

uptake was calculated from the change of gas volume by time. The amount of ethylbenzene was measured after a few percent of $\text{HCo}(\text{CO})_4$ conversion by gas chromatography (Hewlett-Packard 5830/A, SE 30 10-m glass capillary column, 40 °C, 2 mL of Ar/min) from the reaction mixtures after being quenched with pyridine. An aluminum foil covered reaction vessel was used to run the reaction in darkness.

The 2,4-dinitrophenylhydrazone was prepared by adding 10% molar excess of perchloric acid stabilized 2,4-dinitrophenylhydrazine in water to the reaction mixture followed by cooling overnight in the refrigerator and filtration of the precipitate.

The PPh_3 -substituted acylcobalt carbonyls were prepared by adding 20% molar excess of PPh_3 (based on Co) in heptane

to the product mixture after the $\text{Co}_2(\text{CO})_8$ crystals have been removed at -78 °C. Pale yellow crystals formed overnight.

The infrared spectra were made after $\text{Co}_2(\text{CO})_8$ has been removed by crystallization at -78 °C, from the pale yellow supernatant solution with compensation of the solvent, styrene, and traces of remaining $\text{Co}_2(\text{CO})_8$.

Registry No. $\text{PhCH}=\text{CH}_2$, 100-42-5; $\text{HCo}(\text{CO})_4$, 16842-03-8; PhCH_2CH_3 , 100-41-4; $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_4$, 82182-04-5; CO , 630-08-0; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{PhCH}(\text{CH}_3)\text{CHO}$, 93-53-8; $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_3(\text{PPh}_3)$, 82182-05-6; $\text{PhCH}(\text{CH}_3)\text{CHO}$ 2,4-dinitrophenylhydrazone, 5530-36-9; $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_3(\text{PPh}_3)$, 82182-06-7; $\text{PhCH}_2\text{CH}_2\text{CHO}$, 104-53-0; $\text{PhCH}_2\text{CH}_2\text{CHO}$ 2,4-dinitrophenylhydrazone, 1237-68-9; $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_4$, 82182-07-8.

Stereochemically Nonrigid Bis(olefin)rhodium Poly(1-pyrazolyl)borato Complexes. 1. Synthesis and Conversion into New Rhodium(I) and Rhodium(III) Complexes. The Crystal and Molecular Structure of (Tetrakis(1-pyrazolyl)borato)diodocarbonylrhodium(III) Methylene Chloride Solvate

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The bis(olefin)rhodium(I) poly(1-pyrazolyl)borato complexes $\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$, 1, $\text{HB}(\text{pz})_3\text{Rh}(\text{cod})$, 2, and $\text{B}(\text{pz})_4\text{Rh}(\text{LL})$ ($\text{LL} = (\text{C}_2\text{H}_4)_2$, 3; $\text{LL} = \text{cod}$, 4; $\text{LL} = \text{nbd}$, 5; $\text{LL} = \text{duroquinone}$, 6) and related species have been prepared, and their physical and chemical properties have been investigated. ¹H NMR measurements in CDCl_3 at room temperature indicate rapid exchange of all pyrazolyl groups of $\text{B}(\text{pz})_4$ in 3-5. In 6, pyrazolyl group exchange is slow at room temperature but rapid at 85 °C. The olefin ligands in 1, 2, 4 and 6 are kinetically labile and are displaced by CO at atmospheric pressure to give the new rhodium(I) carbonyl complexes $[\text{RB}(\text{pz})_3]\text{Rh}_2(\text{CO})_3$ (8, $\text{R} = \text{H}$; 9, $\text{R} = \text{pz}$). A structure involving three μ -CO ligands is proposed for these complexes on the basis of IR data. 9 reacts with iodine to give the Rh(III) complex $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ (14) and similar complexes have been isolated from the reaction of 8 with Cl_2 and I_2 and of 9 with Br_2 and $\text{C}_3\text{F}_7\text{I}$. Lewis bases displace CO from the Rh(III) complexes, e.g., with triphenylphosphine 14 yields $\text{B}(\text{pz})_4\text{RhI}_2(\text{PPh}_3)$ (17). Crystals of $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ (14) are monoclinic of space group $C2/c$ with eight molecules in a unit cell of dimensions $a = 22.713$ (2) Å, $b = 12.249$ (2) Å, $c = 15.211$ (2) Å, and $\beta = 94.29$ (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations; $R = 0.066$ for 4061 reflections with $I > 3\sigma(I)$. There is disorder (2/3:1/3) of one of the iodine atoms and the CO ligand. The rhodium atom has octahedral coordination. The nondisordered Rh-I bond has a length of 2.634 (1) Å, and the $\text{B}(\text{pz})_4\text{Rh}$ moiety has normal geometry with $\text{Rh-N} = 2.039$ -2.082 (7) Å.

Introduction

Two important groups of bis(olefin)rhodium(I) complexes are typified by the four-coordinate, 16-electron, 2,4-pentanedionato derivative $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$ and the five-coordinate, 18-electron, η -cyclopentadienyl species $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$, respectively. The contrasting structural²⁻⁵ and chemical⁵⁻⁸ properties of these and related

complexes have received much attention in recent years. (Hydrotris(1-pyrazolyl)borato)bis(ethylene)rhodium(I), $\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$ ($\text{pz} = 1$ -pyrazolyl, 1; originally described by Trofimenko⁹) is a potential bridge between the two groups of olefin complexes described above. The hydrotris(1-pyrazolyl)borato ligand may function as a bidentate ligand (resembling *acac*) or in a tridentate fashion (formally analogous to cyclopentadienide).¹⁰ Thus complex 1 may exist as a four-coordinate, 16-electron square-coplanar rhodium(I) complex, 1a, or as a trigonal-bipyramidal five-coordinate 18-electron species, 1b. In solution a dy-

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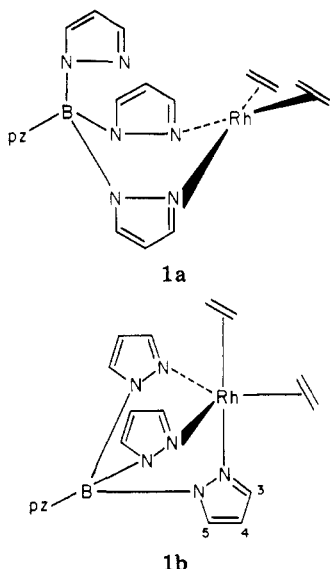
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amic **1a** → **1b** interconversion is also possible and has been observed in related systems (e.g., $B(pz)_4Pt(CH_3)(CO)^{11}$). The 1H NMR spectrum of **1** showed that all three pyrazolyl groups were equivalent on the NMR time scale, as were all ethylene protons.⁹ Complex **1** must therefore be stereochemically nonrigid. However the available evidence did not give any information on the nature of the dynamic processes involved, nor did it indicate which of the possible static structures, **1a** or **1b**, is lower in energy. We describe here the synthesis of a variety of bis(olefin)rhodium(I) complexes of the type $RB(pz)_2Rh(LL)$ ($R = H$ or pz ; $LL = (C_2H_4)_2$ or a chelating unconjugated bis(olefin)) and their use as starting materials for the preparation of new rhodium(I) and rhodium(III) poly(1-pyrazolyl)borato complexes. The crystal and molecular structure of a representative example of the latter, $B(pz)_4RhI_2(CO)$, is also discussed. In subsequent papers we will describe the X-ray crystallographic characterization of three of the bis(olefin)rhodium(I) polypyrazolylborato complexes¹² and present a detailed NMR study of their dynamic properties in solution.¹³ Some of the material described here has previously appeared in an abbreviated form.¹⁴

