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 obsereved with HB(pz)$_3$RhCl$_2$(CO) (**11**) has already been mentioned. Both **11** and B(pz)$_4$RhBr$_2$(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 B(pz)$_4$HBr$_2$(CH$_3$CN) (**16**) in good yield. Triphenylphosphine reacts with B(pz)$_4$RhI$_2$(CO) in boiling benzene to give B(pz)$_4$RhI$_2$(PPh$_3$) (**17**). Useful ^{1}H 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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Registry No. **1**, 33135-94-3; **2**, 82338-07-6; **3**, 82338-08-7; **4**, 81420-85-1; **5**, 81420-83-9; **6**, 82323-69-1; **7**, 52668-37-8; **8**, 82338-09-8; **9**, 82338-10-1; **10**, 33058-09-2; **11**, 73117-44-9; **12**, 82338-11-2; **13**, 82338-12-3; **14**, 82338-13-4; **15**, 82338-14-5; **16**, 82338-15-6; **17**, 82338-16-7.

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 B(pz)$_4$Rh(nbd) (**1**), B(pz)$_4$Rh(cod) (**2**), and B(pz)$_4$R(dp) (**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 β = 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, α = 94.42 (1)°, β = 88.24 (1)°, and γ = 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 series[1] has described the synthesis of (polypyrazolylborato)rhodium complexes. We describe here the crystal and molecular structures of three of these, the closely related complexes B(pz)$_4$Rh(nbd) (**1**), B(pz)$_4$Rh(cod) (**2**), and B(pz)$_4$Rh(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 MoKα radiation Final unit cell parameters were determined from a least-squares fit of

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Table I. Crystal Data and Data Collection Parameters

	RhB(pz)$_4$(nbd)	RhB(pz)$_4$(cod)	RhB(pz)$_4$(dq)
formula	$C_{19}H_{20}BN_8Rh$	$C_{20}H_{24}BN_8Rh$	$C_{22}H_{24}BN_8O_2Rh$
M_r	474.1	490.2	546.2
cryst size, mm	0.27 × 0.26 × 0.14	0.43 × 0.36 × 0.36	0.12 × 0.34 × 0.37
space group	$P2_1/c$	$Pnma$	$A\bar{1}$
a, Å	8.226 (1)	11.923 (2)	10.527 (1)
b, Å	24.500 (4)	10.783 (1)	16.835 (2)
c, Å	9.909 (1)	16.452 (2)	27.725 (3)
α, deg	90	90	94.42 (1)
β, deg	90.96 (1)	90	88.24 (1)
γ, deg	90	90	113.45 (1)
V, Å^3	1996.8	2115.2	4494.5
Z	4	4	8
D_{calcd}, g cm^{-3}	1.58	1.54	1.61
$F(000)$	960	1000	2224
μ(Mo Kα), cm^{-1}	8.61	8.15	7.81
radiation	graphite-monochromatized Mo Kα		
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	0.80	0.80	0.60
steps; width, (deg; duration, s)		40; 0.02; 2	60; 0.01; 1
bkgd counting time, s	20	20	30
collectn range, deg	2-27	2-30	2-25
unique data	4379	3239	5029
unique data with $I > 3\sigma(I)$	2896	2641	4367
final R value	0.035	0.028	0.035
final $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$	0.035	0.037	0.050
largest coordinate shift/error ratio in last cycle	0.02 for x of N(12)	0.01 for z of B	0.06 for x of C(243)
final p parameter in weighting scheme	0.000 13	0.003 58	0.003 00

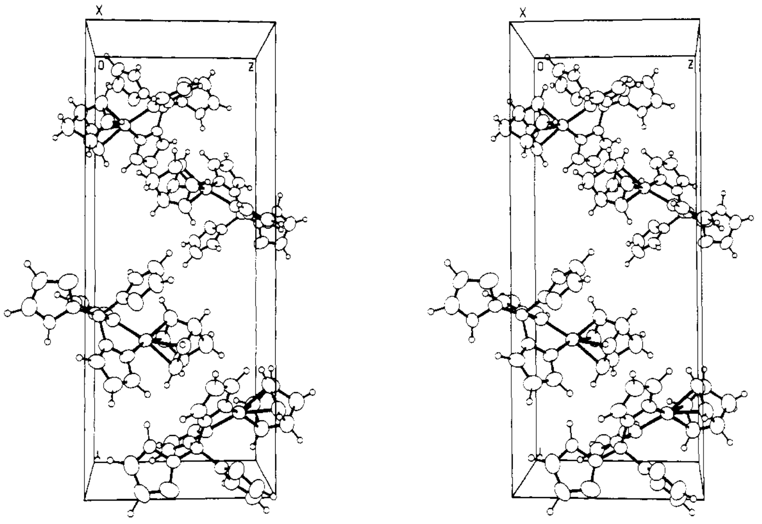

Figure 1. Stereoview of the crystal structure of B(pz)$_4$Rh(nbd) (1).

12 reflections in the range $15 < \theta < 20°$. The crystallographic and data collection details are given in Table I. The observed data were corrected for Lorentz and polarization effects but not for absorption. For B(pz)$_4$Rh(nbd) (1), the systematic absences determine the space group uniquely. For B(pz)$_4$Rh(cod) (2), the systematic absences allow the space group to be either $Pnma$ or $Pn2_1a$; the former was chosen and confirmed by the analysis. For B(pz)$_4$Rh(dq) (3), preliminary oscillation and Weissenberg photographs showed the crystals to be triclinic. Oscillation photographs about the b axis showed that reciprocal lattice layers with k odd, although certainly present, were very weak. The structural significance of this will be dealt with below.

