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Mixed Poly(pyrazolyl)borate–Cyclopentadienyl Zirconium(IV) Complexes. Crystal and Molecular Structure of [Dihydrobis(1-pyrazolyl)borato]dichlorocyclopentadienylzirconium(IV)

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Reaction of the ligand Na[HB(pz)$_3$] or K[HB(3,5-Me$_2$pz)$_3$] (pz = pyrazolyl ring) with CpZrCl$_3$(DME) yields the respective [ligand]CpZrCl$_2$ complex. A similar reaction with K[H$_2$B(pz)$_2$] yields [H(μ-H)B(pz)$_2$]CpZrCl$_2$. This molecule contains a three-center, two-electron B–H–Zr bond as shown by a low $J_{\text{B-H}}$ (88 Hz) value in the ^{11}B NMR spectrum and a ν(B–H) (2160 cm^{-1}) band in the IR spectrum. This was confirmed in the solid state by a single-crystal X-ray structural determination that shows a close B–Zr distance (2.957 (5) Å) indicative of this type of interaction. Crystal data: orthorhombic, *Pnma*, a = 14.902 (6) Å, b = 13.414 (4) Å, c = 7.576 (5) Å, V = 1514 (1) Å^3, Z = 4, D_x = 1.64 g cm^{-3}, λ = 0.71073 Å. Mixing this complex with t-BuNC yields [H$_2$B(pz)$_2$]CpZr(t-BuNC)Cl$_2$, in which the bridging hydrogen atom has been displaced from the metal.

Introduction

We have recently been able to demonstrate that poly(pyrazolyl)borate ligands are useful in the development of the chemistry of alkylmetal complexes of early transition metals. For tantalum,[1] the complexes [RB(pz)$_3$]TaMe$_3$Cl (R = H, pz (pz = pyrazolyl ring)), [HB(3,5-Me$_2$pz)$_3$]TaMe$_3$Cl, and [H(μ-H)B(3,5-Me$_2$pz)$_2$]TaMe$_3$Cl have been prepared. They are very stable for alkyltantalum complexes and show interesting structural features and dynamic processes. With zirconium,[2] many octahedral complexes of the type [RB(pz)$_3$]ZrX$_3$ have been prepared. Most interesting are the alkyl complexes [HB(3,5-Me$_2$pz)$_3$]Zr(O-t-Bu)$_x$R$_{3-x}$ (x = 1, 2; R = Me, CH$_2$Ph, C≡CMe). In this initial work, the introduction of at least one electron-donating alkoxy ligand in addition to the (pyrazolyl)borate ligand was necessary for the preparation of stable alkylzirconium complexes (in the solid,[2c] one of these molecules shows a short Zr–O distance and a Zr–O–C angle of 174°). We have recently been able to prepare [HB(3,5-Me$_2$pz)$_3$]ZrMe$_3$,[3] but this complex is not very stable. Thus, it seems that the introduction of a second auxiliary ligand is important for the development of this chemistry. Two particularly interesting possible choices are either a second poly(pyrazolyl)borate ligand or a cyclopentadienyl (Cp) ligand. Either approach would lead to (ligand)$_2$ZrX$_2$ complexes analogous to the heavily studied Cp$_2$ZrX$_2$ system.[4]

We report here the synthesis of mixed [poly(pyrazolyl)borate]CpZrCl$_2$ complexes, including the solid-state structure of the complex [H(μ-H)B(pz)$_2$]CpZrCl$_2$, a complex with a three-center, two-electron B–H–Zr bond. Only two somewhat similar mixed sandwich compounds have been previously reported. Manzer[5] reported [HB(pz)$_3$]CpTiCl$_2$, a complex that is insoluble in organic solvents. Bagnell and Edwards[6] have reported [HB(pz)$_3$]CpUCl$_2$.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of prepurified nitrogen using either 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 Perkin-Elmer 621 spectrometer. ^{1}H NMR spectra were recorded on Varian EM-390 and EM-360 spectrometers, and chemical shifts are reported in δ vs. Me$_4$Si. Carbon-13 NMR spectra were recorded on an IBM NR-80 spectrometer with CD$_2$Cl$_2$ or CDCl$_3$ as the solvent and internal standard with chemical shifts reported in ppm vs. Me$_4$Si (CDCl$_3$ resonance assigned at 77.0 ppm and CD$_2$Cl$_2$ resonance at 53.8 ppm). All carbon-13 spectra were run with ^{1}H decoupling, and all resonances are singlets. Boron-11 spectra were recorded on a Bruker WH200 spectrometer in CD$_2$Cl$_2$, and chemical shifts are reported in ppm vs. BF$_3$·OEt$_2$. Mass spectra were run as solids on a Finnigan 4521 GC–mass spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by the Robertson Laboratory. K[H$_2$B(pz)$_2$], K[HB(3,5-Me$_2$pz)$_3$], Na[HB(pz)$_3$],[7] and CpZrCl$_3$[8a] were prepared by published methods. CpZrCl$_3$(DME) was prepared by the addition of DME to CpZrCl$_3$ at −78 °C, followed by filtration at room temperature and concentration to give crystals of CpZrCl$_3$(DME).[8b]