Experimental Section

Potassium salts of the dihydrobis-, hydrotris- and tetrakis(1-pyrazolyl)borate anions were prepared as described by Trofimenko.¹⁵ The olefin complexes $[(C_2H_4)_2RhCl]_2$,¹⁶ $[(cod)RhCl]_2$ ¹⁷ ($cod = 1,5$ -cyclooctadiene), $[(nbd)RhCl]_2$ ¹⁸ ($nbd = norbornadiene$), and $[(dq)RhCl]_2$ ¹⁹ ($dq = duroquinone$), as well as $[(CO)_2RhCl]_2$ ²⁰ were synthesized by literature procedures. The preparation of $HB(pz)_3Rh(C_2H_4)_2$ has been described by Trofimenko.⁹ All other reagents and solvents were commercial samples and were used as received. IR spectra were recorded on Perkin-Elmer 257 and 457 spectrophotometers and were calibrated with respect to the spectrum of a standard polystyrene film. Proton NMR spectra

were determined on a Perkin-Elmer/Hitachi R20A instrument operating at 60 MHz. Microanalyses were by the staff of the microanalytical laboratory of University College, Cork, Republic of Ireland.

Thallium(I) Tetrakis(1-pyrazolyl)borate. Saturated aqueous solutions of thallos formate (5.77 g, 23.15 mmol) and $KB(pz)_4$ (7.36 g, 23.15 mmol) were mixed at room temperature. The resulting thick white precipitate was collected by filtration, washed with water and ethanol, and dried in vacuo over P_2O_5 . The yield of $TlB(pz)_4$ was 8.2 g (73%); mp 203–207 °C; 1H NMR ($CDCl_3$, Me_4Si) τ 2.38 (s, 4 H), 2.62 (d, $J = 2.55$ Hz, 4 H), 3.72 (t, $J = 1.95$ Hz, 4 H). Anal. Calcd: C, 29.80; H, 2.48; N, 23.18. Found: C, 29.51; H, 2.53; N, 23.69.

Preparation of $B(pz)_4Rh(C_2H_4)_2$ (2). Solid $TlB(pz)_4$ (0.615 g, 1.27 mmol) was added portionwise over 15 min to a stirred solution of $[(C_2H_4)_2RhCl]_2$ (0.25 g, 0.64 mmol) in 40 mL of dry ether and 10 mL of dry tetrahydrofuran at -70 °C under a nitrogen atmosphere. The solution was stirred for 10 min at -70 °C and then allowed to warm to room temperature over 15 min. After rapid filtration under nitrogen the solvent was removed in vacuo at 40 °C to give a pale yellow unstable solid which was characterized by means of its 1H NMR spectrum (see Discussion).

Preparation of $B(pz)_4Rh(dq)$ (6) and Related Compounds. A solution of $[(dq)RhCl]_2$ (0.90 g, 1.5 mmol) and $KB(pz)_4$ (0.94 g, 3.0 mmol) in ca. 20 mL of *N,N*-dimethylformamide was stirred under nitrogen for ca. 24 h and then poured into ca. 100 mL of water. The mixture was extracted with CH_2Cl_2 until the extracts were colorless. The combined extracts were washed thoroughly with water, dried ($MgSO_4$), and reduced to small volume in vacuo. The concentrated solution was poured onto a 3×16 cm column of neutral alumina. Washing the column with CH_2Cl_2 under gentle suction (water pump) eluted a yellow band containing a little duroquinone. Further elution with methanol removed the main product, orange $B(pz)_4Rh(dq)$, which was further purified by recrystallization from CH_2Cl_2 -hexane; yield 1.19 g (73%). The complexes $HB(pz)_3Rh(cod)$ (2), $B(pz)_2Rh(cod)$ (4), $B(pz)_4Rh(nbd)$ (5), and $H_2B(pz)_2Rh(cod)$ (7) were prepared in a similar fashion²¹ omitting the chromatography step (yields 80–90%).

Preparation of $[HB(pz)_3]_2Rh_2(CO)_3$ (8) and Related Compounds. Method A. $HB(pz)_3Rh(C_2H_4)_2$ (0.18 g, 0.48 mmol) or $HB(pz)_3Rh(cod)$ (0.20 g, 0.47 mmol) were dissolved in ca. 300 mL of dry benzene, and a slow stream of CO was passed through the stirred solution for 24 h. Solvent was removed in vacuo, and the pale greenish-yellow product was washed with benzene and CH_2Cl_2 and dried in vacuo over P_2O_5 ; yield 0.14 g (82%).

Method B. A solution of $[(CO)_2RhCl]_2$ (0.40 g, 1.03 mmol) in the minimum volume of CH_2Cl_2 was treated dropwise under nitrogen with a concentrated methanolic solution of $KHB(pz)_3$ (0.52 g, 2.06 mmol). The resulting greenish yellow precipitate was collected by filtration, washed with water, acetone, and ether, and dried in vacuo over P_2O_5 ; yield 0.42 g (63%). The analogous complex, $B(pz)_4Rh_2(CO)_3$ (9) was prepared from $[(cod)RhCl]_2$ (97% yield) or $[(dq)RhCl]_2$ (65% yield) by method A. Treatment of $H_2B(pz)_2Rh(cod)$ (7) with CO according to method A yielded $H_2B(pz)_2Rh(CO)_2$ (10) in ca. 70% yield.

Preparation of $HB(pz)_3RhI_2CO$ (12) and Related Compounds. An ethereal solution of iodine (0.35 g, 1.40 mmol) was added dropwise under nitrogen to a rapidly stirred suspension of $[HB(pz)_3]_2Rh_2(CO)_3$ (0.5 g, 0.7 mmol) in ca. 30 mL of CH_2Cl_2 . The reaction mixture was stirred overnight at room temperature and filtered and the solvent removed in vacuo. The dark red crystalline residue was washed with water, dried *in vacuo* over P_2O_5 , and recrystallised from CH_2Cl_2 -hexane; yield 0.75 g (90%). The complexes $HB(pz)_3RhCl_2(CO)$ (11), $B(pz)_4RhBr_2(CO)$ (13), $B(pz)_4RhI_2(CO)$ (14), and $B(pz)_4RhI(C_3F_7)(CO)$ (15) were prepared similarly in 75–90% yield except that for **15** an excess of C_3F_7I was employed. 1H NMR ($CDCl_3$, Me_4Si): **12**, δ 8.54 (d, $J = 2.55$ Hz, 1 H; H3/5 of pyrazolyl group trans to CO), 8.06 (d, $J = 1.65$ Hz, 2 H; H3/5 of pyrazolyl groups trans to I), 7.77 (d, $J = 2.25$ Hz, 3 H; 5/3 of pyrazolyl groups), 6.32 (t, $J = 2.40$ Hz, 3 H; H4

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Table II. Interatomic Distances (Å) and Angles (Deg) for 14

