Articles

Organometallic Complexes of Gallium Stabilized by the Dihydrobis(pyrazolyl)borate Ligand

Daniel L. Reger,* Steven J. Knox, and Lukasz Lebioda

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

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The reaction of $GaCl_3$ with 2 and 3 equiv of $K[H_2B(pz)_2]$ (pz = pyrazolyl ring) yields $[H_2B(pz)_2]_2GaCl$ (1) and $[H_2B(pz)_2]_3Ga$ (2), respectively, but the reaction with 1 equiv of the ligand salt yields $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ (3). The complexes $[H_2B(pz)_2]_2GaCH_3$ (4) and $[H_2B(pz)_2]Ga(CH_3)Cl$ (5) are prepared from the reaction of CH_3GaCl_2 with 2 or 1 equiv of $K[H_2B(pz)_2]$, respectively. Complex 5 also forms in the exchange reaction of $(CH_3)_2GaCl$ and $[H_2B(pz)_2]_2GaCl$. $[H_2B(pz)_2]Ga(CH_3)_2$ (6) is prepared by the reaction of $(CH_3)_2GaCl$ and $K[H_2B(pz)_2]$. It is also formed in the reaction of 5 with CH_3Li. The reaction of 3 with 1 equiv of CH_3Li yields a mixture of 4 and 6. The reaction of 3 with 4 equiv of CH_3Li yields 6 exclusively and in high yield based on both gallium atoms in 3. The dimethyl complex 6 reacts with CH_3CO_2H to yield $[H_2B(pz)_2](CH_3)Ga(O_2CCH_3)$ (7). The monomethyl complexes 4 and 7 are stable in the presence of CH_3CO_2H. The organometallic complexes 4–7 are all monomeric in benzene solution and stable to air for extended periods. CH_3CO_2H reacts with $[H_2B(pz)_2]_3Ga$ to yield $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (8). Molecular weight determinations for 8 in benzene solution yield values between a monomer and a dimer. An X-ray crystallographic study shows that in the solid state 8 is monomeric with an octahedral geometry about gallium. Crystal data: monoclinic, $P2_1/n$, $a = 8.492$ (2) Å, $b = 8.087$ (6) Å, $c = 8.278$ (2) Å, $\beta = 103.85$ (2)°, $V = 1917$ Å^3, $Z = 4$, and $\rho = 1.465$ g cm^{-3}.

Introduction

Expanding on earlier studies with group 3 metals and the lanthanides,[1] we have initiated a new investigation exploring the chemistry of group 13, main-group metals using the stabilizing effects of poly(pyrazolyl)borate ligands. The chemistry of these metals is of importance in the diagnosis of disease[2] and in the preparation of new semiconductor materials.[3] Despite this importance, there have been limited efforts in this area, many of them having been quite recent.[4] Our interests in main-group metals lie particularly in the preparation of organometallic complexes stabilized by anionic, chelating ligands.

In our initial publication in this area,[5] we communicated the synthesis of $[H_2B(pz)_2]_2GaCl$ (1) and $[H_2B(pz)_2]_3Ga$ (2), where pz = pyrazolyl ring. These complexes are prepared from the reaction of $GaCl_3$ with the appropriate stoichiometric amount of the ligand salt. The solid-state structure of 1 showed a trigonal-bipyramidal arrangement of the donor atoms with each $[H_2B(pz)_2]$ ligand occupying one axial and one equatorial site. To our knowledge, no other dihydrobis(pyrazolyl)borate complexes of gallium have been reported. Cowley has recently reported the cationic complex $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}[GaCl_4]$, having a substituted hydrotris(pyrazolyl)borate ligand.[6] Reported here are results on the preparation and characterization of organometallic complexes in the [dihydrobis(pyrazolyl)borato]gallium(III) system. Also included are the synthesis and structural characterization by X-ray crystallography of $[H_2B(pz)_2]_2Ga(O_2CCH_3)$.

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. Infrared spectra were recorded on a Nicolet DX V4.56 spectrometer. The ^1H solution NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. Proton chemical shifts are reported in ppm vs Me_4Si. The BH_2 resonance is a broad (covers ca. 1.3 ppm) quartet with the center located as indicated for each compound. Mass spectra were run on a Finnigan 4521 GC–mass spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. $K[H_2B(pz)_2]$[7] and CH_3GaCl_2[8] were prepared by the published methods. Anhydrous $GaCl_3$ was purchased from Aldrich Chemicals and was freshly sublimed prior to each use. Molecular weights were determined by freezing point

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depression measurements in an apparatus similar in basic design to that described by Shriver.[9] The cell contains a Fenwal GB41P2 10-kΩ thermistor, balanced against a Leeds & Northrup bridge circuit. A working calibration curve of ΔΩ vs molality was obtained by using known concentrations of doubly sublimed ferrocene. Data acquisition and processing were automated by interfacing the apparatus to a WYSE 286 computer. Typically, the mass of a sample was determined on a benchtop analytical balance and the sample then quickly transported into the drybox. The solute and the solvent were then introduced to the cryoscopy cell under the nitrogen atmosphere.

