Synthesis and characterization of dihydrobis(3,5-dimethylpyrazolyl)borate complexes of gallium(III) and indium(III) [1]

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Abstract

The reaction of $MeGaCl_2$ with one equivalent of $K[H_2B(3,5-Me_2pz)_2]$ yields $[H_2B(3,5-Me_2pz)_2]GaMeCl$. The structure of $[H_2B(3,5-Me_2pz)_2]GaMeCl$ has been determined crystallographically. The molecular unit is monomeric with a distorted tetrahedral geometry around gallium. The reaction of $GaCl_3$ with two equivalents of MeLi followed by one equivalent of $K[H_2B(3,5-Me_2pz)_2]$ yields $[H_2B(3,5-Me_2pz)_2]GaMe_2$. Similar reactions starting with $MeInCl_2$ or Me_2InCl yield $[H_2B(3,5-Me_2pz)_2]InMeCl$ and $[H_2B(3,5-Me_2pz)_2]InMe_2$, respectively. The reaction of $MeInCl_2$ with two equivalents of $K[H_2B(3,5-Me_2pz)_2]$ in refluxing THF yields $[H_2B(3,5-Me_2pz)_2]_2InMe$. In low-temperature NMR spectra of this complex ($-40°C$), each of the three types of hydrogen atom positions shows as two sharp, equally intense resonances. Each of the pairs of resonances coalesce at higher temperatures.

Keywords: Gallium; Indium; Bis(pyrazolyl)borate

1. Introduction

We, and others, have been interested in developing the coordination and organometallic chemistry of gallium(III) and indium(III) using the versatile poly-(pyrazolyl)borate [1] ligand system [2–4]. Complexes of these ligands are stable and generally monomeric. An important driving force for this chemistry is that Group 13 metals are important in the preparation of new semi-conductor and optoelectronic devices [5] and for nuclear medicine radio labeling studies [6].

We have previously reported complexes of the dihydrobis(pyrazolyl)borate ligand, A, and demonstrated that this bidentate poly(pyrazolyl)borate ligand forms stable, monomeric complexes with gallium(III) and indium(III) [2a–c]. For example, $[H_2B(pz)_2]InMe_2$ (pz = pyrazolyl

ring) is monomeric and air stable [2c]. We anticipated that complexes of the methyl-substituted ligand dihydrobis(3,5-dimethylpyrazolyl)borate, B, would be even more stable, but the increase in steric bulk on the ligand would lead to different chemistry.

A   B
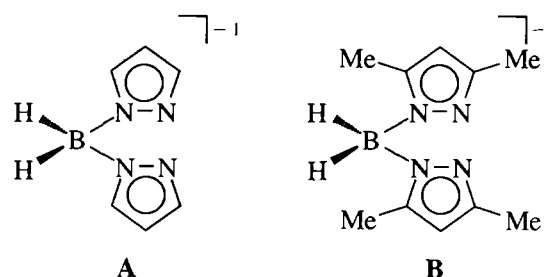
Reported here is the synthesis and characterization of the organometallic complexes of the general formula $[H_2B(3,5-Me_2pz)_2]_mMCl_nMe_p$ (M = Ga, In; $m + n + p = 3$). The complex $[H_2B(3,5-Me_2pz)_2]GaMeCl$ has been characterized in the solid state by X-ray crystallography.

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[1] Dedicated to Professor Marv Rausch on the occasion of his 65th birthday.

2. Experimental

2.1. 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. The ^{1}H solution NMR spectra were recorded on a Bruker AM300 or AM400 spectrometer using a 5 mm broadband probe. Proton chemical shifts are reported in ppm vs. Me$_4$Si. Mass spectra were run on a Finnigan 4521 GC-mass spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present.

K[H$_2$B(3,5-Me$_2$pz)$_2$] was prepared according to published methods [7]. The preparations of MeGaCl$_2$ [8] and MeInCl$_2$ [2c] were carried out following the published methods. Anhydrous GaCl$_3$ was purchased from Aldrich and sublimed as needed. Anhydrous InCl$_3$ was purchased from Cerac Inc. and Strem. MeLi (in diethyl ether) was purchased from Aldrich and used without further purification. Elemental analyses were performed by Robertson Laboratory, Inc., 73 West End Avenue, Florham Park, NJ, 07932 and National Chemical Consulting, Inc., P.O. Box 99, Tenafly, NJ, 07670.

