Synthesis, X-ray Crystal Structure, and Study of Dynamic Behavior of [Dihydrobis(3,5-dimethyl-1-pyrazolyl)borato]-chlorotrimethyltantalum(V), a Molecule with a Strong Three-Center, Two-Electron Bond

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Abstract: Reaction of $TaMe_3Cl_2$ and $K[H_2B(3,5-Me_2pz)_2]$ (3,5-Me_2pz = 3,5-dimethyl-1-pyrazolyl) yields [$H_2B(3,5-Me_2pz)_2]TaMe_3Cl$. X-ray crystallographic analysis shows that the molecule adopts a capped octahedral structure in the solid state with a three-center, two-electron B–H–Ta bond filling the seventh coordination site. A Me ligand is found to cap a face formed from the other two Me and Cl ligands. The Cl atom is disorder in the capped face. The three-center interaction is verified in both the solid and solution phase by IR spectroscopy and, by ^{11}B NMR, shown to be kinetically stable up to at least 110 °C in solution. Of the three possible geometrical isomers, two are observed in the solid phase and, by using low-temperature NMR, all three are observed in solution. Three distinct dynamic processes are observed by variable-temperature $^{13}C\{^1H\}$ NMR studies. These are interpreted as arising from rotational processes involving the different types of triangular faces formed by the Cl and three Me ligands.

As part of a general study of polypyrazolylborate complexes of Zr[1] and Ta, we have prepared the 7-coordinate complexes [RB(pz)₃]TaMe₃Cl (R = H, pz; pz = pyrazolyl) and [HB(3,5-Me₂pz)₃]TaMe₃Cl.[2] Part of our initial plan in using the flexible polypyrazolylborate ligand system[3] with early transition metals was to attempt to prepare complexes by using the tris-chelate [RB(pz)₃] ligands as demonstrated above and to also prepare similar complexes with the bis-chelate [R₂B(pz)₂] ligands. If successful, the second series would potentially have two fewer electrons donated to the metal, and this could drastically alter reaction chemistry. To this end, we report here the synthesis, X-ray structural investigation, and NMR studies of [H₂B(3,5-Me₂pz)₂]TaMe₃Cl. We have been able to show in both the solid and solution phase that this molecule also contains a 7-coordinate Ta with a strong three-center, two-electron B–H–Ta bond filling the seventh coordination site. Two isomers (one enantiomeric) are observed in the solid state and three are observed in solution by ^{11}B and $^{13}C\{^1H\}$ NMR at low temperatures. A study using $^{13}C\{^1H\}$ NMR of the dynamic behavior that interconverts these isomers at higher temperatures has been carried out.

Experimental Section

General Procedure. All manipulations were carried out under a nitrogen atmosphere, either in a Vacuum Atmospheres HE-493 drybox or by using standard Schlenk techniques. All solvents were dried, degassed, and distilled prior to use. $K[H_2B(3,5-Me_2pz)_2]$[4] and $TaMe_3Cl_2$[5] were prepared by published methods. Elemental analysis was performed by Robertson Laboratory. We and others[1] have found that it is difficult to obtain high quality analytical data on polypyrazolylborate complexes that are spectroscopically pure. ^1H NMR spectra were recorded on a Varian Model EM 390 spectrometer, and chemical shifts are reported in δ vs. Me₄Si. Carbon-13 spectra were recorded on IBM NR-80 and Brüker WP200 spectrometers. Chemical shifts are reported in ppm vs. Me₄Si with CD_2Cl_2 (δ = 53.8) and CH_2Cl_2 (δ = 54.0) as solvent and internal standard. Boron-11 spectra were recorded on a Brüker WH400 spectrometer in $C_6D_5CD_3$, and chemical shifts are reported in ppm vs. BF_3·OEt_2. Negative values mean the resonances are shielded with respect to the standard. Infrared spectra were measured on a Perkin-Elmer 621 infrared spectrophotometer. Decomposition point was determined in a sealed capillary and is uncorrected.