Bis[dihydrobis(1-pyrazolyl)borato]gallium Tetrachlorogallate, $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ (3). $GaCl_3$ (0.70 g, 4.0 mmol) was dissolved in THF (15 mL, precooled to −78 °C). $K[H_2B(pz)_2]$ (0.74 g, 4.0 mmol) was added, and the mixture was stirred and warmed to room temperature. After 12 h the solvent was evaporated under vacuum. The white residue was extracted with CH_2Cl_2 (50 mL) and the extract filtered. Evaporation of the CH_2Cl_2 under vacuum yielded a white solid (1.95 g, 3.4 mmol, 85%). ^1H NMR ($CDCl_3$, δ): 7.86, 7.76 (4, 4; d, d; J = 1.7, 1.8 Hz; 3-H, 5-H (pz)); 6.44 (4, t, J = 1.9 Hz, 4-H (pz)); 3.6 (broad, BH_2). IR (CH_2Cl_2, cm^{-1}): 2471, 2417 (BH_2). The FAB mass spectrum shows a cluster for $GaCl_4^-$ at m/e 211. Anal. Calcd for $C_{12}H_{16}N_8Cl_4B_2Ga_2$: C, 25.05; H, 2.81. Found: C, 24.53; H, 3.22.

Bis[dihydrobis(1-pyrazolyl)borato]methylgallium(III), $[H_2B(pz)_2]_2GaCH_3$ (4). $K[H_2B(pz)_2]$ (1.43 g, 7.7 mmol) in THF (30 mL, −78 °C) was added to CH_3GaCl_2 (0.60 g, 3.8 mmol) in THF (10 mL, precooled to −78 °C). The solution was warmed to room temperature and was stirred over a 5-h period. The solvent was evaporated under vacuum, the residue extracted with benzene (40 mL), and the extract filtered. The benzene was removed under vacuum to yield a white solid (1.10 g, 2.9 mmol, 76%). The analytical sample was recrystallized from a benzene/hexane mixture cooled to 0 °C; mp 157–159 °C. ^1H NMR ($CDCl_3$, δ): 7.60, 7.35 (4, 4; d, d; J = 1.8, 1.9 Hz; 3-H, 5-H (pz)); 6.19 (4, t, J = 2.1 Hz, 4-H (pz)); 3.6 (broad, BH_2); 0.39 (3, s, CH_3). IR (benzene, cm^{-1}): 2428 (BH_2). The mass spectrum shows $M^+ - H$ and $M^+ - CH_5$ clusters at m/e 377 and 361. Anal. Calcd for $C_{13}H_{19}N_8B_2Ga$: C, 41.23; H, 5.07. Found: C, 41.00; H, 4.91.

Chloro[dihydrobis(1-pyrazolyl)borato]methylgallium(III), $[H_2B(pz)_2]CH_3GaCl$ (5). $K[H_2B(pz)_2]$ (2.39 g, 13 mmol) in THF (25 mL, −78 °C) was added to CH_3GaCl_2 (2.00 g, 13 mmol) in THF (10 mL, precooled to −78 °C). The solution was warmed to room temperature and was stirred over a 10-h period. The solvent was evaporated under vacuum, the residue extracted with benzene (50 mL), and the extract filtered. The benzene was removed under vacuum to yield a white solid (2.63 g, 9.8 mmol, 75%); mp 52–54 °C. ^1H NMR ($CDCl_3$, δ): 7.78, 7.67 (2, 2; d, d; J = 2.1; 2.0 Hz; 3-H, 5-H (pz)); 6.34 (2, t, J = 2.2 Hz, 4-H (pz)); 3.6 (broad, BH_2); 0.33 (3, s, CH_3). IR (benzene, cm^{-1}): 2464, 2450, 2404 (BH_2). The mass spectrum shows $M^+ - 2H$, $M^+ - CH_4$, and $M^+ - Cl$ clusters at m/e 265, 251, and 231. Anal. Calcd for $C_7H_{11}N_4BClGa$: C, 31.47; H, 4.16; N, 20.96. Found: C, 31.75; H, 4.04; N, 20.86. Cryoscopic molecular weight (benzene solution, formula weight 267; observed molality, observed molecular weight): 0.0555, 263; 0.1065, 266.