Structure Solution and Refinement. All three structures were solved by the heavy atom method, and initial refinement was by full-matrix least-squares calculation.[4] For 1 and 2 difference maps revealed maxima in positions expected for all hydrogen atoms; these were then allowed for in geometrically idealized locations and included in the final rounds of calculations. For each molecule an overall isotropic thermal parameter was refined for hydrogens. In the final cycles, all nonhydrogen atoms were allowed anisotropic motion. There are two independent molecules of 3 in the asymmetric unit; difference maps showed positions for all protons and also showed clearly that one of the methyl groups of one dq ligand had its hydrogen atoms disordered over two sites. Because of computer space limitation only the rhodium atoms and duroquinone molecules were allowed anisotropic vibration in the final rounds of calculation. All hydrogen atoms were placed in geometrically idealized positions and included but not refined in the final cycles.

Details of R factors at convergence are in Table I, and final difference maps for the structures were devoid of chemically significant features. Weights in the refinement cycles were based on counting statistics, $w = 1/(\sigma^2(F) + pF\sigma)^{1/2}$, scattering factors were taken from references 5 and 6, and allowance was made for anomalous dispersion.[7] Tables II, III, and IV contain final fractional coordinates for 1, 2, and 3, respectively. Tables of thermal parameters, calculated hydrogen coordinates, and

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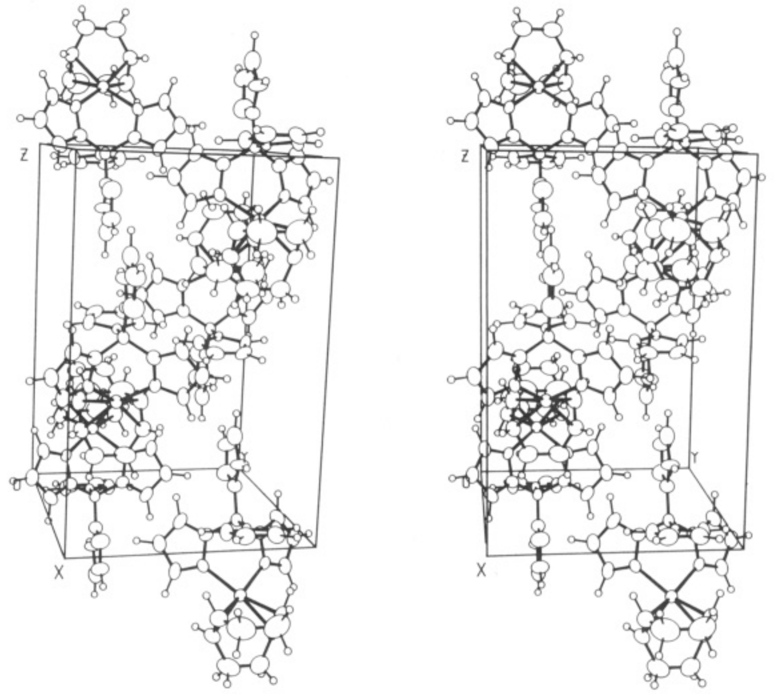

Figure 2. Stereoview of the crystal structure of $B(pz)_4Rh(cod)$ (**2**).

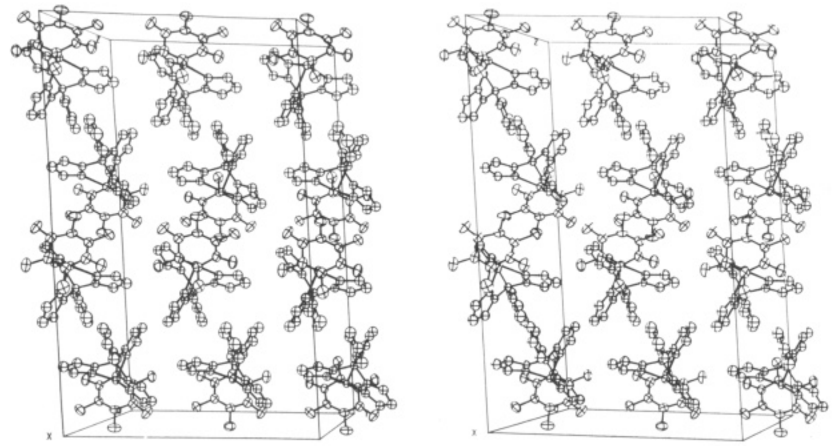

Figure 3. Stereoview of the crystal structure of $B(pz)_4Rh(dq)$ (**3**).

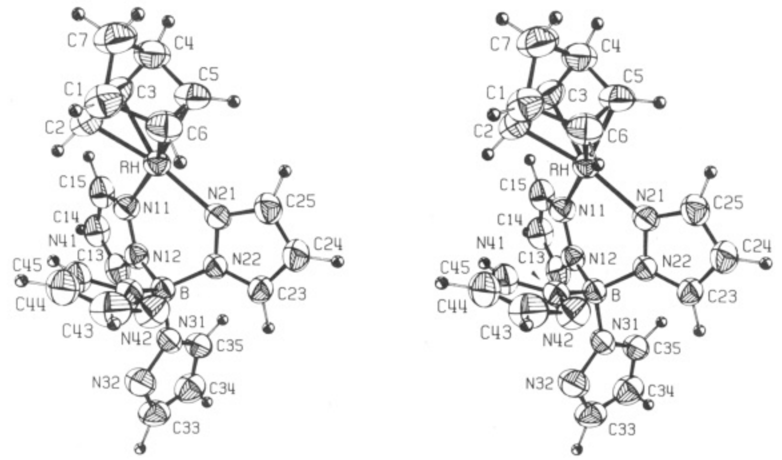

Figure 4. Stereoview of a molecule of $B(pz)_4Rh(nbd)$ (**1**) with the crystallographic numbering scheme.

structure factor are available as supplementary material.

