"intramolecular" corrections were applied. The results given in Table IV favor, slightly, the Wigner lattice. The small energy margin by which the results differ is significant in that a mixed-valence state (U), if not the lowest energy state by the Madelung energy calculation (which always favors the disproportionated Wigner lattice A or B), can be stabilized by a strong electronic coupling between V^{2+} and V^{3+} along *c*.

Conclusion

LiV_2F_6 is a mixed-valence salt that crystallizes in the trirutile (tapiolite) structure, space group $P4_2/mnm$. This structure exhibits pairs of crystallographically equivalent, orthorhombically distorted VF_6 octahedra that share one edge; the VF_6 pairs are separated along the tetragonal *c* axis by LiF_6 octahedra that share edges with the adjacent VF_6 octahedra.

The "rutile-type" distortion of VF_6 octahedra allows one to guess the 3d orbital occupancy in a weak-field scheme and to argue that the nearest-neighbor V–V interaction should be ferromagnetic and that the next-nearest-neighbor V–V interaction should be antiferromagnetic. Implicit in our argument is the assertion that angular distortion of ligands will have an effect on the mixing energy states.

The Madelung energy calculation favors, as expected, the non-mixed-valent Wigner crystal limit by an insignificant energy difference.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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Zirconium(IV) Poly(pyrazolyl)borate *tert*-Butoxide Derivatives. Stereochemically Nonrigid Six-Coordinate Molecules

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The complexes $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ (R = *n*-Bu, *i*-Pr; pz = pyrazolyl ring) and $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ have been prepared from the reaction of the previously reported $[RB(pz)_3]ZrCl_3$ complexes and 1 equiv of KO-*t*-Bu. $[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)_3$ and $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_3$ are prepared with excess KO-*t*-Bu. The two insoluble complexes $[RB(pz)_3]ZrCl_3$ (R = H, pz) have been prepared free of $ZrCl_4$ for the first time and were characterized as their soluble $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ derivatives. The complex $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ shows the expected 2:1 pattern for each type of pyrazolyl reasonance in the ^1H and ^{13}C NMR spectra (one pz is trans to the O-*t*-Bu ligand, the other two are trans to Cl ligands). The other four $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ complexes are fluxional at ambient temperature, but at low temperature limiting static spectra can be obtained. Careful investigation of the variable-temperature ^1H NMR spectra of $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ indicates that a mechanism involving a trigonal twist of the poly(pyrazolyl)borate ligand about the Zr–B axis can explain this dynamic behavior.

Introduction

We have recently described the synthesis of $[RB(pz)_3]ZrCl_3$ (R = *n*-Bu, *i*-Pr; pz = pyrazolyl ring) and $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$,[1] the first well-characterized poly(pyrazolyl)borate complexes of zirconium.[2] Our choice of the alkyl-substituted $[RB(pz)_3]$ ligands was made to avoid potential steric problems offered by the $[HB(3,5\text{-}Me_2pz)_3]$ ligand and to ensure good solubility characteristics in standard organic solvents (complexes of $[HB(pz)_3]^-$ are frequently insoluble[4]). It is anticipated that these complexes represent the starting materials for an extensive series of derivatives of this early transition metal much in the same way that Cp_2ZrCl_2 and to a lesser extent $CpZrCl_3$ have been employed by others.[5]

To this end, we report here the synthesis and investigation of the fluxional behavior of a series of *tert*-butoxide derivatives of these poly(pyrazolyl)borate complexes. For complexes of the type $[RB(pz)_3]Zr(OR)Cl_2$, two of the pz rings are equivalent while the third is distinct. For the complexes of the $[HB(3,5\text{-}Me_2pz)_3]$ ligand, this nonequivalency is observed in both the ^1H and the ^{13}C NMR spectra at all temperatures studied. In contrast, the complexes of the $[RB(pz)_3]$ ligands display temperature-dependent ^1H and ^{13}C NMR spectra. We show that this fluxional behavior can be accounted for by a nondissociative trigonal-twist type mechanism.[6a] Although many stereochemically nonrigid molecules containing poly(pyrazolyl)borate ligands have been described,[6] these molecules

