

suggests simple oxidative addition—1 equiv of Br₂ for each iridium. The presence of four carbonyl stretches in the IR spectra of samples suspended in Nujol or dissolved in methylene chloride implies either isomerization or several mechanisms for oxidative addition. A recent study of the oxidative addition of iodine to rhodium(I) complexes provides evidence for a two-step process in which cis addition of iodine is followed by cis-trans isomerization.²⁵

Conclusion

Two important observations stand out regarding this group of compounds. First, there is residual coordinating tendency in some of these monomeric complexes that can lead to penta-coordination, especially for iridium. Second, when penta-coordination does not occur, there is some tendency toward oligomerization of the monomers, especially in the solid state. These results suggest that these ions are good candidates for the preparation of solid materials with extended interactions,

including those of mixed valency and highly anisotropic conductivity. We are pursuing this possibility by studying the electrochemical oxidation of concentrated solutions.

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Registry No. NEt₄[Rh(COD)(Tcbiim)], 88179-81-1; NEt₄[Rh(CO)₂(Tcbiim)], 88179-82-2; NEt₄[Ir(COD)(Tcbiim)], 88179-83-3; C(NH₂)₃[Ir(COD)(Tcbiim)], 88179-85-5; NMe₄[Ir(COD)(Tcbiim)], 88179-86-6; Na[Ir(COD)(Tcbiim)], 88179-87-7; K[Ir(COD)(Tcbiim)], 88179-88-8; NEt₄[Ir(CO)₂(Tcbiim)], 83312-49-6; NMe₄[Ir(CO)₂(Tcbiim)], 88157-11-3; C(NH₂)₃[Ir(CO)₂(Tcbiim)], 88199-15-9; Na[Ir(CO)₂(Tcbiim)], 88157-12-4; K[Ir(CO)₂(Tcbiim)], 88157-13-5; NEt₄[Ir(CO)₂Br₂(Tcbiim)], 88199-17-1; NEt₄[Ir(COD)(PPh₃)(Tcbiim)]·CH₂Cl₂, 88179-91-3.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, atomic thermal parameters, calculated hydrogen positions, and least-squares planes (27 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Derivatives of Chlorotrimethyltantalum(V). Synthesis, Crystal Structure, and Stereochemically Nonrigid Behavior of Seven-Coordinate Molecules

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The reaction of TaMe₃Cl₂ with the poly(pyrazolyl)borate ligands [RB(pz)₃]⁻ (R = H, pz; pz = pyrazolyl ring) and [HB(3,5-Me₂pz)₃]⁻ yields [RB(pz)₃]TaMe₃Cl and [HB(3,5-Me₂pz)₃]TaMe₃Cl, respectively. These new complexes show remarkable stability for alkyltantalum derivatives. An X-ray crystallographic study of [HB(pz)₃]TaMe₃Cl has shown that the solid-state structure of these molecules is a nearly regular capped octahedron with, in this case, a methyl group capping the face formed by the other two methyl groups and the Cl ligand. The monoclinic crystals are in the space group *P*₂₁/*n* with *a* = 9.425 (6) Å, *b* = 12.567 (5) Å, *c* = 14.315 (5) Å, β = 106.00 (4)°, *V* = 1630 Å³, and *Z* = 4. For [HB(3,5-Me₂pz)₃]TaMe₃Cl, this is also the only isomer observed in solution. For the two [RB(pz)₃]TaMe₃Cl complexes, two isomers are observed in solution, one with a Me ligand in the capping position and the other with the Cl ligand in the capping position. These two molecules show stereochemically nonrigid behavior in solution by NMR. The nonequivalent Me ligands for the Me-capped isomer equilibrate above room temperature. Above 86 °C, the two isomers start to interconvert.

Introduction

We have begun a general investigation into the synthesis and characterization of poly(pyrazolyl)borate complexes of Zr, Nb, and Ta. Although this flexible ligand system has been used extensively with other transition metals,¹ only one well-characterized complex of this type has been reported prior to our work. As part of a general investigation into the synthesis of TaMe₃L₂ (L = bis chelate, monoanionic ligand) compounds, Wilkinson has reported² the synthesis of [H₂B(pz)₂]₂TaMe₃ (pz = pyrazolyl ring).

We have previously reported^{3,4} the synthesis of [RB(pz)₃]ZrCl₃ (R = *i*-Pr, *n*-Bu, H, pz) and [HB(3,5-Me₂pz)₃]ZrCl₃. These complexes react with 1 equiv of KO-*t*-Bu to form [RB(pz)₃]Zr(O-*t*-Bu)Cl₂ complexes. In the octahedral structures expected for these butoxide-substituted compounds, two pz rings remain equivalent and one is distinct. This is observed in the ¹H and ¹³C NMR spectra of [HB(3,5-Me₂pz)₃]Zr(O-*t*-Bu)Cl₂. The [RB(pz)₃]Zr(O-*t*-Bu)Cl₂ complexes are fluxional, showing only one type of pz ring at room

temperature but quenching to the expected 2:1 pattern at low temperature. Careful study of the [B(pz)₄]Zr(O-*t*-Bu)Cl₂ complex allowed us to propose that the mechanism that best explains this dynamic process is a trigonal twist of the [RB(pz)₃] ligand about the Zr-B axis.