(a) Bond Lengths					
Rh-I(1)	2.634 (1)	N(22)-C(23)	1.38 (1)	C(24)-C(25)	1.36 (1)
Rh-I(2)	2.649 (1)	N(31)-N(32)	1.36 (1)	C(33)-C(34)	1.37 (1)
Rh-I(3)	2.521 (2)	N(31)-C(35)	1.34 (1)	C(34)-C(35)	1.41 (1)
Rh-N(11)	2.039 (7)	N(32)-C(33)	1.33 (1)	C(43)-C(44)	1.36 (2)
Rh-N(21)	2.082 (7)	N(41)-N(42)	1.39 (1)	C(44)-C(45)	1.35 (2)
Rh-N(31)	2.075 (7)	N(41)-C(45)	1.42 (1)	B-N(12)	1.52 (1)
N(11)-N(12)	1.36 (1)	N(42)-C(43)	1.26 (2)	B-N(22)	1.56 (1)
N(11)-C(15)	1.32 (1)	C(13)-C(14)	1.33 (2)	B-N(32)	1.55 (1)
N(12)-C(13)	1.36 (1)	C(14)-C(15)	1.36 (2)	B-N(41)	1.49 (1)
N(21)-N(22)	1.34 (1)	C(23)-C(24)	1.42 (2)	C-Cl	1.83 (2)
N(21)-C(25)	1.36 (1)				
(b) Bond Angles					
I(1)-Rh-I(2)	88.9 (1)	B-N(12)-C(13)	130.9 (8)	C(13)-C(14)-C(15)	106.5 (8)
I(1)-Rh-I(3)	90.7 (1)	N(11)-N(12)-C(13)	106.7 (7)	N(11)-C(15)-C(14)	109.6 (9)
I(1)-Rh-N(11)	91.5 (2)	Rh-N(21)-N(22)	121.2 (5)	N(22)-C(23)-C(24)	105.7 (9)
I(1)-Rh-N(21)	176.3 (2)	Rh-N(21)-C(25)	130.9 (7)	C(23)-C(24)-C(25)	106.5 (8)
I(1)-Rh-N(31)	91.0 (2)	N(22)-N(21)-C(25)	107.5 (7)	N(21)-C(25)-C(24)	109.9 (8)
I(2)-Rh-I(3)	83.2 (0)	B-N(22)-N(21)	117.4 (6)	N(32)-C(33)-C(34)	110.9 (9)
I(2)-Rh-N(11)	95.8 (2)	B-N(22)-C(23)	132.3 (8)	C(33)-C(34)-C(35)	103.5 (8)
I(2)-Rh-N(21)	93.5 (2)	N(21)-N(22)-C(23)	110.3 (7)	N(31)-C(35)-C(34)	109.9 (9)
I(2)-Rh-N(31)	178.1 (2)	Rh-N(31)-N(32)	121.0 (5)	N(42)-C(43)-C(44)	116.1 (12)
I(3)-Rh-N(11)	177.6 (2)	Rh-N(31)-C(35)	131.2 (6)	C(43)-C(44)-C(45)	104.0 (10)
I(3)-Rh-N(21)	92.5 (2)	N(32)-N(31)-C(35)	107.2 (7)	N(41)-C(45)-C(44)	107.6 (10)
I(3)-Rh-N(31)	94.9 (2)	B-N(32)-N(31)	117.1 (6)	N(12)-B-N(22)	107.5 (7)
N(11)-Rh-N(21)	85.4 (3)	B-N(32)-C(33)	134.4 (8)	N(12)-B-B(32)	109.6 (7)
N(11)-Rh-N(31)	86.1 (3)	N(31)-N(32)-C(33)	108.6 (7)	N(12)-B-N(41)	109.8 (7)
N(21)-Rh-N(31)	86.7 (3)	B-N(41)-N(42)	124.6 (7)	N(22)-B-N(32)	106.2 (6)
Rh-N(11)-N(12)	117.7 (5)	B-N(41)-C(45)	127.5 (8)	N(22)-B-N(41)	112.4 (7)
Rh-N(11)-C(15)	134.3 (7)	N(42)-N(41)-C(45)	106.5 (8)	N(32)-B-N(41)	111.3 (7)
N(12)-N(11)-C(15)	107.9 (8)	N(41)-N(42)-C(43)	105.8 (10)	Cl-C-Cl	124.7 (10)
B-N(12)-N(11)	122.4 (7)	N(12)-C(13)-C(14)	109.2 (9)		

of pyrazolyl groups); 14, δ 8.57 (d, $J = 1.87$ Hz; H3/5 of pyrazolyl group trans to CO), 8.17 (d, $J = 1.80$ Hz, 2 H; H3/5 of pyrazolyl groups trans to I), 7.88 (d, $J = 2.25$ Hz, 4 H; H5/3 of coordinated pyrazolyl groups and H3/5 of uncoordinated pyrazolyl group), 7.39 (d, $J = 2.62$ Hz, 1 H; H5/3 of uncoordinated pyrazolyl group), 6.57 (t, $J = 2.25$ Hz, 1 H; H4 of uncoordinated pyrazolyl group), 6.25 (t, $J = 1.87$ Hz, 3 H; H4 of coordinated pyrazolyl groups).

The dark red crystals of 14 obtained upon recrystallization from CH_2Cl_2 -Hexane were unstable in air due to loss of solvent of crystallization. For the crystal structure analysis a fresh small ($0.33 \times 0.29 \times 0.19$ mm) crystal was selected and quickly covered with epoxy cement.

Crystal data for $\text{C}_{13}\text{H}_{12}\text{BI}_2\text{H}_8\text{ORh} \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$: $M_r = 706.3$; monoclinic; $a = 22.713$ (2) Å, $b = 12.249$ (2) Å, $c = 15.211$ (2) Å, $\beta = 94.29$ (1)°, $U = 4220.0$ Å³, $Z = 8$, $D_{\text{calc}} = 2.22$ g cm⁻³, $F(000) = 2648$, $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 36.1$ cm⁻¹. Systematic absences hkl when $h + k = 2n + 1$ and $h0l$ when both $h = 2n + 1$ and $l = 2n + 1$ allow the space group to be either $C2/c$ or Cc . $C2/c$ was chosen and confirmed by the successful analysis.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections (with θ in the range 10–20°) measured on a Hilger and Watts four-circle Y290 diffractometer. Intensity data were collected in our usual way²³ to a maximum θ of 27°, and 4613 unique data were obtained. After corrections for Lorentz, polarization effects, and absorption (transmission coefficients 0.38–0.54), the data with $I > 3\sigma(I)$ (4061) were labeled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction; the SHELX²⁴ program system was used in subsequent calculations.