Dimethyl[dihydrobis(1-pyrazolyl)borato]gallium(III), $[H_2B(pz)_2]Ga(CH_3)_2$ (6). Method A. $GaCl_3$ (0.34 g, 1.9 mmol) was placed in a round-bottomed flask, and diethyl ether (5 mL) was added via syringe. The solution was cooled to −78 °C, and CH_3Li (3.8 mL, 3.8 mmol) was added. The mixture was warmed to room temperature and was stirred overnight. $K[H_2B(pz)_2]$ (0.35 g, 1.9 mmol) was added and the mixture stirred for an additional 8 h. The solvent was evaporated under vacuum. The white residue was extracted with hexane (40 mL) and the extract filtered. Evaporation of the hexane under vacuum yielded a colorless oil (0.42 g, 1.7 mmol, 89%). ^1H NMR ($CDCl_3$, δ): 7.64, 7.55 (2, 2; d, d; J = 2.1, 2.2 Hz; 3-H, 5-H (pz)); 6.27 (2, t, J = 2.2 Hz, 4-H (pz)); 3.5 (broad, BH_2); −0.06 (6, s, CH_3). IR (benzene, cm^{-1}): 2433, 2413 (BH_2). The mass spectrum shows $M^+ - H$, $M^+ - CH_3$, and $M^+ - C_2H_7$ clusters at m/e 245, 231, and 215. Anal. Calcd for $C_8H_{14}N_4BGa$: C, 38.94; H, 5.73; N, 22.69. Found: C, 39.13; H, 5.47; N, 22.18. Cryoscopic molecular weight (benzene solution, formula weight 247; observed molality, observed molecular weight): 0.0688, 248; 0.0993, 258.

Method B. $GaCl_3$ (1.00 g, 5.67 mmol) was placed in a round-bottomed flask equipped with a condenser, and diethyl ether (10 mL) was added via syringe. CH_3MgBr (5.87 mL, 17.6 mmol) was added and the mixture stirred for 1 h and then heated at reflux for an additional 3 h. Diethyl ether and $Ga(CH_3)_3$ were distilled under vacuum into a second round-bottomed flask containing $GaCl_3$ (0.45 g, 2.6 mmol) at −196 °C. A condenser was fitted to the flask, and the clear solution was heated at reflux for 16 h. The solution was cooled to −78 °C, and $K[H_2B(pz)_2]$ (1.43 g, 7.7 mmol) was added. The mixture was warmed to room temperature and was stirred for 6 h. The solvent was evaporated under vacuum. The white residue was extracted with hexane (40 mL), and the extract filtered. Evaporation of the hexane under vacuum yielded a colorless oil that was shown by NMR spectroscopy to be a pure sample of **6** (2.9 g, 11.7 mmol, 55%).

Method C. $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ (0.50 g, 0.87 mmol) was placed in a round-bottomed flask, and THF (10 mL) was added via syringe. The solution was cooled to −78 °C, and CH_3Li (3.65 mL, 3.65 mmol) was added. The mixture was warmed to room temperature, while being stirred, over a 4-h period. The solvent was then evaporated under vacuum. The white residue was extracted with hexane (40 mL) and the extract filtered. The hexane was removed under vacuum to yield a colorless oil that was shown by NMR spectroscopy to be a pure sample of **6** (0.41 g, 1.6 mmol, 94% based on both gallium atoms in **3**).

Method D. $[H_2B(pz)_2]Ga(CH_3)Cl$ (0.20 g, 0.75 mmol) was placed in a round-bottomed flask, and THF (10 mL) was added via syringe. The solution was cooled to −78 °C, and CH_3Li (0.75 mL, 0.75 mmol) was added. The mixture was warmed to room temperature, while being stirred, over a 3-h period. The solvent was then evaporated under vacuum. The white residue was extracted with hexane (40 mL) and the extract filtered. The hexane was removed under vacuum to yield a colorless oil that was shown by NMR spectroscopy to be a pure sample of **6** (0.17 g, 0.69 mmol, 92%).

(Acetato)[dihydrobis(1-pyrazolyl)borato]methylgallium(III), $[H_2B(pz)_2](CH_3)Ga(O_2CCH_3)$ (7). Method A. CH_3CO_2H (30.3 μL, 0.53 mmol) was added to $[H_2B(pz)_2]Ga(CH_3)_2$ (0.20 g, 0.53 mmol) in benzene (10 mL). The solution was stirred overnight at room temperature. The solution was filtered and the benzene evaporated under vacuum to yield a white solid (0.15 g, 0.52 mmol, 98%). The analytical sample was recrystallized from a benzene/hexane mixture cooled to 0 °C; mp 80–82 °C. ^1H NMR ($CDCl_3$, δ): 7.63 (4, d, J = 1.5 Hz, 3-H, 5-H (pz)); 6.25 (2, t, J = 2.0 Hz, 4-H (pz)); 3.5 (broad, BH_2); 2.11 (3, s, O_2CCH_3); 0.28 (3, s, CH_3). IR (benzene, cm^{-1}): 2462 (sh), 2441, 2416 (BH_2); 1647, 1621 (CO_2). The mass spectrum shows $M^+ - H$, $M^+ - CH_3$, and $M^+ - O_2CCH_3$ clusters at m/e 289, 275, and 231. Anal. Calcd for $C_9H_{14}N_4O_2BGa$: C, 37.17; H, 4.86. Found: C, 37.07; H, 4.90. Cryoscopic molecular weight (benzene solution, formula weight 290; observed molality, observed molecular weight): 0.0613, 295; 0.1859, 309.