We have attempted to extend this chemistry to Ta. The reactions of these ligands with TaCl₅ yield complex mixtures that have failed to yield pure [RB(pz)₃]TaCl₄ complexes (although mass spectroscopy shows appropriate molecular ion peaks). In contrast, we report here that [RB(pz)₃]TaMe₃Cl complexes readily form, starting with TaMe₃Cl₂. These complexes are stable and exhibit, in certain cases, stereochemically nonrigid behavior that is amenable to study by NMR. Although low-valent seven-coordinate complexes are common, few exhibit dynamic behavior that can readily be studied.⁵ For the [RB(pz)₃]TaMe₃Cl (R = H, pz) molecules reported here, two isomers are observed in solution at room temperature. Both isomers exhibit dynamic behavior, which is shown to be a different type than the behavior we observed earlier for the six-coordinate [RB(pz)₃]Zr(O-*t*-Bu)Cl₂ complexes. We have also carried out a single-crystal X-ray structural analysis of [HB(pz)₃]TaMe₃Cl to verify that the basic structure of these molecules is a capped octahedron.

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Experimental Section

General Procedure. All manipulations were carried out under a nitrogen atmosphere, either in a Vacuum Atmospheres HE-493 drybox or by use of standard Schlenk techniques. All solvents were dried, degassed, and distilled prior to use. $K[HB(3,5-Me_2pz)_3]$, $Na[HB(pz)_3]$, $K[HB(pz)_4]$,⁶ and $TaMe_3Cl_2$ ⁷ were prepared by published methods. Elemental analyses were performed by Robertson Laboratory. We, and others,³ have found that it is difficult to obtain high-quality analytical figures on poly(pyrazolyl)borate complexes that are spectroscopically pure. ¹H NMR spectra were recorded on Varian Model EM 390 and IBM Model NR-80 spectrometers, and chemical shifts are reported in δ vs. Me_4Si . Carbon-13 spectra were recorded on Varian Model CFT-20 and IBM Model NR-80 spectrometers using CH_2Cl_2 and CD_2Cl_2 . Chemical shifts are reported in ppm vs. Me_4Si with $\delta(CD_2Cl_2) = 53.8$ and $\delta(CH_2Cl_2) = 54.0$ as solvent and internal standard. ¹¹B NMR spectra were recorded on a Bruker WP200 spectrometer. Chemical shifts are reported in ppm vs. $B(OMe)_3$. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

[Hydrotris(3,5-dimethylpyrazolyl)borato]chlorotrimethyltantalum(V) ([HB(3,5-Me₂pz)₃]Ta(CH₃)₃Cl). Freshly prepared dichlorotrimethyltantalum (2.18 g, 7.34 mmol) and potassium hydrotris(3,5-dimethylpyrazolyl)borate (2.46 g, 7.34 mmol) were combined in a 250-mL round-bottomed flask containing a Teflon-coated stirring bar. After the flask was cooled to $-78^\circ C$, methylene chloride (40 mL), previously cooled to $-78^\circ C$, was added to the solids by cannula. The reaction mixture was stirred and allowed to warm to ambient temperature. After 18 h, the yellow, milky solution was filtered with a medium-fritted disk. The precipitate was washed with two 5-mL portions of methylene chloride and then discarded. The remaining deep yellow filtrate was evaporated to dryness at ambient temperature under reduced pressure (2.70 g, 4.83 mmol, 66%). This material is spectroscopically pure. The analytical sample was prepared by dissolving this solid in 10 mL of toluene at $50^\circ C$. The solution was filtered at $50^\circ C$ and allowed to slowly cool to $-30^\circ C$. After 24 h the precipitate was collected (0.33 g) and the remaining liquid was reduced to half its volume and recooled to $-30^\circ C$. A second crop was then collected (0.58 g). Anal. Calcd for $C_{18}H_{31}N_6BClTa$: C, 38.70; H, 5.61; N, 15.04; Cl, 6.35. Found: C, 37.45; H, 5.51; N, 14.34; Cl, 6.43. ¹H NMR spectrum ($CDCl_3$): 5.91, 5.80 (1, 2; singlets; 4-H (pz)); 2.50, 1.31 (3, 6; singlets; Ta-Me); 2.43, 2.42, 2.41, 2.34 (3, 6, 3, 6; all singlets; 3-CH₃, 5-CH₃ (pz)). ¹³C NMR spectrum (coupled spectrum in CH_2Cl_2): 151.4, 149.5, 143.9, 143.8 (all multiplets; 3-C, 5-C (pz)); 108.8, 108.5 (doublets, $J = 175$ Hz; 4-C (pz)); 101.2, 87.9 (quartets, $J = 121$ Hz; Ta-Me); 16.5, 16.3, 13.0, 12.7 (quartets, $J = 128$ Hz; 3-CH₃, 5-CH₃ (pz)). ¹¹B NMR spectrum (coupled spectrum in $CDCl_3$): -27.8 (doublet; $J = 107.4$ Hz). Mass spectrum: parent ion (P) was not observed ($P = 558$), 543 ($P - 15$ (CH_3)), 527 ($P - 31$ (C_2H_7)), 513 ($P - 45$ (C_3H_9)). Melting point: 227–233 $^\circ C$ dec.

