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Control of Structure in Lead(II) Complexes Using Poly(pyrazolyl)borate Ligands. Stereochemically Inactive Lone Pair in Octahedral $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (pz = Pyrazolyl Ring)

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Abstract: The reaction of 2 equiv of $K[H_nB(pz)_{4-n}]$ (n = 0–2; pz = pyrazolyl ring) or $K[HB(3,5\text{-}Me_2pz)_3]$ with $PbCl_2$ produces the respective bis[poly(pyrazolyl)borato]lead complex in good yield. The complex $[HB(pz)_3]PbCl$ is formed in a similar reaction using 1 equiv each of the ligand and $PbCl_2$. The structure of $[B(pz)_4]_2Pb$ (**1**) has been determined crystallographically: monoclinic, *Pc*, a = 8.889 (7) Å, b = 8.022 (6) Å, c = 20.901 (18) Å, β = 97.70 (6)°, V = 1447.0 (21) Å^3, Z = 2, $R(F)$ = 5.62%. Complex **1** has a pseudo-trigonal-bipyramidal geometry with each ligand having *bidentate* coordination and spanning an axial and equatorial site. The lead lone pair presumably occupies the remaining equatorial vertex. The ^1H NMR spectra show that **1** is dynamic in solution. All of the pyrazolyl rings are equivalent at ambient temperatures with a 3/1 pattern observed at −89 °C. The low-temperature spectrum can be explained by a low-energy process that equilibrates in each ligand the three pyrazolyl rings close to lead, but the fourth ring remains unique. At higher temperatures, the fourth ring also equilibrates by a boat–boat flip of the six-membered PbN_4B ring (9.1 kcal/mol barrier). The structure of $[HB(pz)_3]_2Pb$ (**2**) has also been determined crystallographically: monoclinic, $P2_1/c$, a = 16.600 (9) Å, b = 8.040 (5) Å, c = 17.214 (9) Å, β = 90.77 (4)°, V = 2297.4 (23) Å^3, Z = 4, $R(F)$ = 5.79%. In the structure of **2**, both ligands are *tridentate*, forming a six-coordinate, monomeric structure. The geometry about the lead atom is best described as based on a capped octahedron with the lone pair on the metal located in the capping position. The structure of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**) has also been determined crystallographically: trigonal, $R\bar{3}$ (No. 148), a = 11.152 (3) Å, c = 25.301 (7) Å, V = 2725.8 (10) Å^3, Z = 3, $R(F)$ = 4.6%. The structure is six-coordinate, and the geometry about the lead atom is a trigonally distorted octahedron. The lead atom sits on a center of inversion, and the planes formed by the three nitrogen donor atoms of each ligand are parallel. The lone pair on lead is clearly stereochemically inactive. Lead-207 NMR studies indicate that these structures are the same in solution. The complex $[H_2B(pz)_2]_2Pb$ (**3**) shows two types of dynamic processes in solution as observed by ^1H NMR spectroscopy. The axial and equatorial pyrazolyl rings in the pseudo-trigonal-bipyramidal structure equilibrate, a process with a very low barrier. Also, a boat–boat flip of the PbN_4B rings formed by each ligand is observed with a barrier 9.4 kcal/mol at −58 °C.

Introduction

Recent studies in these[1] and other[2] laboratories have shown that the poly(pyrazolyl)borate ligand system[3] is especially well suited for the preparation of stable complexes, including organometallics, of the main-group metals. With group 14 metals, we have reported the syntheses of a series of complexes of tin(II) of the formula $[H_nB(pz)_{4-n}]_mSnCl_{2-m}$ (n = 0–2; m = 1, 2).[4] The four-coordinate complexes in this series, such as $[H_2B(pz)_2]_2Sn$ and $[HB(pz)_3]SnCl$, have pseudo-trigonal-bipyramidal structures, with the fifth site occupied by the lone pair on the metal. The complex $[B(pz)_4]_2Sn$ (the $[B(pz)_4]^-$ ligand is potentially tridentate to a single metal) has a very similar four-coordinate structure in the solid state.[4] Given the large size of tin(II) and the fact that others have shown that $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ is five-coordinate in the solid phase,[5] it is surprising that $[B(pz)_4]_2Sn$ is only four-coordinate. It has not proven possible to crystallize $[HB(pz)_3]_2Sn$ for comparison, but ^{119}Sn solution NMR studies[4] of these complexes indicate that this hydrotris(pyrazolyl)borate complex is five-coordinate in solution and $[B(pz)_4]_2Sn$ remains four-coordinate in solution. A number of these tin(II) complexes have also been reported by others.[6]

A driving force for the development of this chemistry is the desire to prepare complexes with these bulky poly(pyrazolyl)borate ligands[7] in which the lone pair on the group 14 metal(II), in violation of VSEPR theory, would be stereochemically inactive. The first example of a molecular species of this type for a group 14 element was decaphenylstannocene, reported in 1984 by Zuckerman.[8a] Solid-state ^{13}C CPMAS NMR data indicate that decaphenylplumbocene has a similar structure,[8b] and a symmetrical structure for decamethylsilicocene also has been published recently.[9] In addition, a series of high coordination number macrocyclic ligand complexes in which the lone pair is claimed to be inactive has been reported.[10,11] Although a structure with a stereochemically inactive lone pair was not found for poly(pyrazolyl)borate complexes of tin(II), we felt that examples might be found with lead(II).

Reported here are results of the synthesis and characterization in both the solid and solution phases of poly(pyrazolyl)borate complexes of lead(II). The syntheses of $[HB(pz)_3]_2Pb$ and $[B(pz)_4]_2Pb$ have been briefly reported by Trofimenko,[3b] and [B-

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$(pz)_4]_2Pb$ has also been reported by Niedenzu,[12] but no structural characterization was given. We anticipated that the extremely large size of lead(II) would yield complexes of higher coordination numbers than observed with tin(II), a result frequently observed with other ligands.[13] The solid-state structures of $[B(pz)_4]_2Pb$, $[HB(pz)_3]_2Pb$, and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ have been determined by X-ray crystallography. The former two structures demonstrate the first clear examples of similar complexes of the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ligands giving totally different coordination environments about the same metal, but in both cases the lead(II) lone pair is stereochemically active. *The* $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ *complex is octahedral in the solid state and thus represents the first example of a six-coordinate, main-group, molecular compound in which the lone pair is stereochemically inactive.* A comparison of the ^{207}Pb and ^{119}Sn solution NMR chemical shifts for these molecules is also presented.