2.2. Chlorodihydrobis(3,5-dimethylpyrazolyl)borato-methylgallium(III) {[H$_2$B(3,5-Me$_2$pz)$_2$]GaMeCl} (1)

Cold THF (60 ml, −78°C) was added to a mixture of K[H$_2$B(3,5-Me$_2$pz)$_2$] (0.55 g, 2.3 mmol) and MeGaCl$_2$ (0.35 g, 2.2 mmol) and the mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum. The residue was extracted with toluene (40 ml) and filtered. The toluene was removed under vacuum to yield a white solid (0.33 g, 46%). Colorless crystals were obtained by recrystallization from hexanes; m.p. 112–114°C. ^{1}H NMR (CDCl$_3$): δ 5.86 (2; s; 4-H (pz)); 2.41, 2.31 (6, 6; s, s; 3-Me, 5-Me (pz)); 0.30 (3; s; Me). The mass spectrum shows clusters for M$^+$–H at m/e 321. The accurate mass spectrum for M$^+$–H is (m/e): Calc. for C$_{11}$H$_{18}$N$_4^{11}$B^{69}Ga^{35}Cl, 321.0569; found, 321.0560. Anal. Calc. for C$_{11}$H$_{19}$N$_4$BGaCl: C, 40.87; H, 5.92; N, 17.33%. Found: C, 40.96; H, 6.03; N, 17.40%.

2.3. Dihydrobis(3,5-dimethylpyrazolyl)boratodimethyl-gallium(III) {[H$_2$B(3,5-Me$_2$pz)$_2$]GaMe$_2$} (2)

GaCl$_3$ (0.34 g, 1.9 mmol) was suspended in diethyl ether (5 ml) and cooled to −78°C. MeLi (3.8 ml, 5.3 mmol) was added via syringe. The mixture was allowed to warm to room temperature and stirred overnight. K[H$_2$B(3,5-Me$_2$pz)$_2$] (0.46 g, 1.9 mmol) suspended in

diethyl ether (5 ml) was added and the mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was extracted with hexanes (40 ml) and filtered. The hexane was removed under vacuum to yield a white solid (0.24 g, 42%). Colorless crystals were obtained by recrystallization from hexanes; m.p. 131–132°C. ^{1}H NMR (CDCl$_3$): δ 5.82 (2; s; 4-H (pz)); 2.32, 2.25 (6, 6; s, s; 3-Me, 5-Me (pz)); −0.07 (6; s; Me). Mass spectrum shows M$^+$–H, M$^+$–CH$_3$ at m/e 301 and 287. The accurate mass spectrum for M$^+$–H is (m/e): Calc. for C$_{12}$H$_{21}$N$_4^{11}$B^{69}Ga, 301.1116; found, 301.1115.

2.4. Chlorodihydrobis(3,5-dimethylpyrazolyl)borato-methylindium(III) {[H$_2$B(3,5-Me$_2$pz)$_2$]InMeCl} (3)

THF (30 ml) was added to a mixture of K[H$_2$B(3,5-Me$_2$pz)$_2$] (0.86 g, 3.5 mmol) and MeInCl$_2$ (0.71 g, 3.5 mmol) and the mixture stirred at room temperature for 5 h. The solvent was removed under vacuum. The residue was extracted with benzene (25 ml) and filtered. The benzene was removed under vacuum to yield a white solid (0.92 g, 70%); m.p. 150–152°C. ^{1}H NMR (CDCl$_3$): δ 5.83 (2; s; 4-H (pz)); 2.36, 2.29 (6, 6; s, s; 3-Me, 5-Me (pz)); 0.51 (3; s; Me). Mass spectrum (m/z): 367 (M$^+$–H); 353 (M$^+$–CH$_3$); 333 (M$^+$–Cl); 317 (M$^+$–CH$_4$–Cl). Anal. Calc. for C$_{11}$H$_{19}$N$_4$BInCl: C, 35.57; H, 5.16; N, 15.09%. Found: C, 35.55; H, 4.88; N, 14.97%.

