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# Structural Characterization of Poly(1-pyrazolyl)borate- and Poly(1-pyrazolyl)methane–Metal Complexes Containing Carbocyclic π-Acceptor Ligands. Synthesis and Crystal and Molecular Structures of [Tetrakis(1-pyrazolyl)borato]($\eta^6$-benzene)ruthenium(II) Hexafluorophosphate and [Hydrotris(1-pyrazolyl)borato]($\eta^5$-pentamethylcyclopentadienyl)rhodium(II) Hexafluorophosphate

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The title compounds were prepared by reaction of [($\eta^6$-benzene)RuCl$_2$]$_2$ or [($\eta^5$-C$_5$Me$_5$)RhCl$_2$]$_2$ with tetrakis(1-pyrazolyl)- and hydrotris(1-pyrazolyl)borate ions, respectively, and isolated as their PF$_6^-$ salts. Their crystal structures and molecular geometries have been determined by single-crystal X-ray diffraction methods. The ruthenium complex crystallizes in the centrosymmetric orthorhombic space group *Cmca* ($D_{2h}^{18}$, No. 64) with $a$ = 13.472 (5) Å, $b$ = 22.034 (4) Å, $c$ = 14.718 (2) Å, and $Z$ = 8. The rhodium compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}^5$, No. 14) with $a$ = 11.852 (10) Å, $b$ = 14.962 (5) Å, $c$ = 13.125 (8) Å, $\beta$ = 92.27 (8)°, and $Z$ = 4. Diffractometer data were collected by the $\theta$–$2\theta$ scan method (742 reflections $>3\sigma(I)$ for the Ru complex, 1448 $>3\sigma(I)$ for the Rh complex). The structures were solved by conventional methods. The ruthenium compound was refined by full-matrix least squares to a conventional final $R$ value of 5.8% whereas that of the rhodium compound was 11.7%. Both structures contain discrete, well-separated cations and PF$_6^-$ anions. In the ruthenium system the [$\eta^6$-C$_6$H$_6$RuB(pz)$_4$]$^+$ cation has crystallographic $m$ symmetry and the PF$_6^-$ anion has crystallographic twofold symmetry. The rhodium complex has a disordered PF$_6^-$ group and there are no symmetry constraints upon the ions. In both systems the pyrazolylborate ligand is tridentate. Principal mean bond lengths in the ruthenium complex are Ru–N = 2.105 (7) Å, N–N = 1.35 (4) Å, N–B = 1.54 (3) Å, and Ru–C(benzene) = 2.20 (3) Å; in the rhodium complex, the corresponding mean distances are Rh–N = 2.15 (1) Å, N–N = 1.39 (12) Å, B–N = 1.54 (9) Å, and Rh–C(cyclopentadiene) = 2.18 (6) Å.

## Introduction

Despite their formal similarity with the cyclopentadienide anion, one of the major anomalies in the chemistry of poly(1-pyrazolyl)borate anions has been the failure of attempts to prepare mixed sandwiches of the type [($\eta^3$-RB(pz)$_3$M($\eta^5$-C$_5$H$_5$)].[2] Recently, however, two of us have briefly reported the isolation of a variety of complexes of this and related types.[3] The syntheses and crystal and molecular structures of two of these unusual mixed-sandwich compounds are presented here in detail. The complexes were prepared by reactions 1 and 2. The two mixed-sandwich cations (isolated as their PF$_6^-$ salts) are yellow (Ru) or yellow-orange (Rh) crystalline solids which are stable in air for periods of at least 1 year. The preparation of these complexes[3] and the structural results,[4] in part, have been the subject of two preliminary communications.

$$[(\eta^6\text{-C}_6\text{H}_6\text{RuCl}_2]_2 + 2\text{B(pz)}_4^- \rightarrow 2[(\eta^6\text{-C}_6\text{H}_6)\text{RuB(pz)}_4]^+ + 4\text{Cl}^- \qquad (1)$$

$$[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2 + 2\text{HB(pz)}_3^- \rightarrow 2[(\eta^5\text{-C}_5\text{Me}_5)\text{RhHB(pz)}_3]^+ + 4\text{Cl}^- \qquad (2)$$

## Experimental Section

Ruthenium and rhodium trichlorides were purchased from Johnson-Matthey Ltd. Potassium salts of the hydrotris- and tetrakis(1-pyrazolyl)borate ions were synthesized as described by Trofimenko.[5] The complexes [($\eta^6$-C$_6$H$_6$)RuCl$_2$]$_2$ and [($\eta^5$-Me$_5$C$_5$)RhCl$_2$]$_2$ were prepared by the published procedures.[6,7] In the case of the ruthenium complex the procedure of Zelonka and Baird[6] occasionally gave erratic results, the initially green reaction mixture failing to turn red even after prolonged heating. In these cases the reaction could be brought to completion by the introduction of a brisk stream of air to the solution. Ir spectra were recorded on a Perkin-Elmer R20A spectrometer operating at 60 MHz.

**[Tetrakis(1-pyrazolyl)borato]($\eta^6$-benzene)ruthenium(II) Hexafluorophosphate.** A solution of [(C$_6$H$_6$)RuCl$_2$]$_2$ (0.5 g) and KB(pz)$_4$ (0.58 g) in 30 ml of acetonitrile was heated to reflux for ca. 5 min. The cooled solution was filtered to remove precipitated KCl and the solvent removed in vacuo. The residue was dissolved in water and the filtered solution treated with excess aqueous NH$_4$PF$_6$. Yellow crystalline [($\eta^6$-C$_6$H$_6$)RuB(pz)$_4$]PF$_6$ precipitated. Analytically pure material, mp 220° dec (0.96 g, 80%), was obtained after two recrystallizations from acetone–ether. Anal. Calcd for C$_{18}$H$_{18}$BF$_6$N$_8$PRu: C, 35.84; H, 3.01; N, 18.58. Found: C, 36.17; H, 3.14; N, 18.33. Ir (KBr): 3160 (w), 3140 (w), 3128 (w), 3105 (w), 2990 (w), 1500 (w), 1440 (m), 1412 (m), 1390 (s), 1312 (s), 1301 (s), 1220 (s), 1188 (w), 1109 (s), 1072 (m), 1063 (m), 1044 (w), 920 (m), 830 (vs, PF$_6^-$), 790 (s), 775 (m), 759 (s) cm$^{-1}$. The $^1$H NMR spectrum in CD$_3$CN showed two doublets ($J$ = 3 Hz) and a triplet ($J$ = 2.5 Hz) at $\tau$ 1.57, 2.38, and 3.65, respectively (relative intensity 3:3:3), associated with the Ru-coordinated pz groups. The uncoordinated pz group appeared as two doublets ($J$ = ~3 Hz) at $\tau$ 2.07 and 2.16 and a triplet ($J$ = ~2 Hz) at $\tau$ 3.42 and the $\eta^6$-C$_6$H$_6$ group exhibited a singlet at $\tau$ 3.8 (relative areas 1:1:1:6). In (CD$_3$)$_2$CO the positions of the pz resonances show only very small shifts but the resonance of the $\eta^6$-C$_6$H$_6$ group moves to $\tau$ 3.69 and partially obscures the triplet resonance of the coordinated pz groups.