[Hydrotris(pyrazolyl)borato]dichlorocyclopentadienylzirconium(IV) ([HB(pz)$_3$]CpZrCl$_2$). CpZrCl$_3$(DME) (0.35 g; 1.0 mmol) and Na[HB(pz)$_3$] (0.24 g; 1.0 mmol) were combined in a 250-mL round-bottom flask containing a magnetic stirring bar. After the flask was cooled to −78 °C, CH$_2$Cl$_2$ (40 mL), previously cooled to −78 °C, was added to the solids via cannula. The reaction mixture was allowed to gradually warm to room temperature with stirring (5 h). The cloudy solution was filtered through a medium-fritted disk. All the volatiles were removed under vacuum, leaving a white solid residue (0.35 g; 79%). The analytical sample was obtained by crystallization from hot–cold toluene, as clear, colorless crystals. ^{1}H NMR spectrum (CDCl$_3$): δ 8.19, 7.85, 7.69, 7.39 (1, 2, 2, 1; d, d, d, d; J = 2.0 Hz; 3-H, 5-H (pz)); 6.74 (5, s, Cp); 6.30, 6.09 (2, 1; t, t; J = 2.0 Hz; 4-H (pz)). ^{13}C NMR spectrum (CDCl$_3$, pz rings nonequivalent in this compound and labeled A and B, the ratio of A:B being 2:1): δ 145.7 (A, B), 136.7 (A), 133.8 (B) (3-C, 5-C (pz)); 119.9 (Cp); 106.2 (A), 104.6 (B) (4-C (pz)). The mass spectrum shows clusters with highest peaks at m/e 439 (M$^+$ + 1) and 373 (M$^+$ − 65 (Cp)). Anal. Calcd for C$_{14}$H$_{15}$N$_6$BCl$_2$Zr: C, 38.36; H, 3.42; N, 19.17; Cl, 15.98. Found: C, 38.64; H, 3.63; N, 18.90; Cl, 15.79.

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichlorocyclopentadienylzirconium(IV) ([HB(3,5-Me$_2$pz)$_3$]CpZrCl$_2$). CpZrCl$_3$(DME) (0.35 g; 1.0 mmol) and K[HB(3,5-Me$_2$pz)$_3$] (0.34 g; 1.0 mmol) were combined in a 250-mL round-bottom flask containing a magnetic stirring bar. After the flask was cooled to −78 °C, CH$_2$Cl$_2$ (50 mL), previously cooled to −78 °C, was added to the solids by cannula. The reaction mixture was gradually allowed to warm to room temperature with stirring (5$^1/_2$ h). The cloudy solution was filtered through a medium-fritted disk. All the volatiles were removed under vacuum, leaving a white solid residue (0.36 g; 68%). ^{1}H NMR spectrum (CDCl$_3$): δ 6.64 (5, s, Cp); 5.88, 5.68 (2, 1; s, s; 4-H (pz)); 2.68, 2.45, 2.25 (9, 6, 3; s, s, s; 3-CH$_3$, 5-CH$_3$(pz)). ^{13}C NMR spectrum (CDCl$_3$, pz rings nonequivalent in this compound and labeled A and B, the ratio of A:B being 2:1): δ 153.8 (A), 153.6 (B), 145.2 (A), 142.5 (B) (3-C, 5-C (pz)); 119.4 (Cp); 109.1 (A), 107.9 (B) (4-C (pz)); 16.6 (B), 15.8 (A), 13.1 (A), 12.9 (B) (3-CH$_3$, 5-CH$_3$ (pz)). The mass spectrum shows a cluster at m/e 457 (M$^+$ − 65 (Cp)); no molecular ion (M$^+$) was observed.