Structure Solution and Refinement. The structure was solved via the Patterson function and subsequent heavy-atom-phased F_o maps. The Patterson function did not have the distribution of peaks expected from a RhI_2 moiety; the presence of additional large peaks was taken as evidence for some positional disorder of the iodines and the CO group similar to that observed with Cl and O atoms in $\text{HB}(\text{Me}_2\text{pz})_3\text{MoOCl}_2$,²⁵ and this was es-

tablished from subsequent electron density maps. From these maps it was apparent that one of the I atoms (I(1)) is little affected by disorder but the other iodine atom (I(2)) and the carbonyl group were obviously disordered; no clear maxima could be discerned for a C–O group in electron density maps, any electron density being effectively swamped by the disordered iodine atom. Accordingly in the refinements that followed two iodine atoms (I(2), I(3)) with partial occupancy were positioned for the disordered I, CO moiety. Since 67 electrons ($53 + 8 + 6$) had to be accounted for, the population parameters of the atoms (I(2) and I(3)) were linked so that their total was 1.26 ($1.26 \times 53 = 67$ electrons). In subsequent refinement the occupancy of I(2) settled to 0.75 and that of I(3) became 0.50, indicating a 2/3:1/3 disorder of the I(2)/CO moiety. A CH_2Cl_2 solvent molecule was also located lying on a crystallographic twofold axis. Refinement was by full-matrix least-squares calculations initially with isotropic and then with anisotropic thermal parameters. A difference map computed at an intermediate stage in the refinement revealed maxima in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealized positions (C–H = 0.95 Å) and included in the final rounds of calculations. Only an overall isotropic thermal parameter was refined for the H atoms. In the final three refinement cycles a weighting scheme of the form $\omega^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$ was employed where the final p parameter was 0.0001. Scattering factors used in the structure factor calculations were taken from ref 26, and allowance was made for anomalous dispersion.²⁷ Refinement converged with $R = 0.066$ and $R_w = [\sum \omega \Delta^2 / \sum \omega F_o^2]^{1/2} = 0.080$ for the 4061 reflections with $I > 3\sigma(I)$. A final difference map was devoid of any significant features. The structure factor listing, hydrogen coordinates, and tables of thermal parameters are available. Final fractional coordinates for the non-hydrogen atoms are in Table I, and molecular dimensions are in Table II.

Preparation of $\text{B}(\text{pz})_4\text{RhI}_2(\text{PPh}_3)$ (17) and Related Compounds. A solution of triphenylphosphine (0.12 g, 0.46 mmol)

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and 14 (0.30 g, 0.45 mmol) in 40 mL of benzene was heated to reflux under nitrogen. Monitoring of the reaction by IR showed complete disappearance of $\nu(\text{CO})$ band of 14 after ca. 20 h. Solvent was removed in vacuo, and the orange residue was recrystallized from CH_2Cl_2 -petroleum (80–100 °C): yield 0.36 g (89%); $^1\text{H NMR}$ (CDCl_3 , Me_4Si) δ 8.85–6.81 (complex multiplet, 23 H; H3 and H5 of free and coordinated pyrazolyl groups with aromatic protons of PPh_3), 6.7 (t, $J = 1.8$ Hz, 1 H; H4 of free pyrazolyl group or H4 of coordinated pyrazolyl group trans to PPh_3), 6.31 (t, $J = 2.25$ Hz, 1 H; H4 of coordinated pyrazolyl group trans to PPh_3 or H4 of free pyrazolyl group), 5.81 (t, $J = 2.40$ Hz, 2 H, H4 of coordinated pyrazolyl groups trans to I). The complex $\text{B}(\text{pz})_4\text{RhBr}_2(\text{CH}_3\text{CN})$ (16) was formed in 79% yield when 12 was refluxed in acetonitrile for 3 h.

Results and Discussion

Reaction of the potassium salt of the appropriate poly-(1-pyrazolyl)borate anion with $[(\text{LL})\text{RhCl}]_2$ in *N,N*-dimethylformamide (DMF) at room temperature gave excellent yields of the polypyrazolylborato complexes $\text{H}_n\text{B}(\text{pz})_{4-n}\text{Rh}(\text{LL})$ (1, $n = 1$, $\text{LL} = (\text{C}_2\text{H}_4)_2$; 2, $n = 1$, $\text{LL} = 1,5$ -cyclooctadiene (cod); 4, $n = 0$, $\text{LL} = \text{cod}$; 5, $n = 0$, $\text{LL} = \text{norbomadiene}$ (nbd); 6, $n = 0$, $\text{LL} = \text{duroquinone}$ (dq); 7, $n = 2$, $\text{LL} = \text{cod}$). This method failed to produce useful yields of $\text{B}(\text{pz})_4\text{Rh}(\text{C}_2\text{H}_4)_2$ (3). Complex 3 was synthesized via the reaction of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ with $\text{TlB}(\text{pz})_4$ in tetrahydrofuran-diethyl ether at -70 °C. Satisfactory microanalytical data could not be obtained for 3²⁸ but the $^1\text{H NMR}$ spectrum was fully in accord with the expected structure (Table III).

Complexes 1–5 and 7 are pale to deep yellow solids while 6 is reddish orange in color. With the exception of 3 all the compounds appear to be indefinitely stable under normal laboratory conditions. Solid complex 3 decomposed in the air over a period of a few days and did so more rapidly in solution. Microanalytical and infrared data for 1–7 are summarized in Table IV. $^1\text{H NMR}$ spectra are in Table III. The 60-MHz $^1\text{H NMR}$ spectrum of $\text{B}(\text{pz})_4\text{Rh}(\text{C}_2\text{H}_4)_2$ (3) at ambient temperatures is very similar to that reported by Trofimenko⁹ for $\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$ (1) and consists of two sharp doublets and a triplet (assignable to the protons at positions 3, 5, and 4 of four equivalent pyrazolyl groups) as well as a singlet corresponding to eight equivalent ethylene protons. Since $[\text{B}(\text{pz})_4]^-$ cannot function as a tetradentate ligand, the coordinated and uncoordinated pyrazolyl groups in 3 must be exchanging rapidly on the NMR time scale. The single ethylene resonance indicates similarly rapid rotation of these ligands around the (ethylene)rhodium bond axis.^{2–5} The spectra of 2, 4, and 5 (apart from resonances characteristic of the olefinic ligands) resemble those of 1 and 3 in also indicating averaging of all pyrazolyl environments. None of these spectra, however, contained any information as to the nature of the averaging process itself. The spectrum of $\text{B}(\text{pz})_4\text{Rh}(\text{dq})$ (6) differs significantly from the other members of the series at room temperature. The resonances in the region of the spectrum characteristic of the $\text{B}(\text{pz})_4$ ligand are markedly broadened. Moreover, the protons at position 4 of the pyrazolyl groups (see 1b above for numbering system) appeared as two broad resonances in a 1:3 ratio. Three broad resonances (with some overlapping) are observed for the protons at positions 3 and 5. A five-coordinate 18-electron structure (i.e., 1b) with three coordinated and one free pyrazolyl group is strongly indicated by the 1:3 ratio of pyrazolyl 4 H resonances. With the assumption of a trigonal-bipyramidal geometry,