**[Hydrotris(1-pyrazolyl)borato]($\eta^5$-pentamethylcyclopentadienyl)rhodium(II) Hexafluorophosphate.** A methanol solution of KHB(pz)$_3$ (0.42 g) was added under nitrogen to [($\eta^5$-C$_5$Me$_5$)RhCl$_2$]$_2$ (0.5 g) in CH$_2$Cl$_2$ and the mixture was stirred for 12 hr. After filtration and removal of solvent in vacuo the residue was dissolved in water and treated with excess aqueous NH$_4$PF$_6$. The yellow precipitate was collected, dried in vacuo, and recrystallized several times from CH$_2$Cl$_2$–ether to give pure [($\eta^5$-C$_5$Me$_5$)RhBH(pz)$_3$]PF$_6$ (0.59 g, 61%), mp 220–227°. Anal. Calcd for C$_{19}$H$_{25}$BF$_6$N$_6$PRh: C, 38.29; H, 4.23; N, 14.10. Found: C, 38.04; H, 4.27; N, 14.59. Ir (KBr): 3150 (w), 2500 (m BH), 1485 (m), 1442 (m), 1410 (s), 1397 (s), 1380 (m), 1311 (s), 1222 (s), 1121 (s), 1077 (m), 1049 (s), 1018 (s), 984 (m), 838 (vs, PF$_6^-$), 792 (w), 778 (m), 766 (s), 741 (m), 719 (s), 660 (w). The $^1$H NMR spectrum in (CD$_3$)$_2$SO showed a pair of doublets ($J$ = 3 Hz) at $\tau$ 1.85 and 2.12 and a triplet ($J$ = 3 Hz) at $\tau$ 3.55 (relative areas 3:3:3) associated with the protons of the coordinated pz groups. The Me groups on the cyclopentadienyl ring appeared as a singlet (relative area 15) at $\tau$ 8.1. In CD$_3$CN the latter resonance appeared at $\tau$ 7.72.

Recrystallization of the ruthenium complex [(C$_6$H$_6$)RuB(pz)$_4$]PF$_6$ from acetone–methylene dichloride solution afforded yellow lath-like crystals suitable for crystallographic study. The $[(C_5Me_5)RhBH(pz)_3]PF_6$ complex yielded orange lath-like crystals on recrystallization from an acetone–methylene dichloride solution.

## Crystal Structure Analyses

**Ruthenium Compound, $C_{18}H_{18}BN_8Ru^+PF_6^-$. Data Collection.** Preliminary unit cell and space group data were determined photographically. Systematic absences (*hkl*, $h + k = 2n + 1$; *hk*0, $h = 2n + 1$; *h*0*l*, $l = 2n + 1$), obtained from Weissenberg and precession films of the 0*kl*–2*kl*, *hk*0, *hk*1, *h*0*l*, and *h*1*l* reciprocal lattice nets (taken with Cu K$\alpha$ radiation; $\lambda$ 1.5418 Å), indicated that the space group was either centrosymmetric *Cmca* ($D_{2h}^{18}$, No. 64) or noncentrosymmetric *C*2*cb* ($C_{2v}^{17}$, No. 41).

A crystal 0.20 × 0.20 × 0.04 mm³, mounted along the *a** axis, was then transferred to a Hilger and Watts Y290 computer-controlled diffractometer and aligned so that the *a** axis was approximately 5° from coincident with $\phi$. Accurate cell constants were determined by the automatic centering of 12 strong reflections; the orientation matrix along with the refined cell constants were fitted to these values by a least-squares process.[8] The results obtained were $a = 13.472$ (5) Å, $b = 22.034$ (4) Å, and $c = 14.718$ (2) Å. The observed density of 1.84 (1) g cm$^{-3}$ obtained by the flotation method in an acetone–methyl iodide mixture agrees well with the calculated value of 1.834 g cm$^{-3}$ for $Z = 8$ formula units of $C_{18}H_{18}BF_6N_8PRu$ (mol wt 603).

Data were collected using a $\theta$–2$\theta$ scanning process with 60 steps of 0.01° each and with approximate monochromatic molybdenum K$\alpha$ ($\lambda$ 0.71079 Å) radiation using a zirconium filter and a pulse height analyzer. A 1-sec count was used for each step and stationary-background counts of 15 sec were measured at the minimum and maximum 2$\theta$ values of the scan. A unique data set of 2044 reflections to $\sin\theta = 0.64$ ($2\theta = 54°$) was collected. Instrument and crystal stabilities were monitored by measuring a set of three reflections, widely separated in reciprocal space, after every 100 reflections. No systematic change in the intensities of the standard reflections was observed; they fluctuated by 2% randomly. Reflections were considered observed if their net count was greater than 3$\sigma$ above background, where $\sigma(I)$ is defined by $\sigma^2(I) = [S + 4(B_1 + B_2)]$ and $S$, $B_1$, and $B_2$ are the scan and first and second background counts, respectively. There were 742 observed reflections which were corrected for Lorentz and polarization factors; the data were not corrected for absorption. With an absorption coefficient, $\mu$, of 8.5 cm$^{-1}$ and the previously mentioned crystal dimensions, transmission factors of the order 85–96% are possible. However, the largest absorption corrections are only present for certain orientations of the crystal (i.e., at $\phi \sim 0$ or 90°). The measured data were converted to observed structure factors making use of locally written data reduction programs and the X-Ray 72 system[9] and were used to calculate a Wilson plot,[10] from which were obtained an approximate absolute scale factor and an initial overall isotropic thermal parameter.

**Structure Solution and Refinement.** A three-dimensional Patterson function was computed and a solution obtained for the ruthenium atom position. The structure analysis was carried out by the heavy-atom method initially in the noncentrosymmetric, *C*2*cb*, space group.[11] The first heavy-atom-phased Fourier synthesis clearly revealed the complete structure showing that the cation had mirror symmetry and that the $PF_6^-$ anion had twofold crystallographic symmetry. Subsequent work was in the centrosymmetric space group *Cmca*. Full-matrix least-squares refinement of the positional and thermal parameters of the Ru, P, F, N, C, and B atoms was then carried out, initially with isotropic thermal parameters and finally with all atoms allowed anisotropic motion. No allowance was made for H atom contributions.

During the course of the refinement the anisotropic thermal parameters of the uncomplexed pyrazolyl group became unduly large, consistent with disorder of this five-membered ring. A Fourier synthesis computed at this stage revealed electron density maxima off the space group mirror plane for three of the ring atoms (C(21), C(22), C(23)). Coordinates were chosen for these atoms and in subsequent refinement cycles they were included with half-weight.[12] At the conclusion of full-matrix anisotropic least-squares refinement, $R = 5.8\%$ for the 742 reflections which had intensities greater than $3\sigma(I)$. During the final part of the refinement, a weighting scheme of the form $w^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$, where the $p$ parameter was $10^{-3}$, was employed. The final weighted $R_w$ was 6.2% ($R_w = 100\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$). The "goodness of fit" index, defined by $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where $n$ and $m$ are numbers of observations and variables, respectively, was 0.23. Scattering factors for the atoms were taken from ref 9. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were made for the ruthenium atom.[13] A final difference synthesis showed a number of small peaks of ~1 e Å$^{-3}$ around the heavy atom and a number of smaller peaks which would correspond to H atom positions, but no attempt was made to locate these precisely.

