.51(4)°$, $\beta = 99.66(4)°$, $\gamma = 93.83(4)°$, $V = 1627$ Å^3, $Z = 2$, $R(F) = 5.9\%$.

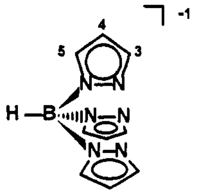
Introduction

We have recently published the preparation and characterization of a series of complexes of the general formula $[H_2B(pz)_2]_mGaCl_n(CH_3)_p$ ($m + n + p = 3$, pz = pyrazolyl ring).[1] This chemistry with the bis(pyrazolyl)borate ligand (**A**) has yielded exceptionally stable, monomeric, group-13 metal complexes. For example, the organometallic complex $[H_2B(pz)_2]Ga(CH_3)_2$ is air stable and monomeric in both the solid and solution phases.



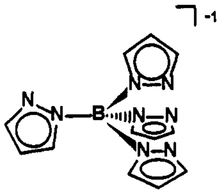
A

$[H_2B(pz)_2]^-$



B

$[HB(pz)_3]^-$



C

$[B(pz)_4]^-$

We have explored related chemistry using the hydrotris(pyrazolyl)borate (**B**) and tetrakis(pyrazolyl)borate (**C**) ligands. These ligands are generally tridentate in transition metal complexes,[2] although they are bidentate in a few cases.[3] In the chemistry of the post transition metals tin(II) and lead(II), it has been shown that these ligands are frequently bidentate.[4] Thus $[B(pz)_4]_2M$ (M = Sn, Pb) complexes are four coordinate with bidentate ligands[4] and $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ is five coordinate with both a tridentate and a bidentate ligand.[5] We wished to determine the bonding modes and properties of gallium complexes of these ligands.

Reported here are the results of reactions of $[HB(pz)_3]^-$, $[B(pz)_4]^-$, and $[HB(3,5\text{-}Me_2pz)_3]^-$ with $GaCl_3$, $GaCH_3Cl_2$,

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and $Ga(CH_3)_2Cl$. The solid state structures of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, and $[B(pz)_4]_2GaCH_3$ have been determined crystallographically, and the fluxional behavior of a number of the new complexes in solution has been studied by variable temperature NMR.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Abbreviations used in the assignment of ^1H NMR resonances are pz = pyrazolyl ring and pz* = 3,5-Me_2pz ring. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. CH_3GaCl_2,[6a] $K[HB(pz)_3]$,[6b] $K[B(pz)_4]$,[6b] and $K[HB(3,5\text{-}Me_2pz)_3]$[6c] were prepared according to the published methods. Anhydrous $GaCl_3$ was purchased from Aldrich Chemical Co. and was freshly sublimed prior to each use. Elemental analyses were performed by Robertson Laboratory, Inc.

Bis[hydrotris(1-pyrazolyl)borato]gallium Tetrachlorogallate, $\{[HB(pz)_3]_2Ga\}GaCl_4$. $GaCl_3$ (1.40 g, 7.95 mmol) was dissolved in THF (10 mL, precooled to −78 °C). A THF solution (20 mL, −78 °C) of $K[HB(pz)_3]$ (2.00 g, 7.94 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated under vacuum. The white residue was extracted with CH_2Cl_2 (35 mL) and the extract filtered. Evaporation of the CH_2Cl_2 under vacuum yielded a white solid (2.42 g, 3.42 mmol, 86%). ^1H NMR ($CDCl_3$, δ): 7.97, 7.11 (d, d; J = 2.3, 2.2 Hz; 3-*H*, 5-*H* pz); 6.34 (t, J = 2.3 Hz, 4-*H* pz). The FAB mass spectrum shows a cluster for $GaCl_4^-$ at *m/e* 211 and a cluster for $[HB(pz)_3]_2Ga^+$ at *m/e* 495. Anal. Calcd for $C_{18}H_{20}B_2Cl_4Ga_2N_{12}$: C, 30.57; H, 2.85. Found: C, 30.31; H, 2.59.

Bis[hydrotris(1-pyrazolyl)borato]gallium Methyltrichlorogallate, $\{[HB(pz)_3]_2Ga\}[Ga(CH_3)Cl_3]$. CH_3GaCl_2 (1.20 g, 7.71 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C. A THF (10 mL, −78 °C) solution of $K[HB(pz)_3]$ (1.90 g, 7.54 mmol) was added. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum. The residue was washed with benzene (20 mL) and extracted with CH_2Cl_2 (20 mL) and the extract filtered. Evaporation of the CH_2Cl_2 under vacuum yielded a white solid (1.87 g, 2.72 mmol, 72%). ^1H NMR ($CDCl_3$, δ): 7.99, 7.11 (6, 6; d, d; J = 2.3, 2.2 Hz; 3-*H*, 5-*H* pz); 6.35 (6, t, J = 2.3 Hz, 4-*H* pz); 0.14 (3, s, CH_3). The FAB mass spectrum shows a cluster for $[HB(pz)_3]_2Ga^+$ at *m/e* 495 and a cluster for $Ga(CH_3)Cl_3^-$ at *m/e* 191. Anal. Calcd for $C_{19}H_{23}B_2Cl_3Ga_2N_{12}$: C, 33.22; H, 3.38; N, 24.47. Found: C, 33.16; H, 3.29; N, 24.72.

Dimethyl[hydrotris(1-pyrazolyl)borato]gallium(III), $[HB(pz)_3]Ga(CH_3)_2$. $GaCl_3$ (0.80 g, 4.5 mmol) was dissolved in diethyl ether (10 mL). The solution was cooled to −78 °C, and CH_3Li (6.0 mL, 1.4 M, 8.4 mmol) was added. The mixture was warmed to room temperature (2 h) and stirred overnight. A THF solution of $K[HB(pz)_3]$ (1.14 g, 4.5 mmol) was added. The mixture was stirred for 3 h. The solvent was removed under vacuum. The residue was extracted with hexane (30 mL) and the extract filtered. Evaporation of the hexane under vacuum yielded a colorless oil (0.90 g, 2.9 mmol, 64%). ^1H NMR ($CDCl_3$, ambient temperature, δ): 7.67, 7.46 (3, 3; br, br; 3-*H*, 5-*H* pz); 6.32 (3, br, 4-*H* pz); −0.18 (6, br, CH_3). ^1H NMR ($CDCl_3$, −48 °C, δ): 7.72, 7.66, 7.58, 7.24 (1, 2, 2, 1; d; J_{HH} = 2 Hz; 3-*H*, 5-*H* pz); 6.40, 6.27 (2, 1; t; J_{HH} = 2 Hz; 4-*H* pz); −0.11, −0.49 (3, 3; s, s; CH_3). Anal. Calcd for $C_{11}H_{16}BGaN_6$: C, 42.24; H, 5.16; N, 26.87. Found: C, 42.59; H, 5.07; N, 26.62.