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Table III. $^1\text{H NMR}$ Spectra (δ) of Bis(olefin)rhodium(I) Poly(1-pyrazolyl)borato Complexes^a

no.	compd	solv	H3/5	H5/3	H4	other
1 ^b	$\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$	CDCl_3	7.8 (d, $J = 1.9$ Hz, 3 H)	7.62 (d, $J = 2.3$ Hz, 3 H)	6.17 (t, $J = 2.1$ Hz, 3 H)	2.54 (d, $J = 1.75$ Hz, 8 H) ^c
2	$\text{HB}(\text{pz})_3\text{Rh}(\text{cod})$	CDCl_3	7.73 (d, $J = 1.7$ Hz, 3 H)	7.56 (d, $J = 2.3$ Hz, 3 H)	6.19 (t, $J = 2.0$ Hz, 3 H)	3.95 (s, br, 4 H), ^d 2.8–1.6 (cm, br, 8 H) ^e
3	$\text{B}(\text{pz})_4\text{Rh}(\text{C}_2\text{H}_4)_2$	CDCl_3	7.65 (d, $J = 1.5$ Hz, 4 H)	7.17 (d, $J = 2.5$ Hz, 4 H)	6.29 (t, $J = 2.0$ Hz, 4 H)	2.85 (s, 8 H) ^e
4	$\text{B}(\text{pz})_4\text{Rh}(\text{cod})$	CDCl_3	7.64 (d, $J = 1.5$ Hz, 4 H)	7.1 (d, $J = 2.3$ Hz, 4 H)	6.21 (t, $J = 2.3$ Hz, 4 H)	4.04 (s, br, 4 H), ^d 2.6–1.5 (cm, br, 8 H) ^e
5	$\text{B}(\text{pz})_4\text{Rh}(\text{nbd})$	CDCl_3	7.5 (d, $J = 1.5$ Hz, 4 H)	7.09 (d, $J = 2.5$ Hz, 4 H)	6.32 (t, $J = 1.9$ Hz, 4 H)	3.81 (d, $J = 1.7$ Hz, 6 H), ^f 1.2 (s, 2 H) ^g
6	$\text{B}(\text{pz})_4\text{Rh}(\text{dq})^h$	CDCl_3	8.17 (d, br, $J = 1.7$ Hz) ⁱ	7.99 (s, br) ^j	6.62 (s, br, 1 H)	1.8 (s, 12 H) ^j
7	$\text{H}_2\text{B}(\text{pz})_2\text{Rh}(\text{cod})$	CDCl_3	7.49 (d, $J = 2.25$ Hz, 2 H)	7.73 (d, br, $J = 1.8$ Hz, 2 H)	6.33 (t, br, $J = 2.0$ Hz, 3 H)	4.26 (s, br, 4 H), ^d 2.9–1.8 (cm, br, 8 H) ^e

^a Spectra measured at room temperature unless stated otherwise. ^b Data from ref 10. ^c Ethylene. ^d Olefinic protons of cod. ^e Methylene protons of cod. ^f Olefinic and bridgehead protons of nbd. ^g Methylene protons of nbd. ^h At 85 °C the following resonances were observed: H3/5, δ 1.89 (s, 4 H); H5/3, 2.21 (d, 2.44, 4 H); H4, 3.60 (d, 1.8, 4 H); CH₃, 1.78 (s, 12 H). ⁱ Overlapping resonances integrating overall for 5 H. ^j Methyl protons of dq.

Table IV. Microanalytical and Infrared Spectroscopic Data (cm⁻¹) for Poly(1-pyrazolyl)borate Complexes of Rhodium

compd	calcd (%)			found (%)			IR ^a
	C	H	N	C	H	N	
1	42.0	4.8	22.6	42.1	4.6	22.4	
2	48.1	5.2	19.8	47.9	5.1	19.8	
4	49.0	4.9	22.9	49.0	4.8	23.0	
5	48.1	4.2	23.6	48.3	4.3	23.5	
6	48.4	4.4	20.5	48.1	4.4	20.3	$\bar{\nu}(\text{CO})^b$ 1640, 1595 cm ⁻¹ (sh)
7	47.0	5.6	15.6	46.6	5.7	15.6	
8	35.2	2.8	23.5	35.6	2.9	23.7	$\bar{\nu}(\text{CO})$ 1845 cm ⁻¹
9	38.2	2.8	26.4	38.2	2.8	26.3	$\bar{\nu}(\text{CO})$ 1839 cm ⁻¹
10	31.4	2.6	18.3	31.3	2.9	18.1	$\bar{\nu}(\text{CO})^c$ 2084, 2020 cm ⁻¹
11 ^d							$\bar{\nu}(\text{CO})^e$ 2129 cm ⁻¹
12 ^f	20.1	1.7	14.0	20.1	1.6	14.0	$\bar{\nu}(\text{CO})^g$ 2095 cm ⁻¹
13	27.4	2.1	19.7	27.8	2.5	19.6	$\bar{\nu}(\text{CO})$ 2120 cm ⁻¹
14	23.5	1.8	16.9	23.9	2.1	16.6	$\bar{\nu}(\text{CO})^h$ 2090 cm ⁻¹
15	27.2	1.7	15.9	27.5	2.0	15.9	$\bar{\nu}(\text{CO})$ 2095 cm ⁻¹
16 ⁱ	28.8	2.6	21.6	28.8	2.5	21.1	
17	40.1	3.0	12.5	40.3	3.1	12.4	

^a KBr disk unless stated otherwise. All absorptions are strong. ^b Carbonyl of quinone ligand. ^c CH₂Cl₂ solution. ^d Not analyzed, see text. ^e $\bar{\nu}(\text{CO})$ 2139 cm⁻¹ in CHCl₃. ^f Iodine calcd 42.5, found, 42.4. ^g $\bar{\nu}(\text{CO})$ 2112 cm⁻¹ in CH₂Cl₂. ^h $\bar{\nu}(\text{CO})$ 2100 cm⁻¹ in CH₂Cl₂. ⁱ Bromine calcd 27.4, found 27.5.

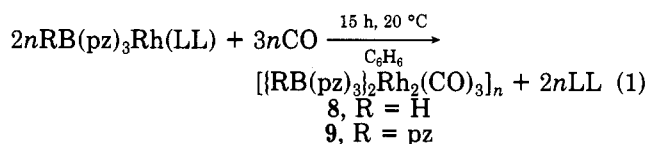
the observed spectrum also suggests that a dynamic process exchanges inequivalent axial and equatorial pyrazolyl groups at a rate which is rapid on the NMR time scale although accidental equivalence of the resonances cannot be completely ruled out. Furthermore, the general broadening of all the pyrazolyl resonances suggests that a second (slow) dynamic process is responsible for exchanging free and coordinated pyrazolyl groups. This presumably proceeds via a four-coordinate intermediate analogous to 1a. When the sample was heated in a sealed NMR tube, the pyrazolyl group resonances begin to coalesce and at 85 °C three sharp resonances are observed, indicating that all four pyrazolyl groups of the B(pz)₄ ligand in 6 are now exchanging rapidly the NMR time scale. On cooling to room temperature the original broadened spectrum reappears. This led us to suspect that complexes 1–5 were also five-coordinate in solution and differed from 6 only in the rate of interchange of free and coordinated pyrazolyl groups. This was confirmed to be so by the results of a detailed variable-temperature NMR study of complexes 4–6 which is described in a subsequent paper.¹³

The room-temperature 60-Mz ¹H NMR spectrum of H₂B(pz)₂Rh(cod) (7) (Table III) indicates equivalence of the two ligand pyrazolyl groups. The IR spectrum of 7 is devoid of bands in the 2000–2200-cm⁻¹ region, ruling out a five-coordinate 18-electron structure in which the fifth coordination position around rhodium is occupied by a B–H–Rh bridge analogous to the B–H–Pt bridge thought to occur in H₂B(pz)₂Pt(CH₃)₃.²⁹ Complex 7 is thus a true 16-electron analogue of (acac)Rh(C₂H₄)₂.