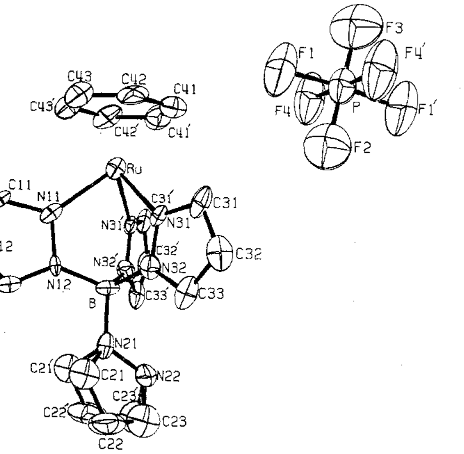

**Figure 1.** Perspective view with 50% probability ellipsoids of $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]PF_6$ showing the molecular geometry and atomic numbering.

**Rhodium Compound, $C_{19}H_{25}BN_6Rh^+PF_6^-$. Data Collection.** Preliminary photographic work was carried out on several crystals, all of which appeared to be multiple in varying degrees. Eventually we obtained one crystal which photographic films indicated to be substantially a single fragment, with only a small number of spurious diffraction spots from a minor fragment. It was realized at this point that analysis of this structure with these data would probably not yield precise parameters for all the atoms. It did seem that it would be possible at least to establish the structure beyond doubt.

Systematic absences (*h*0*l*, $l = 2n + 1$; 0*k*0, $k = 2n + 1$) obtained from Weissenberg and precession films of the 0*kl*–2*kl*, *h*0*l*, *hk*0, and *hk*1 reciprocal lattice nets uniquely determined the monoclinic space group as $P2_1/c$ ($C_{2h}^5$; No. 14). After transferring the 0.13 × 0.12 × 0.08 mm³ crystal to the diffractometer and carefully centering 12 strong reflections, the cell parameters, $a = 11.852$ (10) Å, $b = 14.962$ (5) Å, $c = 13.125$ (8) Å, $\beta = 92.27(8)°$, and $V = 2325.6$ Å³, at 25°, were obtained by a least-squares process.[8]

The density of the complex, found by flotation in an acetone–methylene iodide mixture, was 1.70 (1) g cm$^{-3}$ and agrees well with the calculated value of 1.702 g cm$^{-3}$ which would require 4 molecules of $C_{19}H_{25}BF_6N_6PRh$ (mol wt 596) per asymmetric unit.

Data were collected on the automatic diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ 0.71069 Å). A quarter sphere of intensities in the range $2\theta < 50°$ was collected by a $\theta$–2$\theta$ scanning procedure. The total step-scan width was 0.6° and the background counting time 15 sec. One hundred percent of the Mo K$\alpha$ peak was accepted by the pulse height analyzer. Instrumental and crystal instabilities were checked by monitoring 2 standard reflections every 100 reflections. The intensity of the two standards decreased by less than 2% during data collection and no scaling was applied to the data.

Of the 4096 reflections collected, 1448 reflections ($I > 3\sigma(I)$) were considered observed and corrected for Lorentz and polarization effects. No absorption correction was made; with the previously mentioned crystal dimensions and $\mu = 8.6$ cm$^{-1}$, the range in transmission factors is 89–93%.

**Structure Solution and Refinement.** Inspection of the three-dimensional Patterson synthesis revealed the position of the rhodium atom and a subsequent heavy-atom-phased Fourier synthesis clearly revealed the structure. The atoms of the cation were well-resolved but the fluorine atoms of the anion appeared to be slightly disordered. An initial attempt was made to refine the structure (isotropic thermal parameters, full matrix, using the scattering functions of ref 9 and an anomalous dispersion correction for rhodium[13]) with a disordered model for the $PF_6^-$ group, but this gave physically meaningless results in terms of bond lengths and angles. A difference map computed at

**Table I.** Positional[a] and Thermal Parameters[b] for $[(C_6H_6)RuB(pz)_4]PF_6$

| Atom | *x* | *y* | *z* | pp[c] | *U*, Å$^2$ |
|---|---|---|---|---|---|
| Ru | 0.0 | 0.3426 (1) | 0.5270 (1) | | |
| P | 0.25 | 0.4665 (5) | 0.25 | | |
| F(1) | 0.2451 (11) | 0.4634 (7) | 0.1426 (7) | | |
| F(2) | 0.25 | 0.3959 (9) | 0.25 | | |
| F(3) | 0.25 | 0.5367 (9) | 0.25 | | |
| F(4) | 0.1347 (9) | 0.4669 (7) | 0.2576 (8) | | |
| B | 0.0 | 0.1986 (12) | 0.4870 (20) | | |
| N(11) | 0.0 | 0.2698 (8) | 0.6192 (11) | | |
| N(12) | 0.0 | 0.2101 (8) | 0.5885 (11) | | |
| N(21) | 0.0 | 0.1314 (9) | 0.4653 (15) | | |
| N(22) | 0.0 | 0.1099 (9) | 0.3823 (13) | | |
| N(31) | 0.1043 (9) | 0.2905 (6) | 0.4536 (7) | | |
| N(32) | 0.0929 (9) | 0.2303 (6) | 0.4437 (7) | | |
| C(11) | 0.0 | 0.2690 (10) | 0.7109 (13) | | |
| C(12) | 0.0 | 0.2076 (11) | 0.7386 (18) | | |
| C(13) | 0.0 | 0.1739 (10) | 0.6574 (16) | | |
| C(21) | 0.0837 (26) | 0.0930 (15) | 0.5065 (20) | 0.5 | 5.0 (10) |
| C(22) | 0.0897 (30) | 0.0432 (13) | 0.4481 (27) | 0.5 | |
| C(23) | 0.0283 (28) | 0.0577 (16) | 0.3723 (22) | 0.5 | 6.0 (13) |
| C(31) | 0.1927 (13) | 0.3083 (8) | 0.4123 (8) | | |
| C(32) | 0.2337 (12) | 0.2552 (9) | 0.3723 (10) | | |
| C(33) | 0.1719 (12) | 0.2075 (8) | 0.3936 (9) | | |
| C(41) | 0.0529 (14) | 0.4265 (6) | 0.4644 (13) | | |
| C(42) | 0.1059 (13) | 0.4174 (7) | 0.5483 (11) | | |
| C(43) | 0.0542 (14) | 0.4074 (7) | 0.6325 (11) | | |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ru | 3.2 (1) | 3.9 (1) | 2.7 (1) | 0.0 | 0.0 | −0.3 (1) |
| P | 8.1 (8) | 8.5 (9) | 5.9 (5) | 0.0 | 3.0 (5) | 0.0 |
| F(1) | 11.7 (11) | 19.2 (14) | 5.8 (7) | 0.6 (11) | 1.7 (8) | 1.5 (9) |
| F(2) | 24.7 (29) | 9.9 (17) | 17.1 (21) | 0.0 | 7.8 (22) | 0.0 |
| F(3) | 11.4 (18) | 11.2 (18) | 15.9 (19) | 0.0 | −4.7 (15) | 0.0 |
| F(4) | 6.5 (9) | 22.7 (17) | 8.1 (9) | −0.7 (10) | 3.2 (7) | −1.0 (11) |
| B | 3.3 (16) | 3.1 (17) | 4.3 (19) | 0.0 | 0.0 | −1.5 (14) |
| N(11) | 3.5 (12) | 3.6 (12) | 2.8 (11) | 0.0 | 0.0 | −1.9 (9) |
| N(12) | 4.6 (13) | 3.7 (13) | 0.7 (9) | 0.0 | 0.0 | 0.4 (10) |
| N(21) | 10.8 (17) | 6.0 (13) | 1.6 (11) | 0.0 | 0.0 | −0.7 (12) |
| N(22) | 11.7 (20) | 2.9 (13) | 2.8 (13) | 0.0 | 0.0 | −0.2 (10) |
| N(31) | 3.4 (8) | 3.5 (8) | 1.8 (8) | 0.6 (7) | 0.0 (6) | 0.1 (6) |
| N(32) | 2.6 (7) | 4.4 (9) | 3.1 (8) | 1.2 (7) | −0.3 (6) | 0.8 (6) |
| C(11) | 2.4 (13) | 4.7 (16) | 2.0 (12) | 0.0 | 0.0 | −0.8 (12) |
| C(12) | 7.8 (21) | 5.3 (18) | 4.2 (15) | 0.0 | 0.0 | 1.7 (15) |
| C(13) | 6.0 (17) | 4.7 (18) | 3.3 (13) | 0.0 | 0.0 | −1.6 (13) |
| C(22) | 8.2 (31) | 3.1 (20) | 10.2 (37) | −3.4 (22) | 5.9 (28) | −2.7 (21) |
| C(31) | 4.7 (11) | 7.1 (12) | 0.7 (7) | 1.2 (10) | −0.3 (7) | −0.3 (8) |
| C(32) | 3.0 (11) | 7.7 (13) | 3.0 (10) | −0.7 (11) | −0.8 (8) | 0.7 (10) |
| C(33) | 2.7 (11) | 9.4 (14) | 1.9 (8) | 3.0 (11) | −0.3 (8) | 0.5 (9) |
| C(41) | 10.9 (17) | 2.8 (9) | 5.4 (11) | −2.1 (10) | 0.4 (12) | −0.6 (10) |
| C(42) | 6.6 (13) | 5.5 (12) | 5.2 (14) | −4.0 (10) | 0.5 (10) | −1.8 (9) |
| C(43) | 9.6 (17) | 3.9 (11) | 5.8 (13) | −0.4 (11) | −1.6 (11) | −1.8 (10) |