Method B. CH_3GaCl_2 (0.30 g, 1.9 mmol) was dissolved in THF (10 mL, precooled to −78 °C). $K[H_2B(pz)_2]$ (0.36 g, 1.9 mmol) and $Na[O_2CCH_3]$ (0.16 g, 1.9 mmol) were added, and the mixture was stirred at room temperature overnight. The solvent was evaporated under vacuum and the white residue extracted with benzene (40 mL). The extract was filtered, and the benzene was evaporated under vacuum to yield a white solid that was shown by NMR spectroscopy to be a pure sample of **7** (0.46 g, 1.6 mmol, 84%).

(Acetato)bis[dihydrobis(1-pyrazolyl)borato]gallium(III), $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (8). Method A. $K[H_2B(pz)_2]$ (1.06 g, 5.70 mmol) and $Na[O_2CCH_3]$ (0.234 g, 2.85 mmol) were dissolved in THF (40 mL, −78 °C), and the solution was added to $GaCl_3$ (0.503 g, 2.85 mmol) in THF (10 mL, precooled to −78 °C). This mixture was warmed to room temperature while being stirred for 8 h. The solvent was then evaporated under vacuum. The residue was extracted with benzene (50 mL) and the extract filtered. The benzene was removed under vacuum to yield a white solid (1.18 g, 2.79 mmol, 98%). The analytical sample was recrystallized from a benzene/hexane mixture cooled to 0 °C; mp 125–127 °C. ^1H NMR ($CDCl_3$, δ): 7.61, 7.34 (4, 4; d, d; J = 2.1, 1.7 Hz; 3-H, 5-H (pz)); 6.21 (4, t, J = 2.2 Hz, 4-H (pz)); 3.4 (broad, BH_2); 2.23 (3,

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Table I. Crystallographic Data for the Structural Analysis of $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (8)

formula	$C_{14}H_{19}B_2N_8O_2Ga$
mol wt	422.7
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.492 (2)
b, Å	8.087 (6)
c, Å	8.278 (2)
α, deg	90
β, deg	103.85 (2)
γ, deg	90
V, Å^3	1917
Z	4
cryst size, mm	0.3 × 0.2 × 0.2
monochromator	graphite
radiation	Mo Kα (0.71073 Å)
ρ_{calc}, g cm^{-3}	1.465
temp, °C	23
2θ range, deg	4–50 ($\pm h,+k,+l$)
no. of rflns measd	3698
no. of reflns obsd	3454
linear abs coeff, cm^{-1}	14.54
transmissn factors	
max	1.041
min	0.775
av	0.959
decay cor	
max	1.027
av	1.013
R_F	0.039
R_{wF}	0.047

s, CH_3). IR (benzene, cm^{-1}): 2460 (sh), 2428 (BH_2); 1559, 1539 (CO_2). The mass spectrum shows $M^+ - H$, $M^+ - O_2CCH_3$, and $M^+ - H_2B(pz)_2$ clusters at m/e 421, 363, and 275. Anal. Calcd for $C_{14}H_{19}N_8B_2O_2Ga$: C, 39.78; H, 4.54. Found: C, 39.53; H, 4.54. Cryoscopic molecular weight (benzene solution, formula weight 423; observed molality, observed molecular weight): 0.0272, 535; 0.0965, 547.

Method B. CH_3CO_2H (38.7 μL, 0.64 mmol) was added to $[H_2B(pz)_2]_3Ga$ (0.30 g, 0.59 mmol) in benzene (10 mL). The solution was stirred overnight at room temperature. The resultant suspension was filtered, and hexane (40 mL) was added. Cooling the solution to 0 °C yielded colorless crystals that were shown by NMR spectroscopy to be a pure sample of 8 (0.21 g, 0.50 mmol, 85%).

Crystallographic Analysis of $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (8). A transparent crystal of 8 was mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cell was determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analysis are listed in Table I. Data were collected in the $\omega/2\theta$ scan mode with a 0.7° + (0.35 tan θ)° scan range. The structure was solved by the heavy-atom method and refined by using SDP.[17a] Hydrogen atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements were carried out with weights $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ for reflections with $I > 3\sigma(I)$, where $\sigma(I)$ was derived from counting statistics. Scattering factors and corrections for anomalous dispersion were taken from ref 17b. Absorption corrections were by the method of Walker and Stuart.[10] Table II shows atomic parameters for 8.