Bis[hydrotris(1-pyrazolyl)borato]methylgallium(III), $[HB(pz)_3]_2GaCH_3$. CH_3GaCl_2 (0.60 g, 3.9 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C. A THF solution (10 mL, −78 °C) of $K[HB(pz)_3]$ (1.94 g, 7.70 mmol) was added. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum. The residue was extracted with benzene (20 mL) and the extract filtered. The benzene was removed under vacuum to yield a white solid (1.31 g, 2.57 mmol, 67%). ^1H NMR ($CDCl_3$, ambient temperature, δ): 7.57, 7.20 (6, 6; br, br; 3-*H*, 5-*H* pz); 6.12 (6, br, 4-*H* pz); 0.08 (3, br, CH_3). ^1H NMR (toluene-d^8, −80 °C, δ): 8.16, 8.05, 7.46, 7.26, 7.18, 7.15, 6.73, 6.38 (1, 1, 2, 2, 2, 1, 2, 1; d; J_{HH} = 2 Hz; 3-*H*, 5-*H* pz); 5.79, 5.64, 5.61, 5.22 (1, 2, 2, 1; t; J_{HH} = 2 Hz; 4-*H* pz); 0.77 (3, s, CH_3). The mass spectrum shows a $M^+ + H$ cluster at *m/e* 511. High resolution mass spectrum calculated for $C_{19}H_{22}B_2GaN_{12}$, 509.1532; found, 509.1547

Bis[tetrakis(1-pyrazolyl)borato]gallium Tetrachlorogallate, $\{[B(pz)_4]_2Ga\}GaCl_4$. This compound was prepared as indicated above for the $[HB(pz)_3]^-$ analog in 42% yield. ^1H NMR ($CDCl_3$, δ): 8.27, 8.04, 8.03, 7.25 (1, 1, 3, 3; d; 3-*H*, 5-*H* pz; J = 2 Hz); 6.77, 6.40 (1, 3; t, t; 4-*H* pz; J = 2 Hz). The FAB mass spectrum shows a cluster for $GaCl_4^-$ at *m/e* 211 and a cluster for $[B(pz)_4]_2Ga^+$ at *m/e* 627. Anal. Calcd for $C_{24}H_{24}B_2Cl_4Ga_2N_{16}$: C, 34.34; H, 2.88; N, 26.70. Found: C, 34.15; H, 2.61; N, 26.62.

Dimethyl[tetrakis(1-pyrazolyl)borato]gallium(III), $[B(pz)_4]Ga(CH_3)_2$. $GaCl_3$ (0.89 g, 5.1 mmol) was dissolved in diethyl ether (10 mL, −78 °C), and CH_3Li (7.2 mL, 1.4 M, 10 mmol) was added. The mixture was warmed to room temperature (2 h) and stirred overnight. A THF solution (20 mL) of $K[B(pz)_4]$ (1.60 g, 5.03 mmol) was added. The mixture was stirred for several hours. The solvent was removed under vacuum. The residue was extracted with benzene (30 mL) and the extract filtered. Evaporation of benzene yielded a white solid (1.29 g, 3.40 mmol, 68%). ^1H NMR (toluene-d^8, δ): 7.79, 7.16, 6.97, 6.59 (2, 2, 2, 2; d; J_{HH} = 2 Hz; 3-*H*, 5-*H* pz); 6.08, 5.82 (2, 2; t; J_{HH} = 2 Hz; 4-*H* pz); −0.43 (6, s, CH_3). The mass spectrum shows a $M^+ + H$ cluster at *m/e* 379 and a $M^+ - CH_3$ cluster at *m/e* 363. Anal. Calcd for $C_{14}H_{18}BGaN_8$: C, 44.38; H, 4.79; N, 29.57. Found: C, 44.48; H, 4.80; N, 29.68.

Bis[tetrakis(1-pyrazolyl)borato]methylgallium(III), $[B(pz)_4]_2GaCH_3$. This compound was prepared as indicated above for the $[HB(pz)_3]^-$ analog in 36% yield. Crystals for the X-ray diffraction study were grown from CH_2Cl_2/benzene by slow evaporation of the solvents. These crystals were used for the elemental analysis and contain 0.5 equiv of benzene per gallium complex (verified by NMR). ^1H NMR ($CDCl_3$, δ): 7.60, 7.16 (8, 8; d, d; J = 1.7, 2.4 Hz; 3-*H*, 5-*H* pz); 6.30 (8, t, J = 2.1 Hz, 4-*H* pz); −1.29 (3, s, CH_3). Anal. Calcd for $C_{25}H_{27}B_2GaN_{16}\cdot{}^1/_2C_6H_6$: C, 49.31; H, 4.43; N, 32.86. Found: C, 49.32; H, 4.22; N, 32.77.

Chloro[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]methylgallium(III), $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$. CH_3GaCl_2 (3.92 g, 25.1 mmol) was dissolved in THF (20 mL). This solution was added to a THF solution (30 mL) of $K[HB(3,5\text{-}Me_2pz)_3]$ (8.24 g, 24.5 mmol). The mixture was stirred overnight. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (2 × 30 mL) and the extract filtered. Evaporation of CH_2Cl_2 yielded a white solid (5.39 g, 12.9 mmol, 52.7%). Colorless crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solution by slow evaporation of the solvent. ^1H NMR ($CDCl_3$, δ): 5.77 (3, s, 4-*H* pz*); 2.36, 2.35 (9, 9; s, s; 3,5-$(CH_3)_2$pz*); 0.75 (3, s, Ga-CH_3). Anal. Calcd for $C_{16}H_{25}BClGaN_6$: C, 46.04; H, 6.04; N, 20.14. Found: C, 46.21; H, 6.02; N, 20.20.