[a] The estimated standard deviations of the last digit are in parentheses. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2(U_{11}h^2 \cdot a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}hlb^*c^*)]$ were used for the ruthenium atom and the $PF_6$ group; the resulting thermal coefficients $U_{ij}$ (Å$^2$ × $10^2$), with standard deviations of the last significant figure given in parentheses, are tabulated above. [c] The population parameters are 1.0 except where they are quoted as 0.5.

this stage showed many small maxima in the $PF_6^-$ region, very diffuse maxima where pyrazolyl hydrogen atoms would be expected, and a clear maximum for the hydrogen bonded to boron. No allowance was made for hydrogen atoms in any of the calculations.

It was then decided to use an ordered model for the $PF_6^-$ ion and refine the fluorine atoms anisotropically. Full-matrix least-squares refinement with anisotropic thermal parameters for rhodium, phosphorus, and fluorine atoms converged with $R = 11.7\%$ ($R_w = 16.0\%$ for 1448 observed reflections). The weighting scheme adopted was identical with that used for the ruthenium compound. The standard deviation of an observation of unit weight is 1.2. The anisotropic thermal parameters of the fluorine atoms were anomalously large, consistent with disorder of the $PF_6^-$ group. In view of the suspected poor quality of the observed data, and our inability to refine an isotropic model for a disordered $PF_6^-$ group, we decided against further attempts at refinement as the structure of the cation had been, in any case, clearly established. A final difference synthesis showed features very similar to that found at an earlier stage, viz., small maxima of 1-2 e Å$^{-3}$ around the $PF_6^-$ group, diffuse maxima in

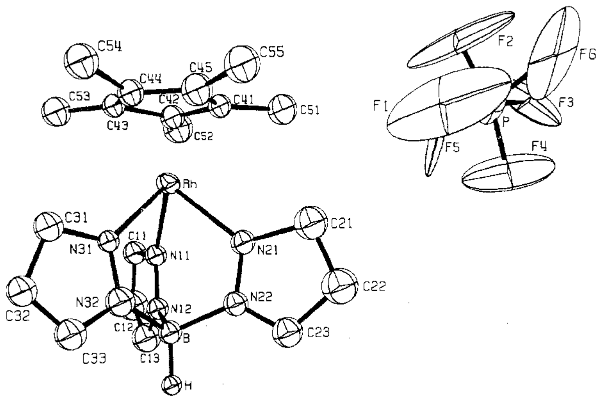

**Figure 2.** Perspective view with 50% probability ellipsoids of $[(\eta^5\text{-}C_5Me_5)RhHB(pz)_3]PF_6$ showing the molecular geometry and atomic numbering.