[Dihydrobis(3,5-dimethyl-1-pyrazolyl)borato]chlorotrimethyltantalum-(V), [H₂B(3,5-Me₂pz)₂TaMe₃Cl] (1). Freshly prepared dichlorotrimethyltantalum (2.16 g, 7.27 mmol), placed in a 250-mL round-bottomed flask with a Teflon-coated stirring bar, was dissolved in diethyl ether (40 mL). The yellow solution was cooled in a -78 °C bath, and $K[H_2B(3,5-Me_2pz)_2]$ (1.76 g, 7.27 mmol) was slowly added with rapid stirring (1 h). The mixture was allowed to warm to ambient temperature with stirring. After 12 h, the milky yellow solution was filtered and the precipitate was washed (two 5-mL portions of diethyl ether) and discarded. The yellow solution was then reduced to ca. 15 mL and cooled to 0 °C (48 h). A bright yellow crystalline product was then collected (0.73 g, 1.57 mmol). These crystals were used in the X-ray analysis. The solution was then halved in volume and recooled to 0 °C (24 h). A second crop (0.93 g, 2.00 mmol) was then collected: total yield 1.66 g (3.57 mmol, 49%). The remaining solution was reduced to dryness to yield 1.09 g of spectroscopically pure material. The analytical sample was prepared by sublimation (95 °C, 0.01 torr): mp 110–116 °C dec; ^1H NMR (CDCl₃, 35 °C) 5.79 (2, s, 4-H(pz)), 2.33, 2.26 (6, 6, s, s, 3,5-Me(pz)), 1.55 (9, br s, Ta–Me); $^{13}C\{^1H\}$ NMR (CD₂Cl₂, 35 °C) 150.0, 145.5 (s, s, 3-C, 5-C(pz)), 107.7 (s, 4-C(pz)), 87.2 (very br s, Ta–Me), 14.4, 10.5 (s, s, 3-Me, 5-Me(pz)); $^{11}B\{^1H\}$ NMR ($C_6D_5CD_3$, -26 °C) -15.11 (s, isomer C), -15.74 (s, isomer B), -16.28 (s, isomer A); ($C_6D_5CD_3$, 110 °C) -15.88 (s) (see Figure 2); mass spectrum, parent ion (P) was not observed (P = 464), 449 (P – 15(CH₃)), 433 (P – 31(C₂H₇)). Anal. Calcd for $C_{13}H_{25}N_4BClTa$: C, 33.61; H, 5.42; N, 12.06; Cl, 7.63. Found: C, 32.73; H, 5.43; N, 12.15; Cl, 7.34.

X-ray Structure Determination. A yellow crystal of approximate dimensions 0.35 × 0.15 × 0.30 mm was mounted in a capillary and used for data collection. The unit cell dimensions obtained from 25 reflections with Mo Kα radiation (λ = 0.71073 Å) were as follows: a = 8.103 (2) Å, b = 25.063 (4) Å, c = 9.425 (2) Å, β = 111.26 (2)°, V = 1784 (1) Å³, space group $P2_1/c$.

A total of 4865 reflections were measured within the range 2° < θ < 27° with a CAD-4 diffractometer. The following parameters were used: scan type ω/2θ, scan width 0.6° + 0.35° tan θ, aperture size 4 mm × (2.0 + 1.0 tan θ) mm; background was measured at the extremes of the scan on a quarter of the scan range. Three standard reflections were measured at every 7200 s of exposure time and showed a crystal decay that was monotonic and isotropic. Maximum decay correction was 1.34 while the average was 1.12. Numerical absorption correction with the linear absorption coefficient of 66.5 cm⁻¹ was applied with the crystal limited by seven faces. The measurements of the crystal dimensions, however, were obscured by the capillary and Vaseline that was used to protect the crystals from air during the process of crystal selection and mounting. Maximum and minimum transmission coefficients were 0.449 and 0.152. Of the 3205 reflections above 3σ(I), 2422 were symmetry independent.

The structure was solved by Patterson techniques and Fourier synthesis. All non-hydrogen atoms were easily located. There are four possible configuromers of the compound with the chlorine atom located in positions 4, 5, 6, or 7 (Figure 1). Of them two are a pair of enantiomers (chlorine atom in positions 5 and 6) and two others have sym-

(1) (a) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840. (b) *Ibid.* **1983**, *22*, 1064.
(2) Reger, D. L.; Swift, C. A.; Lebioda, L. *Inorg. Chem.*, manuscript submitted for publication.
(3) (a) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17. (b) Shaver, A. *J. Organomet. Chem. Libr.* **1976**, *3*, 157.
(4) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.
(5) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
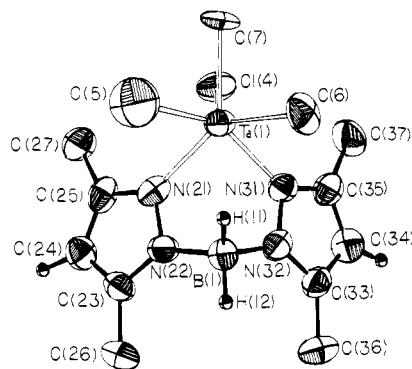
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Figure 1. ORTEP drawing of one isomer of [H₂B(3,5-Me₂pz)₂]TaMe₃Cl. The thermal motion elipsoids are drawn at 50% probability except for H atoms which are at arbitrary levels.

metry C_s (mirror plane). Initial refinement of the structure revealed that in the crystal lattice two isomers occupy the same sites (chlorine in positions 4 and 5 or for sites equivalent by crystal symmetry operations positions 4 and 6). Apparently, in the crystal there was no admixture of the fourth configuromer (with Cl in the capping position 7) and there was no enantiomeric disorder. To allow for the observed partial disorder, three structural models with different constraints were refined. The first with overlapping positions of Cl and Me ligands (atom numbers 4 and 5) tied together, and sums of the occupancy factors for each of the positions equal 1.0 but with no constraint on the global amount of Cl atoms. The refinement of this model with 183 parameters converged at $R = 0.0467$ and $R_w = 0.0625$. In the two other models overlapping positions of the ligands were not constrained. In the second with 191 parameters the global occupancy of Cl was not constrained (refinement of this model was not successful) while in the third with 190 parameters and $R = 0.0467$ and $R_w = 0.0630$ the global occupancy of Cl was constrained to 1.0.