Dimethyl[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]gallium(III), $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$. Method A. This compound was prepared as indicated above for its $[HB(pz)_3]^-$ analog in 91% yield. Crystals suitable for X-ray diffraction were grown from toluene/hexane at −20 °C. ^1H NMR ($CDCl_3$, ambient temperature, δ): 5.8 (3, br, 4-*H* pz*), 2.21 (18, br, 3, 5-$(CH_3)_2$pz*), −0.24 (6, br, Ga–CH_3). ^1H NMR (CD_2Cl_2, −90 °C, δ): 5.97, 5.33 (2, 1; s, s; 4-*H* pz*); 2.34, 2.23, 1.98, 1.73 (6, 6, 3, 3; s, s, s, s; 3,5-$(CH_3)_2$pz*); −0.32, −0.46 (3, 3; s, s; Ga–CH_3). Anal. Calcd for $C_{17}H_{28}BGaN_6$: C, 51.44; H, 7.11; N, 21.17. Found: C, 50.97; H, 7.14; N, 21.36.

Method B. $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ (0.10 g, 0.24 mmol)

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Table I. Crystallographic Data for the Structural Analyses of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, and $[B(pz)_4]_2GaCH_3$

	$[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$	$[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$	$[B(pz)_4]_2GaCH_3\cdot{}^1/_2C_6H_6$
formula	$C_{16}H_{25}BClGaN_6$	$C_{17}H_{28}BGaN_6$	$C_{28}H_{30}BGaN_{16}$
FW	417.40	396.98	681.99
cryst color	colorless	colorless	colorless
cryst habit	prismatic	prismatic	prismatic
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	13.705(7)	7.976(3)	12.316(6)
b, Å	7.780(3)	18.520(11)	15.945(4)
c, Å	18.684(8)	7.942(3)	8.622(4)
α, deg		97.01(4)	101.51(4)
β, deg	93.71(4)	116.28(3)	99.66(4)
γ, deg		93.54(4)	93.83(4)
V, Å^3	1988	1035	1627
Z	4	2	2
cryst size, mm	0.60 × 0.38 × 0.21	0.40 × 0.32 × 0.08	0.48 × 0.30 × 0.28
d_{calcd}, g cm^{-3}	1.395	1.274	1.393
monochromator	graphite	graphite	graphite
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp	ambient	ambient	ambient
scan type	ω/2θ	ω/2θ	ω/2θ
2θ range, deg	4–46	4–46	4–46
data collected	±h,+k,+l	±h,+k,±l	±h,±k,+l
no. of rflns meas	3113	2983	4888
no. of rflns obsd	3009	2878	4530
μ(Mo Kα), cm^{-1}	15.2	13.3	8.8
R	0.061	0.068	0.059
R_w	0.065	0.077	0.073

Table II. Fractional Atomic Coordinates for $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

atom	x/a	y/b	z/c	B (Å^2)
Ga	0.75312(8)	0.1497(1)	0.89827(6)	3.31(2)
Cl	0.6453(2)	0.2893(4)	0.9639(1)	4.79(6)
N11	0.7259(5)	0.2776(9)	0.7526(4)	2.5(1)
N12	0.7598(5)	0.3123(9)	0.8207(4)	2.6(2)
N21	0.6472(5)	−0.0126(9)	0.7762(4)	2.6(2)
N22	0.6651(5)	−0.013(1)	0.8487(4)	2.9(2)
N31	0.8128(5)	0.0026(9)	0.7268(4)	2.6(1)
N32	0.8664(5)	−0.012(1)	0.7913(4)	2.7(2)
C1	0.8632(7)	0.084(1)	0.9619(5)	4.7(3)
C13	0.7809(6)	0.482(1)	0.8244(5)	3.1(2)
C14	0.7615(7)	0.552(1)	0.7585(5)	3.2(2)
C15	0.7264(6)	0.422(1)	0.7127(5)	2.8(2)
C16	0.8235(8)	0.565(1)	0.8907(5)	4.6(2)
C17	0.6981(8)	0.428(1)	0.6352(5)	4.3(2)
C23	0.6053(7)	−0.129(1)	0.8763(5)	4.0(2)
C24	0.5479(7)	−0.200(1)	0.8202(6)	4.5(2)
C25	0.5764(6)	−0.124(1)	0.7588(5)	3.5(2)
C26	0.6066(8)	−0.167(2)	0.9540(6)	5.6(3)
C27	0.5391(8)	−0.164(2)	0.6840(6)	5.7(3)
C33	0.9492(6)	−0.091(1)	0.7773(5)	3.5(2)
C34	0.9490(7)	−0.128(1)	0.7048(5)	4.3(2)
C35	0.8623(7)	−0.064(1)	0.6731(5)	3.4(2)
C36	1.0256(7)	−0.128(2)	0.8345(6)	5.4(3)
C37	0.8250(9)	−0.066(2)	0.5974(6)	5.9(3)
B	0.7137(8)	0.089(1)	0.7259(5)	2.9(2)

Table III. Fractional Atomic Coordinates for $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

atom	x/a	y/b	z/c	B (Å^2)
Ga	0.1553(1)	0.13243(6)	0.3854(2)	4.39(2)
N11	0.3814(8)	0.2650(4)	0.3799(9)	3.2(2)
N12	0.3223(9)	0.1913(4)	0.3166(9)	3.6(2)
N21	0.2082(9)	0.2873(4)	0.5813(9)	3.7(2)
N22	0.1313(9)	0.2151(5)	0.5566(9)	4.4(2)
N31	0.0930(9)	0.3313(4)	0.2671(9)	4.0(2)
N32	−0.0422(9)	0.2729(4)	0.1558(9)	4.1(2)
C1	−0.080(1)	0.0857(6)	0.171(2)	6.8(4)
C2	0.317(1)	0.0697(5)	0.558(1)	5.6(3)
C13	0.439(1)	0.1642(5)	0.250(1)	4.4(2)
C14	0.575(1)	0.2198(6)	0.275(1)	4.7(2)
C15	0.535(1)	0.2830(5)	0.353(1)	4.6(2)
C16	0.415(1)	0.0849(6)	0.168(2)	6.7(3)
C17	0.637(1)	0.3589(7)	0.404(2)	7.4(3)
C23	0.073(1)	0.2100(6)	0.684(1)	5.7(3)
C24	0.118(1)	0.2766(7)	0.800(1)	6.8(3)
C25	0.203(1)	0.3245(6)	0.736(1)	5.7(3)
C26	−0.023(2)	0.1397(8)	0.694(2)	9.0(4)
C27	0.276(2)	0.4047(8)	0.804(2)	8.6(4)
C33	−0.178(1)	0.3023(6)	0.022(1)	5.4(3)
C34	−0.134(1)	0.3763(6)	0.045(1)	6.3(3)
C35	0.037(1)	0.3939(5)	0.206(1)	5.2(3)
C36	−0.347(2)	0.2517(8)	−0.131(2)	7.9(4)
C37	0.152(2)	0.4667(6)	0.294(2)	9.5(5)
B	0.270(1)	0.3169(6)	0.447(2)	4.1(3)

was dissolved in THF (10 mL). The solution was cooled to −78 °C. Methyllithium (0.20 mL, 1.4 M, 0.28 mmol) was added. The mixture was allowed to warm to room temperature (2 h). After 2 h of additional stirring, the solvent was removed under vacuum. The residue was extracted with benzene (20 mL) and the extract filtered. Evaporation of the benzene under vacuum yielded a white solid. The solid was recrystalized in toluene/hexane. NMR spectroscopy showed that the product was a pure sample of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ (0.060 g, 0.15 mmol, 62%).