2.5. Dihydrobis(3,5-dimethylpyrazolyl)boratodimethyl-indium(III) {[H$_2$B(3,5-Me$_2$pz)$_2$]InMe$_2$} (4)

InCl$_3$ (0.50 g, 2.3 mmol) was suspended in diethyl ether (10 ml) and cooled to −78°C. MeLi (3.32 ml, 4.52 mmol) was added via syringe. The mixture was allowed to warm to room temperature and stirred for 2 d. K[H$_2$B(3,5-Me$_2$pz)$_2$] (0.56 g, 2.3 mmol) was added and the mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was extracted with hexanes (20 ml) and filtered. The hexane was removed under vacuum to yield a white solid; m.p. 69–71°C. ^{1}H NMR (CDCl$_3$): δ 5.77 (2; s; 4-H (pz)); 2.30, 2.18 (6, 6; s, s; 3-Me, 5-Me (pz)); 0.04 (6; s; Me). Mass spectrum (m/z): 347 (M$^+$–H), 333 (M$^+$–CH$_3$), 317 (M$^+$–C$_2$H$_7$). Anal. Calc. for C$_{12}$H$_{22}$N$_4$BIn: C, 41.42; H, 6.37; N, 16.10%. Found: C, 42.29; H, 6.50; N, 16.24%.

2.6. Dihydrobis(3,5-dimethylpyrazolyl)boratomethyl-indium(III) {[H$_2$B(3,5-Me$_2$pz)$_2$]$_2$InMe} (5)

MeInCl$_2$ (0.20 g, 1.0 mmol) was mixed with K[H$_2$B(3,5-Me$_2$pz)$_2$] (0.70 g, 2.8 mmol) in THF (30 ml) and allowed to stir at reflux for 4 h. The solvent was removed under vacuum. The residue was extracted

with benzene (30 ml) and filtered. The benzene was removed under vacuum to yield a white solid. The solid was dissolved in a minimal amount of toluene and chilled to $-20°$ overnight. The toluene was removed and the resulting solid dried under vacuum (0.15 g, 28%); m.p. 182–183°C. ^{1}H NMR (CDCl$_3$, ambient temperature): δ 5.68 (4; s; 4-H (pz)); 2.33, 1.94, 1.08 (12, 6, 6; s, br, br; 3-Me, 5-Me (pz)), 0.33 (3; s; Me). ^{1}H NMR (CDCl$_3$, $-40°$C): δ 5.68, 5.66 (2, 2; s; 4-H (pz)); 2.32, 2.31, 1.93, 1.04 (6, 6, 6, 6; s; 3-Me, 5-Me (pz)), 0.31 (3; s; Me). Mass spectrum (m/z): 521(M$^+$–CH$_3$). The accurate mass spectrum for M$^+$–CH$_3$ is (m/e): Calc. for C$_{20}$H$_{32}$N$_8^{11}$B$_2^{115}$In, 521.1975; found, 521.1970.

2.7. Crystallographic studies of {[H$_2$B(3,5-Me$_2$pz)$_2$]-GaMeCl}

Crystal data collection and refinement parameters are given in Table 1. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($19° < 2\theta < 28°$). Axial photographs, unit-cell parameters and occurrence of equivalent reflections indicated a monoclinic crystal system. Systematic absences were uniquely consistent with the space group $P2_1/c$. The structure was solved using direct methods and refined by full-matrix least-squares procedures. All atoms, with the exception of hydrogen, were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. Corrections for absorption were not required because the changes in intensity were less than 10%. All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program libraries (G.

Table 1
Crystallographic data for the structural analyses for [H$_2$B(3,5-Me$_2$pz)$_2$]GaMeCl

Formula	C$_{11}$H$_{19}$BClN$_4$Ga
Mol. wt.	323.3
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.804(2)
b (Å)	18.080(10)
c (Å)	10.613(5)
β (deg)	113.74(10)
V (Å^3)	1546.4(12)
Z	4
Crystal size (mm)	0.25×0.30×0.30
Monochromator	Graphite crystal
Radiation (Å)	MoKα (0.71073)
Temperature	296
2θ range (deg)	4–50 ($\pm h$, $+k$, $\pm l$)
No. of reflections collected	4812
No. of independent reflections	2723
R_F	0.0479
R_{wF}	0.0546