[Hydrotris(1-pyrazolyl)borato]chlorotrimethyltantalum(V) ([HB(pz)₃]Ta(CH₃)₃Cl). Freshly prepared $TaMe_3Cl_2$ (1.15 g, 3.87 mmol) was placed in a 250-mL round-bottomed flask with a Teflon-coated stirring bar. The flask was then cooled to $-78^\circ C$, and precooled diethyl ether (25 mL) was added. Potassium hydrotris(1-pyrazolyl)borate (0.913 g, 3.87 mmol) was slowly added with rapid stirring (1 h), and the yellow mixture was allowed to warm to ambient temperature. After 18 h of stirring, the yellow mixture was filtered on a medium-fritted disk and the precipitate washed with two 5-mL portions of diethyl ether and discarded. The solution was reduced to dryness, yielding a spectroscopically pure sample (0.95 g, 2.00 mmol, 52%). The analytical sample was prepared by dissolving the solid in 5 mL of warm toluene ($50^\circ C$) and filtering. After the solution was cooled to $-30^\circ C$ for 24 h, the yellow precipitate was collected (0.25 g). Anal. Calcd for $C_{12}H_{19}N_6BClTa$: C, 30.37; H, 4.04; N, 17.71. Found: C, 30.69; H, 4.30; N, 17.51. ¹H NMR spectrum ($CDCl_3$): 7.75, 7.67 (3, 3; multiplets, 3-H, 5-H (pz)); 6.25 (3, multiplets, 4-H (pz)); 2.34, 1.16 (1:2 ratio, total of 6.7 integrated intensity; broad singlets; Ta-Me); 0.94 (2.3; singlet; Ta-Me). ¹³C NMR spectrum (CH_2Cl_2): multiple resonances centered at ca. 142 and 134 (3-C, 5-C (pz)); 106.4, 106.1 (4-C (pz)); 98.0, 88.9, 83.4 (Ta-Me). ¹¹B NMR spectrum (coupled in $CDCl_3$): -22.2 (doublet;

$J = 112.3$ Hz). Mass spectrum: parent ion not observed ($P = 474$), 459 ($P - 15$ (CH_3)), 443 ($P - 31$ (C_2H_7)), 429 ($P - 45$ (C_3H_9)). Melting point: 180–185 $^\circ C$ dec.

[Tetrakis(1-pyrazolyl)borato]chlorotrimethyltantalum(V) ([B(pz)₄]Ta(CH₃)₃Cl). The compound was prepared with use of freshly prepared $TaMe_3Cl_2$ (2.17 g, 7.30 mmol) in a procedure similar to that for $[HB(pz)_3]TaMe_3Cl$ except potassium tetrakis(1-pyrazolyl)borate (2.32 g, 7.30 mmol) was used. The spectroscopically pure product (2.56 g, 4.75 mmol, 65%) was dissolved in 8 mL of toluene at $50^\circ C$ and the solution was filtered and allowed to cool at $-30^\circ C$ for 24 h. The precipitate was collected and dried (1.09 g). Anal. Calcd for $C_{15}H_{21}N_8BClTa$: C, 33.33; H, 3.92; N, 20.73; Cl, 6.56. Found: C, 32.82; H, 3.89; N, 20.14; Cl, 7.13. ¹H NMR spectrum ($CDCl_3$): 7.63–8.11 (8; multiplet; 3-H, 5-H (pz)); 6.64 (1; multiplet; 4-H (pz) uncoordinated); 6.27 (3; multiplet; 4-H (pz) coordinated); 2.42, 1.28 (1:2 ratio total of 5.4; broad singlets; Ta-Me); 1.09 (3.6; singlet; Ta-Me). ¹³C spectrum (CH_2Cl_2): multiple resonances centered at 143 and 135 (3-C, 5-C (pz)); five resonances centered at 107 (4-C (pz)); 98.1, 89.3, 83.2 (Ta-Me). Mass spectrum: parent ion not observed ($P = 540$), 525 ($P - 15$ (CH_3)), 509 ($P - 31$ (C_2H_7)), 495 ($P - 45$ (C_3H_9)). Melting point: 189–194 $^\circ C$ dec.

X-ray Structure Determination. The crystals were grown from a dilute toluene solution over 2 weeks at $-30^\circ C$. A fragment of a bigger crystal was carved to the shape of an ellipsoid of approximate dimensions $0.30 \times 0.25 \times 0.25$ mm, mounted in a capillary and used for data collection. Since at room temperature the crystals decomposed rapidly in the X-ray beam, the measurements were carried out at 123 K. The unit cell dimensions obtained from 25 reflections with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) were as follows: $a = 9.425$ (6) Å, $b = 12.567$ (5) Å, $c = 14.315$ (5) Å, $\beta = 106.00$ (4)°, $V = 1630$ Å³, space group $P2_1/n$, $Z = 4$.

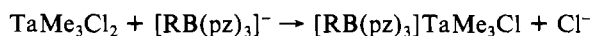
A total of 2254 reflections were measured within the range $2^\circ < \theta < 22^\circ$ with a CAD-4 diffractometer, and 1786 with $F > 6\sigma(F)$ were considered observed. They gave 1578 symmetry-independent reflections with $R_{merge} = 0.076$. The following parameters were used: scan type $\omega/2\theta$, scan width $0.9^\circ + 0.35^\circ \tan \theta$, aperture size $4 \times (2.8 + 1.0 \tan \theta)$ mm, background was measured at the extremes of the scan on a quarter of the scan range. Three standard reflections monitored every 6000 s of exposure time showed only very slow decay (maximum 6%), for which corrections were applied. Absorption corrections were applied with an approximation of the crystal shape by a sphere of radius 0.13 mm and with a linear absorption coefficient of 66.0 cm⁻¹.

The structure was solved by Patterson techniques and Fourier synthesis. On the difference maps approximately half of the hydrogen atoms were located, but except for those on the methyl groups, calculated positions were used in the refinement and kept constant. The function minimized was $\sum w|F_o - F_c|^2$; the weights used were $w = (\sigma^2(F) + 0.0007F^2)^{-1}$. Since the approximations used in the absorption treatment limited the accuracy of the data, refinement was carried out with only heavy atoms (Ta, Cl) anisotropic and others isotropic. It converged at $R = 0.045$, $R_w = 0.056$. The highest peaks on the final Fourier maps were 2.9 e/Å³ in the vicinity of Ta and 0.6 e/Å³ elsewhere.