Results and Discussion

We have previously reported that the reaction of $GaCl_3$ with 2 and 3 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]_2GaCl$ (1) and $[H_2B(pz)_2]_3Ga$ (2), respectively.[5] A similar reaction with 1 equiv of the ligand does not yield $[H_2B(pz)_2]GaCl_2$ but the salt $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ (3; eq 1). The formation

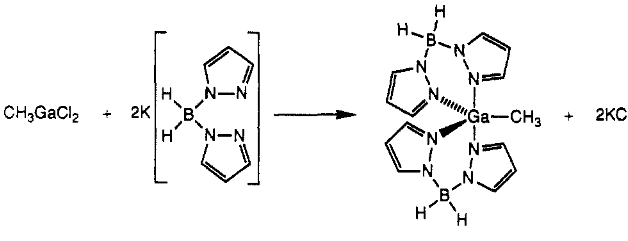
$$2GaCl_3 + 2K[H_2B(pz)_2] \rightarrow \underset{3}{\{[H_2B(pz)_2]_2Ga\}GaCl_4} + 2KCl \quad (1)$$

of a salt of this type has precedent in that Cowley has reported the reaction of $GaCl_3$ with 1 equiv of the substituted hydrotris(pyrazolyl)borate ligand $K[HB(3,5\text{-}Me_2pz)_3]$ yields $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}[GaCl_4]$.[6]

Table II. Positional Parameters for $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B, Å^2
Ga1	0.24760 (7)	0.11136 (2)	0.01210 (7)	3.27 (1)
O1	0.0668 (4)	0.0726 (1)	0.0954 (4)	4.46 (9)
O2	0.3144 (4)	0.0785 (1)	0.2391 (4)	4.22 (9)
N11	0.3978 (5)	0.0498 (2)	−0.2075 (5)	4.2 (1)
N12	0.2934 (5)	0.0504 (2)	−0.1068 (5)	3.9 (1)
N21	0.5518 (5)	0.1240 (2)	−0.1015 (5)	4.2 (1)
N22	0.4678 (5)	0.1355 (2)	0.0136 (5)	3.6 (1)
N31	0.1424 (6)	0.2119 (2)	0.0574 (6)	5.3 (1)
N32	0.1992 (5)	0.1708 (2)	0.1377 (5)	4.2 (1)
N41	0.0520 (5)	0.1789 (2)	−0.2325 (6)	4.9 (1)
N42	0.0919 (5)	0.1329 (2)	−0.1944 (5)	3.9 (1)
C1	0.1728 (6)	0.0628 (2)	0.2236 (6)	3.6 (1)
C2	0.1356 (8)	0.0333 (3)	0.3609 (8)	6.4 (2)
C13	0.2497 (8)	0.0049 (2)	−0.0889 (7)	4.7 (2)
C14	0.3276 (8)	−0.0244 (2)	−0.1789 (8)	6.1 (2)
C15	0.4191 (8)	0.0051 (3)	−0.2508 (7)	5.6 (2)
C23	0.5684 (7)	0.1597 (2)	0.1346 (7)	4.3 (1)
C24	0.7183 (7)	0.1635 (2)	0.0999 (8)	5.2 (2)
C25	0.7037 (6)	0.1407 (3)	−0.0486 (7)	5.2 (2)
C33	0.1988 (7)	0.1774 (2)	0.2982 (8)	5.3 (2)
C34	0.1443 (8)	0.2224 (3)	0.3232 (9)	6.9 (2)
C35	0.1086 (8)	0.2424 (2)	0.1694 (9)	7.0 (2)
C43	−0.0016 (7)	0.1054 (2)	−0.3119 (7)	4.9 (1)
C44	−0.1020 (8)	0.1342 (3)	−0.4280 (8)	6.5 (2)
C45	−0.0648 (7)	0.1794 (3)	−0.3740 (8)	6.5 (2)
B1	0.4694 (9)	0.0959 (3)	−0.2612 (8)	5.4 (2)
B2	0.144 (1)	0.2207 (3)	−0.124 (1)	6.9 (2)

The organometallic complex $[H_2B(pz)_2]_2GaCH_3$ (4) is prepared as in eq 2. The reactions of $[H_2B(pz)_2]_2GaCl$



4

(2)

with a variety of alkylation reagents such as CH_3Li and CH_3MgBr also yield 4, but it is contaminated by other products (mainly 6, vide infra). 4 is a high-melting solid that is freely soluble in aromatic solvents and halocarbon solvents but not saturated hydrocarbon solvents. The complex is stable in air both as a solid and in solution.