Results and Discussion

The crystal structures of **1**, **2**, and **3**, shown in stereoviews in Figures 1, 2, and 3, respectively, contain discrete molecules separated by normal van der Waals distances. Selected interatomic distances and angles for **1**, **2**, and **3** were given in Tables V, VI, and VII, respectively. The bond distances in pyrazolyl rings and olefin ligands of **1**, **2**, annd **3** are in accord with accepted values. Stereoviews

Table V. Principal Interatomic Distances (Å) and Angles (Deg) in B(pz)$_4$Rh(nbd) (1) with Estimated Standard Deviations in Parentheses

(a) Bond Lengths

Rh-N(11)	2.069 (3)	C(13)-C(14)	1.375 (6)	N(41)-C(45)	1.354 (5)
Rh-N(21)	2.065 (3)	C(14)-C(15)	1.387 (7)	N(42)-C(43)	1.328 (6)
Rh-C(2)	2.110 (4)	N(21)-N(22)	1.370 (4)	C(43)-C(44)	1.383 (7)
Rh-C(3)	2.130 (4)	N(21)-C(25)	1.349 (5)	C(44)-C(45)	1.365 (7)
Rh-C(5)	2.127 (5)	N(22)-C(23)	1.343 (5)	C(1)-C(2)	1.537 (7)
Rh-C(6)	2.114 (5)	C(23)-C(24)	1.369 (6)	C(1)-C(6)	1.523 (7)
B-N(12)	1.543 (5)	C(24)-C(25)	1.382 (6)	C(1)-C(7)	1.537 (7)
B-N(22)	1.543 (5)	N(31)-N(32)	1.376 (5)	C(2)-C(3)	1.395 (6)
B-N(31)	1.508 (5)	N(31)-C(35)	1.363 (5)	C(3)-C(4)	1.509 (7)
B-N(41)	1.534 (5)	N(32)-C(33)	1.386 (6)	C(4)-C(5)	1.538 (7)
N(11)-N(12)	1.364 (4)	C(33)-C(34)	1.407 (7)	C(4)-C(7)	1.540 (7)
N(11)-C(15)	1.339 (5)	C(34)-C(35)	1.294 (6)	C(5)-C(6)	1.387 (7)
N(12)-C(13)	1.355 (5)	N(41)-N(42)	1.368 (5)		

(b) Bond Angles

N(11)-Rh-N(21)	90.0 (1)	B-N(12)-N(11)	122.2 (3)	N(42)-N(41)-C(45)	110.7 (4)
N(11)-Rh-C(2)	98.3 (2)	B-N(12)-C(13)	128.7 (4)	N(41)-N(42)-C(43)	104.8 (4)
N(11)-Rh-C(3)	100.5 (2)	N(11)-N(12)-C(13)	108.8 (3)	N(42)-C(43)-C(44)	111.8 (5)
N(11)-Rh-C(5)	161.4 (2)	N(12)-C(13)-C(14)	108.6 (4)	C(43)-C(44)-C(45)	105.4(4)
N(11)-Rh-C(6)	157.1 (2)	C(13)-C(14)-C(15)	105.3 (4)	N(41)-C(45)-C(44)	107.4 (4)
N(21)-Rh-C(2)	157.5 (2)	N(11)-C(15)-C(14)	110.1 (4)	Rh-C(2)-C(1)	95.5 (3)
N(21)-Rh-C(3)	159.3 (2)	Rh-N(21)-N(22)	124.9 (2)	Rh-C(2)-C(3)	71.5 (3)
N(21)-Rh-C(5)	98.2 (2)	Rh-N(21)-C(25)	129.2 (3)	Rh-C(3)-C(2)	70.0 (2)
N(21)-Rh-C(6)	97.2 (2)	N(22)-(21)-C(25)	105.8 (3)	Rh-C(3)-C(4)	96.6 (3)
C(2)-Rh-C(3)	38.4 (2)	B-N(22)-N(21)	119.3 (3)	Rh-C(5)-C(4)	95.8 (3)
C(2)-Rh-C(5)	80.4 (2)	B-N(22)-C(23)	129.4 (3)	Rh-C(5)-C(6)	70.4 (3)
C(2)-Rh-C(6)	67.8 (2)	N(21)-N(22)-C(23)	109.8 (3)	Rh-C(6)-C(1)	95.9 (3)
C(3)-Rh-C(5)	66.9 (2)	N(22)-C(23)-C(24)	108.5 (4)	Rh-C(6)-C(5)	71.4 (3)
C(3)-Rh-C(6)	80.1 (2)	C(23)-C(24)-C(25)	105.7 (4)	C(2)-C(1)-C(6)	100.7 (4)
C(5)-Rh-C(6)	38.2 (2)	N(21)-C(25)-C(24)	110.2 (4)	C(2)-C(1)-C(7)	100.7 (4)
N(12)-B-N(22)	109.4 (3)	B-N(31)-N(32)	127.1 (4)	C(6)-C(1)-C(7)	101.6 (4)
N(12)-B-N(31)	108.8 (3)	B-N(31)-C(35)	121.5 (3)	C(1)-C(2)-C(3)	105.6 (4)
N(12)-B-N(41)	109.0 (3)	N(32)-N(31)-(35)	110.5 (4)	C(2)-C(3)-C(4)	106.4 (4)
N(22)-B-N(31)	110.8 (3)	N(31)-N(32)-C(33)	106.3 (4)	C(3)-C(4)-C(5)	100.7 (4)
N(22)-B-N(41)	107.7 (3)	N(32)-C(33)-C(34)	104.7 (4)	C(3)-C(4)-C(7)	101.5 (4)
N(31)-B-N(41)	111.0 (3)	C(33)-C(34)-C(35)	112.2 (4)	C(5)-C(4)-C(7)	101.2 (4)
Rh-N(11)-N(12)	122.6 (2)	N(31)-C(35)-C(34)	106.4 (4)	C(4)-C(5)-C(6)	105.7 (4)
Rh-N(11)-C(15)	129.9 (3)	B-N(41)-N(42)	118.7 (3)	C(1)-C(6)-C(5)	106.4 (4)
N(12)-N(11)-C(15)	107.1 (3)	B-N(41)-C(45)	130.6 (4)		