[Dihydrobis(1-pyrazolyl)borato]dichlorocyclopentadienylzirconium(IV) ([H$_2$B(pz)$_2$]CpZrCl$_2$). CpZrCl$_3$(DME) (1.4 g; 4.0 mmol) and K[H$_2$B(pz)$_2$] (0.74 g; 4.0 mmol) were combined in a 50-mL round-bottom flask containing a magnetic stirring bar. After the flask was cooled to −78 °C, CH$_2$Cl$_2$ (10 mL), previously cooled to −78 °C, was added to the solids by a cannula. The reaction mixture was allowed to gradually warm to 0 °C with stirring (3 h). The cloudy solution was filtered cold through a medium fritted disk. All the volatiles were removed under vacuum,

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Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{eq},[a] Å^2
Zr(1)	0.05923 (3)	0.750	0.04673 (7)	2.481 (8)
Cl(3)	0.02457 (7)	0.88061 (8)	0.2641 (2)	3.99 (2)
N(1)	0.2466 (2)	0.8421 (2)	0.0259 (4)	2.92 (6)
N(2)	0.1655 (2)	0.8589 (2)	−0.0521 (5)	3.25 (6)
C(3)	0.1779 (3)	0.9375 (3)	−0.1591 (6)	4.3 (1)
C(4)	0.2653 (3)	0.9708 (3)	−0.1484 (7)	4.6 (1)
C(5)	0.3068 (2)	0.9085 (3)	−0.0325 (6)	3.65 (8)
C(6)	−0.0915 (3)	0.6975 (3)	−0.0673 (7)	4.9 (1)
C(7)	−0.0268 (3)	0.6653 (4)	−0.1904 (7)	5.6 (1)
C(8)	0.0129 (4)	0.750	−0.2683 (9)	5.7 (1)
B(1)	0.2515 (4)	0.750	0.1437 (9)	3.3 (1)
H(1)	0.1835	0.750	0.2207	4.0*
H(2)	0.3183	0.750	0.2207	4.0*
H(3)	0.1171	0.9511	−0.2226	4.0*
H(4)	0.3007	1.0175	−0.2500	4.0*
H(5)	0.3671	0.9003	0.0273	4.0*

[a] Values marked with an asterisk indicate that the atoms were not refined; $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j u_{ij}a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

leaving a white solid residue (1.0 g; 70%). The analytical sample was obtained by crystallization from CH_2Cl_2–hexane, as clear, colorless crystals. ^1H NMR spectrum ($CDCl_3$): δ 7.72, 7.52 (2, 2; d, d; $J = 2.0$ Hz; 3-H, 5-H (pz)); 6.89 (5, s, Cp); 6.24 (2, t, $J = 2.0$ Hz, 4-H (pz)). ^{13}C NMR spectrum ($CDCl_3$): δ 138.6, 133.3 (3-C, 5-C (pz)); 119.3 (Cp); 107.0 (4-C (pz)). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −10.5 (s); the coupled spectrum shows a doublet of doublets, $J_{BH} = 88$ and 118 Hz. IR spectrum (Nujol mull), cm^{-1}: 3110 (Cp), 2530 (B–H terminal), 2160 (B–H···Zr). The mass spectrum shows clusters at m/e 373 ($M^+ + 1$) and 307 ($M^+ - 65$ (Cp)). Anal. Calcd for $C_{11}H_{13}N_4BCl_2Zr$: C, 35.33; H, 3.47; N, 14.97; Cl, 18.72. Found: C, 34.77; H, 3.68; N, 14.89; Cl, 18.38.

