Structural Evidence for a New Type of π-Arene Complex containing Poly-(1-pyrazolyl)borate Ligands and Carbocyclic π-Acceptor Ligands. X-Ray Analysis of [Tetrakis-(1-pyrazolyl)borato](h^6-benzene)ruthenium(II) Hexafluorophosphate

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Summary Crystal structure analysis of $\{(C_6H_6)Ru[B(pz)_4]\}^+PF_6^-$ where $B(pz)_4$ represents the tetrakis-(1-pyrazolyl)borate group, has shown that the $B(pz)_4$ ligand is tridentate and the benzene ring is hexahapto.

A number[1–4] of structural studies have been reported on polypyrazolyl complexes of transition metal complexes. These have involved the poly-(1-pyrazolyl)borate ligand alone, *e.g.*, $[HB(pz)_3]_2Co$[1] [where (pz) = 1-pyrazolyl], and also in conjunction with carbonyl, *e.g.*, $B(pz)_4(C_5H_5)(CO)_2Mo$[2] or arylazo co-ligands, *e.g.*, $HB(pz)_3Mo(CO)_2NNPh$.[3] π-Arene complexes containing only one cyclopentadienyl (or similar) ligand and one poly(pyrazolyl)borate or poly-(pyrazolyl)methane ligand,[5] have recently been prepared.[6] We have examined the compounds $\{(C_5H_5)Co[B(pz)_4]\}^+ I^-$, $\{(C_5H_5)Co[B(pz)_4]\}^+B(C_6H_5)_4^-$, $\{(C_5Me_5)Rh[HB(pz)_3]\}^+PF_6^-$, and $\{(C_6H_6)Ru[B(pz)_4]\}^+PF_6^-$, and report here the results of a single crystal *X*-ray study of the lattermost compound, the first true example of a π-arene compound between poly(1-pyrazolyl)boratoruthenium and benzene.

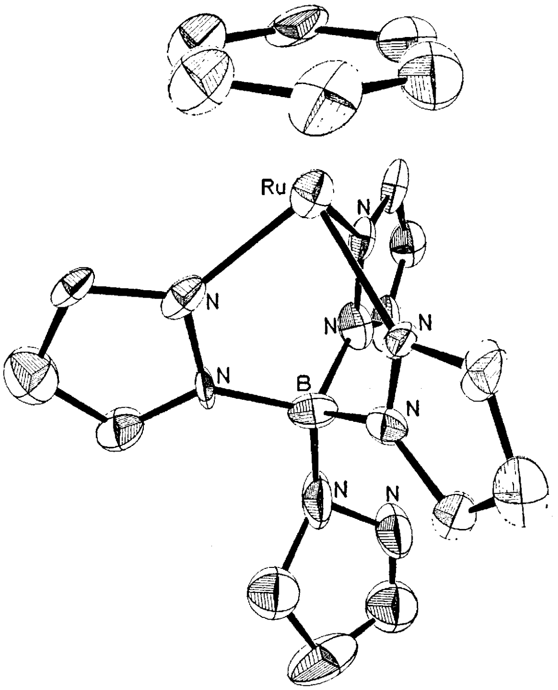

FIGURE. A view of the $\{(C_6H_6)Ru[B(pz)_4]\}^+$ ion. The benzene ring is fully staggered with respect to the RuN_3 group. The thermal ellipsoids are at the 50% probability level.

The crystals consist of discrete, well-separated $\{(C_6H_6)Ru[B(pz)_4]\}^+$ cations which have crystallographic *m*-symmetry (Figure) and $[PF_6^-]$ anions with crystallographic 2-fold symmetry. The poly-(1-pyrazolyl)borate group acts as a tridentate ligand bonded to the ruthenium while the benzene ring is hexahapto. Nitrogen co-ordination to the ruthenium has resulted in a metallo[2,2,2] ring system with mean distances Ru–N 2·107(15), N–N 1·37(2), and N–B 1·52(3) Å. The Ru–C (benzene) distances do not differ significantly from their mean value, 2·20(2) Å. The ruthenium co-ordination may be considered distorted octahedral with the N–Ru–N angles having a mean value 83·8(5)°, distorted from 90° by the bite of the ligand, whereas at the boron atom regular tetrahedral co-ordination occurs with no N–B–N angle significantly different from the mean 109·1(16)°. These angles and bond lengths for the poly-[(1-pyrazolyl)borate ligand are in excellent agreement with those reported for bis[hydrotris-(1-pyrazolyl)borato]cobalt-(II).[1]

Lath-like crystals of $\{(C_6H_6)Ru[B(pz)_4]\}^+$ PF_6^- suitable for crystallographic study were obtained on recrystallization of the powder from acetone–methylene dichloride mixtures. The crystals are orthorhombic with unit cell parameters $a = 13·472(5)$, $b = 22·034(4)$, $c = 14·718(2)$ Å. The systematic absences indicated that the space group was either the centrosymmetric *Cmca* or noncentrosymmetric *C2cb*. $D_m = 1·84$ g/ml, consistent with 8 formula units of $C_{18}H_{18}BF_6N_8PRu$ in the unit cell. Three dimensional intensity data were collected (Mo-K_α radiation) with a Hilger and Watts Y-290 computer controlled diffractometer. With 8 formula units in the unit cell, space group *C2cb* makes no symmetry demands, whereas in *Cmca* the $\{(C_6H_6)Ru[B(pz)_4]\}^+$ ion must have *m* symmetry. The structure solution was carried out by the heavy atom method initially in the non-centrosymmetric, *C2cb*, space group. The first heavy-atom-phased electron-density distribution clearly revealed the complete structure and showed convincingly that the cation had *m*-symmetry and also that the PF_6^- ion had 2-fold crystallographic symmetry. Subsequent refinement was in the centrosymmetric space group *Cmca*. During the course of this refinement it became apparent that the uncomplexed pyrazolyl group was slightly disordered and allowance was made for this; all other positional and thermal parameters refined satisfactorily.† At the conclusion of full-matrix anisotropic refinement $R = 0·060$ for the 742 reflexions which had intensities greater than 3σ(I).

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† It is, of course, possible that the "true" space group is C2*cb* and that the apparent *m* symmetry of the cation and the fact that the PF_6^- ion happens to lie on what is a 2-fold special position in space group *Cmca*, are merely coincidental; however, little would be gained and computing costs much increased, by a *C2cb* refinement.

[1] M. R. Churchill, K. Gold, and C. E. Maw, *Inorg. Chem.*, 1970, **9**, 1597.
[2] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127.
[3] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, B27, 725.
[4] F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J.C.S. Chem. Comm.*, 1972, 777; F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, 1972, **6**, 543; C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Cryst.*, 1971, **B27**, 1859.
[5] S. Trofimenko, *Accounts Chem. Res.*, 1971, **4**, 17; S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
[6] D. J. O'Sullivan and F. J. Lalor, *J. Organometallic Chem.*, **1973**, in the press.