The atomic parameters are presented in Table I, bond lengths in Table II, and selected bond angles in Table III. Most calculations were carried out with the SHELX system of programs.⁸ An ORTEP drawing⁹ of an individual molecule is shown in Figure 1.

Results and Discussion

The new $[RB(pz)_3]TaMe_3Cl$ ($R = H, pz$; $pz =$ pyrazolyl ring) and $[HB(3,5-Me_2pz)_3]TaMe_3Cl$ complexes form readily as shown:



Introduction of the poly(pyrazolyl)borate ligand substantially increases the stability of the Ta complexes. $TaMe_3Cl_2$ is a thermally unstable compound that burns spontaneously in air. The new poly(pyrazolyl)borate complexes can be handled briefly in air and are stable for several months at $25^\circ C$ under nitrogen. These complexes are even more stable than

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Table I. Atomic Fractional Coordinates with Esd's in Parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eqv} , Å ²
Ta(1)	0.0840 (1)	0.1767 (2)	0.2518 (0)	1.78
Cl(4)	0.1198 (3)	0.0055 (2)	0.3257 (2)	2.68
C(6)	0.0959 (12)	0.1709 (8)	0.0978 (8)	1.40
C(5)	0.1927 (15)	0.3106 (10)	0.3430 (10)	2.72
C(7)	0.3221 (14)	0.1490 (10)	0.2585 (9)	2.38
N(11)	-0.0518 (10)	0.3176 (7)	0.1881 (7)	1.66
N(12)	-0.1950 (10)	0.3357 (7)	0.1916 (6)	1.41
C(13)	-0.2417 (12)	0.4286 (9)	0.1503 (8)	1.94
C(14)	-0.1309 (13)	0.4732 (9)	0.1193 (8)	2.10
C(15)	-0.0154 (13)	0.4023 (9)	0.1446 (8)	2.10
N(21)	-0.0485 (10)	0.1984 (7)	0.3612 (6)	1.37
N(22)	-0.1914 (10)	0.2277 (7)	0.3392 (6)	1.45
C(23)	-0.2344 (13)	0.2348 (9)	0.4209 (8)	1.77
C(24)	-0.1165 (13)	0.2052 (9)	0.4981 (9)	2.21
C(25)	-0.0058 (13)	0.1832 (9)	0.4577 (9)	2.27
N(31)	-0.1411 (10)	0.1023 (7)	0.1774 (7)	1.83
N(32)	-0.2748 (9)	0.1474 (7)	0.1779 (6)	1.13
C(33)	-0.3818 (13)	0.0837 (9)	0.1279 (8)	1.98
C(34)	-0.3240 (13)	-0.0012 (9)	0.0929 (9)	2.43
C(35)	-0.1730 (13)	0.0135 (9)	0.1260 (8)	2.22
B(1)	-0.2779 (14)	0.2508 (10)	0.2339 (9)	1.75

Table II. Bond Lengths (Å) with Esd's in Parentheses

Ta(1)-Cl(4)	2.380 (3)	Ta(1)-C(6)	2.24 (1)
Ta(1)-C(5)	2.20 (1)	Ta(1)-C(7)	2.25 (1)
Ta(1)-N(11)	2.228 (9)	Ta(1)-N(21)	2.273 (8)
Ta(1)-N(31)	2.294 (8)	N(11)-N(12)	1.38 (1)
N(11)-C(15)	1.33 (1)	N(12)-C(13)	1.33 (1)
N(12)-B(1)	1.54 (1)	C(13)-C(14)	1.36 (1)
C(14)-C(15)	1.38 (1)	N(21)-N(22)	1.35 (1)
N(21)-C(25)	1.34 (2)	N(22)-C(23)	1.34 (1)
N(22)-B(1)	1.53 (2)	C(23)-C(24)	1.38 (2)
C(24)-C(25)	1.35 (1)	N(31)-N(32)	1.38 (1)
N(31)-C(35)	1.32 (1)	N(32)-C(33)	1.33 (1)
N(32)-B(1)	1.53 (2)	C(33)-C(34)	1.36 (2)
C(34)-C(35)	1.38 (1)		

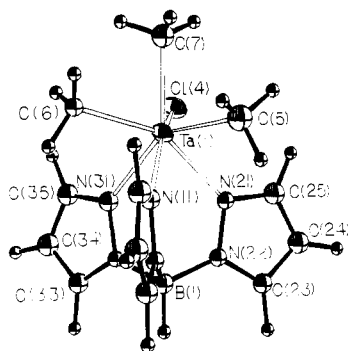


Figure 1. ORTEP⁹ drawing of [HB(pz)₃]TaMe₃Cl. The thermal motion ellipsoids are drawn at 50% probability except for H atoms, which are at an arbitrary level. The unlabeled atom in the pyrazole ring on the left side of the drawing is N(32). The four unlabeled atoms in the pyrazole ring, approximately perpendicular to the plane of the drawing, are C(13), C(14), and C(15) as one goes clockwise around the ring from N(11).

CpTaMe₃Cl, which slowly decomposes over a period of days under nitrogen at 25 °C.⁷ The new complexes are soluble in ethers, CH₂Cl₂, and toluene and slightly soluble in pentane.