Experimental Section

General Procedure. Operations in organic solvents were carried out under a nitrogen atmosphere by using either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. Reactions in water used Schlenk techniques under N_2 atmosphere although the distilled water was not degassed. All organic solvents were dried, degassed, and distilled prior to use. The ^1H NMR spectra were recorded on a Bruker AM-300 or AM-500 spectrometer using a 5-mm broad-band probe. Proton chemical shifts are reported (ppm) downfield from TMS using the solvents $CDCl_3$ (δ_H = 7.24 ppm) and CD_2Cl_2 (δ_H = 5.32 ppm) as internal standards. The reported ^1H coupling constants are $^3J_{HH}$ values unless otherwise indicated. Carbon NMR spectra were recorded on the Bruker AM-500 spectrometer with chemical shifts reported (ppm) downfield from TMS using the solvent $CDCl_3$ as an internal standard (δ_C = 77.0 ppm). All spectra were recorded at room temperature unless otherwise indicated. The ^{207}Pb NMR spectra were recorded on a Bruker AM-500 spectrometer using a 5-mm broad-band probe. The ^{207}Pb NMR spectra were recorded at −49 °C in less than 3 h using a 90° pulse with ca. 0.5-s recycle time in a 1000 ppm window. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using $PbPh_4$ (δ_{Pb} = −178.0 ppm, saturated in $CDCl_3$) as an external standard. Elemental analyses were performed by Robertson Laboratories, Inc. $K[H_2B(pz)_2]$, $K[HB(pz)_3]$, $K[HB(3,5\text{-}Me_2pz)_3]$, and $K[B(pz)_4]$ were prepared by the published methods.[3b] Mass spectra and accurate mass determinations were run on a VG 70SQ mass spectrometer. The clusters assigned to specific ions show the appropriate isotopic patterns as calculated for the atoms present.

Bis[tetrakis(pyrazolyl)borato]lead(II), $[B(pz)_4]_2Pb$ (1). A solution of $PbCl_2$ (0.500 g, 1.80 mmol) in warm (50 °C) water (50 mL) was added, via cannula, to a solution of $K[B(pz)_4]$ (1.14 g, 3.60 mmol) in water (20 mL). A white precipitate formed immediately upon mixing of the two clear, colorless solutions. After being stirred at room temperature for ca. 1 h, the mixture was filtered on a Buchner funnel and washed with H_2O. The white powder was dried overnight in vacuo (1.14 g, 83%); mp 237–239 °C. Crystals for the analytical sample and the X-ray structure were grown from warm/cold (50/5 °C) toluene. ^1H NMR ($CDCl_3$, δ): 7.59, 7.36 (8, 8; d, d, J = 1.5, 2.2 Hz; 3-H, 5-H (pz)); 6.30 (8; t; J = 2.2 Hz; 4-H (pz)). These NMR data match those reported earlier.[12] ^1H NMR (CD_2Cl_2; −89 °C; δ): 7.87, 7.49, 7.41, 7.09, (2, 6, 2, 6; all br; 3-H, 5-H (pz)); 6.35, 6.28 (ca. 2, ca. 6; both br and not separated; 4-H (pz)). ^{207}Pb NMR ($CDCl_3$, −49 °C, δ): −534. MS: *m/e* 766 ($Pb[B(pz)_4]_2$); 487 ($Pb[B(pz)_4]$). Anal. Calcd for $C_{24}H_{24}B_2N_{16}Pb$: C, 37.66; H, 3.16. Found C, 37.87; H, 2.91.

Bis[hydrotris(pyrazolyl)borato]lead(II), $[HB(pz)_3]_2Pb$ (2). Complex **2** was prepared from $PbCl_2$ (0.500 g, 1.80 mmol) and $K[HB(pz)_3]$ (0.910 g, 3.60 mmol) as described above for **1** (0.950 g, 83%); mp 228–231 °C. Crystals for the crystal structure were grown from warm/cold (50/5 °C) toluene. ^1H NMR ($CDCl_3$; δ): 7.75, 7.27 (6, 6; d, d; J = 1.7, 1.8 Hz; 3-H, 5-H (pz)); 6.15 (6; t; J = 2.0 Hz; 4-H (pz)). ^1H NMR (CD_2Cl_2, −89 °C; δ): 7.80, 7.25 (6, 6; d, s, J = 1.9 Hz; 3-H, 5-H (pz)); 6.15 (6; t; J = 1.9 Hz; 4-H (pz)). ^{13}C NMR ($CDCl_3$; δ): 141.0 (3-C (pz)); 136.3 (5-C (pz)); 105.2 (4-C (pz)). ^{207}Pb NMR ($CDCl_3$, −49 °C, δ): −895. MS: *m/e* 633 ($[HB(pz)_3]_2Pb - H$); 421 ($[HB(pz)_3]Pb$). Anal. Calcd for $C_{18}H_{20}B_2N_{12}Pb$: C, 34.14; H, 3.18; N, 26.54. Found C, 34.36; H, 3.13; N, 26.39.

Bis[dihydrobis(pyrazolyl)borato]lead(II), $[H_2B(pz)_2]_2Pb$ (3). Complex **3** was prepared from $PbCl_2$ (0.500 g, 1.80 mmol) and $K[H_2B(pz)_2]$ (0.67 g, 3.60 mmol) as described above for **1** (0.767 g, 85%); mp 168–169 °C. ^1H NMR ($CDCl_3$, δ): 7.61, 7.25 (4, 4; d, d; J = 0.6, 2.0 Hz; 3-H, 5-H (pz)); 6.17 (4; t; J = 2.0 Hz; 4-H (pz)); 4.8–3.8 (very br, BH_2). ^1H NMR (CD_2Cl_2, −89 °C, δ): 7.60, 7.27 (4, 4; s, br; 3-H, 5-H (pz)); 6.17 (4; s; 4-H (pz)); 4.53, 3.55 (2, 2; br, br; BH_2). ^{207}Pb NMR ($CDCl_3$, −49 °C, δ): −139. Anal. Calcd for $C_{12}H_{16}B_2N_8Pb$: C, 28.76; H, 3.22. Found C, 28.77; H, 3.01.