In the refinement, calculated and fixed positions for non-methylenic H atoms were used. All atoms except for partially occupied C atoms were refined with anisotropic thermal parameters. Distances between Ta and partially occupied C atoms were elastically restrained to a value of 2.24 Å in models 2 and 3. The weights used were $(\sigma^2(F) + 0.0007F^2)^{-1}$. In the final cycles of refinement all shifts were less than 0.05.

On the final difference Fourier maps the highest peaks were 1.90 e/Å³ and not close to the Ta position 0.96 e/Å³ for the first and 0.58 e/Å³ for the third model. Statistical analysis (Hamilton test) does not allow the rejection of any of the models but on the basis of the chemical information available we decided to present the results obtained for the last of the above models. The difference between the Ta–Cl and Ta–Me bond length of 0.12 Å is significant, and the distances between overlapping Me and Cl are 0.33 and 0.36 Å. Elemental analysis for Cl correspond to an occupancy of 1.0 while sums of occupancies for the first and second model were 1.08 and 1.10, respectively. It should be pointed out that the occupancies refining on the high side seem to indicate that in the solid state, or at least in the crystal that was used for the crystal structure determination, the admixture of the other configuromer (Cl in position 7) is not significant.

Table I contains the atomic coordinates and thermal parameters. Interatomic distances and angles are in Tables II and III, respectively. An ORTEP drawing of an individual molecule is shown in Figure 1.

Results

Synthesis. The complex [H₂B(3,5-Me₂pz)₂]TaMe₃Cl (3,5-Me₂pz = 3,5-dimethylpyrazolyl ring) is prepared as shown in eq 1. The new complex can be stored for months at −30 °C under

$$K[H_2B(3,5\text{-}Me_2pz)_2] + TaMe_3Cl_2 \rightarrow$$
$$[H_2B(3,5\text{-}Me_2pz)_2]TaMe_3Cl + KCl \quad (1)$$
$$\mathbf{1}$$
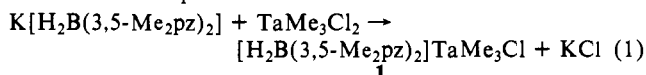
N₂ but decomposes slowly at room temperature. It is freely soluble in all organic solvents other than saturated hydrocarbons, in which it is only slightly soluble.

Solid-State and Molecular Structure. Complex **1** exists as isolated molecules in the solid state. Figure 1 shows an ORTEP drawing of the molecule. The Cl atom is disordered between site 4, as shown, and sites 5 and 6. The molecule with the Cl in position 5 or 6 is chiral, but the crystal is composed of a racemic mixture. Three different structural models with different constraints were refined. The model for the best fit placed no constraints on the

Table I. Fractional Atomic Coordinates Multiplied by 10⁴ [a]

atom	x	y	z	B_{eq}
Ta(1)	2274.0 (6)	1320.9 (2)	2291.3 (5)	3.51
N(31)	4656 (12)	1550 (4)	4314 (9)	3.70
N(32)	4266 (12)	1545 (4)	5620 (10)	3.72
C(33)	5644 (15)	1708 (4)	6824 (12)	3.76
C(34)	6958 (15)	1839 (5)	6245 (14)	4.50
H(34)	8284	1982	6912	5.5
C(35)	6306 (14)	1756 (5)	4708 (13)	4.06
C(36)	5600 (16)	1708 (6)	8412 (12)	5.02
C(37)	7220 (18)	1850 (6)	3591 (16)	6.41
B(1)	2429 (17)	1313 (5)	5411 (14)	3.65
H(11)	1406	1502	4445	5.5
H(12)	2146	1379	6443	5.5
N(21)	2610 (11)	584 (4)	3708 (10)	3.85
N(22)	2490 (11)	703 (4)	5115 (9)	3.66
C(23)	2419 (14)	257 (5)	5855 (12)	3.87
C(24)	2492 (16)	−171 (5)	4958 (13)	4.43
H(24)	2468	−593	5238	5.5
C(25)	2599 (14)	40 (5)	3615 (13)	4.05
C(26)	2328 (17)	281 (6)	7446 (13)	5.64
C(27)	2659 (18)	−249 (6)	2251 (14)	5.78
C(7)	1208 (16)	1527 (5)	−217 (11)	4.31
C(6)	1896 (18)	2194 (5)	2380 (15)	5.56
Cl(4)	4429 (12)	916 (5)	1499 (10)	5.14
C(4)	4232 (89)	1024 (37)	1308 (90)	10.71
Cl(5)	−664 (15)	1017 (6)	1542 (17)	5.90
C(5)	−445 (43)	975 (27)	1292 (67)	8.52

[a] Occupancy factor for Cl(4) and C(5) was 0.557 (18), for C(4) and Cl(5) 0.443 (18).