Crystallographic Analysis of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, and $[B(pz)_4]_2GaCH_3$. A colorless crystal of each complex was mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cells were determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analyses are listed in Table I. Data were collected in the ω/2θ scan mode with a 0.8° + (0.35 tan θ)° scan range. The structure was solved by the heavy atom method and refined by using MolEN.[7] All hydrogen atoms were included in the structure factor calculations and are not refined. Full-matrix least-squares refinements were carried out for reflections with $I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics. Absorption corrections were made by the method of Walker and Stuart.[8] Atomic parameters are shown in Tables II–IV.

Results and Discussion

$[(ligand)_2Ga]^+$ Complexes. The reaction of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCl_3$ yields the respective six coordinate,

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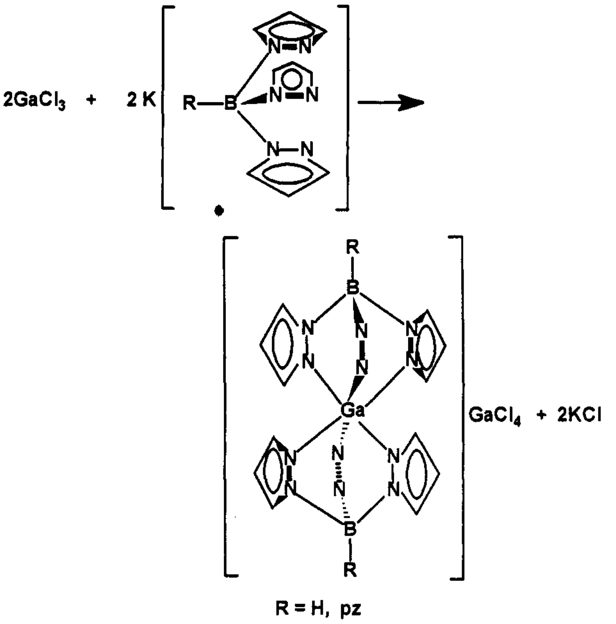
[7] *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

[8] Walker, N.; Stuart, D. *Acta Crystallogr., Sect A* **1983**, *A39*, 158.

Table IV. Fractional Atomic Coordinates for $[B(pz)_4]_2GaCH_3\cdot{}^1/_2C_6H_6$ with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

atom	*x/a*	*y/b*	*z/c*	*B* (Å²)	atom	*x/a*	*y/b*	*z/c*	*B* (Å²)
Ga	0.07070(6)	0.28407(5)	0.16370(9)	2.75(1)	C33	0.0170(7)	0.3786(4)	−0.133(1)	4.6(2)
N11	−0.0073(4)	0.1211(3)	−0.0968(6)	2.4(1)	C34	−0.0572(7)	0.3712(5)	−0.2756(9)	4.7(2)
N12	0.0769(4)	0.1611(3)	0.0259(6)	2.5(1)	C35	−0.1148(6)	0.2919(5)	−0.3029(8)	3.8(2)
N21	−0.1666(4)	0.1892(3)	0.0070(6)	2.7(1)	C43	−0.2426(7)	0.0366(6)	−0.5240(9)	4.9(2)
N22	−0.1003(4)	0.2300(3)	0.1457(6)	2.9(1)	C44	−0.2984(6)	−0.0056(5)	−0.4299(9)	4.4(2)
N31	−0.0740(4)	0.2507(3)	−0.1846(6)	2.8(1)	C45	−0.2620(6)	0.0413(4)	−0.2765(8)	3.3(2)
N32	0.0079(5)	0.3043(4)	−0.0799(7)	3.6(1)	C53	0.0709(6)	0.1814(4)	0.4351(8)	3.6(2)
N41	−0.1889(4)	0.1079(4)	−0.2813(6)	3.0(1)	C54	0.1349(6)	0.1694(5)	0.5750(8)	4.2(2)
N42	−0.1747(5)	0.1033(4)	−0.4386(7)	4.3(1)	C55	0.2356(6)	0.2131(5)	0.5858(8)	4.0(2)
N51	0.2328(4)	0.2525(3)	0.4588(6)	2.8(1)	C63	0.2762(6)	0.3138(6)	0.0072(8)	4.5(2)
N52	0.1288(4)	0.2307(3)	0.3651(6)	2.9(1)	C64	0.3895(7)	0.3284(7)	0.0395(9)	6.2(2)
N61	0.3277(4)	0.3125(4)	0.2581(6)	3.1(1)	C65	0.4208(6)	0.3274(6)	0.2000(9)	5.1(2)
N62	0.2367(4)	0.3056(3)	0.1396(6)	2.8(1)	C73	0.2633(8)	0.5111(6)	0.689(1)	6.6(2)
N71	0.2996(5)	0.4081(4)	0.5118(6)	3.3(1)	C74	0.3008(8)	0.5491(5)	0.576(1)	5.9(2)
N72	0.2628(6)	0.4252(5)	0.6544(8)	5.7(2)	C75	0.3235(7)	0.4827(5)	0.4653(9)	4.3(2)
N81	0.4332(4)	0.2984(4)	0.5243(6)	3.3(1)	C83	0.5670(7)	0.2254(6)	0.583(1)	5.3(2)
N82	0.4723(5)	0.2208(4)	0.4794(8)	5.0(2)	C84	0.5896(7)	0.3013(6)	0.692(1)	5.5(2)
C1	0.0465(6)	0.3992(5)	0.276(1)	4.8(2)	C85	0.5035(6)	0.3477(5)	0.6517(8)	4.0(2)
C13	0.1549(5)	0.1063(4)	0.0319(8)	3.1(1)	B1	−0.1112(6)	0.1666(5)	−0.1441(8)	2.5(1)
C14	0.1231(6)	0.0331(4)	−0.0878(8)	3.4(1)	B2	0.3221(6)	0.3180(5)	0.4386(9)	3.1(2)
C15	0.0206(5)	0.0438(4)	−0.1665(7)	2.9(1)	C1s	0.4673(8)	0.0747(9)	0.088(2)	9.7(4)
C23	−0.1689(6)	0.2538(5)	0.2511(9)	4.4(2)	C2s	0.5152(8)	0.014(1)	0.164(1)	9.9(4)
C24	−0.2760(6)	0.2239(6)	0.1801(9)	4.6(2)	C3s	0.5501(9)	0.9398(9)	0.079(2)	9.9(4)
C25	−0.2731(5)	0.1851(5)	0.0240(9)	3.8(2)					

metallocene–like cations (eq 1). These cations form in



(1)