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotopic displacement coefficients (Å$^2 \times 10^3$) for [H$_2$B(3,5-Me$_2$pz)$_2$]GaMeCl

|	x	y	z	U (eq) [a]
Ga	1576(1)	8975(1)	2094(1)	41(1)
Cl	3111(2)	7970(1)	2470(2)	66(1)
B	−1857(10)	9396(4)	2097(7)	53(3)
N(1)	−593(6)	8656(3)	742(4)	39(2)
N(2)	−1991(6)	8815(2)	965(5)	42(2)
N(3)	1020(6)	9034(3)	3703(4)	45(2)
N(4)	−614(6)	9110(3)	3507(4)	43(2)
C(1)	−3305(8)	8489(3)	−24(6)	48(3)
C(2)	−5028(9)	8589(4)	−99(8)	72(3)
C(3)	−2743(8)	8115(3)	−880(6)	49(3)
C(4)	−1054(8)	8229(3)	−384(6)	42(2)
C(5)	128(9)	7976(4)	−980(6)	61(3)
C(6)	−716(8)	9017(3)	4720(6)	51(3)
C(7)	−2365(10)	9064(4)	4848(7)	72(4)
C(8)	830(9)	8881(3)	5712(6)	55(3)
C(9)	1885(8)	8893(3)	5048(6)	51(3)
C(10)	3733(9)	8795(4)	5636(7)	74(3)
C(11)	2551(9)	9843(3)	1695(7)	64(3)

[a] Equivalent isotopic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Sheldrick, Siemans XRD, Madison, WI). Table 2 contains the atomic coordinates and isotropic thermal parameters.

3. Results and discussion

3.1. Gallium complexes

The reaction of MeGaCl$_2$ with one equivalent of K[H$_2$B(3,5-Me$_2$pz)$_2$] yields [H$_2$B(3,5-Me$_2$pz)$_2$]-GaMeCl (1).

$$K\left[H_2B(3,5\text{-Me}_2pz)_2\right] + MeGaCl_2$$

1
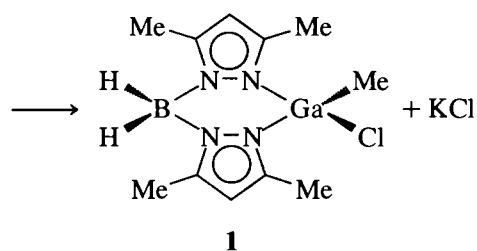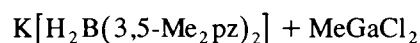
The MeGaCl$_2$ was isolated first from the reaction of GaCl$_3$ and SiMe$_4$ to ensure correct stoichiometry and avoid contamination by [H$_2$B(3,5-Me$_2$pz)$_2$]GaMe$_2$. Complex 1 is freely soluble in aromatic, halocarbon, and saturated hydrocarbon solvents and is stable in air as a solid.

Crystals suitable for X-ray diffraction studies of 1 were grown from hexanes. Fig. 1 shows an ORTEP diagram of the molecule, and selected bond angles and distances given in Table 3.
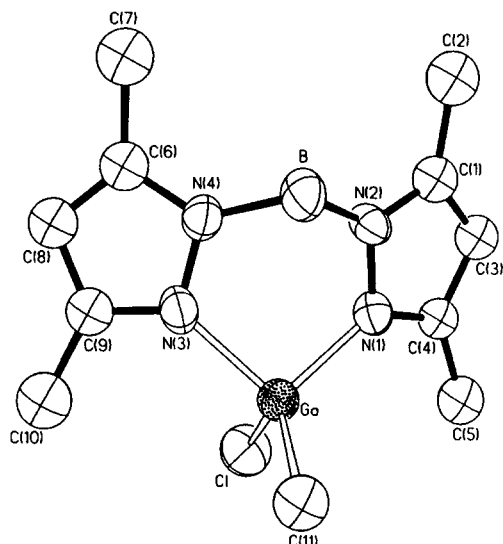
Fig. 1. ORTEP drawing of [H₂B(3,5-Me₂pz)₂]GaMeCl.