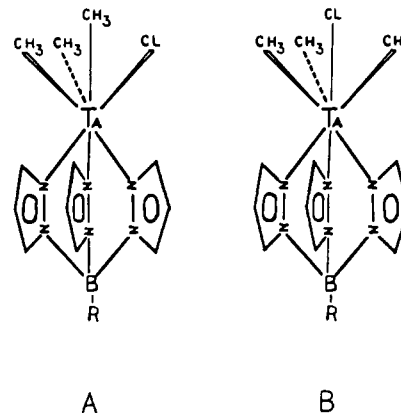
These molecules are not very reactive. For [HB(3,5-Me₂pz)₃]TaMe₃Cl, attempts to replace the Cl ligand with either an alkyl or alkoxide group by stirring the compound in toluene with reagents such as MeLi, MeMgCl, PhCH₂MgCl, KO-*t*-Bu, and NaOMe have failed and only starting material has been recovered. Stirring this complex in either methanol or *tert*-butyl alcohol or with *t*-BuNH₂ in benzene, in hopes of replacing the Me group, yields similar results. This complex is also unreactive toward CO or *t*-BuNC. [B(pz)₄]TaMe₃Cl is similarly unreactive toward replacement of the Cl ligand

Table III. Bond Angles (deg) with Esd's in Parentheses

Cl(4)-Ta(1)-C(6)	111.6 (3)	Cl(4)-Ta(1)-C(5)	116.2 (3)
Cl(4)-Ta(1)-C(7)	79.8 (3)	Cl(4)-Ta(1)-N(11)	153.6 (2)
Cl(4)-Ta(1)-N(21)	80.8 (2)	Cl(4)-Ta(1)-N(31)	80.7 (2)
C(6)-Ta(1)-C(5)	117.9 (4)	C(6)-Ta(1)-C(7)	73.5 (4)
C(6)-Ta(1)-N(11)	78.6 (3)	C(6)-Ta(1)-N(21)	150.3 (3)
C(6)-Ta(1)-N(31)	79.7 (3)	C(5)-Ta(1)-C(7)	78.3 (4)
C(5)-Ta(1)-N(11)	75.9 (3)	C(5)-Ta(1)-N(21)	75.8 (3)
C(5)-Ta(1)-N(31)	143.7 (3)	C(7)-Ta(1)-N(11)	126.5 (3)
C(7)-Ta(1)-N(21)	136.2 (3)	C(7)-Ta(1)-N(31)	137.9 (3)
N(11)-Ta(1)-N(21)	79.9 (3)	N(11)-Ta(1)-N(31)	77.3 (3)
N(21)-Ta(1)-N(31)	75.8 (3)	Ta(1)-N(11)-N(12)	124.9 (6)
Ta(1)-N(11)-C(15)	129.6 (7)	N(12)-N(11)-C(15)	105.5 (8)
N(11)-N(12)-C(13)	109.6 (8)	N(11)-N(12)-B(1)	120.4 (8)
C(13)-N(12)-B(1)	129.9 (8)	N(12)-C(13)-C(14)	108.5 (9)
C(13)-C(14)-C(15)	105.6 (9)	N(11)-C(15)-C(14)	110.8 (9)
Ta(1)-N(21)-N(22)	125.1 (6)	Ta(1)-N(21)-C(25)	128.8 (7)
N(22)-N(21)-C(25)	106.0 (8)	N(21)-N(22)-C(23)	109.7 (8)
N(21)-N(22)-B(1)	120.6 (8)	C(23)-N(22)-B(1)	129.7 (8)
N(22)-C(23)-C(24)	108.0 (9)	C(23)-C(24)-C(25)	104.9 (9)
N(21)-C(25)-C(24)	111.3 (9)	Ta(1)-N(31)-N(32)	123.9 (6)
Ta(1)-N(31)-C(35)	129.8 (7)	N(32)-N(31)-C(35)	106.3 (8)
N(31)-N(32)-B(1)	107.9 (8)	N(31)-N(32)-C(33)	119.9 (7)
C(33)-N(32)-B(1)	132.1 (8)	N(32)-C(33)-C(34)	110.5 (9)
C(33)-C(34)-C(35)	104.4 (9)	N(31)-C(35)-C(34)	110.9 (9)
N(12)-B(1)-N(22)	109.1 (8)	N(12)-B(1)-N(32)	107.3 (8)
N(22)-B(1)-N(32)	105.8 (8)		

by alkyl or alkoxide groups and decomposes when stirred in *tert*-butyl alcohol.

Three basic structural types are generally considered reasonable for seven-coordinate molecules. They are the pentagonal bipyramid, the capped octahedron, and the capped trigonal prism. Calculated energy differences between the three in many cases are small.¹⁰ It was felt that the structure of the molecules reported here is most certainly a capped octahedron. This is because the umbrella-shaped [RB(pz)₃] ligands readily fill three vertices of an octahedron or trigonal prism. The latter shape has never been observed with this ligand and is ruled out by the synthesis of [HB(3,5-Me₂pz)₃]TaMe₃Cl. In this molecule, the 3-methyl substituents would be in close proximity to the three other ligands in the trigonal prism. If the basic octahedral shape is taken, this interaction is greatly reduced. For these Ta complexes, the seventh ligand would clearly cap the face containing no pz-donor groups. Thus two possible isomers, shown as A and B, are possible for these complexes.



In order to verify this prediction, the solid-state structure of [HB(pz)₃]TaMe₃Cl has been determined by X-ray crystallography. As shown in Figure 1, the basic structure is a capped octahedron with a Me group in the capping position (structure A). As expected for a molecule lacking threefold rotational symmetry, some deviations from an idealized geometry are observed, but they are relatively minor. For ex-

(10) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* 1977, 16, 511.