**Table II.** Positional[a] and Thermal Parameters[b] for $[(C_5Me_5)RhBH(pz)_3]PF_6$

| Atom | *x* | *y* | *z* | *U*, Å$^2$ |
|---|---|---|---|---|
| Rh | 0.2533 (3) | 0.0626 (2) | 0.1174 (2) | |
| P | 0.7495 (17) | 0.1207 (8) | 0.3829 (9) | |
| F(1) | 0.7339 (78) | 0.0956 (27) | 0.2715 (23) | |
| F(2) | 0.7149 (62) | 0.0307 (20) | 0.4123 (29) | |
| F(3) | 0.7583 (33) | 0.1467 (24) | 0.4966 (17) | |
| F(4) | 0.7557 (48) | 0.2134 (19) | 0.3519 (28) | |
| F(5) | 0.6327 (45) | 0.1393 (45) | 0.3989 (39) | |
| F(6) | 0.8681 (47) | 0.0876 (40) | 0.3807 (47) | |
| B | 0.2230 (44) | 0.2616 (27) | 0.0138 (26) | 2.7 (9) |
| N(11) | 0.1261 (28) | 0.1632 (19) | 0.1310 (17) | 2.7 (7) |
| N(12) | 0.1321 (30) | 0.2385 (19) | 0.0790 (17) | 2.7 (7) |
| N(21) | 0.3598 (29) | 0.1779 (18) | 0.1316 (18) | 2.8 (7) |
| N(22) | 0.3384 (30) | 0.2535 (19) | 0.0804 (18) | 2.9 (7) |
| N(31) | 0.2379 (26) | 0.1001 (17) | −0.0412 (17) | 2.1 (6) |
| N(32) | 0.2319 (32) | 0.1832 (21) | −0.0649 (21) | 4.0 (8) |
| C(11) | 0.0140 (35) | 0.1565 (26) | 0.1737 (23) | 3.5 (9) |
| C(12) | −0.0374 (52) | 0.2416 (33) | 0.1539 (33) | 6.6 (13) |
| C(13) | 0.0480 (48) | 0.2860 (30) | 0.0903 (29) | 5.1 (12) |
| C(21) | 0.4821 (42) | 0.1830 (29) | 0.1766 (27) | 4.9 (11) |
| C(22) | 0.5110 (46) | 0.2746 (31) | 0.1543 (30) | 5.6 (12) |
| C(23) | 0.4177 (40) | 0.3115 (27) | 0.0938 (25) | 4.1 (10) |
| C(31) | 0.2216 (34) | 0.0491 (23) | −0.1253 (22) | 3.5 (9) |
| C(32) | 0.2091 (37) | 0.1100 (26) | −0.2101 (24) | 3.6 (9) |
| C(33) | 0.2233 (40) | 0.1889 (26) | −0.1725 (26) | 4.1 (10) |
| C(41) | 0.3167 (33) | −0.0132 (22) | 0.2490 (21) | 2.7 (8) |
| C(42) | 0.1994 (35) | −0.0258 (24) | 0.2403 (23) | 3.2 (8) |
| C(43) | 0.1734 (33) | −0.0735 (26) | 0.1392 (20) | 2.7 (8) |
| C(44) | 0.2763 (36) | −0.0756 (24) | 0.0968 (22) | 3.2 (9) |
| C(45) | 0.3641 (40) | −0.0449 (28) | 0.1609 (26) | 4.6 (11) |
| C(51) | 0.3695 (40) | 0.0276 (27) | 0.3491 (26) | 4.7 (10) |
| C(52) | 0.1216 (43) | −0.0072 (31) | 0.3178 (28) | 5.6 (12) |
| C(53) | 0.0649 (41) | −0.0995 (27) | 0.0964 (27) | 4.5 (10) |
| C(54) | 0.3073 (40) | −0.1313 (27) | −0.0012 (26) | 4.6 (11) |
| C(55) | 0.4902 (40) | −0.0491 (30) | 0.1464 (26) | 5.1 (11) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Rh | 3.6 (2) | 2.5 (1) | 1.6 (1) | 0.1 (3) | 0.1 (1) | 0.5 (2) |
| P | 5.2 (10) | 5.9 (7) | 4.1 (5) | −2.1 (12) | −0.6 (5) | −0.4 (6) |
| F(1) | 72.8 (146) | 11.6 (33) | 3.9 (17) | −1.4 (52) | −1.2 (38) | −4.8 (19) |
| F(2) | 51.6 (123) | 2.2 (15) | 13.4 (32) | −2.4 (33) | 9.1 (44) | −3.2 (17) |
| F(3) | 12.6 (34) | 16.2 (30) | 4.9 (14) | 12.4 (30) | −1.6 (15) | −4.1 (17) |
| F(4) | 24.2 (72) | 4.9 (18) | 15.0 (32) | 5.8 (31) | 11.3 (36) | 0.1 (19) |
| F(5) | 6.8 (39) | 28.1 (72) | 24.1 (49) | −13.0 (58) | −0.1 (31) | −8.2 (48) |
| F(6) | 8.1 (42) | 21.7 (70) | 32.9 (69) | −12.1 (64) | 4.7 (39) | 2.0 (49) |

[a] The estimated standard deviations of the last digit are in parentheses. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were used for the rhodium atom and the $PF_6$ group; the resulting thermal coefficients $U_{ij}$ (Å$^2$ × $10^2$), with standard deviations of the last significant figure given in parentheses, are tabulated above.

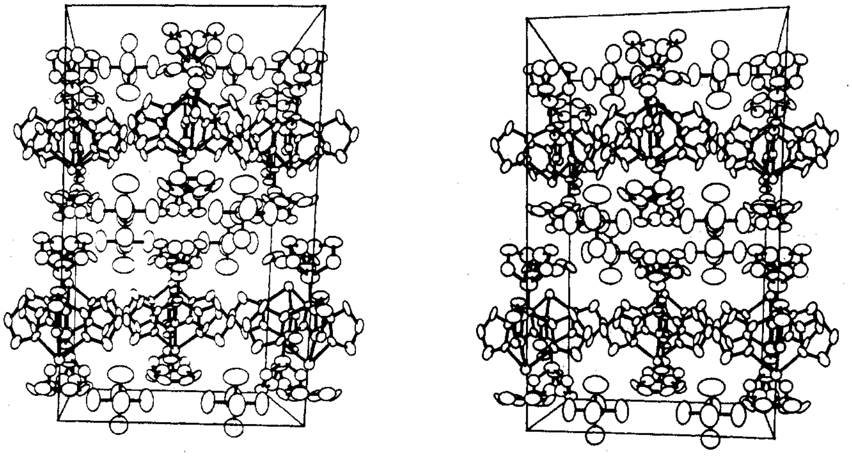

**Figure 3.** Stereoview of the molecular packing diagram of $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]PF_6$.

positions which would correspond to pyrazolyl hydrogens, and a clear maximum for the hydrogen bonded to boron.

## Results

The final atomic parameters for the ruthenium and rhodium compounds are given in Tables I and II, respectively. The molecular structures of the two compounds are shown in Figures 1 and 2. The packing diagrams are given in Figures 3 and 4. Tables III and IV list bond lengths and bond angles for the ruthenium and rhodium compounds, respectively.

**Table III.** Principal Intermolecular Bond Distances (A)[a] and Bond Angles (deg)[a] for $[(C_6H_6)RuB(pz)_4]PF_6$

(a) Distances from Ruthenium

| | | | |
|---|---|---|---|
| Ru-N(11) | 2.10 (2) | Ru-C(41) | 2.18 (2) |
| Ru-N(31) | 2.11 (2) | Ru-C(42) | 2.20 (2) |
| | | Ru-C(43) | 2.23 (2) |

(b) Distances within Tetrakis(1-pyrazolyl)borato Ligand

| | | | |
|---|---|---|---|
| B-N(12) | 1.52 (3) | N(11)-N(12) | 1.39 (3) |
| B-N(21) | 1.52 (3) | N(21)-N(22) | 1.31 (3) |
| B-N(32) | 1.57 (2) | N(31)-N(32) | 1.34 (2) |
| N(11)-C(11) | 1.35 (3) | C(11)-C(12) | 1.41 (3) |
| N(12)-C(13) | 1.29 (3) | C(12)-C(13) | 1.41 (3) |
| N(21)-C(21) | 1.54 (4) | C(21)-C(22) | 1.40 (5) |
| N(22)-C(23) | 1.22 (4) | C(22)-C(23) | 1.43 (5) |
| N(31)-C(31) | 1.39 (2) | C(31)-C(32) | 1.42 (2) |
| N(32)-C(33) | 1.39 (2) | C(32)-C(33) | 1.38 (2) |

(c) Distances within Benzene Ring

| | | | |
|---|---|---|---|
| C(41)-C(41′) | 1.43 (3) | C(42)-C(43) | 1.44 (2) |
| C(41)-C(42) | 1.44 (3) | C(43)-C(43′) | 1.46 (3) |