[Dihydrobis(1-pyrazolyl)borato]dichlorocyclopentadienyl(*tert*-butyl isocyanide)zirconium(IV) ($[H_2B(pz)_2]CpZr(CNCMe_3)Cl_2$). $CpZrCl_3$-(DME) (0.70 g; 2.0 mmol) and $K[H_2B(pz)_2]$ (0.37 g; 2.0 mmol) were combined in a 50-mL round-bottom flask containing a magnetic stirring bar. After the flask was cooled to −78 °C, CH_2Cl_2 (5 mL), previously cooled to −78 °C, was added to the solids by cannula. The reaction mixture was allowed to gradually warm to 0 °C with stirring (3 h). *tert*-Butyl isocyanide (220 μL; 2.0 mmol) was added to the solution. The solution was stirred at 0 °C for 2 h. The cloudy beige solution was filtered through a medium-fritted disk. All the volatiles were removed under vacuum, leaving a beige oil. It proved impossible to obtain a pure sample of this material due to decomposition during attempted purification procedures. The compound was characterized spectroscopically. ^1H NMR spectrum ($CDCl_3$): δ 8.11, 7.70 (2, 2; d, d; $J = 2.0$ Hz; 3-H, 5-H (pz)); 6.70 (5, s, Cp); 6.20 (2, t, $J = 2.0$ Hz, 4-H (pz)); 2.41 (9, s, CH_3's). ^{13}C NMR spectrum ($CDCl_3$): δ 138.5, 138.1 (3-C, 5-C (pz)); 120.4 (Cp); 104.9 (4-C (pz)); 59.0 ($C(CH_3)_3$); 30.1 (CH_3's). IR spectrum (Nujol mull), cm^{-1}: 3120 (Cp), 2423 (B–H terminal), 2218 (isocyanide). $^{11}B\{H\}$ NMR ($CDCl_3$, 80 °C): δ −8.31 (s); the coupled spectrum shows a triplet, $J_{BH} = 95$ Hz. The mass spectrum shows clusters at m/e 455 (M^+), 440 ($M^+ - 15$ (CH_3)), and 372 ($M^+ - 83$ (t-BuNC)).

Table II. Bond Angles (deg) and Distances (Å) with Estimated Standard Deviations in Parentheses[a]

Cl(3)–Zr(1)–N(2)	84.79 (7)	C(7)–Zr(1)–C(8)	33.0 (1)
Cl(3)–Zr(1)–N(2)*	145.28 (7)	C(7)–Zr(1)–H(1)	147.2
Cl(3)–Zr(1)–C(6)	104.1 (1)	N(2)–N(1)–C(5)	109 (3)
Cl(3)–Zr(1)–C(6)*	80.9 (1)	N(2)–N(1)–B(1)	115.4 (3)
Cl(3)–Zr(1)–C(7)	134.6 (1)	C(5)–N(1)–B(1)	134.5 (3)
Cl(3)–Zr(1)–C(7)*	92.9 (1)	Zr(1)–N(2)–N(1)	111.6 (2)
Cl(3)–Zr(1)–C(8)	125.80 (7)	Zr(1)–N(2)–C(3)	142.8 (2)
Cl(3)–Zr(1)–H(1)	77.47	N(1)–N(2)–C(3)	105.6 (3)
Cl(3)–Zr(1)–Cl(3)*	90.87 (5)	N(2)–C(3)–C(4)	110.4 (3)
N(2)–Zr(1)–N(2)*	79.7 (1)	C(3)–C(4)–C(5)	105.5 (3)
N(2)–Zr(1)–C(6)	133.5 (1)	N(1)–C(5)–C(4)	108.6 (3)
N(2)–Zr(1)–C(6)*	109.2 (1)	Zr(1)–C(6)–C(6)*	73.68 (9)
N(2)–Zr(1)–C(7)	114.5 (1)	Zr(1)–C(6)–C(7)	72.7 (2)
N(2)–Zr(1)–C(7)*	80.1 (1)	C(6)*–C(6)–C(7)	107.9 (3)
N(2)–Zr(1)–C(8)	83.0 (1)	Zr(1)–C(7)–C(6)	74.5 (2)
N(2)–Zr(1)–H(1)	67.94	Zr(1)–C(7)–C(8)	73.5 (3)
C(6)–Zr(1)–C(6)*	32.6 (2)	C(6)–C(7)–C(8)	108.4 (4)
C(6)–Zr(1)–C(7)	32.8 (1)	Zr(1)–C(8)–C(7)	73.4 (3)
C(6)–Zr(1)–C(7)*	54.3 (1)	C(7)–C(8)–C(7)*	107.3 (5)
C(6)–Zr(1)–C(8)	54.6 (2)	N(1)–B(1)–N(1)*	108.1 (4)
C(6)–Zr(1)–H(1)	158.39	N(1)–B(1)–H(1)	104.6
C(7)–Zr(1)–C(7)*	54.5 (2)	N(1)–B(1)–H(2)	109.7
		H(1)–B(1)–H(2)	119.7