Table VI. Principal Interatomic Distances (Å) and Angles (Deg) in B(pz)$_4$Rh(cod) (2) with Estimated Standard Deviations in Parentheses[a]

(a) Bond Lengths

Rh-N(11)	2.099 (2)	B-N(12)	1.543 (3)	N(22)-C(23)	1.361 (4)
Rh-C(2)	2.139 (2)	B-N(21)	1.526 (4)	N(31)-C(35)	1.340 (5)
Rh-C(3)	2.124 (3)	B-N(31)	1.526 (4)	N(32)-C(33)	1.337 (6)
C(1)-C(1)$^{\mathrm{I}}$	1.412 (10)	N(11)-N(12)	1.361 (2)	C(13)-C(14)	1.367 (4)
C(1)-C(2)	1.521 (4)	N(21)-N(22)	1.349 (3)	C(14)-C(15)	1.388 (4)
C(2)-C(3)	1.382 (4)	N(31)-N(32)	1.374 (5)	C(23)-C(23)$^{\mathrm{I}}$	1.369 (7)
C(3)-C(4)	1.494 (5)	N(11)-C(15)	1.338 (3)	C(33)-C(34)	1.360 (9)
C(4)-C(4)$^{\mathrm{I}}$	1.502 (12)	N(12)-C(13)	1.347 (3)	C(34)-C(35)	1.392 (7)

(b) Bond Angles

C(2)-Rh-C(2)$^{\mathrm{I}}$	81.4 (2)	C(1)-C(2)-C(3)	123.7 (3)	N(11)-C(15)-C(14)	110.8 (2)
C(3)-Rh-C(3)$^{\mathrm{I}}$	82.1 (2)	Rh-C(3)-C(2)	71.7 (2)	B-N(21)-N(22)	124.1 (2)
C(2)-Rh-C(3)	37.8 (1)	Rh-C(3)-C(4)	111.9 (3)	N(22)-N(21)-N(22)$^{\mathrm{I}}$	111.2 (3)
N(11)-Rh-C(2)	163.1 (1)	C(2)-C(3)-C(4)	125.4 (3)	N(21)-N(22)-C(23)	106.0 (2)
N(11)-Rh-C(3)	159.0 (1)	C(3)-C(4)-C(4)$^{\mathrm{I}}$	115.6 (2)	N(22)-C(23)-C(23)$^{\mathrm{I}}$	108.4 (2)
N(11)-Rh-N(11)$^{\mathrm{I}}$	86.6 (1)	Rh-N(11)-N(12)	120.4 (1)	B-N(31)-N(32)	121.9 (3)
N(12)-B-N(12)$^{\mathrm{I}}$	108.5 (2)	Rh-N(11)-C(15)	133.3 (2)	B-N(31)-C(35)	127.4 (4)
N(12)-B-N(21)	109.0 (2)	N(12)-N(11)-C(15)	106.2 (2)	N(32)-N(31)-C(35)	110.7 (3)
N(12)-B-N(31)	110.1 (2)	B-N(12)-N(11)	120.8 (2)	N(31)-N(32)-C(33)	104.3 (4)
N(21)-B-N(31)	109.9 (3)	B-N(12)-C(13)	129.9 (2)	N(32)-C(33)-C(34)	112.8 (4)
C(1)-C(1)-C(2)$^{\mathrm{I}}$	116.9 (2)	N(11)-N(12)-C(13)	109.3 (2)	C(33)-C(34)-C(35)	104.7 (4)
Rh-C(2)-C(1)	111.4 (2)	N(12)-C(13)-C(14)	109.1 (2)	N(31)-C(35)-C(34)	107.6 (5)
Rh-C(2)-C(3)	70.5 (2)	C(13)-C(14)-C(15)	104.6 (2)		

[a] The superscript I refers to the equivalent position x, $0.5 - y$, z.

of the individual molecules of **1**, **2**, and one of the molecules of **3**, with our crystallographic numbering schemes, are shown in Figures 4, 5, and 6, respectively.