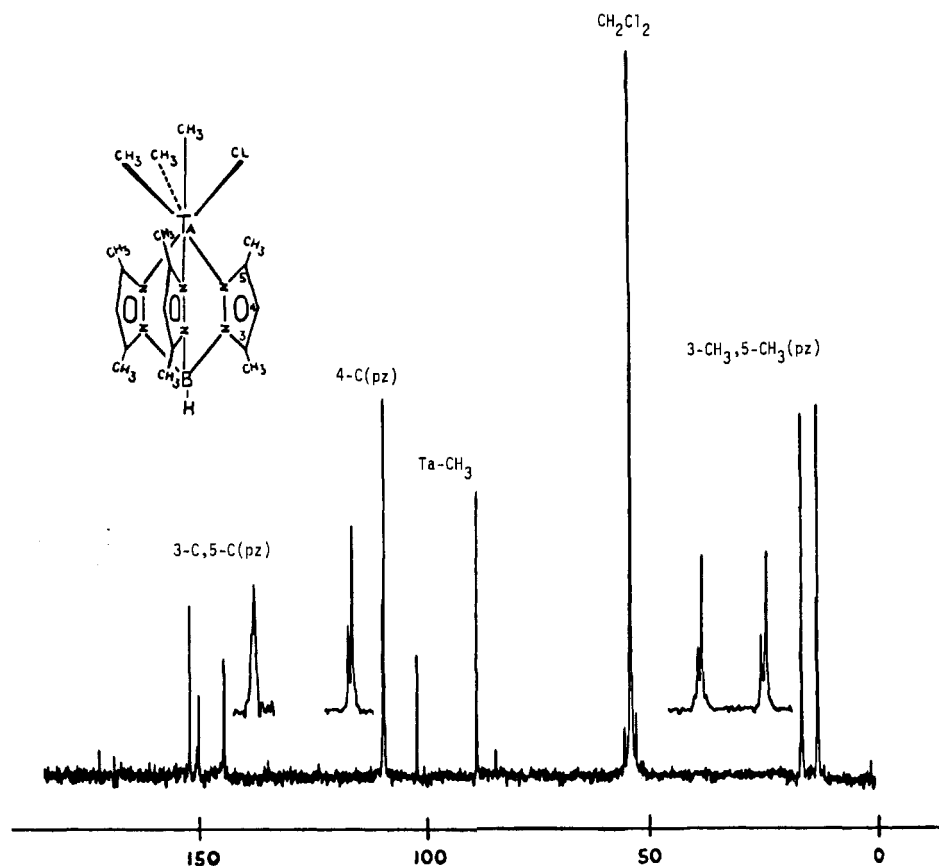


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{TaMe}_3\text{Cl}$. The inserts are expansions of proximate regions.

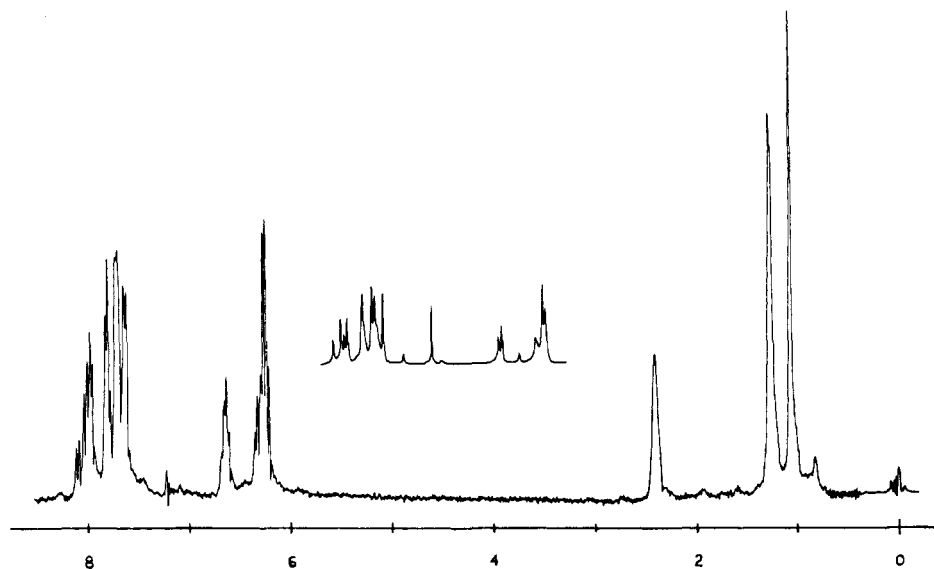


Figure 3. ^1H NMR spectrum in CDCl_3 (90 MHz) of $[\text{B}(\text{pz})_4]\text{TaMe}_3\text{Cl}$ taken at -8°C . The insert is the δ 8.2–6.2 region run at 400 MHz.

ample, the angles formed through the metal from the capping Me group with the other two Me groups and the Cl ligand are 78.2 (4), 73.3 (4), and 79.9 (3) $^\circ$, respectively, and 126.4 (3), 136.1 (3), and 137.9 (3) $^\circ$ with the three nitrogen donor atoms of the poly(pyrazolyl)borate ligand. These angles average to 77.1 and 133.4° and can be compared with calculated values for a d^0 configuration of an idealized ML_7 capped-octahedral arrangement of 84 and 138° .¹⁰ This theoretical paper also predicted that, for a d^0 system, π -donor ligands would be preferentially located in the triangular face of the octahedron that is capped by the seventh ligand. The π -donor nitrogen atoms are restricted to the uncapped triangular face of the octahedron, but the only remaining π -donor ligand, Cl, is located in the capped triangular face of the octahedron as

predicted. Although this does fit these calculated results, in solution a substantial amount of isomer B, with the Cl in the capping position, is also observed (vide infra).