Zr(1)–Cl(3)	2.459 (1)	N(2)–C(3)	1.344 (4)
Zr(1)–N(2)	2.280 (3)	C(3)–C(4)	1.380 (5)
Zr(1)–C(6)	2.507 (3)	C(4)–C(5)	1.369 (5)
Zr(1)–C(7)	2.483 (4)	C(6)–C(6)	1.409 (8)
Zr(1)–C(8)	2.484 (5)	C(6)–C(7)	1.409 (6)
Zr(1)–H(1)	2.274	C(7)–C(8)	1.411 (6)
N(1)–N(2)	1.364 (4)	B(1)–H(1)	1.167
N(1)–C(5)	1.339 (4)	B(1)–H(2)	1.155
N(1)–B(1)	1.526 (4)		

[a] Atoms marked with an asterisk are related by the x, $0.5 - y$, z symmetry operation.

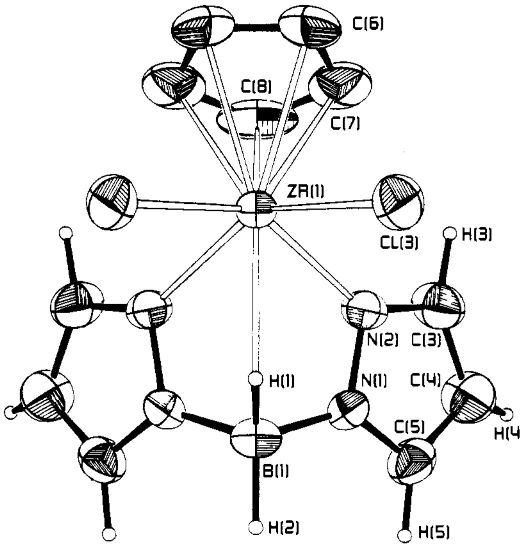

Figure 1. ORTEP[11] drawing of the molecule of $[H(\mu\text{-}H)B(pz)_2]CpZrCl_2$. The thermal motion ellipsoids are at 50% probability level.

X-ray Structure Determination. Colorless crystals of $[H_2B(pz)_2]$-$CpZrCl_2$ were grown from a mixed CH_2Cl_2–hexane solution. An irregular fragment of a larger crystal with dimensions 0.2 × 0.2 × 0.2 mm was mounted in a glass capillary and used for measurements. The crystals are orthorhombic, in space group *Pnma*, with $a = 14.902$ (6) Å, $b = 13.414$ (4) Å, $c = 7.576$ (5) Å, $V = 1514$ (1) Å^3, $Z = 4$, $D_x = 1.64$ g cm^{-3}, linear absorption coefficient $\mu = 10.60$ cm^{-1}, fw = 374.19, $F(000) = 744$, and $T = 291$ K. The data were collected with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) in the $2° < \theta < 25°$ range and a graphite monochromator; 25 general reflections were used for the orientation matrix and parameter measurements. The data were collected in the ω–2θ scan mode with $0.65° + (0.35 \tan \theta)°$ scan range and variable scan speed; the orientation was checked every 100 reflections. The intensities of three standard reflections were monitored every 2.5 h of exposure time. The crystal showed very little decay in the X-ray beam over 48 h of exposure. The corrections for decay were applied (maximum 1.01, average 1.005). A total of 1385 reflections were measured, and 1038 were observed with $I > 3\sigma(I)$. Absorption corrections were applied by using the method of Walker and Stuart.[9] Minimum, maximum, and average corrections were 0.891, 1.067, and 0.992, respectively. The Zr position was determined from a Patterson map, the rest of the structure was found in difference Fourier maps. The structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2(F) + 0.0004F^2)^{-1}$, with anisotropic temperature factors for all non-H atoms. Atomic scattering factors were corrected for anomalous dispersion. In the difference Fourier maps the hydrogen atoms bonded to B(1) corresponded to the highest peaks. The hydrogen atoms bonded to the carbon atoms of the pyrazolyl rings were also found, but those of the Cp ring could not be located in the map. The parameters of the H atoms were not refined.[10] The final $R = 0.027$, $R_w = 0.036$, and $S = 1.33$. On the final difference Fourier map the maximum was 0.32 e Å^{-3}

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(10) All calculations were carried out with the Enraf-Nonius Structure Determination Package by B. A. Frenz, 1983.

and was in the vicinity of the Zr atom. The atomic coordinates are listed in Table I; important bond distances and angles are in Table II. An ORTEP[11] drawing of the molecule is shown in Figure 1.