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(2) A brief report[3] of $[B(pz)_4]_2ZrX_2$ (X = Cl, Br) and $[B(pz)_4]_4Zr$ has appeared. Following the preparations outlined in that publication, we have been unable to reproduce the reported NMR data.
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represent the first discrete six-coordinate complexes of this type amenable to a variable-temperature investigation.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of prepurified nitrogen with the use of standard Schlenk techniques or an efficient drybox. All solvents were dried, degassed, and distilled prior to their use. Infrared spectra were recorded on a Beckman Model IR 4210 spectrometer. Proton NMR spectra were recorded on Varian EM-390 and Bruker WP-200 spectrometers, and chemical shifts are reported in δ vs. Me_4Si. Carbon-13 NMR spectra were recorded on Varian CFT-20 and IBM NR-80 spectrometers with CD_2Cl_2 or $CDCl_3$ as the solvent and internal standard. Chemical shifts are reported in ppm vs. Me_4Si, with the CD_2Cl_2 resonance assigned at 53.8 ppm and the $CDCl_3$ resonance at 77.0 ppm. All carbon-13 spectra were run with ^1H decoupling, and all resonances are singlets. Carbon atoms bound to boron were not observed. Mass spectra were run as solids with a Finnigan 4021 GC–mass spectrometer using an ionization voltage of 70 eV. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$, $[i\text{-}PrB(pz)_3]ZrCl_3$, $[n\text{-}BuB(pz)_3]ZrCl_3$, and $[HB(3,5\text{-}Me_2pz)_3]Zr(OMe)Cl_2$ were prepared as previously described.[1] In our initial paper, $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ was purified by a Soxhlet extraction. We have now found that the crude reaction residue is best purified by crystallization from hot–cold toluene (1.0 g, 75 mL) in 71% yield. $ZrCl_4$ was freshly sublimed prior to its use. Elemental analyses were performed by Robertson Laboratory. Melting points were determined in sealed capillaries and are uncorrected.

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloro-*tert*-butoxyzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\}$. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ (0.50 g, 1.0 mmol) and potassium *tert*-butoxide (0.12 g, 1.1 mmol) were combined in a 250-mL round-bottom flask containing a magnetic stirring bar. Toluene (50 mL) was added via syringe, and the reaction was allowed to stir overnight (~10 h) at room temperature. The cloudy, white solution was filtered through a medium-fritted disk, and the solvent was evaporated from the clear, colorless filtrate under reduced pressure at room temperature, yielding a white solid (0.44 g, 82%). The analytical sample was obtained by crystallization of this solid (0.50 g) from 80 mL of hot–cold (−30 °C) hexane. White crystals (0.31 g, 62%, mp 243–246 °C) were recovered. Anal. Calcd for $C_{19}H_{31}N_6BCl_2OZr$: C, 42.86; H, 5.87. Found: C, 43.04; H, 5.77. ^1H NMR spectrum ($CDCl_3$): 5.78 (3, s, 4-H (pz)); 2.66, 2.60, 2.36 (3, 6, 9; s, s, s; 3-CH_3, 5-CH_3 (pz)); 1.57 (9, s, $OC(CH_3)_3$). IR spectrum (cm^{-1} in CH_2Cl_2): ν(BH) 2562. ^{13}C NMR spectrum (in $CDCl_3$, the pz rings are nonequivalent in this compound and are labeled A and B; the ratio A:B is 2:1): 153.7 (B), 152.1 (A), 145.9 (A), 144.4 (B) (3-C, 5-C (pz)); 107.3 (B), 106.7 (A) (4-C (pz)); 83.4 (O–C); 30.9 ($OC(CH_3)_3$); 15.39 (B), 15.35 (A), 12.83 (A), 12.73 (B) (CH_3 (pz)). The mass spectrum shows multiple clusters (appropriate isotopic pattern for an ion containing two Cl atoms) at m/e 515 (P − 15 (CH_3)) and a base peak at m/e 459 (P − 73 (O-*t*-Bu)). No parent ion (P) was observed.

[Isopropyltris(1-pyrazolyl)borato]dichloro-*tert*-butoxyzirconium(IV) $\{[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\}$. This compound was prepared by the same procedure as for $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, yielding a white solid (49%). The analytical sample was obtained by crystallization of this solid (0.30 g) from 150 mL of hot–cold (−30 °C) hexane. White crystals (0.17 g, 57%, mp 198–201 °C) were recovered. Anal. Calcd for $C_{16}H_{25}N_6BCl_2OZr$: C, 39.19; H, 5.14. Found: C, 39.47; H, 5.07. ^1H NMR spectrum ($CDCl_3$): 8.02, 7.81 (3, 3; d, d; J = 2.7 Hz, J = 2.4 Hz; 3-H, 5-H (pz)); 6.24 (3, t, J = 2.1 Hz, 4-H (pz)); 2.0 (1, m, CH); 1.50 (6, d, J = 6.9 Hz, $C(CH_3)_2$); 1.42 (9, s, $OC(CH_3)_3$). ^{13}C NMR spectrum ($CDCl_3$): 143.2, 134.8 (3-C, 5-C (pz)); 104.8 (4-C (pz)); 82.6 (O–C); 31.1 ($OC(CH_3)_3$); 20.6 ($C(CH_3)_2$). The mass spectrum shows multiple clusters (appropriate isotopic pattern for an ion containing two Cl atoms) at m/e 473 (P − 15 (CH_3)) and a base peak at m/e 415 (P − 73 (O-*t*-Bu)). No parent ion was observed.