The reaction of CH_3GaCl_2 with 1 equiv of the dihydrobis(pyrazolyl)borate ligand yields $[H_2B(pz)_2]Ga(CH_3)Cl$ (5; eq 3). In contrast to the reaction of 1 equiv of the ligand

$$CH_3GaCl_2 + K[H_2B(pz)_2] \rightarrow \underset{5}{[H_2B(pz)_2]Ga(CH_3)Cl} + KCl \quad (3)$$

and $GaCl_3$ that yields the salt 3, introduction of the methyl group in the gallium starting material blocks salt formation. 5 also forms in the exchange reaction of 1 with $(CH_3)_2GaCl$ (eq 4). In this reaction, a dihydrobis(pyrazolyl)borate ligand as well as a methyl group must undergo transmetalation.

$$[H_2B(pz)_2]_2GaCl + (CH_3)_2GaCl \rightarrow 2[H_2B(pz)_2]Ga(CH_3)Cl \quad (4)$$

Complex 5 is also freely soluble in aromatic solvents and halocarbon solvents and slightly soluble in saturated hydrocarbon solvents. The compound is stable in air both

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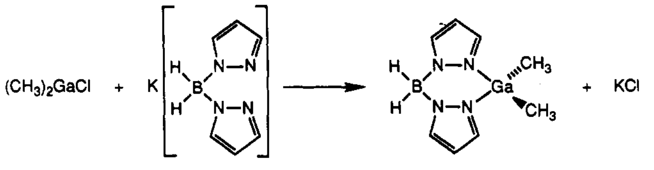
[10] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159.

as a solid and in solution. Molecular weight studies in benzene show that this complex is monomeric in solution.

The dimethyl complex $[H_2B(pz)_2]Ga(CH_3)_2$ (**6**) is prepared from $(CH_3)_2GaCl$ as shown in eq 5. In this reaction,



6

(5)

$(CH_3)_2GaCl$ is prepared from $GaCl_3$ and 2 equiv of CH_3Li in diethyl ether followed by in situ addition of the dihydrobis(pyrazolyl)borate salt, a method that avoids the difficult isolation procedures for the reactive compounds $(CH_3)_3Ga$[11] and $(CH_3)_2GaCl$.[12] In our initial preparation of **6**, $(CH_3)_2GaCl$ was prepared by a modified version of the exchange reaction of isolated $(CH_3)_3Ga$ with $GaCl_3$.[12b] This procedure avoids the presence of magnesium or lithium chloride in reaction 4, an impurity that could also react with the dihydrobis(pyrazolyl)borate ligand salt. Yields of **6** are higher in the CH_3Li preparation, and the success of the reaction demonstrates that the presence of lithium chloride does not interfere with the reaction in this case.

Complex **6** can be also be prepared by the reaction of **5** with CH_3Li (eq 6). The reaction of cationic **3** or

$$[H_2B(pz)_2]Ga(CH_3)Cl + CH_3Li \rightarrow [H_2B(pz)_2]Ga(CH_3)_2 + LiCl \quad (6)$$

$\{[H_2B(pz)_2]_2Ga\}PF_6$ (formed in situ from **1** and $TlPF_6$) with 1 equiv of CH_3Li under a variety of conditions does not cleanly yield **4** but an approximately equal mixture of **4** and **6**. Addition of 4 equiv of CH_3Li to **3** yields **6** in high yield *based on both gallium atoms in* **3** (eq 7). In this

$$\{[H_2B(pz)_2]_2Ga\}GaCl_4 + 4CH_3Li \rightarrow 2[H_2B(pz)_2]Ga(CH_3)_2 + 4LiCl \quad (7)$$

reaction, as with reaction 4, a dihydrobis(pyrazolyl)borate ligand undergoes transmetalation. As outlined above, the reaction of **1** with 1 equiv of CH_3Li or CH_3MgBr yields a mixture of **4** and **6** and other uncharacterized byproducts. Reaction of **1** with 2 equiv of CH_3Li or CH_3MgBr yields **6**, but again it is contaminated with other dihydrobis(pyrazolyl)borate-containing byproducts. Clearly, these types of reagents readily induce transmetalation of a dihydrobis(pyrazolyl)borate ligand from $[H_2B(pz)_2]_2Ga$-type compounds but not from complexes **5** and **6**, which contain one dihydrobis(pyrazolyl)borate ligand.

Parkin has recently shown that organometallic hydrotris(pyrazolyl)borate complexes of magnesium and aluminum can be prepared by displacement of methyl ligands.[13] An attempted preparation of **6** from $Ga(CH_3)_3$ and $K[H_2B(pz)_2]$ was not successful.

Complex **6** is an oil at ambient temperature, although an oily white solid can be obtained from a concentrated hexane solution at −78 °C. This solid melts below room temperature. It is freely soluble in aromatic solvents, halocarbon solvents, and saturated hydrocarbon solvents. The complex is stable in air both as an oil and in solution. Molecular weight studies in benzene show that **6** is a monomer in solution.