Results and Discussion

The new mixed tris(pyrazolyl)borate–cyclopentadienyl zirconium(IV) complexes are readily prepared as shown in eq 1. These

$$\mathrm{CpZrCl_3(DME)} \xrightarrow[{[\mathrm{HB(3,5\text{-}Me_2pz)_3}]^-}]{[\mathrm{HB(pz)_3}]^- \text{ or}} [\text{ligand}]\mathrm{CpZrCl_2} \quad (1)$$

reactions are carried out in stoichiometric amounts. In contrast, our earlier preparation of $[HB(pz)_3]ZrCl_3$ from $ZrCl_4$ and the ligand salt required 2 equiv of $ZrCl_4$,[2a] the second equivalent acting as a Lewis acid for the displaced chloride. Clearly, the formally 16-electron starting material in eq 1 is not as strong a Lewis acid as $ZrCl_4$. The mixed-ligand complexes are thermally very stable but decompose in air. Although electronically equivalent to Cp_2ZrCl_2, these complexes have not yet proven useful as precursors to new hydride or alkyl derivatives. Starting material is consumed in reactions with RLi, RMgBr, or *t*-BuOK, but no new resonances are observed in the alkyl region of spectra taken on the residues formed in these reactions. No reaction is observed when $[HB(pz)_3]CpZrCl_2$ is mixed with *t*-BuNC.

In the NMR of both of the new tris(pyrazolyl)borate complexes, the pyrazolyl ring carbon and hydrogen atoms each show resonances in a 2:1 pattern, showing that these molecules possess a mirror plane in solution. This pattern is retained up to 100 °C. In contrast, $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ type molecules are fluxional[2b] by a mechanism involving a trigonal twist of the poly(pyrazolyl)borate ligand about the Zr–B axis with the barrier to rotation of ca. 13 kcal/mol. The increased bulk of the cyclopentadienyl ligand must substantially increase the barrier to this type of ligand rotation. The complex $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$,[2b] with the bulky dimethyl-substituted ligand, and seven-coordinate $[RB(pz)_3]TaMe_3Cl$ type molecules[1] also do not show this type of fluxional behavior. (Zr(IV) and Ta(V) are about equal in size.) In contrast, in the NMR spectrum of the paramagnetic complex $[HB(pz)_3]CpUCl_2$ only one resonance is reported for each type of pyrazolyl-ring hydrogen atom.[6] Presumably, the larger size of U(IV) (ionic radius 0.97 Å) vs. Zr(IV) (ionic radius 0.79 Å) lowers the barrier to rotation of the ligand about the Zr–B axis. Thus, this type of fluxional process is very sensitive to steric constraints.

In order to prepare a complex similar to those prepared in eq 1 that might have two fewer electrons at the metal and thus be more reactive, the reaction with a bis(pyrazolyl)borate ligand, eq 2, was carried out. This reaction must be carried out at a high

$$\mathrm{CpZrCl_3(DME)} \xrightarrow{[\mathrm{H_2B(pz)_2}]^-} [\mathrm{H}(\mu\text{-}\mathrm{H})\mathrm{B(pz)_2}]\mathrm{CpZrCl_2} \quad (2)$$