[*n*-Butyltris(1-pyrazolyl)borato]dichloro-*tert*-butoxyzirconium(IV) $\{[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\}$. This compound was prepared by the same procedure as for $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, yielding a white solid (61%, mp 134–135 °C). Anal. Calcd for $C_{17}H_{27}N_6BCl_2OZr$: C, 40.48; H, 5.36; N, 16.67; Cl, 14.09. Found: C, 39.98; H, 5.29; N, 15.94; Cl, 13.56. ^1H NMR spectrum ($CDCl_3$): 8.00, 7.71 (3, 3; d, d; J = 2.4 Hz, J = 2.7 Hz; 3-H, 5-H (pz)); 6.23 (3, t, J = 2.1 Hz, 4-H (pz)); 1.6, 1.1 (9, m, *n*-Bu); 1.40 (9, s, $OC(CH_3)_3$). ^{13}C NMR spectrum ($CDCl_3$): 143.4, 134.1 (3-C, 5-C (pz)); 104.9 (4-C (pz)); 82.6 (O–C); 31.0 ($OC(CH_3)_3$); 27.5, 26.8 (CH_2); 14.0 (CH_3).

[Hydrotris(3,5-dimethylpyrazolyl)borato]tri-*tert*-butoxyzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_3\}$. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ (2.00 g, 4.05 mmol) and potassium *tert*-butoxide (1.81 g, 16.2 mmol) were combined in a 250-mL flask containing a magnetic stirring bar. Benzene (75 mL) was added via syringe, and this mixture was refluxed for 3 h. The benzene was evaporated under reduced pressure at room temperature, leaving a white residue. The solid was stirred with hexane (100 mL), this mixture was filtered, and the hexane was evaporated at room temperature, yielding a white solid (2.01 g, 82%). The analytical sample was obtained by crystallization of 1.00 g of this solid from 30 mL of hot–cold (−30 °C) hexane. White crystals (0.41 g, 41%, mp 236–239 °C) were recovered. Anal. Calcd for $C_{27}H_{49}N_6O_3BZr$: C, 53.36; H, 8.13. Found: C, 52.52; H, 7.76. ^1H NMR spectrum ($CDCl_3$): 5.64 (3, s, 4-H (pz)); 2.61, 2.33 (9, 9; s, s; 3-H, 5-H (pz)); 1.31 (27, s, $OC(CH_3)_3$). IR spectrum (cm^{-1} in CH_2Cl_2): ν(BH) 2555. ^{13}C NMR spectrum ($CDCl_3$): 150.0, 143.7 (3-C, 5-C (pz)); 105.1 (4-C (pz)); 75.8 (OC); 32.8 ($OC(CH_3)_3$); 17.1, 13.1 (CH_3 (pz)).

[Isopropyltris(1-pyrazolyl)borato]tri-*tert*-butoxyzirconium(IV) $\{[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)_3\}$. $[i\text{-}PrB(pz)_3]ZrCl_3$ (3.00 g, 6.64 mmol) and potassium *tert*-butoxide (3.00 g, 26.8 mmol) were combined in a 250-mL flask containing a magnetic stirring bar. Toluene (150 mL) was added via syringe, and the reaction was allowed to proceed overnight (~12 h) at room temperature. The cloudy, white solution was filtered through a medium-fritted disk, and the solvent was evaporated from the clear, colorless filtrate under reduced pressure at room temperature, yielding a white solid (3.18 g, 85%). This solid was pure by NMR but proved too soluble to crystallize even from hexane. ^1H NMR spectrum ($CDCl_3$): 7.82, 7.71 (3, 3; d, d; J = 2.1 Hz, J = 2.4 Hz; 3-H, 5-H (pz)); 6.09 (3, t, J = 2.1 Hz, 4-H (pz)); 2.0 (1, m, CH); 1.49 (6, d, J = 6.7 Hz, $C(CH_3)_2$); 1.23 (27, s, $OC(CH_3)_3$). ^{13}C NMR spectrum ($CDCl_3$): 141.6, 133.2 (3-C, 5-C (pz)); 103.1 (4-C (pz)); 74.7 (O–C); 32.6 ($OC(CH_3)_3$); 21.0 ($C(CH_3)_2$).

[Tetrakis(1-pyrazolyl)borato]trichlorozirconium(IV) $\{B(pz)_4]ZrCl_3\}$. Freshly sublimed $ZrCl_4$ (8.15 g, 35.0 mmol) was stirred in CH_2Cl_2 (200 mL) at −78 °C. Diethyl ether (50 mL) was added via syringe, and the mixture was warmed to room temperature, yielding a homogeneous solution presumably containing an Et_2O adduct of $ZrCl_4$ ($ZrCl_4$ is only sparingly soluble in CH_2Cl_2). Potassium tetrakis(1-pyrazolyl)borate (5.60 g, 17.6 mmol) was slowly added as a solid to this stirred solution, and the reaction was allowed to proceed overnight (~12 h). All volatiles were removed under vacuum, leaving a white residue. This crude solid was triturated with a solution of CH_2Cl_2–Et_2O (1:1, 100 mL) at room temperature. The solid that remained was collected and dried under vacuum (8.72 g, 92%, with the assumption that 1 equiv of KCl is present); this mixture was used in subsequent reactions as a source of $[B(pz)_4]ZrCl_3$. The very limited solubility of this compound precluded further purification and solution spectroscopic characterization. The mass spectrum shows a multiple cluster (appropriate isotopic pattern for an ion containing three Cl atoms) at m/e 476 (parent) and a base peak at m/e 439 (P − 37 (^{37}Cl), appropriate isotopic pattern for an ion containing two Cl atoms).