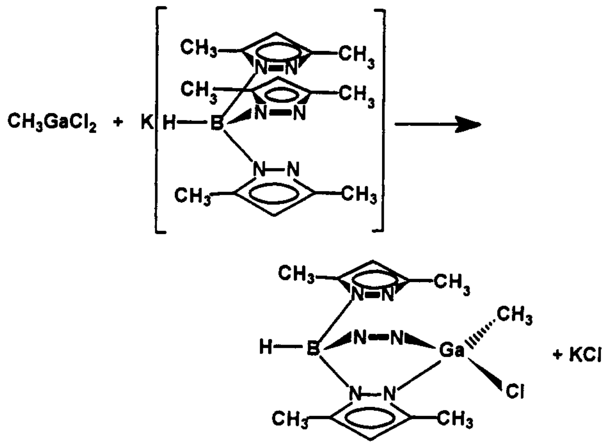
reactions with either 1 or 2 equiv of the ligand. An analogous preparation of $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}^+$ has been reported earlier, including the determination of the solid state structure.[9] Surprisingly, the cation is also formed in the reaction of 1 equiv of $[HB(pz)_3]^-$ and $GaCH_3Cl_2$ (eq 2). In this case, a methyl group,

$$CH_3GaCl_3 \xrightarrow{K[HB(pz)_3]} \{[HB(pz)_3]_2Ga\}[Ga(CH_3)Cl_3] \quad (2)$$

as well as the chlorides, must be displaced by the $[HB(pz)_3]^-$ ligands. The anion isolated from the reaction contains one methyl group, and a small amount of $[HB(pz)_3]Ga(CH_3)_2$ is also formed. Although $[B(pz)_4]^-$ reacts in a similar fashion, it did not prove possible to isolate the product in pure form. The driving force for these unusual reactions must be the formation of the extremely stable, octahedral cations. In contrast, both $[H_2B(pz)_2]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$ (vide infra) react with $GaCH_3Cl_2$ to form neutral [poly(pyrazolyl)borato]Ga(CH₃)Cl complexes.[1]

These six coordinate gallium cations are air stable in both the solid and solution phases. They do not react with nucleophiles. In contrast, four coordinate $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ reacts with CH_3Li (4 equiv) to yield $[H_2B(pz)_2]Ga(CH_3)_2$. Also, $\{[B(pz)_4]_2Ga\}^+$ is the only gallium complex of the tetrakis(pyrazolyl) borate ligands reported here that is not fluxional at ambient temperature, showing the expected 3/1 pattern (three coordinated and one noncoordinated pyrazolyl ring) for each of the three types of hydrogen atoms in the pyrazolyl rings.

$[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$. One equivalent of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand reacts with $GaCH_3Cl_2$ to yield $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ (eq 3). This complex is



(3)

partially soluble in aromatic solvents and freely soluble in halocarbons. It is air stable in solution. Its solubility in benzene was too low for a molecular weight determination.

The pyrazolyl rings in this complex are equivalent in ¹H NMR spectra, even at −90 °C. Given that there is no arrangement of the ligands in which the rings can be

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[9] Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277.

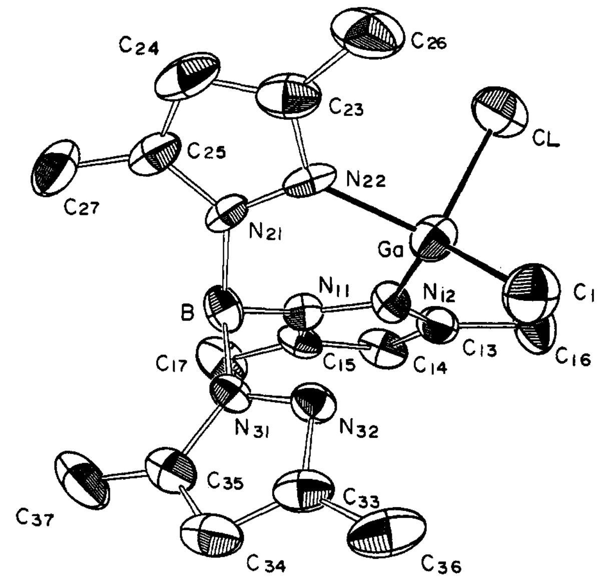


Figure 1. ORTEP diagram of [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)Cl.

equivalent in this molecule, the structure in the solid state was determined by X-ray crystallography.

An ORTEP drawing of [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)Cl is shown in Figure 1; selected bond distances and angles are shown in Table V. The complex is four coordinate, with the [HB(3,5-Me$_2$pz)$_3$] ligand exhibiting only bidentate coordination. The shortest intermolecular Ga···Cl distance is 7 Å, indicating that there are no bridging interactions.

The geometry about the gallium atom can be described as distorted tetrahedral. The N12–Ga–N22 angle is restricted by the chelate ring to 97.3(3)°, but the C1–Ga–Cl angle trans to it is 107.9(3)°. The chloride ligand is rotated toward the nitrogen donor atoms, reducing the Cl–Ga–N angles to an average of 99.3(2)°, and the methyl ligand is rotated away from the nitrogen donor atoms, giving an average C1–Ga–N angle of 124.1(4)°.