Table II. Bond Distances (Å)

Ta(1)–N(21)	2.237 (10)	Ta(1)–N(31)	2.241 (9)
Ta(1)–C(6)	2.216 (12)	Ta(1)–C(7)	2.263 (9)
Ta(1)–C(5)	2.234 (19)	Ta(1)–C(4)	2.235 (19)
Ta(1)–Cl(5)	2.351 (10)	Ta(1)–Cl(4)	2.363 (7)
Ta(1)–H(11)	2.42	Ta(1)–B(1)	2.897 (12)
B(1)–N(22)	1.560 (15)	B(1)–N(32)	1.542 (15)
N(21)–N(22)	1.396 (11)	N(31)–N(32)	1.377 (11)
N(22)–C(23)	1.330 (13)	N(32)–C(33)	1.335 (13)
C(23)–C(24)	1.379 (16)	C(33)–C(34)	1.400 (16)
C(24)–C(25)	1.404 (16)	C(34)–C(35)	1.366 (16)
C(25)–N(21)	1.366 (14)	C(35)–N(31)	1.354 (14)
C(23)–C(26)	1.529 (14)	C(33)–C(36)	1.510 (14)
C(25)–C(27)	1.491 (16)	C(35)–C(37)	1.510 (16)

Table III. Selected Bond Angles (deg)

C(7)–Ta(1)–C(6)	78.9 (5)	N(21)–Ta(1)–N(31)	79.8 (3)
N(21)–Ta(1)–C(7)	136.9 (4)	N(31)–Ta(1)–C(7)	135.7 (4)
N(21)–Ta(1)–C(6)	141.9 (4)	N(31)–Ta(1)–C(6)	78.7 (4)
N(21)–Ta(1)–Cl(4)	83.7 (4)	N(31)–Ta(1)–Cl(4)	82.6 (3)
C(6)–Ta(1)–Cl(4)	129.9 (4)	C(7)–Ta(1)–Cl(4)	79.3 (4)
N(21)–Ta(1)–C(4)	91.2 (24)	N(31)–Ta(1)–C(4)	85.3 (23)
C(6)–Ta(1)–C(4)	118.2 (25)	C(7)–Ta(1)–C(4)	72.7 (22)
Cl(5)–Ta(1)–C(5)	8.5 (18)	Cl(4)–Ta(1)–C(4)	7.7 (25)
N(21)–Ta(1)–Cl(5)	78.6 (4)	N(31)–Ta(1)–Cl(5)	143.5 (5)
C(6)–Ta(1)–Cl(5)	101.1 (6)	C(7)–Ta(1)–Cl(5)	78.4 (5)
		C(4)–Ta(1)–Cl(5)	124.2 (24)
N(21)–Ta(1)–C(5)	79.6 (19)	N(31)–Ta(1)–C(5)	150.7 (17)
C(6)–Ta(1)–C(5)	105.7 (19)	C(7)–Ta(1)–C(5)	72.8 (17)
C(4)–Ta(1)–C(5)	115.9 (28)	Cl(4)–Ta(1)–Cl(5)	115.9 (16)

overlapping positions of the ligands, but the total occupancy of Cl was constrained to 1.0. This yielded two sets of bond angles and distances for the disordered positions, Tables II and III, one set for each geometrical isomer. The Cl ligand was found in position 4 55.7 (1.8)% and evenly distributed in positions 5 and 6 44.3 (1.8)% of the time. It is not found in position 7.

The most important point in the structure is the extreme puckering of the 6-membered chelate ring, making the B–Ta distance 2.897 (12) Å. In general, these ligands form this boat-type puckering, but it is usually quite shallow and M–B distances are ca. 3.8 Å.[6] Two important exceptions are [H₂B-(3,5-Me₂pz)₂]Mo(CO)₂(η³-C₃H₅)[7] and [H₂B(3,5-Me₂pz)₂]Mo-(CO)₂(η³-C₇H₇)[8] where the Mo–B distance is ca. 2.8 Å. In both

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of these structures a three-center, two-electron B–H–Mo interaction was proposed to explain the short Mo–B distance. The short Ta–B distance in 1 coupled with the obvious open coordination site at Ta in this region (N(21)–Ta–C(6) angle = 141.9 (4)°, C(5)–Ta–N(31) angle = 150.7 (17)°) clearly indicates a three-center, two-electron B–H–Ta interaction. Given the high absorption coefficient of Ta and the Cl disorder problem, we were unable to definitively locate the bridging H atom. Hydrogen atoms H(11) and H(12) and those on carbon atoms C(24) and C(34) were placed into the model prior to the final stages of the refinement using standard considerations. H(11) was placed assuming no interaction with Ta.

With the three-center interaction occupying a coordination site, the structure of the molecule is best described as a capped octahedron. Atoms N(21), N(31), and the three-center bond occupy one triangular face; atoms Cl(4), C(5), and C(6) the second, and C(7) caps the latter face. We have recently determined[2] the solid-state structure of [HB(pz)₃]TaMe₃Cl (2), a discreet 7-coordinate molecule that has a very similar structure to 1, which we also described as a capped octahedron. Although exchanging the third pz ring in 2 for the three-center interaction in 1 makes the structure appear more irregular, the various angles are very similar. For example, the angles formed through the metal from the capping Me group in 1 to the other two Me groups and the Cl ligand are 78.9 (5), 72.8 (17), and 79.3 (4)° for 1 and 78.2 (5), 74.1 (4), and 79.8 (3)° for 2. Also, the angles formed in 1 from the capping Me group with the two nitrogen donor atoms are 136.9° and 135.7 (4)° compared to an average of 133.5° for 2. Thus, in the solid state there is clearly a B–H–Ta interaction filling the seventh coordination site for 1, leading to an approximately capped octahedral structure.