Table I. Crystallographic Data for $[B(pz)_4]_2Pb$ (**1**), $[HB(pz)_3]_2Pb$ (**2**), and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**)

	1	**2**	**4**
formula	$PbC_{24}H_{24}N_{16}B_2$	$PbC_{18}H_{20}N_{12}B_2$	$PbC_{30}H_{44}N_{12}B_2$
mol wt	743.65	611.56	801.58
cryst syst	monoclinic	monoclinic	trigonal
space group	Pc	$P2_1/c$	$R\bar{3}$ (No. 148)
a, Å	8.889 (7)	16.600 (9)	11.152 (3)
b, Å	8.022 (6)	8.040 (5)	
c, Å	20.901 (18)	17.214 (9)	25.301 (7)
β, deg	97.70 (6)	90.77 (4)	
V, Å^3	1447.0 (21)	2297.4 (23)	2725.8 (10)
Z	2	4	3
cryst size, mm	0.41 × 0.40 × 0.20	0.45 × 0.45 × 0.45	0.10 × 0.36 × 0.38
cryst color	colorless	colorless	colorless
D_{calc}, g cm^{-3}	1.707	1.768	1.465
μ(Mo Kα), cm^{-1}	56.68	72.65	46.09
temp, K	297	297	297
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2θ range, deg	4–46	4–50	4–50
data collected (h,k,l)	±10,+9,+23	±20,+10,+21	+14,+14,±31
rflns collcted	2276	4519	1258
indep rflns	2035	4049	1258
indep rflns obsd	1857	2351	1219
$R(F)$, %	5.62	5.79	4.60
$R(wF)$, %	5.78	5.96	4.84

Bis[hydrotris(3,5-dimethylpyrazolyl)borato]lead(II), $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (4). Complex **4** was prepared from $PbCl_2$ (0.250 g, 0.900 mmol) and $K[HB(3,5\text{-}Me_2pz)_3]$ (0.605 g, 1.80 mmol) as described above for **1** (0.363 g, 50%); mp 317–319 °C. Crystals for the crystal structure were grown from hot/cold (70/25 °C) toluene. ^1H NMR ($CDCl_3$, δ): 5.77 (6, s, 4-H (pz)); 2.30 (18, s, 3-Me); 1.77 (18, s, 5-Me). ^{13}C NMR ($CDCl_3$, δ): 149.0 (3-C (pz)); 145.5 (5-C (pz)); 105.8 (4-C (pz)); 13.5 (Me); 13.3 (Me). ^{207}Pb NMR ($CDCl_3$, −49 °C, δ): −1481. MS: *m/e* 802 ($Pb[HB(Me_2pz)_3]_2$); 505 ($Pb[HB(Me_2pz)_3])^+$. Anal. Calcd for $C_{30}H_{44}B_2N_{12}Pb$: C, 44.95; H, 5.53. Found C, 45.02; H, 5.46.

[Hydrotris(pyrazolyl)borato]chlorolead(II), $[HB(pz)_3]PbCl$ (5). A solution of $K[HB(pz)_3]$ (0.45 g, 1.8 mmol) in warm (50 °C) water (20 mL) was added, via cannula, to a solution $PbCl_2$ (0.500 g, 1.80 mmol) in water (50 mL). A white precipitate formed immediately upon mixing of the two clear, colorless solutions. After being stirred at room temperature for ca. 1 h, the mixture was filtered on a Buchner funnel and washed with H_2O. The white powder was dried overnight in vacuo (0.467 g, 56%); mp 284–287 °C. ^1H NMR ($CDCl_3$, δ): 7.74, 7.35 (3, 3; s, s; 3-H, 5-H (pz)); 6.16 (3; s; 4-H (pz)). Accurate mass spectrum for $M^+ - H$ (*m/e*): calcd for $^{206}PbC_9H_9{}^{11}B^{35}ClN_6$, 453.0415; found, 453.0410.

X-ray Crystal Structure Determination for 1, 2, and 4. Crystal, data collection and refinement parameters are collected in Table I. Colorless crystals of **1**, **2**, and **4** were each mounted on fine glass fibers with epoxy cement. The unit cell parameters of **1**, **2**, and **4** were each obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed $2/m$ Laue symmetry for both **1** and **2** and $\bar{3}$ or $\bar{3}m$ Laue symmetry for **4**. The systematic absences in the diffraction data of **2** uniquely established the space group as $P2_1/n$. The systematic absences in the diffraction data of **1** establish the space group as Pc or $P2/c$. E-statistics suggested the noncentrosymmetric alternative, and the chemical sensible results of refinement showed that Pc is the correct space group for **1**. Refinement of a multiplicative term (−0.312) for $\Delta f''$ for **1** indicated that the enantiomorph might not be correct, and refinement in the other hand produced a positive multiplicative term (0.312) of $\Delta f''$ but these values are too small to prove one hand is correct as opposed to the other. The systematic absences in the diffraction data of **4** established the space group as $R3$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$. A solution was obtained in each of the space groups above, but the chemically sensible result of the refinement showed that $R\bar{3}$ is the correct space group for **4**. An empirical absorption correction (XEMP) was applied to the data sets of **1**, **2**, and **4** (216 Ψ-scan reflections, pseudoellipsoid

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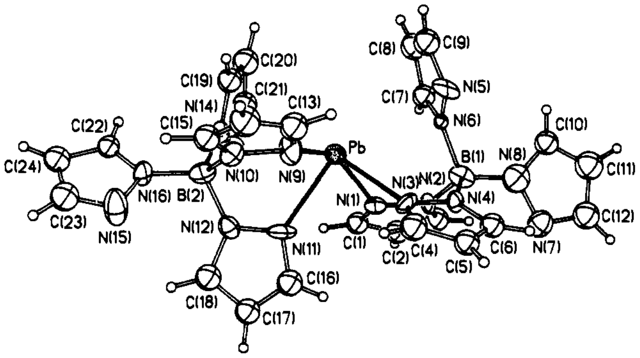


Figure 1. ORTEP drawing and labeling scheme for $[B(pz)_4]_2Pb$ (**1**). Ellipsoids are at 30% probability.