The molecular unit is monomeric with a distorted tetrahedral geometry around gallium. The Ga–ligand bond distances are normal and similar to those observed in [η^2-HB(3,5-Me₂pz)₃]GaMeCl [2d] and [Me₂-B(pz)₂]GaMe₂ [3b]. The N(1)–Ga–N(3) bond angle is restricted by the chelate ring to 98.2(2)° with the C(11)–Ga–Cl angle opening to 114.7(2)°. The C(11)–Ga–N angles are similar (average 117°) and larger than the essentially identical Cl–Ga–N angles (average 104°). The GaN₄B six-membered ring is in the normal boat configuration with the boron oriented toward C(11), presumably causing the larger C–Ga–N angles. A similar but larger distortion is observed with four-coordinate
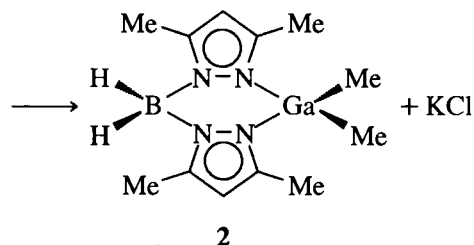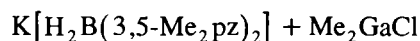
Table 3
Selected bond distances and bond angles for [H₂(B(3,5-Me₂pz)₂]GaMeCl with estimated standard deviations in parenthesis

Bond lengths (Å)	
Ga–Cl	2.203(2)
Ga–N(1)	1.957(4)
Ga–N(3)	1.959(6)
Ga–C(11)	1.917(7)
Bond angles (deg)	
Cl–Ga–N(1)	103.6(2)
Cl–Ga–N(3)	103.8(2)
N(1)–Ga–N(3)	98.2(2)
Cl–Ga–C(11)	114.7(2)
N(1)–Ga–C(11)	118.1(2)
N(3)–Ga–C(11)	116.0(3)
N(2)–B–N(4)	108.9(5)
Ga–N(1)–N(2)	119.3(3)
Ga–N(1)–C(4)	132.8(5)
Ga–N(3)–N(4)	119.1(3)
Ga–N(3)–C(9)	133.0(5)
B–N(2)–C(1)	132.0(6)
B–N(4)–C(6)	133.3

[η^2-HB(3,5-Me₂pz)₃]GaMeCl. Again, the boron is oriented toward the methyl ligand, but the third 3,5-Me₂pz ring is also oriented toward the methyl ligand causing a larger distortion. A similar distortion to that in **1** is observed in [Me₂B(pz)₂]GaMe₂ where the C–Ga–N angles are larger for the methyl ligand oriented toward the boron.

It is interesting to compare the monomeric structure of **1** to that of {[H₂B(pz)₂]InMeCl}₂ [2c]. In this case, in the solid state structure there are two independent dimeric units held together by long (average of 3.13 Å) bridging chlorine interactions. There are no indications in the structure of **1** of any intermolecular association.
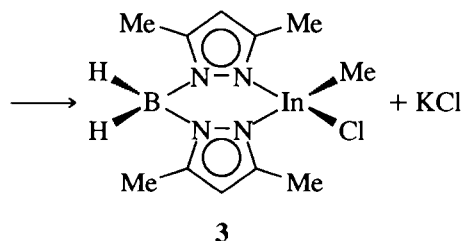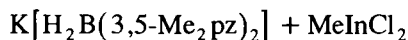
The reaction of GaCl₃ with two equivalents of MeLi, followed by one equivalent of K[H₂B(3,5-Me₂pz)₂] yields [H₂B(3,5-Me₂pz)₂]GaMe₂ (2).

K[H₂B(3,5-Me₂pz)₂] + Me₂GaCl

2

The complex is a crystalline solid that is stable in air and is freely soluble in aromatic, halocarbon, and saturated hydrocarbon solvents. In contrast, the unsubstituted analog, [H₂B(pz)₂]GaMe₂, is an oil [2b].

3.2. Indium complexes

The reaction of MeInCl₂ with one equivalent of K[H₂B(3,5-Me₂pz)₂] yields [H₂B(3,5-Me₂pz)₂]In-MeCl (3).

K[H₂B(3,5-Me₂pz)₂] + MeInCl₂

3

The MeInCl₂ was isolated first from the reaction of InCl₃ and Me₄Sn. Complex **3** is freely soluble in both aromatic and halocarbon solvents, but is insoluble in saturated hydrocarbon solvents. The complex is stable in air as a solid but decomposes in solution over several weeks.