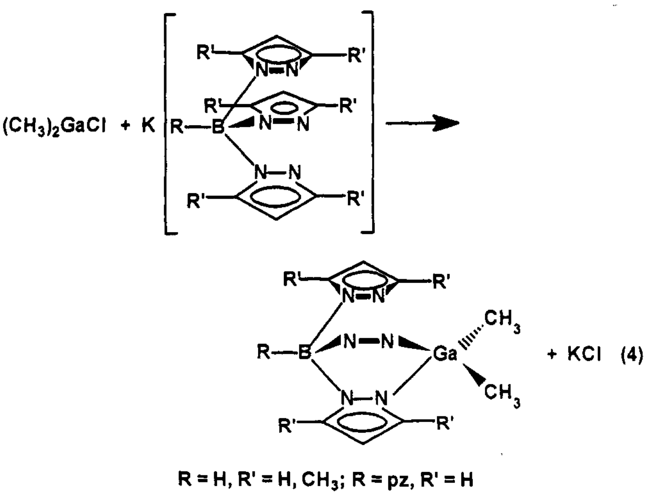
The long pyrazolyl ring Ga···N32 distance is 2.897(7) Å, nearly 1 Å longer than the normal bonding interactions. The proximity of this donor atom to the metal appears to be the reason for the asymmetric arrangement of C1 and the chloride ligand. The asymmetry can be explained by either the presence of a weak bonding interaction with the lone pair on N32 or simply nonbonding steric effects. If the long interaction is considered as a weak bond, the geometry about the gallium atom can be viewed as trigonal bipyramidal with the long bond and the chlorine atom in the axial positions.

We have previously reported the structure of [H$_2$B(pz)$_2$]In(CH$_3$)Cl, an indium analog of this gallium structure.[10] In the indium structure there are two independent dimeric units held together by long (average of 3.13 Å) bridging chlorine interactions. The bond distances in the gallium and indium structures are similar after correcting for the 0.15 Å larger radius of indium(III),[11] but the bond angles are different because of the bridging interactions. The weak Ga···N32 interaction in the gallium complex can be viewed as replacing the chloride bridging interaction in the indium compound, although the impact on the coordination geometry of the remaining ligands is greater in the indium complex.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)Cl and [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)$_2$ with Esd's in Parentheses

	[HB(3,5-Me$_2$pz)$_3$]-Ga(CH$_3$)Cl	[HB(3,5-Me$_2$pz)$_3$]-Ga(CH$_3$)$_2$
	Bond Lengths	
Ga–N12	1.930(7)	1.968(8)
Ga–N22	1.943(7)	1.998(8)
Ga···N32	2.897(7)	3.420(8)
Ga–C1	1.93(1)	1.968(9)
Ga–Cl(C2)	2.259(3)	1.97(1)
N11–N12	1.353(9)	1.371(9)
N11–C15	1.35(1)	1.36(1)
N11–B	1.55(1)	1.55(1)
N12–C13	1.35(1)	1.35(1)
C13–C14	1.36(1)	1.37(1)
C13–C16	1.48(1)	1.50(1)
C14–C15	1.39(1)	1.38(1)
C15–C17	1.48(1)	1.49(1)
	Bond Angles	
N12–Ga–N22	97.3(3)	95.4(3)
N12–Ga–N32	73.3(3)	66.0(2)
N12–Ga–C1	124.3(4)	114.6(5)
N12–Ga–Cl(C2)	99.0(2)	105.6(4)
N22–Ga–N32	74.5(3)	66.8(3)
N22–Ga–C1	123.9(4)	115.5(4)
N22–Ga–Cl(C2)	99.5(2)	105.0(4)
N32–Ga–C1	123.9(4)	75.4(4)
N32–Ga–Cl(C2)	169.2(2)	166.6(3)
C1–Ga–Cl(C2)	107.9(3)	117.9(4)
N12–N11–C15	109.9(7)	108.7(7)
N12–N11–B	120.9(7)	122.7(7)
C15–N11–B	127.8(7)	128.3(7)
Ga–N12–N11	123.1(5)	124.8(6)
Ga–N12–C13	128.5(6)	125.2(6)
N11–N12–C13	107.6(6)	107.4(7)
N12–C13–C16	122.5(8)	121.9(9)
C14–C13–C16	128.8(9)	129(1)
C13–C14–C15	107.6(8)	107.2(9)
N11–C15–C14	106.3(7)	107.7(8)
N11–C15–C17	124.1(8)	123.8(9)
C14–C15–C17	129.5(8)	128(1)
N11–B–N21	109.8(7)	113.5(8)
N11–B–N31	109.8(7)	108.3(8)
N21–B–N31	108.9(7)	109.5(8)

(ligand)Ga(CH$_3$)$_2$. All three poly(pyrazolyl)borate ligands studied here react with Ga(CH$_3$)$_2$Cl to yield the respective (ligand)Ga(CH$_3$)$_2$ complexes in good yield (eq 4). [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)$_2$ can also be prepared by



the reaction of [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)Cl and CH$_3$Li. These complexes are soluble in aromatic and halocarbon solvents and are air stable in solution.

At ambient temperature, [HB(3,5-Me$_2$pz)$_3$]Ga(CH$_3$)$_2$ and [HB(pz)$_3$]Ga(CH$_3$)$_2$ show single resonances in ^{1}H

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[10] (a) Reger, D. L.; Knox, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* 1990, *9*, 2581. (b) Reger, D. L.; Mason, S. S.; Rheingold, A. L. *Inorg. Chem.*, submitted for publication.

[11] Shannon, R. D. *Acta Crystallogr., Sect. A* 1976, *A32*, 751.

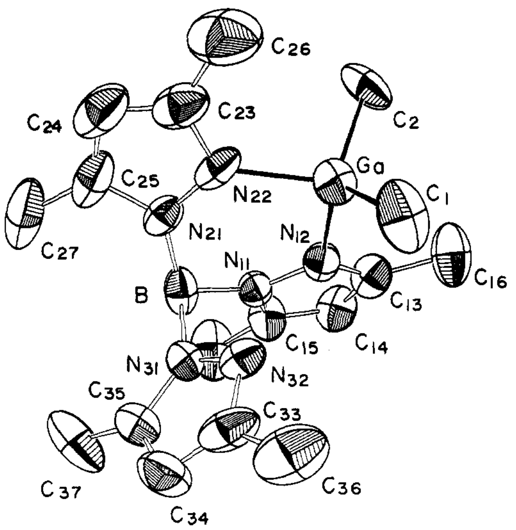

Figure 2. ORTEP diagram of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$.