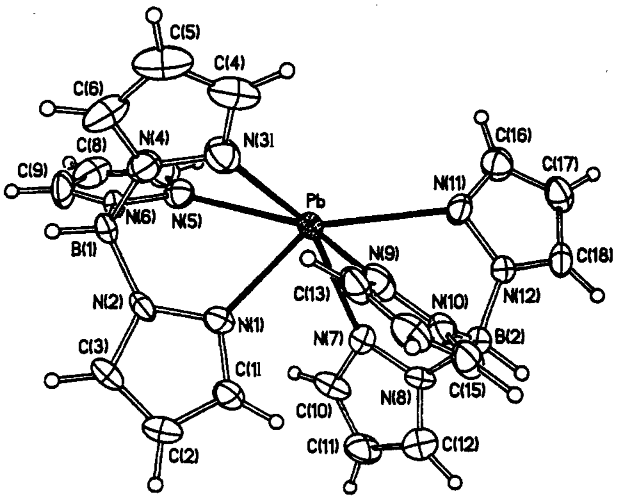


Figure 2. ORTEP drawing and labeling scheme for $[HB(pz)_3]_2Pb$ (**2**). Ellipsoids are at 30% probability.

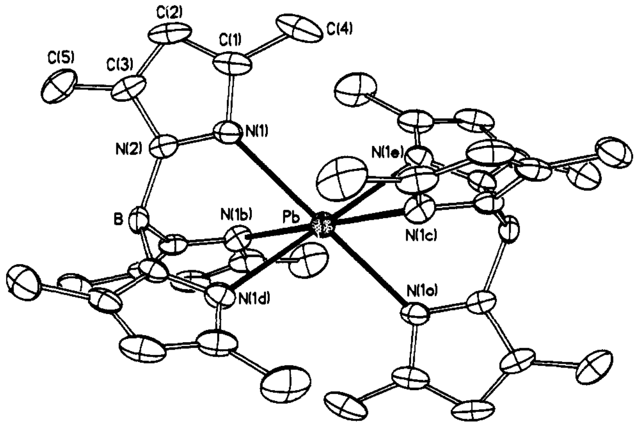


Figure 3. ORTEP drawing and labeling scheme for $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**). Ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.

model), and for all three structures the semiempirical absorption correction program XABS was used.

The structures of **1**, **2**, and **4** were solved by heavy-atom methods which located the Pb atoms. The remaining non-hydrogen atoms were located through subsequent least squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, U = 1.2U for attached C). All non-hydrogen atoms of **1**, **2**, and **4** were refined with anisotropic thermal parameters.

Figures 1–3 show the ORTEP drawings of **1**, **2**, and **4**, respectively. Tables II–IV contain selected bond distances and bond angles for **1**, **2**, and **4**, respectively.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1) (G. Sheldrick, Nicolet (Siemens), Madison, WI).

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for $[B(pz)_4]_2Pb$ (**1**)

Bond Distances			
Pb–N(1)	2.478 (18)	Pb–N(3)	2.414 (15)
Pb–N(9)	2.518 (20)	Pb–N(11)	2.423 (16)
N(1)–N(2)	1.415 (24)	N(3)–N(4)	1.369 (24)
N(5)–N(6)	1.394 (20)	N(7)–N(8)	1.363 (29)
N(9)–N(10)	1.401 (28)	N(11)–N(12)	1.377 (28)
N(13)–N(14)	1.409 (24)	N(15)–N(16)	1.354 (24)
Pb···B(1)	3.433 (17)	Pb···B(2)	3.517 (17)
Pb···N(5)	3.245 (14)	Pb···N(13)	3.037 (14)
Bond Angles			
N(1)–Pb–N(3)	75.4 (5)	N(1)–Pb–N(9)	148.1 (5)
N(3)–Pb–N(9)	84.7 (6)	N(1)–Pb–N(11)	82.2 (6)
N(3)–Pb–N(11)	86.6 (6)	N(9)–Pb–N(11)	71.8 (6)
Pb–N(1)–N(2)	118.8 (11)	Pb–N(3)–N(4)	117.3 (10)
Pb–N(9)–N(10)	120.2 (12)	Pb–N(11)–N(12)	119.7 (12)
N(2)–B(1)–N(4)	110.8 (14)	N(2)–B(1)–N(6)	105.2 (15)
N(2)–B(1)–N(8)	109.9 (18)	N(4)–B(1)–N(6)	107.4 (17)
N(4)–B(1)–N(8)	111.5 (16)	N(6)–B(1)–N(8)	111.8 (15)
N(10)–B(2)–N(12)	107.0 (17)	N(10)–B(2)–N(14)	105.0 (14)
N(10)–B(2)–N(16)	115.4 (19)	N(12)–B(2)–N(14)	106.2 (17)
N(12)–B(2)–N(16)	114.3 (15)	N(14)–B(2)–N(16)	108.3 (16)
N(1)–N(2)–B(1)	117.6 (16)	N(3)–N(4)–B(1)	122.4 (15)
N(5)–N(6)–B(1)	121.4 (13)	N(7)–N(8)–B(1)	119.8 (17)
N(9)–N(10)–B(2)	118.0 (18)	N(11)–N(12)–B(2)	122.4 (15)
N(13)–N(14)–B(2)	121.2 (15)	N(15)–N(16)–B(2)	118.8 (17)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[HB(pz)_3]_2Pb$ (**2**)