(d) Distances within Hexafluorophosphate Group

| | | | |
|---|---|---|---|
| P-F(1) | 1.58 (1) | P-F(3) | 1.55 (2) |
| P-F(2) | 1.56 (2) | P-F(4) | 1.56 (1) |

(e) Bond Angles

| | | | |
|---|---|---|---|
| N(11)-Ru-N(31) | 85.1 (5) | N(32)-N(31)-C(31) | 109.2 (12) |
| N(31)-Ru-N(31′) | 83.4 (5) | N(31)-C(31)-C(32) | 106.3 (14) |
| N(12)-B-N(32) | 109.1 (13) | C(31)-C(32)-C(33) | 107.4 (14) |
| N(21)-B-N(12) | 111.8 (21) | C(32)-C(33)-N(32) | 107.9 (15) |
| N(21)-B-N(32) | 110.5 (14) | N(21)-N(22)-C(23) | 117.0 (22) |
| N(32)-B-N(32′) | 105.8 (17) | N(22)-N(21)-C(21) | 99.7 (16) |
| Ru-N(11)-N(12) | 120.8 (12) | N(21)-C(21)-C(22) | 103.5 (26) |
| Ru-N(31)-N(32) | 121.1 (9) | C(21)-C(22)-C(23) | 105.8 (29) |
| Ru-N(11)-C(11) | 131.0 (14) | C(22)-C(23)-N(22) | 107.4 (28) |
| Ru-N(31)-C(31) | 129.7 (10) | C(41)-C(42)-C(43) | 121.3 (16) |
| B-N(12)-N(11) | 118.5 (17) | C(42)-C(43)-C(43′) | 118.9 (15) |
| B-N(32)-N(31) | 119.2 (13) | C(42)-C(41)-C(41′) | 119.7 (17) |
| B-N(12)-C(13) | 132.2 (20) | F(1)-P-F(2) | 87.5 (6) |
| B-N(32)-C(33) | 131.7 (15) | F(1)-P-F(4) | 91.7 (7) |
| B-N(21)-N(22) | 123.4 (20) | F(1)-P-F(3) | 92.5 (6) |
| B-N(21)-C(21) | 117.1 (17) | F(1)-P-F(1′) | 174.9 (11) |
| N(11)-N(12)-C(13) | 109.3 (16) | F(1)-P-F(4′) | 88.3 (7) |
| N(12)-N(11)-C(11) | 108.2 (16) | F(2)-P-F(4) | 90.3 (7) |
| N(11)-C(11)-C(12) | 107.5 (19) | F(2)-P-F(3) | 180.0 (21) |
| C(11)-C(12)-C(13) | 105.1 (21) | F(3)-P-F(4) | 89.7 (7) |
| C(12)-C(13)-N(12) | 109.9 (20) | F(4)-P-F(4′) | 179.4 (9) |
| N(31)-N(32)-C(33) | 109.1 (12) | | |

[a] The esd's shown in parentheses are right adjusted.

Table V gives the least-squares planes for the two compounds.

## Discussion

The $C_{3v}$ tridentate ligands tetrakis(1-pyrazolyl)borate, $B(pz)_4$, and hydrotris(1-pyrazolyl)borate, $BH(pz)_3$, have been treated successfully to yield derivatives $[(\eta^6\text{-}C_6H_6)RuB(pz)_4](PF_6)$ and $[(\eta^5\text{-}C_5Me_5)RhBH(pz)_3](PF_6)$ whose structures have been established by crystal structure analyses. Both complexes have conformational features which indicate that the (1-pyrazolyl)borate ligands retain $C_{3v}$ symmetry. The well-resolved $^1H$ NMR spectra of both cations (Experimental Section) are indicative of their expected diamagnetism. The spectra of the two complexes show the triplet and pair of doublets characteristic[14] of three equivalent coordinated pyrazole groups. In the case of the $RuB(pz)_4$ complex, a total of six pz resonances are observed at 35°C (relative areas 3:3:3:1:1:1) indicating that under these conditions the free and coordinated pyrazole groups do not interconvert. Both $\eta^6\text{-}C_6H_6$ and $\eta^5\text{-}C_5Me_5$ protons showed singlet resonance patterns. All resonance positions were to some extent solvent dependent, the largest effects being shown by the protons attached to the carbocyclic ligands.

In the molecular structure of $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]PF_6$, the coordination around the ruthenium atom in the cation is distorted octahedral (Figure 1). The central ruthenium atom is bonded directly to the three nitrogen atoms [N(11), N(31), N(31')] of the pyrazolyl groups, with a mean ruthenium–nitrogen bond distance of 2.11 (2) Å. The N–Ru–N angles have a mean value of 84.3 (0.5)° distorted from 90° by the bite of the pyrazolylborate ligand. The ruthenium atom is in addition π bonded to the $\eta^6$-benzene group with a mean Ru–C length of 2.20 (3) Å. This corresponds to the Ru atom being 1.67 Å from the benzene plane. The orientation of the benzene ring with respect to the three Ru-bonded nitrogen atoms of the poly(pyrazolyl) system is shown in Figure 5a; a fully staggered conformation is adopted similar to that found in analogous π-bonded benzene systems (e.g., benzenechromium tricarbonyl[15]).

**Table IV.** Principal Intermolecular Bond Distances (A)[a] and Bond Angles (deg)[a] for $[(C_5Me_5)RhBH(pz)_3]PF_6$

(a) Distances from Rhodium

| | | | |
|---|---|---|---|
| Rh-N(11) | 2.14 (3) | Rh-C(41) | 2.18 (4) |
| Rh-N(21) | 2.14 (3) | Rh-C(42) | 2.20 (3) |
| Rh-N(31) | 2.16 (3) | Rh-C(43) | 2.27 (4) |
| | | Rh-C(44) | 2.11 (4) |
| | | Rh-C(45) | 2.14 (4) |

(b) Distances within Hydrotris(1-pyrazolyl)borato Ligand

| | | | |
|---|---|---|---|
| B-N(12) | 1.44 (6) | N(11)-N(12) | 1.32 (4) |
| B-N(22) | 1.60 (6) | N(21)-N(22) | 1.34 (4) |
| B-N(32) | 1.57 (5) | N(31)-N(32) | 1.28 (4) |
| N(11)-C(11) | 1.47 (5) | C(11)-C(12) | 1.43 (6) |
| N(12)-C(13) | 1.24 (6) | C(12)-C(13) | 1.49 (8) |
| N(21)-C(21) | 1.55 (6) | C(21)-C(22) | 1.45 (6) |
| N(22)-C(23) | 1.29 (5) | C(22)-C(23) | 1.44 (6) |
| N(31)-C(31) | 1.35 (4) | C(31)-C(32) | 1.44 (5) |
| N(32)-C(33) | 1.42 (4) | C(32)-C(33) | 1.29 (5) |

(c) Distances within Pentamethylcyclopentadiene Group

| | | | |
|---|---|---|---|
| C(41)-C(42) | 1.40 (6) | C(41)-C(51) | 1.56 (5) |
| C(42)-C(43) | 1.53 (4) | C(42)-C(52) | 1.43 (6) |
| C(43)-C(44) | 1.36 (6) | C(43)-C(53) | 1.44 (6) |
| C(44)-C(45) | 1.39 (6) | C(44)-C(54) | 1.58 (5) |
| C(41)-C(45) | 1.39 (5) | C(45)-C(55) | 1.51 (7) |

(d) Distances within Hexafluorophosphate Group

| | | | |
|---|---|---|---|
| P-F(1) | 1.51 (3) | P-F(4) | 1.45 (3) |
| P-F(2) | 1.46 (4) | P-F(5) | 1.44 (6) |
| P-F(3) | 1.54 (3) | P-F(6) | 1.49 (6) |