The rhodium coordination in B(pz)$_4$Rh(nbd) (**1**), is square planar (Figure 4) with the nbd ligand occupying two cis sites (deviations (Å) from square plane are as follows: Rh −0.026, N(11) + 0.016, N(21) −0.002, midpoint of C(2)═C(3) −0.005, midpoint of C(5)═C(6) + 0.017). Figure 7a shows a view of **1** viewed normal to the olefin coordination plane. The principal coordination dimensions

Table VII. Principal Interatomic Distances (Å) and Angles (Deg) in $B(pz)_4Rh(dq)$ (3) with Estimated Standard Deviations in Parentheses

(a) Bond Lengths

	molecule 1	molecule 2		molecule 1	molecule 2
Rh-N(11)	2.085 (3)	2.071 (3)	N(21)-C(25)	1.337 (7)	1.347 (7)
Rh-N(21)	2.130 (4)	2.129 (4)	N(22)-C(23)	1.346 (8)	1.346 (8)
Rh-N(31)	2.184 (3)	2.167 (3)	C(23)-C(24)	1.359 (6)	1.356 (6)
C(1)-C(2)	1.448 (6)	1.459 (7)	C(24)-C(25)	1.389 (9)	1.377 (9)
C(1)-C(6)	1.473 (8)	1.466 (8)	N(22)-B	1.542 (6)	1.543 (6)
C(1)-O(1)	1.239 (6)	1.237 (6)	N(31)-N(32)	1.360 (5)	1.361 (5)
C(2)-C(3)	1.438 (6)	1.442 (7)	N(31)-C(35)	1.332 (6)	1.341 (6)
C(2)-C(21)	1.506 (7)	1.503 (8)	N(32)-C(33)	1.360 (5)	1.360 (5)
C(3)-C(4)	1.451 (7)	1.460 (7)	C(33)-C(34)	1.363 (7)	1.362 (7)
C(3)-C(31)	1.516 (6)	1.505 (7)	C(34)-C(35)	1.385 (6)	1.383 (6)
C(4)-C(5)	1.485 (6)	1.467 (6)	N(32)-B	1.548 (6)	1.544 (6)
C(4)-O(2)	1.224 (5)	1.236 (6)	N(41)-N(42)	1.382 (6)	1.385 (7)
C(5)-C(6)	1.385 (6)	1.396 (6)	N(41)-N/C(45)	1.378 (6)	1.366 (5)
C(5)-C(51)	1.502 (8)	1.500 (8)	N(42)-C(43)	1.338 (7)	1.393 (8)
C(6)-C(61)	1.513 (6)	1.515 (7)	C(43)-C(44)	1.362 (7)	1.345 (8)
N(11)-N(12)	1.368 (5)	1.365 (5)	C(44)-N/C(45)	1.371 (8)	1.328 (8)
N(11)-C(15)	1.341 (7)	1.347 (7)	N(41)-B	1.501 (6)	1.498 (6)
N(12)-C(13)	1.356 (5)	1.361 (6)	Rh···C(1)	2.450 (5)	2.459 (3)
C(13)-C(14)	1.372 (8)	1.369 (8)	Rh-C(2)	2.164 (5)	2.172 (6)
C(14)-C(15)	1.373 (6)	1.376 (7)	Rh-C(3)	2.166 (4)	2.179 (5)
N(12)-B	1.553 (7)	1.562 (7)	Rh···C(4)	2.480 (4)	2.439 (4)
N(21)-N(22)	1.361 (5)	1.359 (5)	Rh-C(5)	2.263 (4)	2.272 (4)
			Rh-C(6)	2.230 (4)	2.236 (4)