NMR spectra for each of the three types of hydrogen atoms in the pyrazolyl rings and a single resonance for the two methyl groups on gallium. At low temperatures for both complexes each of the resonance types for the pyrazolyl rings are in a 2/1 ratio and the methyl groups on gallium become nonequivalent. The barrier to the dynamic process for $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ is 13.7 kcal/mol, as measured for the methyl ligand resonances at 6 °C. The temperature dependent behavior for the methyl group resonance is interesting. At −90 °C they are separated by 70 Hz, but as the temperature increases the resonance that is initially more shielded moves dramatically to lower field while both remain sharp. At −40 °C only a single sharp resonance is observed which separates again at −27 °C. Line broadening does not start until −15 °C.

The low temperature spectra are consistent with either a five coordinate, trigonal bipyramidal coordination sphere or a four coordination geometry with a noncoordinated pyrazolyl ring, the geometry observed in the solid state for $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$. We initially favored the former interpretation on the basis of the fact that $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ shows equivalent rings in its ^1H NMR spectra even at −90 °C, a result very different from that observed with the [tris(pyrazolyl)borato]$Ga(CH_3)_2$ complexes.

The solid state structure of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ has been determined in order to definitively establish the coordination geometry. The structure is shown in Figure 2 and bond angles and distances are given in Table V. The molecule is monomeric and four coordinate at gallium. One of the pyrazolyl rings is clearly not bonded to the gallium with a Ga···N32 distance of 3.420(8) Å.

The geometry about the gallium is best described as tetrahedral. As with $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, the methyl ligands are rotated away from the noncoordinated pyrazolyl ring with average C1–Ga–N angles of 115.1(5)° and C2–Ga–N angles of 105.3(4)°, but the distortion is considerably less in this case. A similar, but even less pronounced, distortion is observed in the structure of $[Me_2B(pz)_2]Ga(CH_3)_2$.[12] In this case, the methyl groups on gallium rotate away from the methyl group on the boron that is closer to the gallium due to the boat arrangement of the BN_4Ga ring. Other bond distances and angles are also similar in these two structures.

There is a significant difference between these two gallium structures and the related structure of $[H_2B(pz)_2]In(CH_3)_2$.[10] The Cl–Ga–C2 angles are 117.9(4) and 121.3(3)°, whereas the C1–In–C2 angle opens to 141.1(1)°. As we have noted previously, large C–In–C angles are a feature that seems to be general for four coordinate $In(CH_3)_2$ structures.[13] This type of distortion appears to not be very important for gallium.

The differences in the observed NMR behavior of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ and $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ are surprising. In both cases, the most reasonable dynamic process to explain the equilibration of the resonances for the ring hydrogen atoms and the equilibration of the methyl ligands is an intramolecular rearrangmenet involving an association–dissociation of the pyrazolyl rings, going through a five coordinate intermediate. The proximity of the third pyrazolyl ring to the gallium for $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ may considerably lower the barrier to such a process for this molecule in comparioson to $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, leading to the observed lower rearrangement barrier.

The ambient temperature ^1H NMR spectrum of $[B(pz)_4]Ga(CH_3)_2$ shows two equal intensity resonances for each of the three types of hydrogen atoms in the pyrazolyl rings and a single resonance for the methyl groups on gallium. The resonances broaden at lower temperatures, but a limiting spectra was not observed at −90 °C. A tetrahedral structure with the tetrakis(pyrazolyl)borate ligand undergoing a rapid flip of the BN_4Ga ring to equilibrate the noncoordinated pyrazolyl rings and the methyl groups explains the ambient temperature spectrum. It is also reasonable to assign a similar four coordinate structure to $[HB(pz)_3]Ga(CH_3)_2$.

(Ligand)₂GaCH₃. The reaction of 2 equiv of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCH_3Cl_2$ yields the respective (ligand)$_2$$GaCH_3$ complexes (eq 5). In contrast, a similar reaction with 2 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ yields $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$.

$$CH_3GaCl_2 + 2K[RB(pz)_3] \rightarrow [RB(pz)_3]_2GaCH_3 + 2KCl \quad (5)$$

$$R = H, pz$$

The ^1H NMR spectra of $[HB(pz)_3]_2GaCH_3$ and $[B(pz)_4]_2GaCH_3$ show single resonances for each type of pyrazolyl ring hydrogen atom at ambient temperature. Although a limiting spectra could not be observed for $[B(pz)_4]_2GaCH_3$, each of the pyrazolyl ring resonances for $[HB(pz)_3]_2GaCH_3$ freeze out at low temperatures to a 1/1/2/2 pattern. These spectra can be explained by a five coordinate square pyramidal structure (**D**), by a six coordinate octahedral structure (**E**), or by a seven coordinate capped octahedral arrangement with the methyl group in the capping position (**F**). Efforts to obtain

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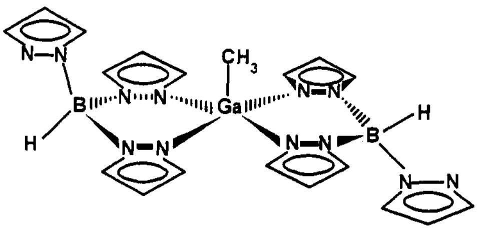

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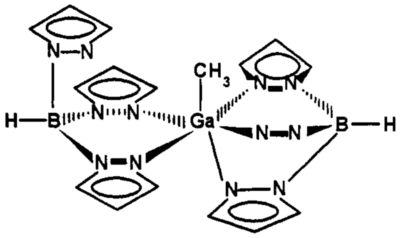

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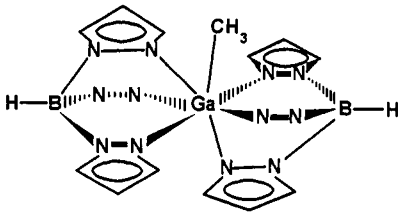

F

suitable crystals of $[HB(pz)_3]_2GaCH_3$ for a crystallographic study failed, but the structure of $[B(pz)_4]_2GaCH_3$ in the solid state has been determined.

An ORTEP drawing of $[B(pz)_4]_2GaCH_3$ is shown in Figure 3, and important bond distances and angles are shown in Table VI. The molecule is monomeric in the solid phase with 0.5 equiv of benzene also present (verified by NMR).

The most important feature in the structure is that gallium is six coordinate (structure E) with both a tridentate and bidentate tetrakis (pyrazolyl) borate ligand. The arrangement of the donor atoms is nearly octahedral. The intraligand N–Ga–N bond angles range from 79.7 to 87.6°, with the largest angle formed by the nitrogen atoms of the chelate ring of the bidentate ligand. The C–Ga–N angles range from 94.1 to 100.6°. The two angles from the bidentate ligand are the larger ones, a consequence of the orientation of the boat configuration of the BN_4Ga ring. In this ligand, the noncoordinated pyrazolyl ring distant from the metal straddles the two coordinated rings, and the remaining ring is oriented perpendicular to the distant ring to avoid intraligand contacts. This orientation places the potential nitrogen donor atom of the noncoordinated pyrazolyl ring closer to the metal, N72, such that the lone pair is not pointing at the metal. In contrast, the noncoordinated rings in the two structures of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand discussed above are orientated such that the lone pair on the nitrogen donor atom points at the metal.