Bond Distances			
Pb–N(1)	2.462 (13)	Pb–N(3)	2.623 (16)
Pb–N(5)	2.806 (13)	Pb–N(7)	2.523 (14)
Pb–N(9)	2.477 (13)	Pb–N(11)	2.750 (14)
N(1)–N(2)	1.386 (18)	N(3)–N(4)	1.352 (20)
N(5)–N(6)	1.350 (18)	N(7)–N(8)	1.364 (18)
N(9)–N(10)	1.345 (19)	N(11)–N(12)	1.349 (17)
Bond Angles			
N(1)–Pb–N(3)	73.5 (4)	N(1)–Pb–N(5)	73.2 (4)
N(1)–Pb–N(7)	78.8 (4)	N(1)–Pb–N(9)	77.6 (4)
N(1)–Pb–N(11)	139.1 (4)	N(3)–Pb–N(5)	72.5 (4)
N(3)–Pb–N(7)	150.1 (4)	N(3)–Pb–N(9)	84.7 (5)
N(3)–Pb–N(11)	124.9 (4)	N(5)–Pb–N(7)	110.1 (4)
N(5)–Pb–N(9)	147.0 (4)	N(5)–Pb–N(11)	143.5 (4)
N(7)–Pb–N(9)	78.6 (5)	N(7)–Pb–N(11)	71.6 (4)
N(9)–Pb–N(11)	69.4 (4)	Pb–N(1)–N(2)	125.2 (9)
Pb–N(3)–N(4)	133.0 (12)	Pb–N(5)–N(6)	119.8 (9)
Pb–N(7)–N(8)	122.3 (10)	Pb–N(9)–N(10)	124.2 (11)
Pb–N(11)–N(12)	118.2 (9)	N(1)–N(2)–B(1)	123.6 (12)
N(3)–N(4)–B(1)	123.9 (14)	N(5)–N(6)–B(1)	120.6 (12)
N(7)–N(8)–B(2)	120.7 (12)	N(9)–N(10)–B(2)	123.5 (13)
N(11)–N(12)–B(2)	120.6 (13)	N(2)–B(1)–N(4)	111.8 (13)
N(2)–B(1)–N(6)	109.1 (14)	N(4)–B(1)–N(6)	110.0 (13)
N(8)–B(2)–N(10)	109.6 (14)	N(8)–B(2)–N(12)	107.6 (14)
N(10)–B(2)–N(12)	113.8 (15)		

Table IV. Bond Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**)

Bond Distances			
Pb–N(1)	2.610 (5)	N(1)–C(1)	1.323 (8)
N(1)–N(2)	1.358 (8)	N(2)–C(3)	1.348 (8)
N(2)–B	1.554 (6)	C(1)–C(2)	1.399 (13)
B–H(1)	1.047 (155)	C(2)–C(3)	1.374 (11)
B–N(2B)	1.553 (4)	C(3)–C(5)	1.491 (12)
C(1)–C(4)	1.502 (15)		
Bond Angles			
N(1)–Pb–N(1A)	180.0 (1)	N(1)–Pb–N(1B)	75.2 (1)
N(1A)–Pb–N(1B)	104.8 (1)	Pb–N(1)–N(2)	118.2 (4)
Pb–N(1)–C(1)	130.6 (5)	N(2)–C(3)–C(5)	123.6 (7)
N(1)–N(2)–B	122.3 (5)	N(2)–N(1)–C(1)	107.1 (6)
B–N(2)–C(3)	127.8 (6)	N(1)–N(2)–C(3)	109.9 (5)
N(2)–B–N(2A)	110.6 (4)	C(2)–C(1)–C(4)	129.3 (7)
N(1)–C(1)–C(4)	120.8 (8)	N(2)–C(3)–C(2)	107.7 (7)
C(1)–C(2)–C(3)	105.4 (6)	C(2)–C(3)–C(5)	128.7 (7)

Results

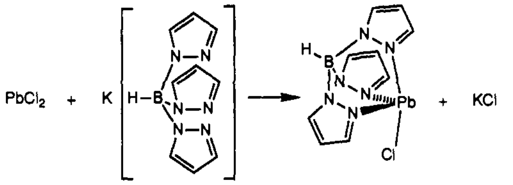
Syntheses of Complexes. Complexes with two bis-, tris-, and tetrakis(pyrazolyl)borate ligands coordinated to lead(II) are readily prepared by the addition of aqueous solutions of $PbCl_2$ to solutions of 2 equiv of the ligand salt (eqs 1 and 2). In a analogous manner,

$$2K[H_nB(pz)_{4-n}] + PbCl_2 \rightarrow [H_nB(pz)_{4-n}]_2Pb + 2KCl \quad (1)$$

$$n = 0\ (\mathbf{1}),\ 1\ (\mathbf{2}),\ 2\ (\mathbf{3})$$

$$2K[HB(3,5\text{-}Me_2pz)_3] + PbCl_2 \rightarrow [HB(3,5\text{-}Me_2pz)_3]_2Pb\ (\mathbf{4}) + 2KCl \quad (2)$$

$[HB(pz)_3]PbCl$ is prepared in water by addition of solutions of 1 equiv of the ligand salt to $PbCl_2$ solutions (eq 3). Attempts to prepare $[B(pz)_4]PbCl$ and $[H_2B(pz)_2]PbCl$ by similar reactions in water, CH_2Cl_2, or THF failed. With the tetrakis(pyrazolyl)borate ligand, the only product isolated from a reaction with this stoichiometry is $[B(pz)_4]_2Pb$. Reactions with the dihydrobis(pyrazolyl)borate ligand produced an insoluble white solid that was not further characterized.



(3)

5

All five complexes are stable in air. They are high-melting solids that are soluble in aromatic and halocarbon solvents, with the chloro complex **5** being considerably less soluble.

Solid-State Structures. The structures of $[B(pz)_4]_2Pb$ (**1**), $[HB(pz)_3]_2Pb$ (**2**), and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**) have been determined crystallographically.

Structure of $[B(pz)_4]_2Pb$ (1). Figure 1 shows an ORTEP drawing of **1**; Table II shows selected bond angles and distances. The molecule is monomeric with no short intermolecular contacts. Each ligand is coordinated to the lead atom in only a bidentate fashion. The geometry about the lead atom is best described as a distorted pseudotrigonal bipyramid with the lone pair on the lead atom presumably occupying an equatorial site. Each ligand spans an axial and equatorial site with the N–Pb–N bond angles formed by the chelate rings of 71.8 (6)° and 75.4 (5)°. The axial N(1)–Pb–N(9) bond angle is 148.1 (5)°, and the axial Pb–N distances are 2.478 (18) and 2.518 (20) Å. The equatorial N(3)–Pb–N(11) bond angle is 86.6 (6)°, and the equatorial Pb–N distances are 2.414 (15) and 2.423 (16) Å. The average Pb–N axial bond distance is 2.498 Å, just slightly longer than the average equatorial bond distance of 2.418 Å.