Infrared Spectrum. A strong absorption at 2490 (Nujol mull) or 2497 cm⁻¹ (CH₂Cl₂ solution) is observed and is readily assigned to the terminal B–H stretch. Two other strong bands at 2013 and 2072 (Nujol mull) or 2012 and 2069 cm⁻¹ (CH₂Cl₂ solution) are also observed and are assigned to the B–H–Ta interaction.[9] As a single band would be expected for one isomer, the two bands observed in the solid state reflect the two isomers found in the crystal structure. In one case the B–H–Ta interaction would be trans to a Cl ligand and in the other trans to a Me ligand, so the spread of 69 cm⁻¹ is not unreasonable.

¹¹**B NMR.** Figure 2 shows the ¹¹B NMR at three temperatures, with and without proton decoupling. The ¹¹B{¹H} spectrum at –26 °C (line narrowed) shows three resonances. As supported by ¹³C{¹H} data (vide infra) these three resonances arise from the two isomers A and B observed in the solid state and the third possible i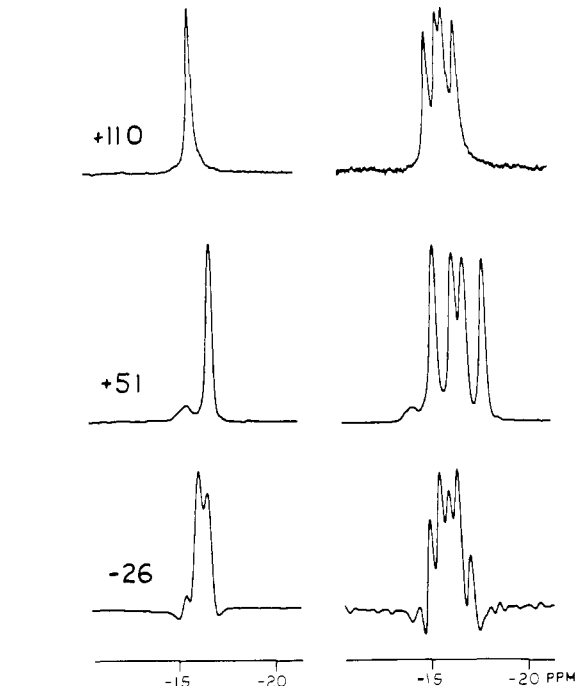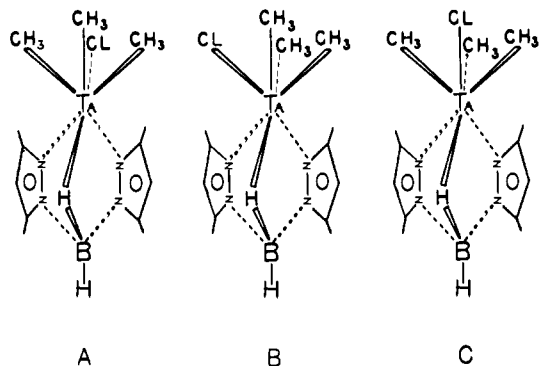somer C, with Cl in position 7. At 51 °C the two major isomers have coalesced, but the minor isomer is still distinct. At 110 °C, the resonances for all three isomers have become equivalent. The coupled spectrum at 110 °C shows as a double

Figure 2. ¹¹B NMR spectra of [H₂B(3,5-Me₂pz)₂]TaMe₃Cl, both ¹H coupled (right) and decoupled, recorded at 128.4 MHz. The –26 and +51 °C spectra are line narrowed.
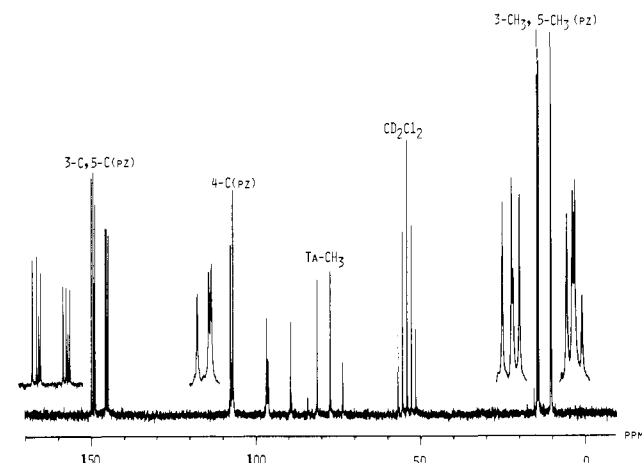
Figure 3. ¹³C{¹H} spectrum of [H₂B(3,5-Me₂pz)₂]TaMe₃Cl recorded at –58 °C in CD₂Cl₂. The inserts are expansions of proximate regions.

doublet with J_{BH} = 76 and 118 Hz. As J_{BH} = 112 Hz for 2,[2] we assign the 118-Hz coupling as arising from the terminal B–H and the 76-Hz coupling as arising from the B–H–Ta interaction. Coupling constants of 60–70 Hz have been observed in molecules containing similar B–H–Mn type interactions.[10] The –26 °C coupled spectrum (line narrowed) is appropriate for two overlapping double doublets given the known chemical shift difference in the two major isomers from the decoupled spectrum and using the same coupling constants as observed at 110 °C.