[Hydrotris(1-pyrazolyl)borato]trichlorozirconium(IV) $\{[HB(pz)_3]ZrCl_3\}$. This complex was prepared by a method analogous to the one for $[B(pz)_4]ZrCl_3$ with $Na[HB(pz)_3]$ and yields a mixture of the desired white complex and NaCl (95%). The mixture was used in subsequent reactions as a source of $[HB(pz)_3]ZrCl_3$. The very limited solubility of this compound precluded further purification and solution spectroscopic characterization. The mass spectrum shows a multiple cluster (appropriate isotopic pattern for an ion containing three Cl atoms) at m/e 410 (parent) and a base peak at m/e 373 (P − 37 (^{37}Cl), appropriate isotopic pattern for an ion containing two Cl atoms).

[Hydrotris(1-pyrazolyl)borato]dichloro-*tert*-butoxyzirconium(IV) $\{[HB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\}$. This compound was prepared by the same procedure as for $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\}$, yielding a white solid (48% yield). The analytical sample was obtained by crystallization of this solid (0.60 g) from 200 mL of hot–cold (−30 °C) hexane. White crystals (0.20 g, 33%, mp 203–204 °C) were recovered. Anal. Calcd for $C_{13}H_{19}N_6OBCl_2Zr$: C, 34.83; H, 4.27. Found: C, 34.75; H, 4.38. ^1H NMR spectrum ($CDCl_3$): 8.01, 7.65 (3, 3; d, d; J = 2.4 Hz, J = 2.4 Hz; 3-H, 5-H (pz)); 6.21 (3, t, J = 2.2 Hz, 4-H (pz)); 1.42 (9, s, $OC(CH_3)_3$). IR spectrum (cm^{-1} in CH_2Cl_2):

ν(BH) 2497. ^{13}C NMR spectrum ($CDCl_3$): 143.5, 135.7 (3-C, 5-C (pz)); 105.2 (4-C (pz)); 82.8 (OC); 31.0 ($OC(CH_3)_3$). The mass spectrum shows multiple clusters (appropriate isotopic pattern for an ion containing two Cl atoms) at m/e 431 (P − 15 (CH_3)) and a base peak at m/e 373 (P − 73 (O-*t*-Bu)). No parent ion was observed.

[Tetrakis(1-pyrazolyl)borato]dichloro-*tert*-butoxyzirconium(IV) {[B(pz)$_4$]Zr(O-*t*-Bu)Cl$_2$}. This compound was prepared by the same procedure as for {[HB(3,5-Me_2pz)$_3$]Zr(O-*t*-Bu)Cl_2}, yielding a white solid (27%, mp 187–190 °C). Anal. Calcd for $C_{16}H_{21}N_6BCl_2OZr$: C, 37.36; H, 4.12. Found: C, 37.60; H, 4.30. ^{1}H NMR spectrum (CD_2Cl_2): 8.10, 7.80 (3, 3; d, d; J = 1.9 Hz, J = 2.2 Hz; 3-H, 5-H (pz coord)); 8.03, 7.98 (1, 1; d, d; J = 2.4 Hz, J = 1.4 Hz; 3-H, 5-H (pz uncoord)); 6.67 (1, t, J = 2.0 Hz, 4-H (pz uncoord)); 6.31 (3, t, J = 2.3 Hz, 4-H (pz coord)); 1.32 (9, s, $OC(CH_3)_3$). ^{13}C NMR spectrum ($CDCl_3$): 144.4, 135.7 (3-C, 5-C (pz coord)); 136.0, 135.8 (3-C, 5-C (pz uncoord)); 107.6 (4-C (pz uncoord)); 105.5 (4-C (pz coord)); 83.2 (O–C); 31.1 ($OC(CH_3)_3$). The mass spectrum shows multiple clusters (appropriate isotopic pattern for an ion containing two Cl atoms) at m/e 497 (P − 15 (CH_3)) and a base peak at m/e 439 (P − 73 (O-*t*-Bu)). No parent ion was observed.

Determination of the Barrier to Rotation for [*n*-BuB(pz)$_3$]Zr(O-*t*-Bu)Cl$_2$. ^{13}C Spectra. The ^{13}C spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer equipped with a variable-temperature controller. The sample was prepared in a drybox with CD_2Cl_2 as the solvent and internal standard. The temperature was determined with a thermocouple before and after each run and was constant to ±2 °C. Samples were allowed to equilibrate in the probe for at least 30 min before data acquisition was initiated. Spectra were collected over an 89-deg range from +35 to −54 °C.