The Ga–Cl distance is normal and very close to those observed in the tetrahedral structures, even though the average Ga–N distance is 0.18 Å longer, as expected in going from four to six coordination.[11] The shortest Ga–N bond distance is that trans to the methyl ligand. This result is surprising given that the trans influence of a methyl ligand would be expected to be greater than that of nitrogen donor ligand.[14] The Ga–N distances for the bidentate ligand are almost as short, and the Ga–N distances in the tridentate ligand cis to the methyl ligand are approximately 0.1 Å longer.

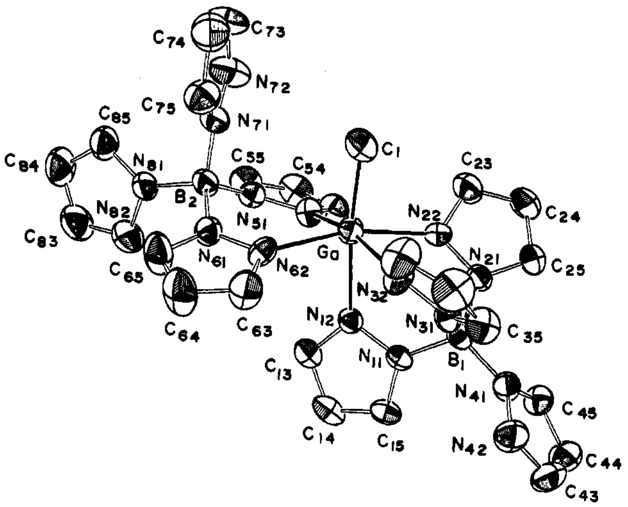

Figure 3. ORTEP diagram of $[B(pz)_4]_2GaCH_3$.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for $[B(pz)_4]_2GaCH_3 \cdot {}^1/_2C_6H_6$ with Esd's in Parentheses

	Bond Lengths		
Ga–N12	2.093(5)	N11–C15	1.352(8)
Ga–N22	2.190(5)	N11–B1	1.547(9)
Ga–N32	2.207(6)	N12–N22	2.767(8)
Ga–N52	2.122(5)	N12–N32	2.756(8)
Ga–N62	2.102(6)	N12–C13	1.343(9)
Ga–C1	1.965(8)	C13–C14	1.380(8)
N11–N12	1.369(6)	C14–C15	1.367(9)
	Bond Angles		
N12–Ga–N22	80.4(2)	N52–Ga–N62	87.6(2)
N12–Ga–N32	79.7(2)	N52–Ga–C1	99.6(3)
N12–Ga–N52	85.4(2)	N62–Ga–C1	100.6(3)
N12–Ga–N62	84.7(2)	N12–N11–C15	109.4(5)
N12–Ga–C1	172.8(3)	N12–N11–B1	121.1(4)
N22–Ga–N32	83.3(2)	C15–N11–B1	129.4(4)
N22–Ga–N52	92.7(2)	Ga–N12–C13	131.4(4)
N22–Ga–N62	165.1(2)	Ga–N12–C15	157.5(3)
N22–Ga–C1	94.1(3)	N11–N12–C13	106.2(4)
N32–Ga–N52	165.0(2)	N12–C13–C14	110.3(5)
N32–Ga–N62	92.6(2)	C13–C14–C15	105.8(6)
N32–Ga–C1	95.1(3)	N11–C15–C14	108.3(5)

The structure of $[HB(pz)_3]_2GaCH_3$ is also likely to be six coordinate. As observed here for gallium, in the analogous chemistry of indium[10b] the metal shows a very strong tendency to form six coordinate complexes. The tendency of indium to prefer six coordination, especially with hard donor atoms, has been well documented previously.[15] Gallium shows a similar tendency.

Conclusion

The stable six coordinate cations, $[(ligand)_2Ga]^+$, form in the reaction of $GaCl_3$ with any of the ligands $[HB(pz)_3]^-$, $[B(pz)_4]^-$, and $[HB(3,5\text{-}Me_2pz)_3]^-$. These cations are also formed in the reactions of 1 equiv of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCH_3Cl_2$, but the neutral complex $[HB(3,5\text{-}Me_2pz)_3](CH_3)Cl$ forms with the methyl substituted ligand.

All three poly(pyrazolyl) borate ligands studied here react with $Ga(CH_3)_2Cl$ to yield the respective (ligand)$Ga(CH_3)_2$ complexes. X-ray crystallography has shown

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[14] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience: New York, 1988; p 1300.

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that $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ and $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ are four coordinate in the solid state with an approximate tetrahedral geometry about the gallium atom. In both complexes the nitrogen donor atom of the noncoordinated ring points toward the metal. For $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$, it is only 2.897(7) Å away from the gallium atom, possibly indicating a weak interaction. The observation that the metal does not form a strong bond with a donor atom held in close proximity by the potentially tridentate poly(pyrazolyl)borate ligands shows that gallium strongly prefers four over five coordination in these complexes. These four coordinate complexes are fluxional in solution, and a five coordinate intermediate is proposed in the mechanism for the equilibration of the rings. The five coordinate complexes $[H_2B(pz)_2]_2GaCl$ and $[H_2B(pz)_2]_2GaCH_3$ have been synthesized previously.[1]

The complexes $[HB(pz)_3]_2GaCH_3$ and $[B(pz)_4]_2GaCH_3$ have been prepared, and the latter has been shown to be six coordinate in the solid state, containing both a tridentate and a bidentate $[B(pz)_4]^-$ ligand. In these complexes, gallium shows a preference for six over either seven or five coordination. The $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is too bulky to form $[HB(3,5\text{-}Me_2pz)_3]_2GaCH_3$.

An overall structural conclusion is that in complexes with polydentate ligands in which more than one coordination number is reasonable, gallium(III) prefers four over five coordination and prefers six over either five or seven coordination.

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Supplementary Material Available: Tables of complete bond distances, angles, anisotropic thermal parameters, and positional parameters of H atoms (23 pages). Ordering information is given on any current masthead page.

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