¹³**C{¹H} NMR.** Figure 3 shows the ¹³C{¹H} NMR spectrum of 1 taken at –58 °C. Assignments as shown on the figure of the various regions are straightforward from previous work.[2] As seen best in the expansions, each type of pyrazolyl ring carbon shows as four resonances, three of fairly equal size, one much smaller. There are seven resonances in the Ta–Me region.

Figure 4 shows the variable temperature data for the Ta–Me region and the 3 and 5 position pyrazolyl ring carbon atoms. In the Ta–Me region, three types of resonances can be identified.

(6) Cotton, F. A.; Frenz, B. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2118.

(7) Kosky, C. A.; Ganis, P.; Avitabile, G. *Acta Crystallogr. Sect. B* **1971**, *B27*, 1859.

(8) Cotton, F. A.; Jeremic, M.; Shaver, A. *Inorg. Chim. Acta* **1972**, *6*, 543.

(9) (a) King, R. B.; Bond, A. *J. Am. Chem. Soc.* **1974**, *96*, 1338. (b) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(10) (a) Calabrese, J. C.; Fischer, M. B.; Gaines, D. F.; Lott, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 6318. (b) Lott, J. W.; Gaines, D. F. *Inorg. Chem.* **1974**, *13*, 2261.
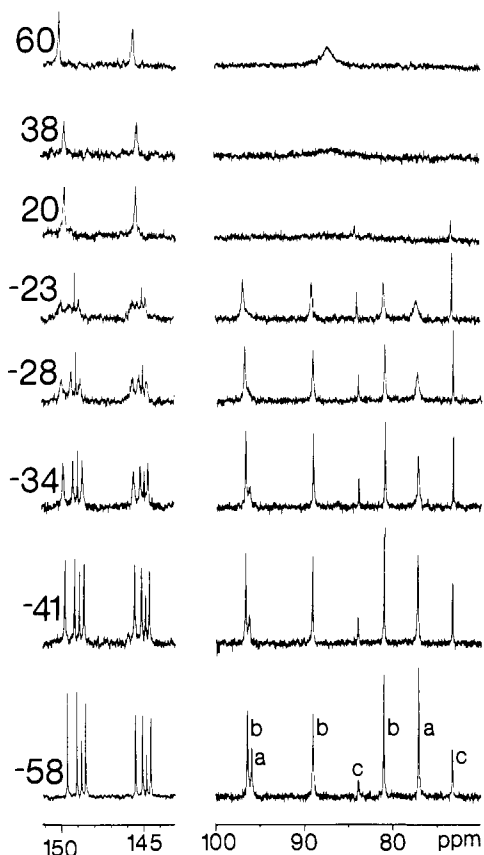
Figure 4. Variable-temperature $^{13}C\{^1H\}$ spectra of $[H_2B(3,5-Me_2pz)_2]$-TaMe$_3$Cl in the Ta–Me and 3,5-pyrazolyl ring carbon atom regions.

The resonances labeled a in the −58 °C spectrum, which are in an approximate 1:2 ratio, show line broadening already at −41 °C. This can be observed by the decrease in relative peak heights and, when greatly expanded data are used, in a 50% increase in the half-height peak width while the other five resonances do not change. Note that a careful check at −23 °C showed that the pulsing sequence being used did not lead to saturation at that temperature, so this peak broadening at −41 °C cannot be attributed to some unusual relaxation problem. By −34 °C, the a resonances are quite broad and the three resonances labeled b, of approximately equal intensity, have started to broaden. The c peaks, which are in a 1:2 ratio, remain sharp until the 20 °C spectrum. At 60 °C, the highest temperature measured, all the peaks have coalesced into a single broad resonance.

For the pyrazolyl ring carbon resonances (shown in Figure 4 for the 3-C, 5-C(pz)), the three large resonances of each set coalesce with increasing temperature while the small resonance remains sharp until the 20 °C spectrum.

Discussion

The solid-state structure of $[H_2B(3,5-Me_2pz)_2]TaMe_3Cl$ (**1**) clearly shows that the Ta is 7-coordinate with a B–H–Ta three-center, two-electron bond filling the seventh coordination site. This interaction is verified in both the solid and solution phase by observation of bands in the 2000 cm^{-1} region, typical of a B–H–M interaction,[9] in the IR spectra. More definitive is the coupled ^{11}B NMR spectrum (Figure 2) at 110 °C, which shows two different B–H coupling constants, one appropriate for a terminal B–H and one for a B–H–Ta bonding situation. Thus at 110 °C, the three-center bond remains intact on the NMR time scale. Clearly the electron-deficient Ta strongly interacts with the electron density in one of the B–H bonds.

Of the three possible geometrical isomers for **1**, two are observed in the solid state. The two place the Cl ligand in the capped face,

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

for A trans and for B cis to the B–H–Ta interaction. (Note: for B, placing the Cl in position 5 or 6, Figure 1, generates enantiomers, not different geometrical isomers.) In solution, the third possible isomer C, with the Cl in the capping position, is also observed.