Our results show that 1–6 genuinely bridge the gap between (acac)Rh(LL) and (η-C₅H₅)Rh(LL) (LL = (C₂H₄)₂ or chelating nonconjugated diene) since both four-coordinated 16-electron and five-coordinated 18-electron species are present in solutions of the poly(1-pyrazolyl)borato complexes. The chemistry of (acac)Rh(C₂H₄)₂ differs from that of coordinatively saturated (η-C₅H₅)Rh(C₂H₄)₂ in that the vacant coordination site on the former facilitates rapid displacement of ethylene by other Lewis bases via an associative pathway.⁶ The chemical behavior of the poly(1-pyrazolyl)borato complex is, on balance, closer to that of the coordinatively unsaturated acetylacetonato complex (Complexes 1 and 2 form approximate 1:1 adducts with mercuric halides, i.e., HB(pz)₃Rh-

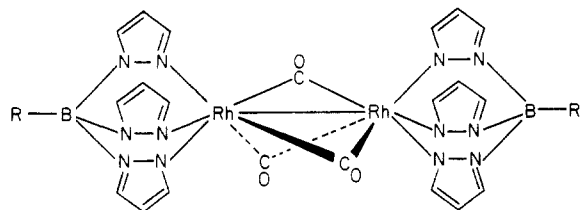
(C₂H₄)₂·HgCl₂, HB(pz)₃Rh(C₂H₄)₂·HgBr₃, and Hb-(pz)₃Rh(cod)·HgCl₂. The low solubility of the adducts prevented their full characterization, and it is uncertain whether or not they are structurally analogous to the known mercuric halide adducts of (η⁵-C₅H₅)Rh(C₂H₄)₂.⁵

Complexes 1, 2, and 4 react readily with Lewis bases such as Ph₃P, Ph₂PCH₂CH₂PPh₂, and *t*-BuNC in CH₂Cl₂ to give mixtures of products which have not so far yielded to characterization. No reaction took place between 4 and either phenylacetylene or diphenylacetylene in benzene solution at room temperature or at reflux. In contrast the reaction of CO at atmospheric pressure with 1, 2, 4, or 6 in benzene proceeded cleanly to give a single product in high yield (e.g., eq 1). The products are very stable pale



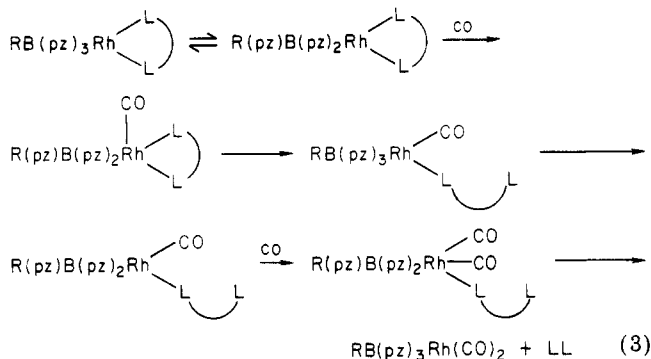
greenish yellow solids, the microanalyses of which were consistent with the formulae $[\{\text{HB}(\text{pz})_{3/2}\text{Rh}_2(\text{CO})_3\}_n]$ (8) and $[\{\text{B}(\text{pz})_{4/2}\text{Rh}_2(\text{CO})_3\}_n]$ (9). Complex 8 was also prepared²² by the reaction of $[(\text{CO})_2\text{RhCl}]_2$ with KHB(pz)₃ in CH₂Cl₂-CH₃OH (e.g., eq 2). Compounds 8 and 9 have only very limited solubility in organic solvents. This raises the possibility that they may have polymeric structures with exopolydentate¹⁰ poly(1-pyrazolyl)borate ligands linking $[\text{Rh}_2(\text{CO})_3]$ units. However, intrinsically low solubility has been observed for poly(1-pyrazolyl)borato complexes which do not have cross-linked structures.³⁰ The insolubility of 8 and 9 precludes an NMR study, nor were we able to grow crystals for an X-ray investigation. In the absence of definitive information we will assume that *n* = 1 in the formulae of 8 and 9, and this conclusion is supported to some extent by the chemical behavior of the complexes (see below).

The IR spectra of 8 and 9 show one broad intense $\bar{\nu}(\text{CO})$ band at 1845 cm⁻¹, 8, and 1839 cm⁻¹, 9 (Table IV). The single peak and its low-frequency suggest that all three CO ligands in 8 and 9 are doubly bridging. The 18-electron rule also requires that the complexes contain a rhodium-



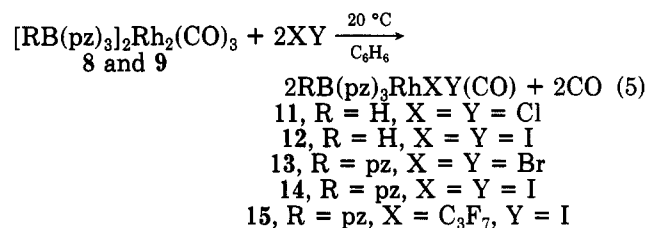
8, R = H
9, R = pz

rhodium single bond. Complexes 8 and 9 are formally related to the dimeric η -cyclopentadienyl complexes (η -C₅H₅)₂M₂(CO)₃ (M = Co³¹ Rh³²) and (η -C₅H₅)₂Rh₂(*t*-BuNC)₃³³ and to the η^5 -indenyl complex (η^5 -C₉H₇)₂Rh₂(*t*-BuNC)₃.³⁴ A structure involving one μ -carbonyl (or isocyanide) and two terminal ligands is suggested for these complexes by their IR spectra³¹⁻³⁴ and has been established crystallographically in the case of (η -C₅H₅)₂Rh₂(CO)₃.³⁵ The (μ -CO)₃ structure suggested for 8 and 9 is consistent with the greater steric demand of the poly(1-pyrazolyl)borato ligands. Reaction of H₂B(pz)₂Rh(cod) (7) with CO in benzene at room temperature and atmospheric²¹ pressure yielded the known complex H₂B(pz)₂Rh(CO)₂ (10) (previously prepared from [(CO)₂RhCl]₂ and KH₂B(pz)₂^{23,36}) which showed no tendency under these conditions to condense to a dirhodium species. A reasonable mechanism for the formation of 8 and 9 from RB(pz)₂Rh(LL) (R = H, pz; LL = diene) would involve attack of CO upon the thermally accessible four-coordinate 16-electron form of the latter, followed by a sequence of displacement and associative steps in which the poly(1-pyrazolyl)borato is alternately bidentate and tridentate, leading ultimately to formation of RB(pz)₃Rh(CO)₂, two molecules of the latter than condensing to form 8 or 9 with extrusion of CO (eq 3 and 4). Support for this proposal may be drawn



from a study³⁴ of the reactions of the η^5 -indenyl complex (η -C₉H₇)Rh(C₂H₄)₂. The ethylene ligands in this complex are readily displaced by CO or *t*-BuNC due, it has been suggested, to the ease of η^5 -C₉H₇ \rightarrow η^3 -C₉H₇ "slippage" which generates a coordinatively unsaturated (16-electron) rhodium atom resembling the five-coordinate/four-coordinate equilibrium proposed for 2-6. The initial products of olefin substitution are (η^5 -C₉H₇)Rh(CO)₂ and (η^5 -C₉H₇)Rh(*t*-BuNC)₂. These readily undergo condensation