(b) Bond Angles

	molecule 1	molecule 2		molecule 1	molecule 2
N(11)-Rh-N(21)	83.7 (1)	83.3 (2)	N(12)-B-N(32)	105.6 (4)	105.9 (4)
N(11)-Rh-N(31)	82.0 (1)	81.7 (1)	N(12)-B-N(41)	111.7 (3)	109.7 (3)
N(21)-Rh-N(31)	87.0 (1)	87.2 (1)	N(22)-B-N(32)	110.4 (3)	109.7 (3)
Rh-N(11)-N(12)	120.1 (3)	119.6 (3)	N(22)-B-N(41)	108.6 (4)	109.0 (4)
Rh-N(11)-C(15)	133.2 (3)	133.9 (3)	N(32)-B-N(41)	112.7 (3)	114.6 (3)
N(12)-N(11)-C(15)	106.5 (3)	106.3 (3)	C(6)-C(1)-C(2)	113.3 (4)	113.4 (4)
N(11)-N(12)-C(13)	109.2 (4)	109.1 (4)	C(2)-C(1)-O(1)	123.0 (5)	122.8 (5)
N(11)-N(12)-B	120.9 (3)	121.9 (3)	C(6)-C(1)-O(1)	122.7 (4)	122.8 (4)
C(13)-N(12)-B	129.4 (3)	128.8 (4)	C(1)-C(2)-C(3)	120.5 (4)	120.5 (5)
N(12)-C(13)-C(14)	107.9 (4)	108.3 (4)	C(1)-C(2)-C(21)	115.0 (4)	115.3 (4)
C(13)-C(14)-C(15)	106.2 (5)	105.8 (5)	C(3)-C(2)-C(21)	123.3 (4)	123.0 (4)
C(14)-C(15)-N(11)	110.2 (5)	110.5 (5)	C(2)-C(3)-C(4)	121.1 (4)	120.8 (4)
Rh-N(21)-N(22)	119.1 (3)	120.0 (3)	C(2)-C(3)-C(31)	122.8 (4)	122.9 (5)
Rh-N(21)-C(25)	134.5 (3)	133.6 (3)	C(4)-C(3)-C(31)	114.5 (4)	115.3 (4)
N(22)-N(21)-C(25)	106.4 (4)	106.4 (4)	C(3)-C(4)-C(5)	112.6 (3)	114.1 (4)
N(21)-N(22)-C(23)	109.3 (3)	109.0 (3)	C(3)-C(4)-O(2)	123.8 (4)	122.9 (4)
N(21)-N(22)-B	120.9 (4)	119.9 (4)	C(5)-C(4)-O(2)	122.4 (5)	122.0 (5)
C(23)-N(22)-B	129.0 (4)	130.4 (4)	C(4)-C(5)-C(6)	121.5 (5)	121.8 (5)
N(22)-C(23)-C(24)	108.8 (5)	109.0 (5)	C(4)-C(5)-C(51)	116.8 (4)	117.4 (4)
C(23)-C(24)-C(25)	105.3 (5)	105.7 (5)	C(6)-C(5)-C(51)	120.9 (4)	120.3 (4)
C(24)-C(25)-N(21)	110.1 (4)	109.9 (4)	C(5)-C(6)-C(1)	121.1 (4)	121.1 (4)
Rh-N(31)-N(32)	121.7 (2)	122.8 (3)	C(5)-C(6)-C(61)	120.6 (5)	120.8 (5)
Rh-N(31)-C(35)	130.2 (3)	130.8 (3)	C(1)-C(6)-C(61)	117.4 (4)	117.0 (4)
N(32)-N(31)-C(35)	106.4 (3)	106.0 (3)	C(1)-Rh-C(2)	35.9 (2)	36.1 (2)
N(31)-N(32)-C(33)	109.1 (4)	109.6 (4)	C(1)-Rh-C(3)	65.4 (2)	65.4 (2)
N(31)-N(32)-B	117.1 (3)	116.1 (3)	C(1)-Rh-C(4)	72.7 (2)	73.5 (2)
C(33)-N(32)-B	131.9 (3)	133.3 (4)	C(1)-Rh-C(5)	63.6 (2)	63.5 (2)
N(32)-C(33)-C(34)	108.6 (4)	108.1 (4)	C(1)-Rh-C(6)	36.3 (2)	36.0 (2)
C(33)-C(34)-C(34)	105.1 (4)	105.7 (4)	C(2)-Rh-C(3)	38.8 (2)	38.7 (2)
C(34)-C(35)-N(31)	110.9 (4)	110.6 (4)	C(2)-Rh-C(4)	65.2 (2)	66.1 (2)
B-N(41)-N(42)	117.5 (3)	125.6 (4)	C(2)-Rh-C(5)	79.2 (2)	79.2 (2)
B-N(41)-N/C(45)	131.7 (4)	124.6 (4)	C(2)-Rh-C(6)	67.5 (2)	67.4 (2)
N(42)-N(41)-N/C(45)	109.5 (4)	109.7 (4)	C(3)-Rh-C(4)	35.6 (2)	36.3 (2)
N(41)-N(42)-C(43)	105.0 (4)	106.8 (4)	C(3)-Rh-C(5)	66.9 (2)	66.9 (2)
N(42)-C(43)-C(44)	112.1 (5)	104.5 (5)	C(3)-Rh-C(6)	79.7 (1)	79.7 (2)
C(43)-C(44)-N/C(45)	106.4 (5)	114.5 (5)	C(4)-Rh-C(5)	36.1 (1)	36.1 (2)
C(44)-N/C(45)-N(41)	107.0 (4)	104.5 (4)	C(4)-Rh-C(6)	64.0 (1)	64.5 (1)
N(12)-B-N(22)	107.7 (3)	107.7 (3)	C(5)-Rh-C(6)	35.9 (2)	36.1 (2)

(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, N–Rh–N = 90.0(1)°) are in accord with values reported for other Rh(nbd) complexes, e.g., Rh–C = 2.087–2.104 (3) Å and C=C = 1.384–1.406 (5) Å in $[Rh(nbd)(OAc)]_2$[8] and Rh–C = 2.04–2.16 (1) Å and C=C = 1.39–1.45 (1) Å in Rh $(C_5H_5N)(C_5HF_6O)(nbd)$.[9] The olefin coordination in 1 is slightly asymmetric with in a and Rh–C(6) (2.110 (4) and 2.114 (5) Å, mean 2.112 Å) less than Rh–C(3) and Rh–C(5) (2.130 (4) and 2.127 (5) Å, mean 2.129 Å). The cause of this

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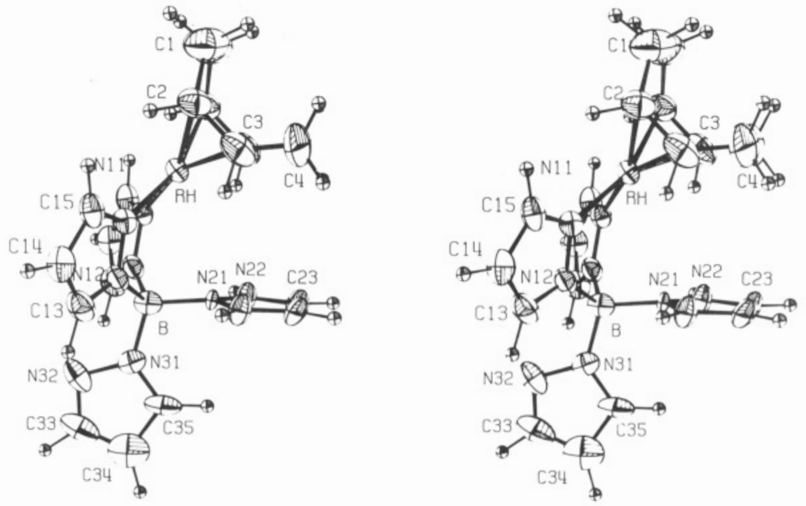

Figure 5. Stereoview of a molecule of $B(pz)_4Rh(cod)$ (**2**) with the crystallographic numbering scheme. The molecule has crystallographic mirror symmetry.