In solution, $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{TaMe}_3\text{Cl}$ also adopts structure A. This is best demonstrated in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this complex shown in Figure 2. In structure A, two of the pz rings are equivalent (trans to Me groups) and one distinct (trans to Cl) and, similarly, two Me groups are equivalent with one unique. Thus each type of carbon atom in this molecule should appear as two resonances in a ratio of 2:1. For structure B, the pz rings and the Me groups are equivalent. As assigned on the spectrum,⁴ each type of carbon atom shows as two resonances in a 2:1 ratio. The two Ta-Me resonances were more deshielded than we anticipated but were

verified by the coupled spectrum, which showed these resonances as quartets with $J_{\text{CH}} = 121$ Hz. This slightly low coupling constant for a methyl group ($J_{\text{CH}} = 128$ Hz for the methyl groups on the pz rings) has been observed for other Ta-Me complexes.¹¹ Also, we ran the spectrum of $[\text{H}_2\text{B}(\text{pz})_2]\text{TaMe}_3$.² For this complex, the single Ta-Me resonance is at 110.4 ppm with $J_{\text{CH}} = 122$ Hz.

The situation is more complex for the two $[\text{RB}(\text{pz})_3]\text{-TaMe}_3\text{Cl}$ complexes. Although the X-ray structural analysis of $[\text{HB}(\text{pz})_3]\text{TaMe}_3\text{Cl}$ shows only structure A, in solution both this molecule and $[\text{B}(\text{pz})_4]\text{TaMe}_3\text{Cl}$ exist as a mixture of structures A and B. Figure 3 shows the 90-MHz ¹H NMR spectrum (at -8 °C) for $[\text{B}(\text{pz})_4]\text{TaMe}_3\text{Cl}$. In the Ta-Me region, three resonances are observed. The slightly broader two resonances at lower field are in a 1:2 ratio and are assigned to the Ta-Me groups in isomer A. The third, sharp resonance is assigned to the three equivalent Ta-Me groups of isomer B. The spectrum of $[\text{HB}(\text{pz})_3]\text{TaMe}_3\text{Cl}$ is very similar in this region. The pyrazolyl region of the spectrum is complex. The insert shows the 400-MHz spectrum (no spin-spin coupling is observed at this level of expansion) of this region. The two more shielded multiplets at ca. δ 6.6 and 6.2 (integrated intensity 1:3) are assigned to the 4-H (pz).⁴ The smaller resonance is assigned to the noncoordinated pz ring for both isomers. The expected two separate resonances are observed at 400 MHz. The larger resonance is shown at 400 MHz to be composed of three signals as expected if both isomers are present (two for isomer A, one for B). The remaining downfield resonances are due to the 3-H, 5-H (pz) hydrogen atoms. The complex region from δ 7.8 to 7.6, which cannot be fully resolved even at 400 MHz, arises from the coordinated pz rings of both isomers. The smaller complicated resonance centered at ca. δ 8.0 shows as four resonances at 400 MHz and is assigned to the noncoordinated pz rings (two signals for each isomer). Final proof of these assignments is that the resonances assigned to the free pz rings are absent in the spectrum of $[\text{HB}(\text{pz})_3]\text{TaMe}_3\text{Cl}$ and irradiation of the δ 6.6 peak causes collapse only of the resonance centered at δ 8.0.

Thus at -8 °C, both isomers A and B are observed in solution for $[\text{B}(\text{pz})_4]\text{TaMe}_3\text{Cl}$ (3:2 ratio) and $[\text{HB}(\text{pz})_3]\text{-TaMe}_3\text{Cl}$ (2.8:1 ratio). As one heats these samples near room temperature, the two Ta-Me resonances assigned to isomer A start to broaden as shown in Figure 4 for $[\text{B}(\text{pz})_4]\text{TaMe}_3\text{Cl}$. At 65 °C they have started to coalesce while the remaining Ta-Me resonance remains sharp. Importantly, the pz region of the spectrum does not change (the loss of the doublet pattern in the δ 8.0 signal is caused by temperature-dependent chemical shifts) in this temperature range. At 86 °C, the Ta-Me resonance of isomer B starts to collapse with a concomitant change in the pz region. This process continues so that at 140 °C (the highest temperature measured) the Ta-Me resonances have merged into a single broad peak. Although slight sample decomposition is noted in the high-temperature spectra, the temperature dependence is reversible.

Clearly two separate dynamic processes are needed to account for these data. In the region 23–65 °C, the three methyl groups of isomer A are equilibrating without equilibrating the three pz rings of this isomer. Two mechanisms can account for those observations (Scheme I). One is the exchange of the capping methyl group with either of the methyl ligands in the octahedron (path A). The other is a rotation of the triangular face formed by the three Me groups (path B). This second mechanism seems more reasonable to us. In both mechanisms the Cl ligand retains its position in the capped

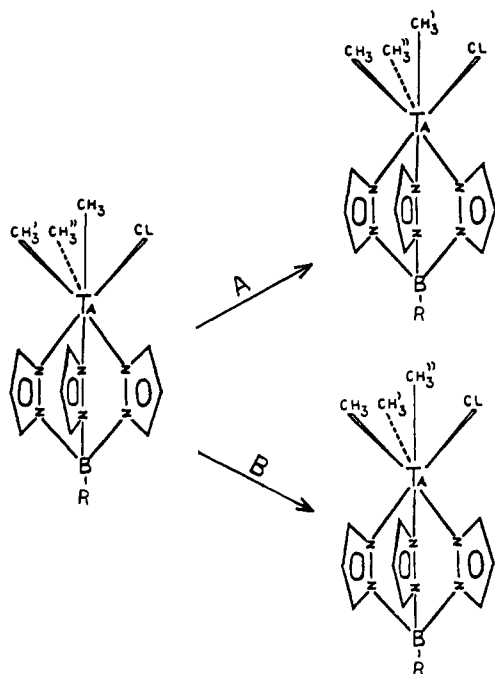


Figure 4. ¹H NMR spectrum in C₂D₂Cl₄ (80 MHz) of $[\text{B}(\text{pz})_4]\text{-TaMe}_3\text{Cl}$ at various temperatures (°C). The × peaks are due to residual toluene and sample decomposition.