This structure is similar to the structure observed for $[B(pz)_4]_2Sn$,[4] especially the overall pseudo-trigonal-bipyramidal shape with compressed axial and equatorial bond angles. Major differences in the tin structure are that the axial Sn–N bond distances are very different (2.336 (4) and 2.625 (4) Å) and the average axial distance is 0.222 Å longer than the average equatorial distance. Compression of the bond angles and shorter equatorial bond distances are general features of four-coordinate tin(II) structures.[14] Although fewer data are available, the structures of a number of lead(II) complexes also show these features.[15] For example, the complex $(EtOCS_2)_2Pb$ has this basic structural type, but the axial bond distances are 0.13 Å longer than the equatorial bonds.[15b] In general, in higher coordinate lead structures, bonds adjacent to the presumed location of the lead(II) lone pair are over 0.1 Å longer than bonds remote from the lone pair.[13,16] This trend is less pronounced in **1**.

The six-membered BN_4Pb rings are arranged in shallow boat configurations with Pb···B distances of 3.433 (17) and 3.517 (17) Å. One of the noncoordinated pyrazolyl rings on each ligand is close to the lead atom with Pb···N(5) and Pb···N(13) distances of 3.245 (14) and 3.037 (14) Å, respectively. There are clearly no bonding interactions between these nitrogen atoms and the lead atom because the planes of these pyrazolyl rings, the planes in which the lone pairs on the nitrogen atoms are located, are oriented approximately at right angles from the Pb–N vectors. Rotation of these rings so as to move the N(5) and/or N(13) atoms toward the lead atom would bring them into bonding range.

Structure of $[HB(pz)_3]_2Pb$ (2). Figure 2 shows an ORTEP drawing of $[HB(pz)_3]_2Pb$ (**2**); Table III shows selected bond angles and distances. In contrast to **1**, both ligands are *tridentate*, forming a six-coordinate, monomeric structure. The geometry about the lead atom is best described as based on a capped octahedron, with the lone pair on the metal located in the capping position of the triangular face formed by N(3), N(5), and N(11). The three Pb–N bond distances to these donor atoms average 2.726 Å, whereas the average of the other three is much shorter at 2.487 Å. As pointed out above, lengthening of lead-donor atom bonds proximate to the lone pair is generally observed in lead(II) structures. The interligand bond angles in the capped face are much larger (average 134° vs 78°), as expected. Of the three basic seven-vertex geometries generally considered important, pentagonal bipyramid, capped trigonal prism, and capped octahedron, clearly the latter is favored for complexes containing two η^3-poly(pyrazolyl)borate ligands. These umbrella-shaped ligands readily fill the vertices of an octahedron, but a trigonal-prismatic arrangement of two ligands is prevented by interligand contacts of the pyrazolyl rings.

Structure of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (4). Figure 3 shows an ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (**4**); Table IV shows the bond angles and distances. The complex is six-coordinate, and the geometry about the lead atom is a trigonally distorted octahedron. The lead atom sits on a center of inversion, and the planes formed by the three nitrogen donor atoms of each ligand are parallel. Intraligand N–Pb–N bond angles are all 75.2 (1)°, and the interligand N–Pb–N bond angles are 104.8 (1)° (cis) and 180 (1)° (trans). The lone pair on lead is clearly stereochemically inactive.

Variable-Temperature NMR Data. The variable-temperature ^1H NMR spectra of $[H_2B(pz)_2]_2Pb$ (**3**) indicate that this four-coordinate complex shows two types of dynamic processes in solution. The ambient-temperature spectrum shows three resonances in the aromatic region, one for each of the three types of hydrogen atoms in the pyrazolyl rings, and a broad resonance (ca. 1.2 ppm wide) for the BH_2 hydrogen atoms. At −89 °C, two of the pyrazolyl ring hydrogen atom resonances are still sharp, but line broadening of the middle resonance is observed. At −89 °C, two nonequivalent BH resonances with a half-height width of 70 Hz are observed. At ambient temperature, the BH_2 resonance is broad due to quadrupolar coupling and relaxation effects from the boron atom, but at low temperatures the boron becomes self-decoupled from the hydrogen atoms leading to sharper resonances.[17] At low temperatures, the BH_2 hydrogen atoms are nonequivalent, as expected for an axial and equatorial orientation in the boat configuration observed for the six-membered BN_4Pb ring of a bidentate poly(pyrazolyl)borate ligand (e.g., the structure of **1**). Coalescence of the two BH resonances is observed at −58 °C (500 MHz). The barrier to the dynamic process at −58 °C is calculated to be 9.4 kcal/mol.

The ambient-temperature ^1H NMR spectrum of **1** also shows three resonances, one for each of the three types of hydrogen atoms in the pyrazolyl rings. At −89 °C, each resonance type has split

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Table V. Tin-119 and Lead-207[a] NMR Chemical Shift and Line Width Data in $CDCl_3$

	^{119}Sn	^{207}Pb	Pb $w_{1/2}$ (Hz)
$[H_2B(pz)_2]_2M$	−652	−139	150
$[B(pz)_4]_2M$	−743	−534	200
$[HB(pz)_3]_2M$	−877	−895	600
$[HB(3,5\text{-}Me_2pz)_3]_2M$	−934	−1481	300

[a] At −49 °C.

into two resonances with *3/1 integrated intensities*. Appropriate line broadening is observed at intermediate temperatures with a barrier to the fluxional process of 9.1 kcal/mol, as calculated from the coalescence at −75 °C of the two downfield resonances. Both **2** and **4** show equivalent rings, even at low temperatures.

Lead-207 NMR. Shown in Table V are the ^{207}Pb chemical shift and line width data for the complexes reported here. Also shown in Table V are the ^{119}Sn chemical shifts for the tin(II) complexes, with the analogous ligand combinations, that we had reported earlier.[4] The ^{207}Pb spectra were recorded at −49 °C since no peaks were observed at room temperature. A value for $[HB(pz)_3]PbCl$ could not be recorded due to low solubility.