(e) Bond Angles

| | | | |
|---|---|---|---|
| N(11)-Rh-N(21) | 80.9 (12) | C(42)-C(43)-C(44) | 102.4 (31) |
| N(11)-Rh-N(31) | 82.2 (10) | C(43)-C(44)-C(45) | 113.9 (30) |
| N(21)-Rh-N(31) | 84.3 (10) | C(44)-C(45)-C(41) | 107.5 (38) |
| N(12)-B-N(22) | 107.5 (26) | C(45)-C(41)-C(42) | 108.6 (31) |
| N(12)-B-N(32) | 106.4 (32) | C(51)-C(41)-C(42) | 119.0 (30) |
| N(22)-B-N(32) | 103.0 (31) | C(51)-C(41)-C(45) | 132.4 (37) |
| Rh-N(31)-N(32) | 119.2 (19) | C(52)-C(42)-C(41) | 125.6 (31) |
| Rh-N(31)-C(31) | 130.2 (21) | C(52)-C(42)-C(43) | 126.6 (37) |
| Rh-N(21)-N(22) | 122.7 (24) | C(53)-C(43)-C(42) | 127.8 (33) |
| Rh-N(21)-C(21) | 127.9 (23) | C(53)-C(43)-C(44) | 129.5 (29) |
| Rh-N(11)-N(12) | 120.2 (24) | C(54)-C(44)-C(43) | 125.8 (34) |
| Rh-N(11)-C(11) | 129.4 (23) | C(54)-C(44)-C(45) | 118.2 (37) |
| N(31)-N(32)-C(33) | 107.5 (27) | C(55)-C(45)-C(44) | 128.9 (34) |
| N(32)-N(31)-C(31) | 110.2 (25) | C(55)-C(45)-C(41) | 123.5 (34) |
| N(31)-C(31)-C(32) | 106.3 (29) | F(1)-P-F(2) | 90.1 (24) |
| C(31)-C(32)-C(33) | 106.0 (30) | F(1)-P-F(3) | 176.8 (40) |
| C(32)-C(33)-N(32) | 109.3 (33) | F(1)-P-F(4) | 88.4 (22) |
| N(21)-N(22)-C(23) | 112.3 (32) | F(1)-P-F(5) | 96.2 (41) |
| N(22)-N(21)-C(21) | 107.9 (30) | F(1)-P-F(6) | 88.8 (42) |
| N(21)-C(21)-C(22) | 101.3 (35) | F(2)-P-F(3) | 89.2 (21) |
| C(21)-C(22)-C(23) | 107.0 (41) | F(2)-P-F(4) | 166.7 (39) |
| C(22)-C(23)-N(22) | 110.9 (36) | F(2)-P-F(5) | 81.8 (39) |
| N(11)-N(12)-C(13) | 111.6 (34) | F(2)-P-F(6) | 88.5 (37) |
| N(12)-N(11)-C(11) | 109.0 (30) | F(3)-P-F(4) | 91.6 (20) |
| N(11)-C(11)-C(12) | 104.8 (35) | F(3)-P-F(5) | 80.6 (26) |
| C(11)-C(12)-C(13) | 101.8 (43) | F(3)-P-F(6) | 94.3 (29) |
| C(12)-C(13)-N(12) | 112.2 (39) | F(4)-P-F(5) | 85.2 (35) |
| C(41)-C(42)-C(43) | 107.4 (30) | F(4)-P-F(6) | 104.7 (34) |
| | | F(5)-P-F(6) | 169.1 (35) |

[a] The esd's shown in parentheses are right adjusted.

In similar fashion, the rhodium coordination in the cation of the $[(\eta^5\text{-}C_5Me_5)RhBH(pz)_3]PF_6$ complex is distorted

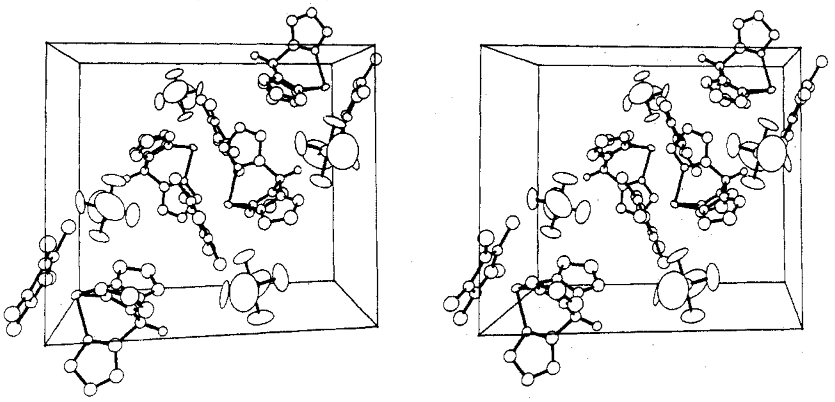

Figure 4. Stereoview of the molecular packing diagram of $[(\eta^5\text{-}C_5Me_5)RhHB(pz)_3]PF_6$.

Table V. Least-Squares Planes[a] within the $[(C_6H_6)RuB(pz)_4]^+$ and $[(C_5Me_5)RhBH(pz)_3]^+$ Cations and Deviations (Å) of Atoms Therefrom

(a) Ruthenium Cation

Plane a: C(41), C(42), C(43), C(41′), C(42′), C(43′)
Equation: $0.986Y + 0.168Z = 10.414$
C(41), −0.003; C(42), 0.007; C(43), −0.004; C(41′), −0.003; C(42′), 0.007; C(43′), −0.004; Ru, 1.67

Plane b: N(21), N(22), C(21), C(22), C(23)
Equation: $0.775X + 0.484Y - 0.407Z = -1.254$
N(21), −0.13; N(22), 0.14; C(21), 0.09; C(22), −0.03; C(23), −0.06

Plane c: N(31), N(32), C(31), C(32), C(33)
Equation: $0.507X - 0.165Y + 0.846Z = 5.317$
N(31), −0.012; N(32), 0.005; C(31), 0.014; C(32), −0.011; C(33), 0.004

(b) Rhodium Cation

Plane a: C(41), C(42), C(43), C(44), C(45)
Equation: $-0.112X + 0.901Y - 0.420Z = -1.947$
C(41), −0.007; C(42), 0.023; C(43), −0.033; C(44), 0.032; C(45), −0.015; Rh, 1.82; C(51), −0.074; C(52), −0.044; C(53), −0.006; C(54), −0.223; C(55), −0.163

Plane b: N(11), N(12), C(11), C(12), C(13)
Equation: $-0.380X - 0.404Y - 0.832Z = -2.913$
N(11), −0.046; N(12), 0.030; C(11), 0.043; C(12), −0.027; C(13), 0.001

Plane c: N(21), N(22), C(21), C(22), C(23)
Equation: $-0.428X + 0.335Y + 0.840Z = 0.493$
N(21), 0.048; N(22), −0.037; C(21), −0.042; C(22), 0.025; C(23), 0.006

Plane d: N(31), N(32), C(31), C(32), C(33)
Equation: $0.995X + 0.029Y - 0.094Z = 2.154$
N(31), 0.024; N(32), −0.040; C(31), 0.002; C(32), −0.028; C(33), 0.042

[a] The orthogonal vectors $X$, $Y$, $Z$ are related to the unit cell vectors $a$, $b$, $c$ as follows: $X$ is parallel to $a$, $Y$ is perpendicular to the $ac$ plane, and $Z$ is in the $ac$ plane perpendicular to $a$.