The reaction of InCl₃ with two equivalents of MeLi

and followed by one equivalent of $K[H_2B(3,5-Me_2pz)_2]$ yields $[H_2B(3,5-Me_2pz)_2]InMe_2$ (4).

$$K[H_2B(3,5-Me_2pz)_2] + Me_2InCl$$

4
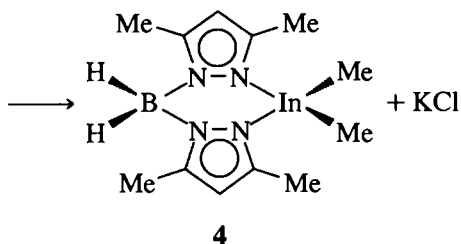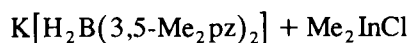
Complex **4** is freely soluble in aromatic, halocarbon, and saturated hydrocarbon solvents and is stable in air as a solid. It is also prepared from the reaction of **3** with MeLi.

The reaction of $MeInCl_2$ with two equivalents of $K[H_2B(3,5-Me_2pz)_2]$ in refluxing THF yields $[H_2B(3,5-Me_2pz)_2]_2InMe$ (5).

$$2K[H_2B(3,5-Mepz)_2] + MeInCl_2$$

5
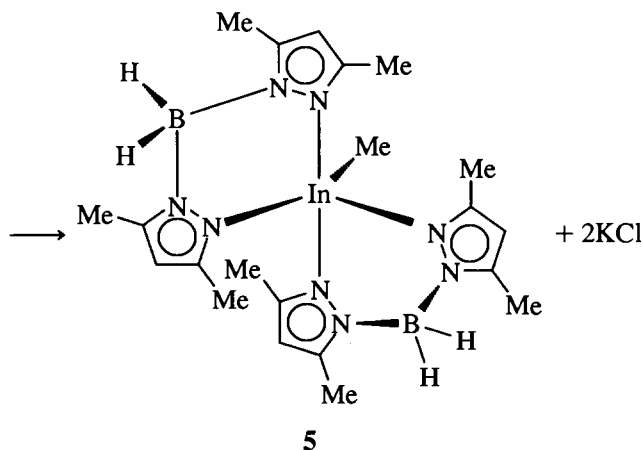
The forcing conditions of refluxing THF are needed to drive this reaction to completion. Reactions carried out at ambient temperature, the temperature used in the other reactions in this work and for the preparation of $[H_2B(pz)_2]_2GaMe$, lead to the isolation of a mixture of complexes **3** and **5**. Complex **5** is freely soluble in halocarbon and aromatic solvents but is insoluble in saturated hydrocarbon solvents.

The ambient temperature ^1H NMR spectrum of **5** shows the 4-position hydrogen atoms and the 5-position methyl groups each as single resonances, but the 3-position methyl groups show as two broad resonances separated by nearly 1 ppm. At $-40°C$ each of the three types of hydrogen atom positions shows as two sharp, equally intense resonances. For both the 4-position hydrogen atoms and the 5-position methyl groups, the pairs of resonances are separated by less than 0.02 ppm The 3-position resonances are separated by 0.89 ppm. This greater separation of the low-temperature resonance pairs explains why the 4-position hydrogen atoms

and the 5-position methyl groups are sharp single lines in the ambient temperature, whereas the resonances for the 3-position methyl groups have not yet coalesced.

The dynamic behavior of **5** observed in these variable temperature spectra can be explained by either a trigonal bipyramid or square planar arrangement of the ligands. We favor a trigonal bipyramid arrangement in which each $[H_2B(3,5-Me_2pz)_2]^-$ ligand spans an axial and equatorial position, as pictured in the equation, because this structure is found by X-ray crystallography for $[H_2B(pz)_2]_2GaCl$ [1a]. At higher temperatures the trigonal bipyramid undergoes fast exchange of the axial and equatorial positions, equilibrating all of the pyrazolyl rings. At $-40°C$ this dynamic process is slow on the NMR time scale. Separate resonances would be expected for the axial and equatorial pyrazolyl rings, as observed.

4. Supplementary material available

Tables of complete data collection information, bond distances, angles, anisotropic thermal parameters and positional parameters of H atoms are available from the authors.

Acknowledgment

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