Identification of three isomers along with the fact that isomers A and C have a plane of symmetry allows assignment of the $^{13}C\{^1H\}$ NMR spectrum in the Ta–Me region and partial assignment of the other resonances. In isomers A and C, (3,5-Me$_2$pz) rings are equivalent and the Ta–Me groups are in a 2:1 ratio. For B, the two rings are nonequivalent, as are all three Ta–Me groups. Thus, one predicts four resonances for each type of pyrazolyl ring carbon atom (one from A, one from C, and two from B) and seven resonances (two each for A and C in a 2:1 ratio and three for B) in the Ta–Me region, as observed. Clearly, B must predominate in solution with A at about half this abundance (the nonequivalent pyrazolyl rings in **B** need to be twice as abundant as the equivalent rings in A to give an equal size resonance). We chose A over C as the second major isomer in solution because it is observed in the solid state and it has the lowest barrier to a dynamic rearrangement process (vide infra). Also, theory predicts that for a d^0 system, π-donor ligands would preferentially locate in the capped face.[11] C is then the minor isomer. Peaks in the Ta–Me region can be assigned based on the variable temperature data. The two peaks for A are labeled as a in Figure 4. These are in a 1:2 ratio and show line broadening first. The three equal height resonances b, which all coalease in a similar way, are assigned to isomer B. The two smallest resonances c are then assigned to isomer C. For pyrazolyl ring resonances, the smallest one in each type is clearly isomer C with the other three from A and B.

We have previously observed two types of dynamic behavior for similar molecules. First, for $[B(pz)_4]Zr(Cl)_2O-t-Bu$,[1b] a fluxional process was observed in the temperature range of −60 to 30 °C involving a trigonal twist of the polypyrazolylborate ligand about the Zr–B axis leading to equilibration of the three coordinated pz rings in these octahedral molecules. Second, the capped octahedral molecules $[RB(pz)_3]TaMe_3Cl$ (R = H, pz) exist as two isomers in solution, one with a Me group in the capping position and the other with a Cl ligand in the cap.[2] In the temperature range 30 to 86 °C, a process most likely involving rotation of the triangular face formed by the three Me groups equilibrates these three ligands. The pz ligands do not equilibrate in this temperature range and are thus not undergoing the type of rotation observed for $[B(pz)_4]Zr(Cl)_2O-t-Bu$. Above 86 °C, the two isomers interconvert, presumably by a similar rotation of the triangular faces formed from two Me groups and the Cl ligand.

We believe the dynamic processes observed for **1** can be explained by similar arguments. First, for isomer A, rotation of the face formed by the three Me groups explains the initial line broadening of these resonances in the −41 °C spectrum. This process does not interconvert the isomers and is similar to the lowest energy process observed for **2**. Second, above −41 °C isomers A and B equilibrate by partial rotation of the 3-fold faces formed by the Cl ligand and two Me groups. Only rotation that carries the Cl ligand between the capped face positions can be taking place up to −23 °C because isomer C remains unique in this temperature range. We feel this is not an unreasonable restriction because for $[RB(pz)_3]TaMe_3Cl$ the rotation process that exchanges the Cl ligand in the capping position with the capped face is at higher energy than the rotation that equilibrates a Me ligand in this position. Finally, complete rotation of all of these faces starts to take place at 20 °C, equilibrating the resonances for all three isomers. As expected, for the pyrazolyl ligand carbon atoms, the three intense resonances coalesce up to −23 °C while the one small resonance, assigned to isomer C, remains sharp, finally coalescing at 20 °C.

We point out that a different process, a trigonal twist rotation of the polypyrazolylborate ligand around the Ta–B axis, cannot be completely ruled out as a mechanism for the intermediate temperature range where isomers A and B become equivalent. This type of mechanism has been previously proposed for [H$_2$B-

$(3,5\text{-Me}_2\text{pz})_2]\text{Mo(CO)}_2(\eta^3\text{-C}_7\text{H}_7).$[12] A main argument against this mechanism is that it cannot explain, by itself, equilibration of the Me ligands for isomers A and B because the Me ligand in the cap would remain distinct. Thus, at a minimum, equilibration of the Me ligands by the triangular face rotational mechanism is necessary. Also, this mechanism was not observed for **2**, a molecule structurally very similar to **1**, up to 86 °C. One might also anticipate that the 3-Me substituents on the pyrazolyl rings would impede such a rotation as observed with [HB(3,5-Me$_2$pz)$_3$]Zr(Cl)$_2$O-*t*-Bu, a nonfluxional molecule up to 110 °C.[1b]

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(12) Calderon, J. L.; Cotton, F. A.; Shaver, A. *J. Organomet. Chem.* **1972**, *42*, 419.