concentration to obtain the desired product, a product that decomposes in a few hours in solution. X-ray crystallography (vide infra) demonstrates unequivocally that there is a three-center, two-electron, B–H–Zr interaction in this molecule in the solid state. In the IR spectrum of the solid, ν(B–H) bands are observed at 2530 cm^{-1} (terminal) and 2160 cm^{-1} (three-center). ^{11}B NMR shows that this interaction is retained in solution. In the coupled ^{11}B NMR spectrum, one observes a doublet of doublets with J_{BH} = 88 and 118 Hz. Coupling constants of 60–70 Hz have been observed in molecules containing B–H–Mn interactions[12] and in $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]TaMe_3Cl$, a molecule with a very similar bonding pattern[1b] (J_{BH} = 118 and 76 Hz). Three other relevant coupling constants are 112 Hz for $[HB(pz)_3]TaMe_3Cl$,[1a] 105 Hz for $K[HB(pz)_3]$,[7] and 96 Hz for $K[H_2B(pz)_2]$.[7] Thus, the 118-Hz coupling for $[H(\mu\text{-}H)B(pz)_2]CpZrCl_2$ arises from the terminal BH and the 88-Hz coupling from the bridging BH. The spectrum is not typical of that expected for a BH_2 group in a normal η^2-$[H_2B(pz)_2]$ ligand because one would expect that the hydrogen atoms would equilibrate through a ring inversion, the barrier to which has been estimated to be ca. 6 kcal/mol.[13]

Due to the three-center bond, the $[H_2B(pz)_2]$ ligand donates as many electrons to the zirconium atom as the tris ligands. As anticipated, however, the molecules differ in that the three-center bond is a potential site of reactivity. Thus, mixing $[H(\mu\text{-}H)B(pz)_2]CpZrCl_2$ with *t*-BuNC yields $[H_2B(pz)_2]CpZr(t\text{-}BuNC)Cl_2$, in which the isocyanide ligand has displaced the bridging hydrogen atom. As outlined above, a similar reaction with the two tris(pyrazolyl)borate complexes fails. Displacement of the bridging hydrogen atom is demonstrated by the ^{11}B NMR spectrum. In this case, a triplet with J_{BH} = 95 Hz is observed. As outlined above, this is the spectrum expected for a normal η^2-$[H_2B(pz)_2]$ ligand (virtually the same as observed for $K[H_2B(pz)_2]$) in which the BH_2 hydrogen atoms are equilibrating via a rapid ring inversion. In order to resolve the coupling, it was necessary to run the spectrum at 80 °C, a well-known phenomenon in ^{11}B NMR.[14] Cooling the sample to −20 °C resulted in a continual broadening of the signal, eliminating the possibility that the broadening observed at ambient temperature was the result of a dynamic process of some type. We are exploring the usefulness of this partially open coordination site for developing new chemistry.

Description of Structure. $[H(\mu\text{-}H)B(pz)_2]CpZrCl_2$ exists as isolated molecules in the solid state. Figure 1 shows an ORTEP drawingof the molecule. The molecule contains a crystallographically imposed mirror plane passing through B(1), Zr(1), and C(8). The most interesting feature of the structure is the extreme puckering of the six-membered chelate ring. This places Zr(1), B(1), and H(1), 1.368, 0.770, and 1.74 Å, respectively, above the plane formed by N(2), N(1), N(1)*, and N(2)* and makes a 106.9° angle between the normals to the plane formed by B(1), N(1), N(2), and Zr(1) and the symmetry-equivalent plane. The B–Zr distance is very short at 2.957 (5) Å. These data clearly indicate a three-center, two-electron B–H–Zr bonding situation, and in fact, the bridging hydrogen atom was located close to Zr (2.27 Å). This type of bonding has been observed previously in three cases, $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]TaMe_3Cl$,[1b] $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]Mo(CO)_2(\eta^3\text{-}C_3H_5)$,[15] and $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]Mo(CO)_2(\eta^3\text{-}C_7H_7)$.[16] For cases where no three-center interaction exists, the puckering of the six-membered chelate ring is shallow with M–B distances of ca. 3.8 Å.[17]

The overall geometry in this mixed Cp–poly(pyrazolyl)borate complex in the solid state is very similar to that of the large number of bent sandwich[18] Cp_2MX_n type structures. The Zr–C and Zr–Cl distances are very similar to those reported for Cp_2ZrCl_2, but the Cl–Zr–Cl angle is 6° smaller. The angle between normals to the Cp plane and the H(1), N(2), N(2)* plane is 127.8°, which compares closely to the average value of 127.0° found between the Cp planes of Cp_2ZrCl_2. (It is an average value because two independent molecules, one of which is disordered, were found in this structure.)

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Supplementary Material Available: Table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (11 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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