octahedral. Three nitrogen atoms [N(11), N(21), N(31)] of the pyrazolyl rings coordinate to the rhodium atom (mean Rh–N distance 2.15 (3) Å) while the $\eta^5$-pentamethylcyclopentadiene group completes the coordination, with a mean Rh–C length of 2.18 (6) Å corresponding to a Rh–$C_5$ plane distance of 1.82 Å. The mean N–Rh–N angle of 82.5 (1.2)° is not significantly different from that found in the ruthenium complex. In the $C_5Me_5$ system, although the ring atoms are coplanar, four of the methyl groups are significantly displaced from this plane away from the poly(1-pyrazolyl)borate ligand. This distortion comes about to relieve intramolecular interactions between the pyrazolyl groups and the methyl carbons. A view of the orientation of the $C_5Me_5$ system with respect to the poly(1-pyrazolyl)borate cage is given in Figure 5b. Methyl carbon C(53) is not involved in any close contacts with the pyrazolyl groups and is essentially coplanar with the $C_5$ ring. The remaining four methyl carbon atoms C(51), C(52), C(54), and C(55) make contacts in the ranges C(methyl)···C(pyrazolyl) = 3.29–3.54 Å and C(methyl)···N = 3.54–3.70 Å which would have been much shorter in the absence of out-of-plane bending of the C(cyclopentadienyl)–C(methyl) bonds. It may also be seen from Figure 5b that there is some distortion of the pyrazolyl framework as a result of intraion overcrowding. Thus one might have expected the projections of Rh–N(11)–C(11), Rh–N(21)–C(21), and Rh–N(31)–C(31) to be linear; Figure 5b shows that these are clearly nonlinear and implies a slight twisting of the pyrazolyl rings relative to the metallo[2.2.2] cage as

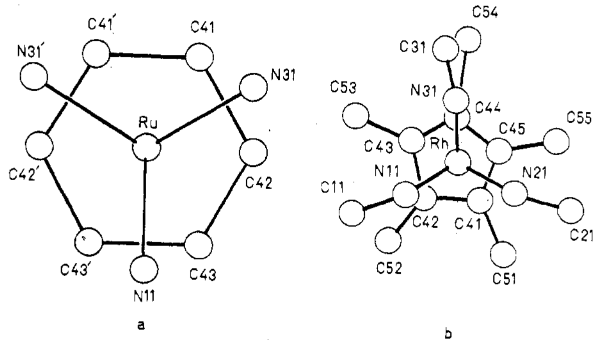

Figure 5. View of the central region of the $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]^+$ (a) and $[(\eta^5\text{-}C_5Me_5)RhHB(pz)_3]^+$ (b) cations projected onto the plane of the $\eta^6$-benzene and the $\eta^5$-pentamethylcyclopentadienyl rings, respectively, so as to show the mutual orientation of the ring and the nitrogens bonded to the metal ion.

Table VI. Metallo[2.2.2] Ring System for Various Poly(1-pyrazolyl)borate Complexes

| No.[a] | Compd | M–N[b] | B–N | N–N | N–C | C–C |
|---|---|---|---|---|---|---|
| 1 | $[HB(pz)_3]_2Co$ | 2.129 (7) | 1.544 (21) | 1.364 (3) | 1.335 (15) | 1.386 (24) |
| 2 | $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]PF_6$ | 2.105 (7) | 1.54 (3) | 1.35 (4) | 1.36 (1) | 1.41 (2) |
| 3 | $[(\eta^5\text{-}C_5Me_5)RhBH(pz)_3]PF_6$ | 2.15 (1) | 1.54 (9) | 1.31 (3) | 1.39 (12) | 1.42 (7) |
| 4 | $H_2B(Me_2pz)_2(\eta^3\text{-}C_7H_7)(CO)_2Mo$ | 2.20 (3) | 1.540 (15) | 1.376 (8) | 1.346 (10) | 1.399 (15) |
| 5 | $(\eta^5\text{-}C_5H_5)MoB(pz)_4(CO)_2$ | 2.21 (4) | 1.54 (3) | 1.35 (3) | 1.37 (17) | 1.40 (0) |
| 6 | $BH(pz)_3Mo(CO)_2NNC_6H_5$ | 2.218 (12) | 1.541 (19) | 1.368 (9) | 1.339 (10) | 1.394 (16) |
| 7 | $H_2B(Me_2pz)_2Mo(CO)_2(\eta^3\text{-}C_3H_5)$ | 2.21 (6) | 1.542 (7) | 1.36 (16) | 1.354 (10) | 1.38 (2) |

[a] Source: **1**, ref 16; **2** and **3**, this work; **4**, ref 17; **5**, ref 18; **6**, ref 19; **7**, ref 20. [b] Mean bond distances (Å) are quoted.

a result of C(methyl)···C(pyrazolyl) interactions. Another way of describing this twist is via the torsion angles Rh–N(11)–N(12)–B, Rh–N(21)–N(22)–B, and Rh–N(31)–C(32)–B which would be zero in the absence of any deformation; the values here are −2.5, 5.8, and −6.3°, respectively. In the Ru complex, there is no intraion overcrowding and no distortion of the [2.2.2] cage. (Compare torsion angles Ru–N(11)–N(12)–B = 0° and Ru–N(31)–N(32)–B = 0.4°.)

In both complexes, the boron atoms exhibit tetrahedral coordination with N–B–N angles in the range 106–112 (1)° for the Ru complex and 103–108 (3)° in the Rh complex.

A comparison of bond distances for the unique metallo-[2.2.2] ring system for a number of poly(1-pyrazolyl)borate–metal complexes is given in Table VI. As can be seen the bond lengths and angles obtained for the two complexes under study are in good agreement with those previously reported.

Each of the pyrazolyl rings in the ruthenium and rhodium compounds is planar within the limits of experimental error as seen in Table V. The mean bond lengths and angles for the pyrazolyl systems in the two complexes are essentially the same and are also in reasonable agreement with structural values obtained for other compounds as indicated in Table VI. In particular, the pyrazolyl bonding in the ruthenium complex is quite similar to that found for $[HB(pz)_3]_2Co$.[2b] As has been noted for the $[HB(pz)_3]_2Co$ structure,[2b] the N–N bonds of the pyrazolyl rings are not parallel to the M–B axis but are slanted toward the boron atoms since the B–N bond distances are shorter than the M–N distances. The average intraligand N(1)···N(1′) contact is 2.85 (2) Å while the N(2)···N(2′) contact is shorter (2.51 (2) Å). The corresponding mean distances in the rhodium complex are 2.83 (6) and 2.45 (4) Å.

The molecular packing within the crystal lattice is seen in Figures 3 and 4 for the ruthenium and rhodium complexes, respectively. The individual $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]$ and $[\eta^5\text{-}C_5Me_5)RhBH(pz)_3]$ cations as well as the $PF_6$ anions are all separated by normal van der Waals distances. All interion contacts less than 3.5 Å were calculated for both complexes. The shortest contacts were in the Ru complex and involved the disordered pyrazolyl group (i.e., C(21)···C(22) = 3.07 (4) Å involving a molecule at $x$, $y$, $z$ and another at $x$, $-y$, $1 - z$).

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**Registry No.** $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]PF_6$, 52015-89-1; $[(\eta^5\text{-}C_5Me_5)RhBH(pz)_3]PF_6$, 52015-82-4; $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, 37366-09-9; $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$, 12354-85-7.

**Supplementary Material Available.** Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material for this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50439U-12-75.

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(12) It is, of course, possible that the "true" space group is *C2cb* and that the apparent *m* symmetry of the cation and the fact that the $PF_6^-$ ion happens to lie on what is a twofold special position in space group *Cmca* are merely coincidental; however little would be gained and computing costs much increased by a *C2cb* refinement.

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