Synthesis, Linkage Isomerism, and Ligand Reactivity of (Urea)pentaamminerhodium(III) Complexes

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Abstract: The synthesis and reactions in aqueous solution of both O- and N-bonded linkage isomers of the [(urea)pentaamminerhodium(III)](3+) complex ion are described. Under neutral and basic conditions, the O-bonded isomer rearranges and hydrolyzes to give mixtures of the deprotonated N-bonded form and the [(NH$_3$)$_5$RhOH]$^{2+}$ ion. Under acidic conditions, the two isomers interconvert and ultimately produce mixtures of [(NH$_3$)$_5$RhOH$_2$]$^{3+}$ and [(NH$_3$)$_6$Rh]$^{3+}$ ions. The former arises by hydrolysis of the O-bonded isomer while the latter derives from the N-bonded species, at least in part by way of intermediate [(NH$_3$)$_5$RhNCO]$^{2+}$ ion. At pH 2.05 and 25 °C, the decomposition of the [(NH$_3$)$_5$RhNH$_2$CONH$_2$]$^{3+}$ ion by this path occurs ca. 30 000 times faster than the analogous reaction of urea under similar conditions.

The very slow decomposition of urea[1-3] in aqueous solution is ascribed to an elimination reaction producing ammonia and cyanic acid as sole products (eq 1, $k = 6 \times 10^{-10}$ s^{-1} at 25 °C).[4] The

$$\text{NH}_2\text{CONH}_2 \rightarrow \text{NH}_3 + \text{HNCO} \rightleftharpoons \text{NH}_4^+ + \text{NCO}^- \quad (1)$$

rate of reaction is insensitive to pH over a wide range but rises above pH 12 and decreases at very low pH. The increase under basic conditions is ascribed to specific-base catalysis, rather than any change in mechanism, while the decrease in rate in acidic solutions is attributed to protonation of the substrate.[5,6]

By contrast, the enzymatic decomposition of urea catalyzed by jack bean urease is a hydrolytic process producing carbamate and ammonium ions as the initial products[7] (eq 2). Since the

$$\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{COO}^- + \text{NH}_4^+ \quad (2)$$

spontaneous hydrolysis of urea has never been observed in competition with the slow elimination reaction and since $k_{\text{cat.}}$ for the urease-catalyzed reaction[8] is 3.5×10^3 s^{-1} at 25 °C, it is apparent that the urea molecule is activated to hydrolysis by a factor[6] in excess of 10^{14}. Jack bean urease is a nickel(II) metalloenzyme[9] with each of its six identical subunits containing one active site[10,11]

and two metal ions,[12] and at least one of these nickel ions is implicated in the hydrolysis.[8-12] On the basis of studies of the substrate specificity and inhibition data, a mechanism involving both nickel ions has been proposed.[8] Coordination of the substrate to one nickel ion through its carbonyl oxygen is argued to activate it toward attack by hydroxide ion coordinated at the other metal center. Such activation, at least for the individual processes, has been proposed for the reactions of zinc metalloenzymes,[13] and there is ample precedence for both roles for the metal ion in the hydrolysis of amino acid esters and amides.[14]

In order to assess the effect of coordination to a metal ion on the susceptibility of urea to hydrolysis, we have examined the reactions of pentaamminecobalt(III) complexes of urea (O-coordinated)[15] and *N,N*-dimethylurea (N-bonded).[16] In neither study was hydrolysis of coordinated urea observed, although for the former a small percentage of [(NH$_3$)$_5$CoOH] produced in the base hydrolysis arose via carbonyl rather than cobalt–oxygen cleavage.[15] It was clear from these studies that any reaction at

(1) Werner, A. E. "The Chemistry of Urea"; Longmans, Green and Co.: London, 1923; pp 31–48.
(2) Warner, R. C. *J. Biol. Chem.* **1942**, *142*, 705–23.
(3) Shaw, W. H. R.; Bordeaux, J. J. *J. Am. Chem. Soc.* **1955**, *77*, 4729–33.
(4) Calculated from data in ref 3, extrapolated to 25 °C.
(5) Shaw, W. H. R.; Walker, D. G. *J. Am. Chem. Soc.* **1958**, *80*, 5537–42.
(6) Blakeley, R. L.; Treston, A.; Andrews, R. K.; Zerner, B. *J. Am. Chem. Soc.* **1982**, *104*, 612–4.
(7) Blakeley, R. L.; Hinds, J. A.; Kunze, H. E.; Webb, E. C.; Zerner, B. *Biochemistry*, **1969**, *8*, 1991–2000.
(8) Dixon, N. E.; Riddles, P. W.; Gazzola, C.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 1335–44.

(9) Dixon, N. E.; Gazzola, C.; Blakeley, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975**, *97*, 4131–3. Dixon, N. E.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 469–73. Dixon, N. E.; Gazzola, C.; Asher, C. J.; Lee, D. S. W.; Blakeley, R. L.; Zerner, B. *Ibid.* **1980**, *58*, 474–80.
(10) Dixon, N. E.; Hinds, J. A.; Fihelly, A. K.; Gazzola, C.; Winzor, D. J.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 1323–34.
(11) Dixon, N. E.; Gazzola, C.; Watters, J. J.; Blakeley, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975**, *97*, 4130–1.
(12) Dixon, N. E.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 481–8.
(13) Brown, R. S.; Huguet, J.; Curtis, N. J. In "Metal Ions in Biological Systems", Sigel, H., Ed.; Marcel Dekker: New York, 1983; Vol. 15, pp 55–99.
(14) Dixon, N. E.; Sargeson, A. M. In "Zinc Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1983; pp 253–352.
(15) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688–97.
(16) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M., submitted for publication.