Spectral Simulations. The simulated spectra were calculated with use of the DNMR-3 computer program, which had been converted to double precision. The upfield resonance of the pair for the 3-C, 5-C (pz) carbon atoms was used. The spectra were calculated with an A′AB ⇌ ABA′ ⇌ BA′A spin system with mutual exchange. The parameters that were read into the program were as follows: the chemical shifts in Hz relative to an arbitrary reference, the effective transverse relaxation time T_2 (in s), which is calculated from the line width at half-height $\Delta\nu_{1/2}$ (in Hz) by $T_2 = 1/(\pi\Delta\nu_{1/2})$, and rate constants in s^{-1}. The calculated spectra were plotted on a Calcomp plotter. The experimental and simulated spectra were matched by visual comparison of the spectra. The Eyring plot of ln (k/T) vs. $1/T$ was made on a Hewlett-Packard 9810A calculator using a standard least-squares analysis. The slope and y intercept of the line were obtained directly from the calculator.

Results

Synthesis of Compounds. The mono-*tert*-butoxide derivatives of the three [RB(pz)$_3$]$ZrCl_3$ starting materials described earlier[1] form readily as shown in reaction 1. Addition of the

$$[RB(pz)_3]ZrCl_3 + KO\text{-}t\text{-}Bu \xrightarrow{\text{toluene}} [RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2 + KCl \quad (1)$$

butoxide ligand increases the solubility of the products such that simple filtration of the reaction mixture followed by evaporation of the toluene yields spectroscopically pure material. The products can be crystallized from hot–cold hexane. Two complexes in which all three chloride ligands are replaced with *tert*-butoxide groups have been prepared as shown in eq 2. For the [HB(3,5-Me_2pz)$_3$]-ligand case, refluxing benzene

$$[RB(pz)_3]ZrCl_3 + 3KO\text{-}t\text{-}Bu \rightarrow [RB(pz)_3]Zr(O\text{-}t\text{-}Bu)_3 + 3KCl \quad (2)$$

with an excess of KO-*t*-Bu is necessary for this reaction to go to completion. If less forcing conditions or a stoichiometeric amount of KO-*t*-Bu is used, NMR analysis indicates the formation of [HB(3,5-Me_2pz)$_3$]Zr(O-*t*-Bu)$_2$Cl in addition to the tributoxide complex. Attempts to prepare the dibutoxide complex free of mono- or trisubstituted complexes have not yet succeeded. The [*i*-PrB(pz)$_3$]Zr(O-*t*-Bu)$_3$ complex forms at room temperature, but again some of the dibutoxide complex forms unless an excess of butoxide is used. This bis complex could not be isolated in pure form.

Monobutoxide complexes of the two ligands containing unsubstituted pz rings display fluxional NMR behavior at room temperature, but static spectra can be obtained at low temperature. As part of our investigation of this fluxional process (vide infra), synthesis of the complex [B(pz)$_4$]Zr(O-*t*-Bu)Cl_2 became important. In our earlier work, we had attempted the preparation of [HB(pz)$_3$]$ZrCl_3$ and [B(pz)$_4$]-$ZrCl_3$ but had been unsuccessful, due (we felt) to the insolubility of these complexes. This insolubility is a major problem because 2 equiv of $ZrCl_4$/equiv of ligand are needed for the exclusive preparation of [RB(pz)$_3$]$ZrCl_3$ complexes.[1] Thus one faces the problem of trying to separate the desired product from the excess $ZrCl_4$, both of which are insoluble in common organic solvents. The solution to this problem is to add Et_2O to the CH_2Cl_2 solution of $ZrCl_4$ at the start of the reaction. This solubilizes the $ZrCl_4$ as an Et_2O adduct. At the end of the reaction, the crude solid obtained by evaporation of the solvent is stirred with a 1:1 solution of CH_2Cl_2–Et_2O. This dissolves the Et_2O adduct of $ZrCl_4$, which is soluble in this solution, but the desired zirconium complexes are insoluble and can be collected, contaminated with KCl or NaCl. Although the [HB(pz)$_3$]$ZrCl_3$ and [B(pz)$_4$]$ZrCl_3$ complexes thus isolated could not be characterized spectroscopically, mass spectrometry clearly indicates that they have formed. More importantly, these complexes will react with KO-*t*-Bu as in eq 1 to yield [HB(pz)$_3$]Zr(O-*t*-Bu)Cl_2 and [B(pz)$_4$]Zr(O-*t*-Bu)Cl_2, respectively. These more soluble complexes were fully characterized, thus indirectly characterizing the parent trichloride complexes.

The alkoxide ligands in these molecules can be exchanged with free alcohols in certain cases as shown in eq 3. This

$$[HB(3,5\text{-}Me_2pz)_3]Zr(OMe)Cl_2 + t\text{-}BuOH \rightarrow [HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2 + MeOH \quad (3)$$

reaction cannot be reversed although EtOH will exchange with the butoxide complex.

One butoxide ligand increases the stability of these complexes to hydrolysis in air. Thus [*i*-PrB(pz)$_3$]$ZrCl_3$ decomposes as a solid in air in a couple of hours whereas [*i*-PrB(pz)$_3$]-Zr(O-*t*-Bu)Cl_2 is only 50% decomposed after 15 h. The [*i*-PrB(pz)$_3$]Zr(O-*t*-Bu)$_3$ complex shows intermediate stability. [HB(pz)$_3$]Zr(O-*t*-Bu)Cl_2 is considerably more stable than all three of these complexes, showing only slight decomposition after 15 h as a solid. The thermal stability of [*i*-PrB(pz)$_3$]-$ZrCl_3$ (evaluated by running periodic ^{1}H NMR spectra of samples heated to 60 °C) is actually a little greater than that of [*i*-PrB(pz)$_3$]Zr(O-*t*-Bu)Cl_2.