(11) The methyl group of $(\text{Cp})_2\text{Ta}(\text{CH}_2)\text{CH}_3$ resonates at -5 ppm ($J_{\text{CH}} = 122$)⁷ and for $(\eta^3\text{-C}_3\text{Me}_5)\text{TaMe}_2(\eta^2\text{-C}(\text{Me}_2)\text{O})$ at 55.6 ppm ($J_{\text{CH}} = 119$).¹²

(12) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

Scheme I



octahedron, rendering the pz rings nonequivalent. Thus, as observed, no changes are expected in the low-field part of the spectrum from this dynamic behavior. Above 65 °C, the Cl ligand must start to exchange with the methyl ligands so as to interconvert isomers A and B. Again, this process could take place by a simple exchange with the capping methyl ligand or a rotation of one of the triangular faces that these two atoms form with either of the two remaining methyl lig-

ands. This process now equilibrates the pz rings in isomer A with each other and with the pz rings of isomer B. The noncoordinated pz ring does not exchange with coordinated pz rings at any temperature studied.

It is interesting to compare the dynamic processes observed for these seven-coordinate Ta molecules with the six-coordinate $[\text{RB}(\text{pz})_3]\text{Zr}(\text{O}-t\text{-Bu})\text{Cl}_2$ complexes studied earlier.⁴ For the six-coordinate molecules, the three pz rings exchange at room temperature by a trigonal-twist rotation of the poly(pyrazolyl)borate ligand about the Zr-B axis. This process can be quenched below 0 °C. Clearly for isomer A, in which the pz rings are similarly nonequivalent, this type of rotation does not take place up to 65 °C. This can be simply explained by an increased steric barrier to the rotation in these seven-coordinate molecules. A similar steric argument was used to explain the fact that $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{Zr}(\text{O}-t\text{-Bu})\text{Cl}_2$ is static up to 140 °C.

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Registry No. $[\text{HB}(\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer A), 88181-28-6; $[\text{HB}(\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer B), 88243-98-5; $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$, 88181-29-7; $[\text{B}(\text{pz})_4]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer A), 88181-30-0; $[\text{B}(\text{pz})_4]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer B), 88243-97-4; TaMe_3Cl_2 , 3020-02-8.

Supplementary Material Available: Tables of fractional coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for $[\text{HB}(\text{pz})_3]\text{TaMe}_3\text{Cl}$ (9 pages). Ordering information is given on any current masthead page.

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Solvento Complexes of Tungsten, Rhenium, Osmium, and Iridium and the X-ray Crystal Structure of $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$

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$[\text{WH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{ReH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{ReH}_7(\text{PPh}_3)_2]$, $[\text{OsH}_4(\text{PMe}_2\text{Ph})_3]$, and $[\text{IrH}_5(\text{PPh}_3)_2]$ react with HBF_4 in MeCN (=S) to give $[\text{WH}_2\text{S}_2(\text{PMe}_2\text{Ph})_3]^{2+}$, $[\text{ReHS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$, $[\text{ReHS}_4(\text{PPh}_3)_2]^{2+}$, $[\text{OsS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$, and $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]^{2+}$ as the BF_4 salts. The reaction mechanism and evidence for the initial protonation of some of the d^0 polyhydrides at an M-H bond is discussed. In all but the iridium case, MeOH and Me_2CO failed to give analogous complexes and no alkane or alkene dehydrogenation reactions were ever observed with the acetonitrile complexes. In the iridium case a variety of solvento complexes can be obtained. Where S = Me_2CO , these are active in alkene and alkane dehydrogenation, and in this case a single-crystal X-ray diffraction study was performed: monoclinic unit cell; $a = 10.565$ (2) Å; $b = 25.315$ (7) Å; $c = 15.460$ (4) Å; $\beta = 95.74$ (2)°; $V = 4114$ (4) Å³; space group $P2_1/c$; $Z = 4$; $R = 5.6\%$. The trans influence of the hydride ligands on the O-bound acetone groups was pronounced: Ir-O = 2.228 (5) Å (av), ca. 10% longer than the expected 2.02 Å. This is consistent with the high reactivity of the acetone complex.

We have been studying solvento complexes of the transition metals¹ as possible precursors to reactive, ligand-deficient species for the catalytic and stoichiometric activation of normally unreactive substrates, such as alkanes. For example we found that $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]\text{BF}_4$ (**1**) is active for alkane dehydrogenation² where S = Me_2CO (**1a**) but not where S

= MeCN (**1b**) and that **1** can be obtained by acidolysis of $\text{IrH}_5(\text{PPh}_3)_2$ with HBF_4 in the solvent S.³ We therefore decided to attempt the preparation of a variety of similar solvento complexes of other metals. While this work was in progress, Caulton et al.^{4a} showed that acidolysis of MoH_4 -

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