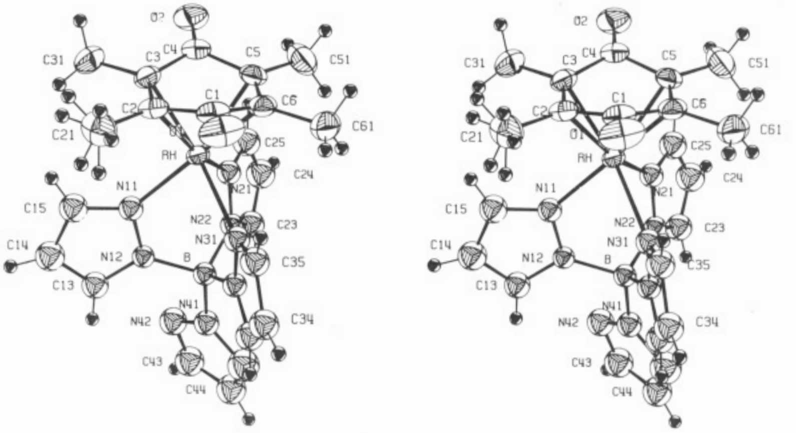

Figure 6. Stereoview of molecule 1 of $B(pz)_4Rh(dq)$ (**3**) with the crystallographic numbering scheme. One methyl group has its hydrogens disordered over two sites.

asymmetry appears to be the close approach of pyrazolyl hydrogens at C(15)–H and C(25)–H (Figure 4) to nbd hydrogens at C(3)–H and C(5)–H (H···H = 2.28, 2.15 Å). The presence of the pz ring N(41)···C(45) above the coordination plane causes no distortion to the coordination.

In an attempt to quantify the steric demand of the nbd ligand, we have calculated from the coordinates of Table II a maximum cone angle θ^{10} in a manner exactly analogous to our previous work on bulky phosphine complexes.[11] Our calculations lead to a maximum θ value of 183° (corresponding to the angles subtended by C(2)–H, C(3)–H, C(5)–H, and C(6)–H). It is obvious that the nbd ligand is at best an irregular cone and the *minimum* cone angle is also relevant and is ~109° (for the C(1)–H and C(4)–H segment). The Rh···N(42) distance which would become an Rh–N bond in a five-coordinate complex is 4.096 (3) Å, and the Rh···N(42) vector lies close to the direction of minimum nbd cone angle which would provide the least encumbrance of five-coordination.

In $B(pz)_4Rh(cod)$ (**2**) the rhodium atom also has square-planar coordination and the molecule possesses crystallographic mirror symmetry (Figure 5), the mirror plane passing through the Rh, B, and N(21) atoms and pyrazolyl ring N(31)···C(35) (deviations (Å) from the square plane are as follows: Rh–0.028, N(11) and $N(11)^I$ + 0.007, midpoints of C(2)═C(3) and $C(2)^I$═$C(3)^I$ + 0.007). Figure 7b is a view normal to the olefin coordination plane. Because of the mirror plane, the pyrazolyl ring containing N(21) is disordered over two sites with equal probability but the only effect of this, is to interchange the uncomplexed N atom with a CH moiety. The principal coordination dimensions (Rh–C = 2.124 and 2.139 (2) Å, Rh–N = 2.099 (2) Å, C═C = 1.382 (4) Å, N–Rh–N = 86.6 (1)°) are in accord with those reported in other Rh(cod) complexes, e.g., Rh–C = 2.101–2.129 (5) Å, C═C = 1.39 (1) Å in Rh (cod) $(C_5H_4CO_2Me)^{12}$ and Rh–C = 2.06–2.38 (1) and C═C = 1.41 and 1.43 (2) Å in $Rh(cod)(C_8H_{11})$.[13] The olefin coordination in **2** closely resembles that found in **1** and is slightly asymmetric. Thus Rh–C(2) = 2.139 (2) Å is longer than Rh–C(3) = 2.124 (2) Å again to relieve H···H intramolecular interactions between C(2)–H and C(15)–H atoms (H···H = 2.04 Å). Cone angle calculations for cod in **2** lead to a maximum cone angle θ of 210° (at the C(2)–H, C(3)–H, C(2′)–H, and C(3′)–H segments) and also to a minimum value of ~120° between the C(1)–H, C(1′)–H and C(4)-H, C(4′)–H segments. The Rh···N(22) distance which would be a Rh–N bond in a five-coordinate species is 3.694 (2) Å, and as in **1** the Rh···N(22) vector lies close to the direction of the minimum cod cone angle which