Investigation of Fluxional Behavior. As can be readily seen in the drawings in Figures 1 and 2, for the five complexes of formula [RB(pz)$_3$]Zr(O-*t*-Bu)Cl_2 two of the pz rings are equivalent and one is distinct. With the bulky [HB(3,5-Me_2pz)$_3$] ligand, this nonequivalence is observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra at temperatures up to 140 °C. For example, as shown in Figure 1, each pz-ring resonance in the ^{13}C{^{1}H} spectrum is doubled in a ratio of 2:1. For all four of the ligands containing unsubstituted pz rings, the three coordinated rings show as equivalent in the room-temperature ^{1}H and ^{13}C{^{1}H} spectra, but at lower temperature each type of pz resonance collapses and sharpens into two peaks in a ratio of 2:1 as expected for a static spectrum.

Two molecules were studied in detail. The first, [*n*-BuB-(pz)$_3$]Zr(O-*t*-Bu)Cl_2, was studied by ^{13}C{^{1}H} NMR spectroscopy. Figure 2 shows the room-temperature spectrum, and the insert shows the limiting low-temperature spectrum for the 3-C, 5-C (pz) carbon atoms. With use of the upfield resonance of this pair for spectral simulation, the following activation parameters were calculated: $\Delta G^\ddagger$ = 13.4 kcal mol^{-1}, $\Delta H^\ddagger$ = 11.5 kcal mol^{-1}, and $\Delta S^\ddagger$ = −6.5 eu. Taking into account errors inherent in this determination, we believe the

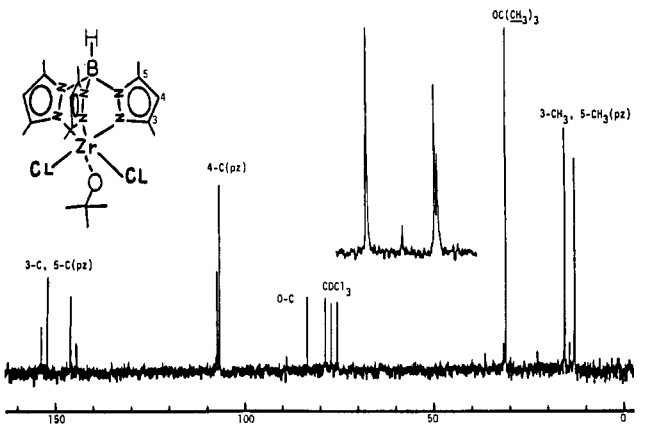

Figure 1. $^{13}C\{^1H\}$ spectrum of $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ in $CDCl_3$. The insert is an expansion of the 12–17-ppm region showing each line is split into two resonances.

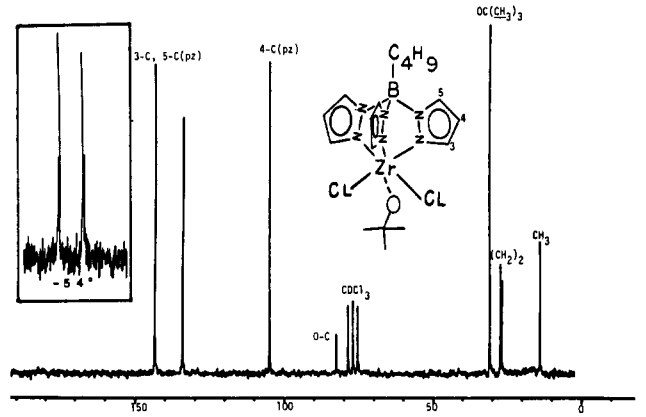

Figure 2. $^{13}C\{^1H\}$ spectrum of $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ in $CDCl_3$ at 35 °C. The insert shows the 134–144-ppm region at the same expansion but at −54 °C.

$\Delta G^{\ddagger}$ value is accurate within ±0.5 kcal/mol.

More mechanistic information can be obtained from the complex $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$. Figure 3A shows the room-temperature ^1H NMR spectrum in the pz region for this molecule. The two upfield triplet resonances are assigned as the 4-H (pz) and integrate in a 1:3 ratio. Thus three pz rings are equivalent and one is distinct at this temperature. The resonance that appears as a triplet at about 8.0 ppm is assigned as two overlapping doublets of the 3-H, 5-H (pz) type associated with the unique pz ring and the two doublets as these same hydrogen atoms on the three equivalent pz rings. As shown in Figure 3B, this assignment was verified by a decoupling experiment where irradiation of the unique 4-H (pz) triplet causes the triplet at 8.0 ppm to collapse to a pair of singlets, leaving the other resonances unchanged.