to (η^5 -C₉H₇)₃Rh₃(CO)₃ (boiling heptane) or (η^5 -C₉H₇)₂Rh₂(*t*-BuNC)₃ (room temperature), respectively.³⁴ It seems probable that species of the type RB(pz)₃Rh(CO)₂ (R = H, pz) are formed in the reactions reported here, but we have not been able to detect their intervention under our reaction conditions. Such dicarbonyls must be much more susceptible to condensation than either their η -cyclopentadienyl³⁷ or η^5 -indenyl³⁰ analogues, and it is not entirely obvious why this should be so. Interestingly, in this context, a closely related dicarbonyl HB(Me₂pz)₃Rh(CO)₂ (Me₂pz = 3,5-dimethyl-1-pyrazolyl) has been reported.³⁸ This complex could be a four-coordinate analogue of (acac)Rh(CO)₂³⁹ but is more likely to be a fluxional five-coordinate analogue of the hypothetical RBpz₃Rh(CO)₂. That this complex does not undergo spontaneous condensation to dimetallic species related to 8 and 9 is presumably a result of the steric effect of the ligand methyl substituents (eq 5).



A suspension of [HB(pz)₃]₂Rh₂(CO)₃ (8) in benzene showed no evidence for reaction with NO at room temperature or with PPh₃ under reflux conditions. Neither was 8 reduced to a carbonyl anion by sodium amalgam in tetrahydrofuran. However, when benzene suspensions of 8 or 9 were treated with halogens or heptafluoro-*n*-propyl iodide, a smooth oxidative displacement of CO led to the formation of the rhodium(III) complexes 11-15 in high yield (e.g., eq 5). Microanalytical and IR data for 11-15 are summarized in Table IV. A different synthesis of 11 has also recently been described;²⁸ in our hands HB(pz)₃RhCl₂(CO) (11) underwent slow partial decarbonylation in the solid state and lost CO more rapidly on attempted recrystallization. Satisfactory microanalytical data were not obtained for this complex, and it was identified on the basis of its IR spectrum (Table I) which was identical with that reported in ref 28. The ¹H NMR spectrum of HB(pz)₃RhI₂(CO) (12) (Experimental Section) is similar to the spectrum²⁸ of its dichloro analogue, 11. The protons at the 3-position of the ligand pyrazolyl groups (or, alternatively, at the 5-position, since an unambiguous assignment is not possible) appear as a pair of doublets in a 1:2 ratio, indicating a rigid octahedral geometry for 12 and the more complex NMR spectrum of B(pz)₄RhI₂(CO) (14) may be similarly interpreted. We were unable to obtain satisfactory NMR spectra for 13 or 15 possibly due to the presence of traces of paramagnetic impurities, but a similar octahedral structure may also be safely inferred for these complexes.

Complexes 11-15 show a single strong $\bar{\nu}$ (CO) absorption between 2090 and 2129 cm⁻¹ in pressed KBr disks (Table I, $\bar{\nu}$ (CO) is ca. 10 cm⁻¹ higher in CH₂Cl₂ solution). As expected the complexes with the more electronegative halogen substituents show the higher carbonyl stretching frequencies. The large increase in $\bar{\nu}$ (CO) vis-à-vis the precursors 8 and 9 (ca. 260 cm⁻¹) is compatible with oxidation from Rh(I) to Rh(III) accompanied by a shift from

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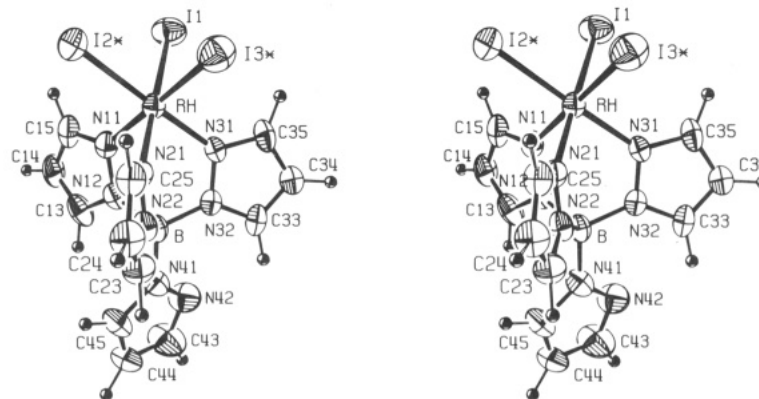


Figure 1. Stereoview of 14 with ellipsoids at the 50% probability level. I2* and I3* are disordered iodine and CO moieties.

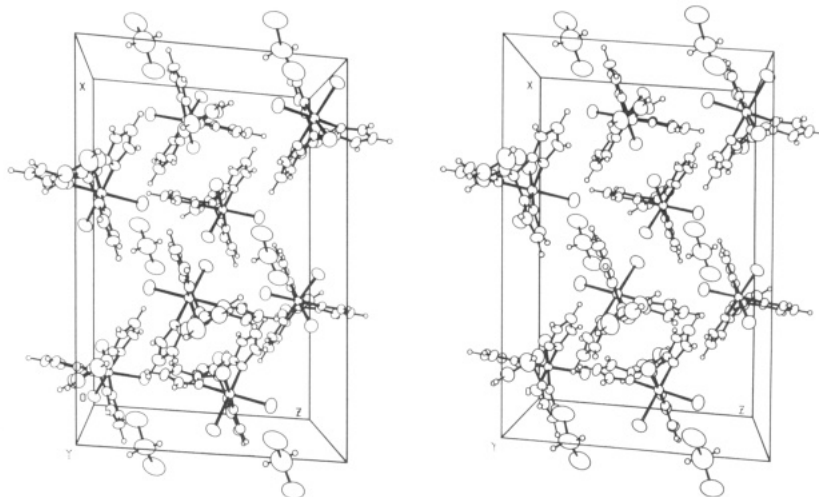
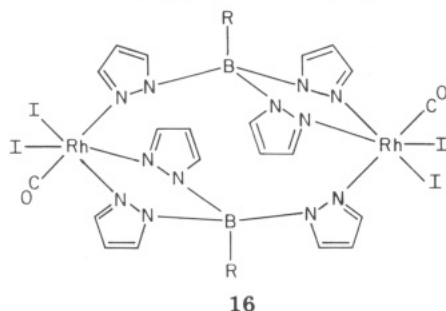


Figure 2. Stereoview of the crystal structure of 14.

μ - to terminal character for the remaining carbonyl group. The carbonyl stretching frequencies of $(\text{RBpz}_3)\text{RhI}_2(\text{CO})$ (12 and 14) are ca. $30\text{--}60\text{ cm}^{-1}$ higher than in the related η -cyclopentadienyl complexes $(\eta\text{-C}_5\text{H}_5)\text{RhI}_2(\text{CO})$ (2065 cm^{-1})⁴⁰ and $(\eta\text{-C}_5\text{Me}_5)\text{RhI}_2(\text{CO})$ (2035 cm^{-1}).⁴¹ This result is unexpected since poly(1-pyrazolyl)borato ligands are stronger net electron donors than cyclopentadienide.⁹ If complexes 11–15 have been correctly formulated as mononuclear octahedral Rh(III) species, then their formation from 8 and 9 provides support for our suggestion that the latter are discrete dirhodium compounds. However, the available ¹H NMR evidence (although compatible with a mononuclear structure for 11–15) would also fit a dirhodium structure (e.g., 16) with exopolydentate poly(1-



pyrazolyl)borato ligands derived from oxidative cleavage of the $\text{Rh}_2(\text{CO})_3$ moiety in polymeric $[\{\text{RB}(\text{pz})_3\}_2\text{Rh}_2(\text{CO})_3]_n$

($n > 1$). In order to resolve unambiguously whether 11–15 are monorhodium or dirhodium species, we have determined the crystal and molecular structure of a sample compound $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ (14).