Discussion

Structures. The most important result of the structures of **1** and **2** is the demonstration for the first time that a matched pair of complexes of the same metal with the tetrakis(pyrazolyl)borate and hydrotris(pyrazolyl)borate ligands *have very different structures*. Complex **1** is four-coordinate with a structure very similar to $[B(pz)_4]_2Sn$.[4] Given the large size of lead(II), its known propensity toward high coordination numbers,[13] and the six-coordinate structures of **2** and **4**, four-coordination in **1** is initially a surprising result. We suggest that even though there are numerous examples of $[B(pz)_4]^-$ acting as a tridentate ligand,[18] intraligand contacts among the pyrazolyl rings favor bidentate coordination. In bidentate coordination, intraligand contacts can be minimized. The noncoordinated ring farthest from the metal can orient so as to bisect the planes of the two coordinated rings, minimizing contacts among these three rings. The fourth ring avoids any close contacts with these three rings by orienting perpendicular to the distant noncoordinated ring. This arrangement is observed in our $[B(pz)_4]_2M$ (M = Sn, Pb) structures and in other cases where this ligand is bidentate.[19] If the ligand is tridentate, the noncoordinated pyrazolyl ring cannot avoid unfavorable steric interactions with the coordinated rings.

This type of steric control of structure has been discussed previously in relationship to the inability of the $[Ph_2B(pz)_2]^-$ ligand to show a C–H agostic interaction in electron-deficient transition-metal complexes. Specifically, Cotton[20] has pointed out that an orientation of one of the phenyl groups such as to form a M–H–C three-center interaction with an ortho hydrogen atom on a phenyl ring (which would be analogous to the $[B(pz)_4]^-$ ligand becoming tridentate) in $[Ph_2B(pz)_2](CO)_2$(2-methylallyl)Mo would cause unfavorable contacts between the ortho hydrogen atoms of the remaining phenyl ring and those on the pyrazolyl rings. This point has been emphasized again very recently.[21] Also, the somewhat similar ligand $PhHC(3,5\text{-}Me_2pz)_2$, a ligand containing only one phenyl group and thus removing the unfavorable contact in η^3 coordination, has been shown in the complex $[PhHC(3,5\text{-}Me_2pz)_2]Mo(CO)_3$,[22] to have a structure in which there is an interaction of the phenyl ring with the metal atom. Although the unfavorable interactions of the pyrazolyl rings should not be as great for a tridentate $[B(pz)_4]^-$ ligand as in $[Ph_2B(pz)_2]^-$ because of the smaller five-membered rings, the interactions still can influence structural arrangement.

Two other molecules in which the $[B(pz)_4]^-$ ligand coordinates bidentate where tridentate coordination may have been anticipated are $[\eta^2\text{-}B(pz)_4]Rh(\eta^4$-1,5-cyclooctadiene) and $[\eta^2\text{-}B(pz)_4]Rh(\eta^4$-norbornadiene). However, tridentate coordination is observed in the very similar molecule $[\eta^3\text{-}B(pz)_4]Rh(\eta^4$-1,4-duroquinone).[19] As suggested above, in the stereoview of $[\eta^3\text{-}B(pz)_4]Rh(\eta^4$-1,4-duroquinone) there does appear to be a close contact between the hydrogen atom at the 5-position of the noncoordinated pyrazolyl ring and one on a coordinated ring. Both tridentate and bidentate coordination of tetrakis(pyrazolyl)borate ligands also have been observed in very similar platinum complexes.[23] In addition, although steric factors from the isopropyl groups may also be important, it has been shown that a series of $[B(3\text{-}i\text{-}Prpz)_4]_2M$ complexes with first-row metals are four-coordinate whereas analogous $[HB(i\text{-}Prpz)_3]_2M$ complexes (in these complexes one of the 3-*i*-Prpz rings isomerizes to a 5-*i*-Prpz ring for each ligand) are six-coordinate.[24]

Clearly, whether $[B(pz)_4]^-$ will coordinate bidentate or tridentate is determined by a balance between the desire of the metal to attain higher coordination numbers and repulsive intramolecular forces between the noncoordinated pyrazolyl ring and the three-coordinated rings in tridentate coordination of this ligand. This work shows that it cannot be assumed that very similar hydrotris(pyrazolyl)borate and tetrakis(pyrazolyl)borate complexes will have analogous structures with the same coordination numbers.

The highly symmetrical structure of **4** with the bulky $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand demonstrates that the lone pair on the lead(II) atom is stereochemically inactive in this complex. Although Zuckerman raised interest in this point in 1984 with his structure of decaphenylstannocene[8] and review article,[25] ***4** is the first six-coordinate, main-group, molecular complex in which the lone pair is stereochemically inactive*. The difference in structure between **4** and the similar six-coordinate complex **2**, where the lone pair is stereochemically active, can be attributed to steric effects. The cone angle of $[HB(pz)_3]^-$ is 184° whereas $[HB(3,5\text{-}Me_2pz)_3]^-$ has a much larger cone angle of 224°.[26] Interestingly, the attempt to use the same strategy in tin(II) chemistry to prepare a complex with a stereochemically inactive lone pair was not successful because $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ is only five-coordinate.[5] As we had anticipated, the larger size of lead(II) accommodates two tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligands, but only in a symmetrical arrangement with an inactive lone pair.