Figure 4 shows the effect on the two 4-H (pz) resonances of lowering the temperature of the sample. The larger resonance broadens and splits into two triplets of area 1:2 while the other resonance remains unchanged. Clearly, the resonance that remains unchanged can be assigned to a pz ring that is not coordinated to the zirconium (there must be at least one). The other three pz rings are coordinated to the zirconium atom and display fluxional behavior at room temperature analogous to that observed above for $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$. At low temperature, the expected quenched spectrum is observed.

Discussion

The complexes $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ readily form from reaction of the 12-electron species $[RB(pz)_3]ZrCl_3$ and KO-*t*-Bu. Although forcing reaction conditions are necessary, a surprising result is the formation of $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_3$. The dimethyl-substituted pyrazolyl ligand is sterically quite large,[7] and the introduction of the three large *tert*-butoxide ligands must lead to a congested molecule.

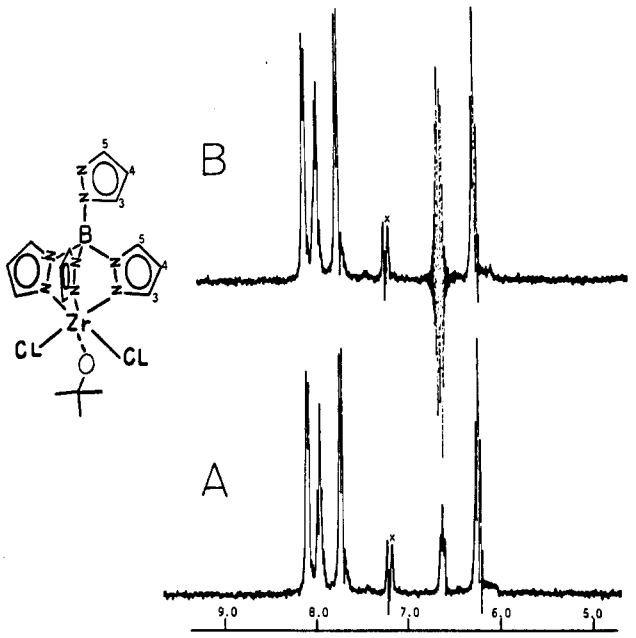

Figure 3. ^1H NMR spectra (90 MHz) of $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ at ambient temperature in $CDCl_3$: (A) normal spectrum; (B) spectrum with decoupling of the 6.7-ppm resonance. The peaks marked with × are $CHCl_3$ and residual toluene. For assignments see the Results section.

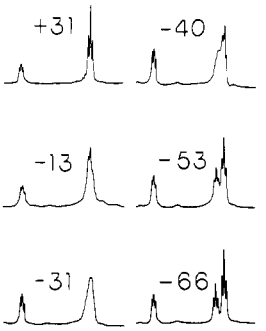

Figure 4. ^1H NMR spectra of the 4-H (pz) resonances of $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ at various temperatures (°C). The spectra were run at 200 MHz in CD_2Cl_2.

There has recently been considerable discussion on the ability of alkoxide ligands to form multiple M–O bonds with electron-deficient transition-metal complexes through $p\pi$–$d\pi$ donation from oxygen to the metal.[8] McCleverty et al.[4] have suggested that the deshielding of the O–C carbon resonance vs. the resonance of the free alcohol in the ^{13}C NMR spectra is reflective of M–O multiple bonding. For $[HB(3,5\text{-}Me_2pz)_3]Mo(NO)Br(O\text{-}i\text{-}Pr)$, a shift of nearly 25 ppm was observed and an X-ray structural analysis of the chloride analogue of this molecule clearly indicated multiple Mo–O bonding. For our monobutoxide complexes a shift of 15 ppm

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is observed, which drops to 7 ppm for the tributoxide derivatives. The strong back-bonding ability of the NO ligand in the molybdenum complex may account for the larger shift with that molecule. The usefulness of this parameter to measure the degree of M-O multiple bonding needs further investigation.

The fluxional behavior of the three $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ (R = H, *i*-Pr, *n*-Bu) complexes can reasonably be explained by a number of possible mechanisms. The first is dissociation of one of the pz rings from coordination to the metal and rapid rearrangement of the five-coordinate intermediate thus produced, followed by reassociation of the free pz ring. Although no direct demonstration of this sequence has been observed, the equilibration of the fourth pz ring in complexes such as $[B(pz)_4]Pd(\eta^3\text{-}C_3H_5)$[9] or $[B(pz)_4]Cu(CO)$[10] must require the dissociation step and five-coordinate molecules are well-known to have a low barrier to rearrangement.[11]