Reaction of **6** with CH_3CO_2H, even in excess, leads to the elimination of only one of the methyl ligands as methane (eq 8). Compound **7** can also be prepared from

$$[H_2B(pz)_2]Ga(CH_3)_2 + CH_3CO_2H \rightarrow \underset{\mathbf{7}}{[H_2B(pz)_2](CH_3)Ga(O_2CCH_3)} + CH_4 \quad (8)$$

CH_3GaCl_2 and stoichiometric amounts of the two ligand salts (eq 9). Molecular weight studies in benzene show

$$CH_3GaCl_2 + K[H_2B(pz)_2] + Na[O_2CCH_3] \rightarrow [H_2B(pz)_2](CH_3)Ga(O_2CCH_3) + KCl + NaCl \quad (9)$$

that this air-stable complex is a monomer in solution. In contrast, $(CH_3CO_2)Ga(CH_3)_2$ is dimeric[14] and $(CH_3CO_2)_2Ga(CH_3)$ is oligomeric[15] in solution with bridging acetate ligands.

Both **4** and **7** do not react with CH_3CO_2H. Thus, it is possible to eliminate one methyl ligand from the dimethyl complex **6** with acetic acid to yield **7**, but it is not possible to eliminate a methyl ligand with acetic acid from the organometallics **4** and **7**, containing two chelate ligands. It has been shown previously that acetic acid will cleave either one or two methyl ligands from $(CH_3)_3Ga$, but not the third.[15]

The solid-state structure of complex **1** shows the geometry of the donor ligands to be in a trigonal-bipyramidal arrangement with each dihydrobis(pyrazolyl)borate ligand bridging an axial and an equatorial site. We assume a similar geometry for both **4** and **7**. For all three, there should be two sets of pyrazolyl ring resonances in the ^1H NMR spectra, one for the axial and one for the equatorial pyrazolyl rings. The ambient-temperature NMR spectra of all of the complexes reported here show only three resonances in the aromatic region, one for each of the nonequivalent hydrogen atoms on the pyrazolyl rings. At −83 °C, the resonances in **1** and **7** show no indication of line broadening. The onset of line broadening is observed for **4** at −83 °C, but limiting low-temperature spectra could not be obtained. These data indicate that **1**, **4**, and **7** are fluxional in solution with a low barrier to rearrangement, as expected for five-coordinate complexes.

Although acetic acid does not cleave the methyl ligand in **4**, the product that would have formed, $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (**8**), can be prepared by the exchange of one of the dihydrobis(pyrazolyl)borate ligands in **2** with acetic acid (eq 10). No attempt was made to isolate

$$[H_2B(pz)_2]_3Ga + CH_3CO_2H \rightarrow \underset{\mathbf{8}}{[H_2B(pz)_2]_2Ga(O_2CCH_3)} + H[H_2B(pz)_2] \quad (10)$$

$H[H_2B(pz)_2]$, a known compound.[7] **8** is also prepared directly from $GaCl_3$ and stoichiometric amounts of the ligand salts (eq 11). Attempts to form **8** from **4** and CO_2

$$GaCl_3 + 2K[H_2B(pz)_2] + Na(O_2CCH_3) \rightarrow [H_2B(pz)_2]_2Ga(O_2CCH_3) + 2KCl + NaCl \quad (11)$$

lead to the reisolation of **4**.

Complex **8** is soluble in aromatic solvents and halocarbon solvents but not in saturated hydrocarbon solvents. This complex is air-stable, both as a solid and in solution. Molecular weight studies in benzene were carried out with five independent samples at eight different concentrations (solubility limited the range of concentrations) and yield

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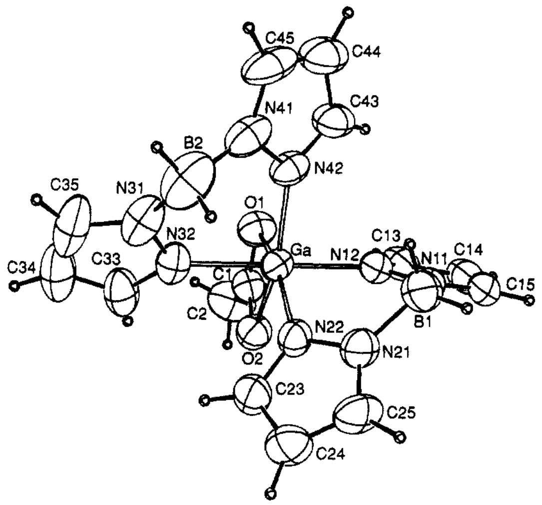

Figure 1. Numbered ORTEP drawing of $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ (8).