The X-ray analysis establishes that 14 is indeed a monorhodium complex with octahedral coordination (Figure 1) and also provides some confirmatory evidence that the precursor tricarbonyl is the dirhodium species 9. Although the 2/3:1/3 disorder of one of the iodine atoms and the carbonyl group precludes any detailed discussion of the Rh–I and Rh–C distances, we note that the apparently undistorted Rh–I distance ($2.634(1)\text{ \AA}$) is much less than values found for other Rh–I bond lengths ($2.652\text{--}2.699(2)\text{ \AA}$) surveyed in ref 42, but although the electron density at I(1) was consistent with it being an undistorted iodine, we cannot rule out the possibility that it too is slightly disordered with the CO moiety.

The $\text{B}(\text{pz})_4\text{Rh}$ moiety has normal geometry with a Rh–N distances of $2.039\text{--}2.082(7)\text{ \AA}$ in accord with values noted previously;⁴³ the longest distance is trans to the non-disordered iodine I(1) and the shortest is trans to the disordered site with 2/3 CO occupancy. The N–Rh–N angles $85.4\text{--}86.7(3)^\circ$ are distorted from 90° by the bite of the ligand; other dimensions (mean B–N = $1.53(1)$, N–N = $1.36(1)\text{ \AA}$, N–C = $1.35(1)\text{ \AA}$, C–C = $1.37(1)\text{ \AA}$) and the planarity of the individual pyrazolyl rings are also in accord with previous findings.

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(43) See, for example: Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Inorg. Chem.* 1975, 14, 3046 and references therein.

In the crystal structure, the octahedral molecules of the complex are separated by normal van der Waals distances. The dichloromethane of solvation lies on a crystallographic twofold axis and fills what would have been a void in the crystal lattice.

The high carbonyl stretching frequencies observed for complexes 11-15 imply that the carbonyl ligands in these species should be quite labile. Slow partial decarbonylation observed with $\text{HB}(\text{pz})_3\text{RhCl}_2(\text{CO})$ (11) has already been mentioned. Both 11 and $\text{B}(\text{pz})_4\text{RhBr}_2(\text{CO})$ (13) underwent complete decarbonylation in refluxing toluene, but we have been unable to obtain meaningful microanalytical data on the products. Smooth displacement of CO from 13 in boiling acetonitrile generates $\text{B}(\text{pz})_4\text{HBr}_2(\text{CH}_3\text{CN})$ (16) in good yield. Triphenylphosphine reacts with $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ in boiling benzene to give $\text{B}(\text{pz})_4\text{RhI}_2(\text{PPh}_3)$ (17). Useful ^1H NMR data could not be recorded for 16 but the spectrum of 17 (Experimental Section) was fully in accord

with its proposed formulation.

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Supplementary Material Available: Table I and tables of structure factors, thermal parameters, and calculated hydrogen coordinates for 14 (27 pages). Ordering information is given on any current masthead page.

Stereochemically Nonrigid Bis(olefin)rhodium Poly(1-pyrazolyl)borato Complexes. 2.¹ X-ray Crystallographic Studies. The Crystal and Molecular Structures of the Norbornadiene, Cycloocta-1,5-diene, and Duroquinone Complexes

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The crystal and molecular structures of $\text{B}(\text{pz})_4\text{Rh}(\text{nbd})$ (1), $\text{B}(\text{pz})_4\text{Rh}(\text{cod})$ (2), and $\text{B}(\text{pz})_4\text{Rh}(\text{dq})$ (3) have been determined. Crystals of 1 are monoclinic of space group $P2_1/c$ with four molecules in a cell of dimensions $a = 8.226$ (1) Å, $b = 24.500$ (4) Å, $c = 9.909$ (1) Å, and $\beta = 90.96$ (1)°. Crystals of 2 are orthorhombic of space group $Pnma$ with four molecules with crystallographic mirror symmetry in a cell of dimensions $a = 11.923$ (2) Å, $b = 10.783$ (1) Å, and $c = 16.452$ (2) Å. Crystals of 3 are triclinic of space group $A\bar{1}$ with eight molecules in a cell of dimensions $a = 10.527$ (1) Å, $b = 16.835$ (2) Å, $c = 27.725$ (3) Å, $\alpha = 94.42$ (1)°, $\beta = 88.24$ (1)°, and $\gamma = 113.45$ (1)°. The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations: for 1 $R = 0.035$ for 2896 observed reflections, for 2, $R = 0.028$ for 2641 reflections, and for 3, $R = 0.035$ for 4367 reflections. The analyses establish that in the nbd, 1, and cod, 2, complexes, only two pz moieties complex to rhodium yielding a square-planar coordination, whereas in the dq complex, 3, three pz groups coordinate to produce trigonal-bipyramidal coordination. Principal dimensions are as follows: for 1, Rh-O = 2.110-2.130 (4) Å, Rh-N = 2.069 and 2.065 (3) Å, C=C = 1.395 and 1.387 (6) Å; for 2, Rh-C = 2.124 and 2.139 (2) Å, Rh-N = 2.099 (2) Å, C=C = 1.382 (4) Å; for 3, mean Rh-C(ax) = 2.250 (4) Å, Rh-C(eq) = 2.170 (5) Å, Rh-N(ax) = 2.078 (3) Å, Rh-N(eq) = 2.129-2.184 (3) and mean 2.153 (3) Å, C=C(ax) = 1.390 (6) Å, C=C(eq) = 1.440 (7) Å.

Introduction

The preceding paper in this series¹ has described the synthesis of (polypyrazolylborato)rhodium complexes. We describe here the crystal and molecular structures of three of these, the closely related complexes $\text{B}(\text{pz})_4\text{Rh}(\text{nbd})$ (1), $\text{B}(\text{pz})_4\text{Rh}(\text{cod})$ (2), and $\text{B}(\text{pz})_4\text{Rh}(\text{dq})$ (3) (where nbd = norbornadiene, cod = cycloocta-1,5-diene, dq = 1,4-duroquinone, and pz = pyrazolyl) of interest because NMR data^{1,3} have indicated different degrees of coordination at

different temperatures in these complexes. Our X-ray analyses establish unequivocally the room-temperature solid-state structures of 1-3 and provide data for comparison with our NMR work.³

Experimental Section

Data Collection. Compounds 1-3 were prepared as described previously and suitable small crystals were readily available.¹ Preliminary Weissenberg and precession photographs yielded initial cell data. Diffraction data were collected on a Hilger & Watts Y290 four-circle diffractometer using $\text{MoK}\alpha$ radiation. Final unit cell parameters were determined from a least-squares fit of

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(3) Cocivera, M.; Ferguson, G.; Lalor, F. J.; Szczecinski, P., part 3 following in this issue.