The second mechanism is a simple rotation of the pyrazolylborate ligand about the Zr-B axis, a trigonal-twist mechanism. That this mechanism is most likely to be correct was demonstrated by the study, shown in Figures 3 and 4, on $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$. In this case, if the dissociative mechanism was correct, the fluxional process would equilibrate all four pz rings. This is not the case. A similar trigonal-twist mechanism was shown earlier for $[B(pz)_4]Mo(CO)_2(\eta^3\text{-allyl})$ complexes,[6a] where the barrier was calculated for a number of complexes to be ca. 14 kcal mol^{-1}. A similar process was also proposed for $[B(pz)_4]Pt(CO)CH_3$,[6b] where the barrier was measured to be 10.5 kcal mol^{-1}. Our measured barrier of 13.4 kcal mol^{-1} for $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ is in this same range. These studies represent the first investigation of this type of fluxional behavior for discrete six-coordinate complexes. On the basis of 60-MHz ^1H NMR data, the molecules $[B(pz)_4]Mn(CO)_2PR_3$ (R = OMe, Me) were reported to be fluxional at 5 °C but solubility problems prevented a low-temperature study.[12] From the spectrum of $[B(pz)_4]Mn(CO)_2P(OMe)_3$ pictured in this paper, the interpretation of fluxional behavior at 5 °C is questionable. In fact, this spectrum more closely matches our low-temperature spectrum for $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ than the high-temperature spectrum. Higher field ^1H or ^{13}C NMR data are needed to conclusively prove this point. Numerous other six-coordinate complexes, mainly of molybdenum (e.g., $[RB(pz)_3]Mo(CO)_2(N_2Ph)$[13a]), show static NMR spectra at room temperature.[4,13]

A final reasonable mechanism would be dissociation of either a Cl or an O-*t*-Bu ligand and rapid rearrangement of the five-coordinate species thus produced, followed by reassociation of the ligand. Two points argue against this type of mechanism. First, these molecules are 12-electron species and should be reluctant to dissociate a ligand, particularly the O-*t*-Bu ligand in which multiple M-O bonding is likely. Second, and more important, is the fact that the complex $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ is not fluxional up to 140 °C. Dissociation of a ligand from this more sterically hindered molecule (this ligand should also be a better electron donor) would be expected to be a lower energy process, not higher as observed. One can easily explain the higher barrier for this molecule if the trigonal-twist mechanism is correct in that the 3-Me (pz) groups would seemingly lock like gears with the O-*t*-Bu and Cl ligands, hindering the rotation.

Acknowledgment. We wish to thank Dr. Ron Garber and Mr. Neil Swift for assistance in obtaining the computer-simulated NMR spectra and Mr. Michael Walla for the computer-simulated mass spectral data.

Registry No. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-13-6; $[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-14-7; $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-15-8; $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_3$, 84695-16-9; $[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)_3$, 84695-17-0; $[B(pz)_4]ZrCl_3$, 84695-18-1; $[HB(pz)_3]ZrCl_3$, 84695-19-2; $[HB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-20-5; $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-21-6; $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$, 80041-67-4; $[i\text{-}PrB(pz)_3]ZrCl_3$, 80041-70-9; $[n\text{-}BuB(pz)_3]ZrCl_3$, 80041-69-6; $K[B(pz)_4]$, 14782-58-2; $Na[HB(pz)_3]$, 18583-62-5.

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Isotopic ^{18}O Exchange between $VO^{2+}(aq)$ and Water

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The intrinsic rate of yl-oxygen exchange ($t_{1/2}$ = 400 min at 0 °C) of $VO^{2+}(aq)$ with solvent water follows the rate law rate = $k_0[VO^{2+}(aq)] + k_{OH}K_{eq}[VO^{2+}(aq)]/[H^+]$ with $k_0 = (2.4 \pm 0.8) \times 10^{-5}$ s^{-1}, $k_{OH} = 1.32 \pm 0.11$ s^{-1}, and $K_{eq} = 3.98 \times 10^{-7}$ M at 0.0 °C and $I = 2.54$. At $[VO^{2+}] = 0.18$ M, $I = 0.64$, and $[H^+] = 0.10$ M as chloride salts, $\Delta H^* = 20.5 \pm 1.1$ kcal/mol and $\Delta S^* = -4.4 \pm 0.2$ cal/(mol deg). The exchange is catalyzed by VO_2^+, giving a $k_{VO_2^+}$ of 3.91 ± 0.09 M^{-1} s^{-1} at 0.0 °C, $[H^+] = 0.1$ M, and $I = 0.37$. $[VO(NCS)(OH_2)_4]^+$ exchanges with $k_{NCS} = (5.56 \pm 0.14) \times 10^{-7}$ M^{-1} s^{-1} at 0.0 °C and $I = 0.7$, considerably lower than the parent aquo ion. When complexation was by oxalate or $EDTA^{4-}$, the exchange rate increased with acidity and had a very small k_0 term while with NTA^{3-}, where an equatorial water was probably present, the faster rate was inversely related to the acidity.

Introduction

In recent years a knowledge of the aqueous structure and rates of solvent exchange with oxyions has become essential to an understanding of a host of other experimental studies including oxidation-reduction mechanisms, atom-transfer reactions, and ligand substitution processes. For oxygen exchange, processes in water that are relatively slow, static methods employing ^{18}O have proven highly successful. These studies coupled with X-ray crystal studies have led to significant progress with species such as $V_{10}O_{28}^{6-}$,[1] $Mo_2O_4^{2+}$,[2] and

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