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ with Estimated Standard Deviations in Parentheses

	Bond Distances		
Ga–O1	2.127 (3)	Ga–O2	2.048 (3)
Ga–N12	2.057 (4)	Ga–N22	1.986 (4)
Ga–N32	2.059 (4)	Ga–N42	1.988 (4)
B1–N11	1.538 (8)	B1–N21	1.555 (8)
B2–N31	1.53 (1)	B2–N41	1.567 (9)
	Bond Angles		
O1–Ga–O2	62.3 (1)	O1–Ga–N12	87.9 (1)
O1–Ga–N22	157.5 (1)	O1–Ga–N32	90.3 (1)
O1–Ga–N42	93.0 (1)	O2–Ga–N12	91.2 (1)
O2–Ga–N22	95.4 (1)	O2–Ga–N32	87.0 (2)
O2–Ga–N42	155.1 (1)	N12–Ga–N22	90.1 (2)
N12–Ga–N32	177.9 (2)	N12–Ga–N42	90.3 (2)
N22–Ga–N32	91.2 (2)	N22–Ga–N42	109.4 (2)
N32–Ga–N42	90.9 (2)	N11–B1–N22	108.0 (2)
N31–B2–N41	108.7 (5)		

an average value of 544 (with a standard deviation of 17). This value lies between those of a monomer (423) and a dimer (846). An attempt to observe both isomers by ^1H NMR spectroscopy failed. At ambient temperatures, only one set of resonances is observed for the pyrazolyl rings. At −83 °C the onset of line broadening is observed for both the ring and acetate methyl group resonances, but limiting low-temperature spectra could not be obtained. Because of these results, the solid-state structure of 8 was determined crystallographically.

Molecular Structure of $[H_2B(pz)_2]_2Ga(O_2CCH_3)$. An ORTEP drawing of 8 is shown in Figure 1; selected bond lengths and angles are shown in Table III. The structure clearly shows that the molecule is a monomer in the solid state. The molecular geometry is a distorted octahedron. The main distortion is caused by the small bite angle of the acetate ligand, leading to an O–Ga–O angle of 62.3 (1)°. This low bond angle is mainly compensated for in the octahedron by an opening of the opposite N22–Ga–N42 bond angle to 109.4 (2)°. No other bond angle of the octahedron is distorted away from 90° by more than 5°. As was found in the structure of 1, the intraligand N–Ga–N bond angles are very close to 90°. The size of gallium(III) and the normal bite angle for the dihydrobis(pyrazolyl)borate ligand are appropriately matched for forming bonds at 90°. This angle has been observed to decrease for larger metals such as indium[16] and yttrium.[1] The six-membered GaN_4B rings of the dihydrobis(pyrazolyl)borate ligands are in a shallow boat arrangement with Ga···B nonbonding distances of 3.301 (4) (B1) and 3.317 (4) (B2) Å.

Summary

With one exception, all possible neutral gallium dihydrobis(pyrazolyl)borate complexes of the general formula $[H_2B(pz)_2]_mGaCl_n(CH_3)_p$ $(m + n + p = 3)$ have been prepared by using the appropriate gallium starting material and ligand stoichiometry (eq 12). The exception is the

$$(CH_3)_pGaCl_{n+m} + mK[H_2B(pz)_2] \rightarrow [H_2B(pz)_2]_mGaCl_n(CH_3)_p + mKCl \quad (12)$$

reaction of $GaCl_3$ with 1 equiv of $K[H_2B(pz)_2]$ to yield the salt 3, in which two ligands coordinate to one gallium with the formation of the tetrachlorogallate anion. The dimethyl derivative 6 can also be prepared by reaction of 3 or 5 with CH_3Li. All of the $[H_2B(pz)_2]_mGaCl_n(CH_3)_p$ complexes are monomeric in solution. Introduction of the dihydrobis(pyrazolyl)borate ligand converts the highly reactive $(CH_3)_xGaCl_{3-x}$ starting materials into complexes that are stable in solution to air. An interesting feature of the reactivity of these complexes is the propensity of one of the dihydrobis(pyrazolyl)borate ligands in $[H_2B(pz)_2]_2Ga$-type compounds to undergo transmetalation reactions. The mixed dihydrobis(pyrazolyl)borate–acetate complexes $[H_2B(pz)_2](CH_3)Ga(O_2CCH_3)$ and $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ have also been prepared, and the latter was shown to have a distorted-octahedral geometry in the solid state.

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Note Added in Proof. The preparation of $[R_2B(pz)_2]Ga(CH_3)_2$ (R = H, CH_3) complexes and the crystal structure of the R = CH_3 derivative have been recently reported.[18]

Registry No. 3, 127916-02-3; 4, 127943-62-8; 5, 127916-03-4; 6, 126795-91-3; 7, 127916-04-5; 8, 127916-05-6; $K[H_2B(Pz)_2]$, 18583-59-0; $GaCl_3$, 13450-90-3; CH_3GaCl, 6917-74-4; $Ga(CH_3)_3$, 1445-79-0; $[H_2B(Pz)_2]_3Ga$, 122174-43-0.

Supplementary Material Available: Tables of complete bond distances and angles, positional parameters of H atoms, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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