Tridentate poly(pyrazolyl)borate ligands have frequently been compared to cyclopentadienyl ligands, and the $[HB(pz)_3]^-$ and $(\eta^5\text{-}C_5Me_5)^-$ ligands have been shown to have similar electronic properties.[27] The structure of **2** can be described as having a bent metallocene-type arrangement, considering the N_3 donor atoms plane of each ligand as analogous to the plane of a cyclopentadienyl ligand. The solid-state structure of $(\eta^5\text{-}C_5Me_5)_2Pb$ shows that this molecule is monomeric with a bent metallocene structure.[28] The ring centroid–Pb–ring centroid angle is 151° compared to the analogous B–Pb–B angle of 137.1 (5)° for **2**. One other molecule formed from a tridentate, umbrella ligand that is similar

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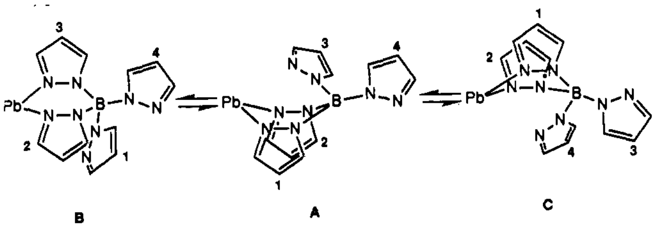
Scheme I



to **2** and **4** is $\{(\eta^5\text{-}C_5H_5)Co[P(OC_2H_5)_2O]_3\}_2Pb$. As observed with **2**, the lone pair is stereochemically active with a Co–Pb–Co angle of 150.96 (7)°.[29]

The differences in structure of **1**, **2**, and **4** demonstrate that changes in very similar ligands can have pronounced structural effects. Changes in structure with these variations in the ligands might not occur for other metals, but lead(II) can accommodate a variety of different structural types.[13] In **1**, the structure is dominated by *intraligand* steric effects. The structure of **2** is not dominated by steric effects from the ligand and is a six-coordinate arrangement with a stereochemically active lone pair. The symmetrical structure of **4** is dominated by *interligand* steric effects.

It is also interesting to compare the average Pb–N bond distances in **1**, **2**, and **4**. It has been suggested previously that metal–ligand distances are shorter in lead(II) structures where the lone pair is stereochemically active.[10] The average Pb–N distance in **2** is 2.607 (14) Å while the Pb–N distances in **4** are essentially the same at 2.610 (5) Å. Although the lone pair is clearly active in **2** and not in **4**, there is no difference in the Pb–N bond lengths. The average Pb–N distance in **1** is 2.458 Å, but because this complex has a lower coordination number this distance is not directly comparable to those in **2** or **4**.

The solution- and solid-state structures of **3** and **5** can be assigned by analogy to the tin(II) complexes[4] and other known complexes of lead(II)[13] and the structure of **1** to the pseudo-trigonal-bipyramidal structure shown in eq 3. The fifth vertex of the polyhedra is presumably occupied by the lead(II) lone pair. Because of the low solubility of **5**, a dimeric structure with bridging chloride ligands is also possible.

^{207}Pb NMR. The chemical shift range observed for the lead(II) complexes (Table V) is greater than observed for tin(II), as expected.[30] For both metals, chemical shifts move to higher fields as the coordination number of the complexes increases. Correlations of chemical shift between analogous tin(II) and lead(II) complexes have been noted previously.[29] Particularly notable is the large shift to higher field for **4**, a complex with a structure different from that of the tin(II) analogue and in which the lone pair is stereochemically inactive. It has been shown previously that lead(II) salts (e.g., $Pb(ClO_4)_2 \cdot H_2O$) with the inactive lone pair isolated in the 6s orbital have resonances at high fields.[31]

Variable-Temperature NMR. In the pseudo-trigonal-bipyramidal structure of **3**, there are axial and equatorial pyrazolyl rings. These rings show as equivalent at ambient temperatures in ^{1}H NMR spectra, and line broadening of only one of the ring hydrogen resonances is observed even at −89 °C. This behavior for **3** is very similar to that observed previously with $[H_2B(pz)_2]_2Sn$. For tin, the barrier is higher, 10.2 kcal/mol at −58 °C, and each resonance type appears as two equal-intensity resonances.[4] A second dynamic process for **3**, the boat-boat flip of the BN_4Pb ring, equilibrates the BH_2 resonances at ambient temperatures, and this process can be frozen out at low temperatures with a barrier of 9.4 kcal/mol at −58 °C. Again, this barrier is lower than observed for the same process with $[H_2B(pz)_2]_2Sn$ (10.3 kcal/mol). We attribute these lower lead(II) barriers, for both the intramolecular rearrangement that equilibrates the axial and equatorial pyrazolyl rings and the boat–boat flip, to the larger size of lead.

For **1**, the observations of equivalent pyrazolyl rings at ambient temperature and a 3/1 pattern at −89 °C also parallel those observed with $[B(pz)_4]_2Sn$, except again the barrier is lower by 1.4 kcal/mol for the lead(II) complex. As with the tin(II) complex, we assign the solution structure of **1** to be the same as observed in the solid-state structure. In this structure, all eight pyrazolyl rings are nonequivalent. Nevertheless, the 3/1 integrated intensities of the two resonances observed at −89 °C for each type of ring hydrogen atom can be explained if a low-energy process equilibrates for each ligand the three rings that are "close" to the lead atom. Such a process would involve the coordination of the pyrazolyl ring nitrogen donor atom that is 3.0–3.2 Å away from the lead atom with dissociation of one of the coordinated rings (A → B, Scheme I), presumably through a five-coordinate intermediate. Repetition of this process for the three "close" rings of each ligand (rings 1, 2, and 3) would equilibrate these six rings, but leave the remaining two rings (rings 4) unique. At higher temperatures, a boat-boat flip of the BN_4Pb rings of the bidentate ligand (A → C) equilibrates all four rings on each ligand. Consistent with this interpretation is the fact that the barrier to the ring flip for both **1** and **3** is essentially the same and both ca. 1 kcal/mol lower than observed with the tin(II) analogues.

Our assignment of a four-coordinate solution structure and a low barrier to the bond breaking–bond making process A → B for both $[B(pz)_4]_2M$ (M = Sn, Pb) complexes is supported by a recent publication by Jones and Hessell.[32] They show that the hydrotris(3,5-dimethylpyrazolyl)borate ligand in $[HB(3,5\text{-}Me_2pz)_3]Rh(CNCMe_3)_2$ is *bidentate* in both the solid state and in solution, but the ^{1}H NMR spectra show all three rings as equivalent, even at −100 °C. A similar bond breaking–bond making process to that proposed above is a reasonable explanation for these observations.

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Supplementary Material Available: Tables of positional parameters, complete bond distances, angles, anisotropic thermal parameters and positional parameters of H atoms (15 pages); listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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