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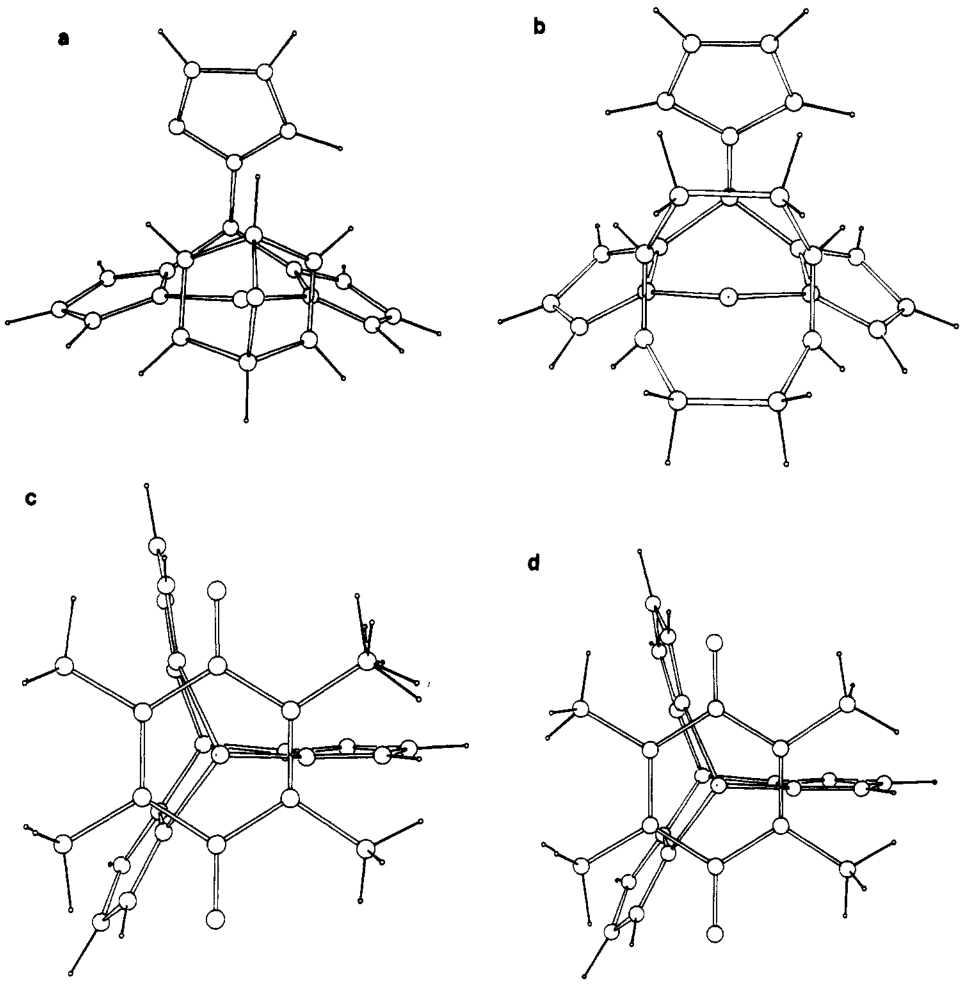

Figure 7. Views of the complexes looking approximately along the normal to the olefin coordination plane (the *exo*-pyrazolyl ring has been excluded for clarity): (a) B(pz)$_4$Rh(nbd) (1); (b) B(pz)$_4$Rh(cod) (2); (c) moleule 1 of B(pz)$_4$Rh(dq) (3); (d) molecule 2 of B(pz)$_4$Rh(dq).

would provide the minimum hindrance to five-coordination.

The asymmetric unit of B(pz)$_4$Rh(dq) (**3**) contains two independent essentially identical molecules (labeled molecule A and molecule B in Tables III and VII) which differ slightly in the orientation of the pyrazolyl rings and also in that in one molecule, the hydrogen atoms of one methyl group are disordered over two sites. The Rh coordination geometry (Figure 6) is trigonal bipyramidal with one Rh–olefin and one Rh–N bond axial: Rh–(C(5) or C(6)) = 2.230–2.272 (4) Å, mean 2.250 Å; Rh–N(11) = 2.085 and 2.071 (3) Å, mean 2.078 Å. The remaining equatorial coordination distances are as follows: Rh–(C(2) or C(3)) = 2.164–2.179 (5) Å, mean 2.170 Å; Rh–N(21) = 2.130 and 2.129 (4) Å, mean 2.130 Å; Rh–N(31) = 2.184 and 2.167 (3) Å, mean 2.176 Å. The equatorial moiety (Rh, N(21), N(31), midpoint of C(2)=C(3)) is planar to within 0.003 Å (molecule A) and 0.062 Å (molecule B), and the axial N(11)–Rh–(midpoint of C(5)=C(6)) angles are 170.8 and 169.9 (2)° for molecules A and B, respectively. The mean olefin distances C(2)=C(3) = 1.440 (7) Å and C(5)=C(6) = 1.390 (6) Å are significantly different, the axial olefin (C(5)=C(6)) having the shorter C=C distance and the longer Rh–C bonds. The small differences between the two molecules are what give rise to the layers with weak *k* odd reflections in space group $A\bar{1}$. If these weak reflections were ignored, the cell would reduce to one with one molecule of **3** in the asymmetric unit; the new **b** and **c** cell dimensions being half of those reported for the $A\bar{1}$ cell. There are no previous reports of Rh(dq) complexes stored in the Cambridge Crystallographic Data Base.[14]

Complex formation causes deformation of both the dq and B(pz)$_3$Rh skeletons in **3**. Thus the dq ligand adopts a boat conformation with dihedral angle (26.7° molecule A, 23.9° molecule B) between the C(1), C(2), C(3), C(4) and C(1), C(4), C(5), C(6) planes. This has the effect of placing the carbonyl oxygen atoms 0.36–0.57 Å off the olefin plane on the side away from the rhodium atom. Views of the two molecules of **3** normal to the olefin coordination plane are in parts c and d of Figure 7. Formation of the five-coordinate complex produces some distortion of the B(pz)$_3$Rh framework with values of interplanar angles between RhNNB and pyrazolyl ring planes in the range 5.1–13.6°.

From a study of the crystal structures of **1**–**3**, one might anticipate that **1** and **2** should be able to form five-coordinate complexes. Our cone-angle calculations show that there is a minimum cone-angle pathway about both nbd and cod ligands for a third pyrazolyl nitrogen to approach a rhodium atom. The fact that no five-coordinate solid-state structures occur with **1** and **2** presumably reflects the fine balance which must exist between crystal packing and intramolecular interactions. This balance is seen to favor four-coordinate structures for **1** and **2** in the solid but our NMR work[3] shows that **2** is certainly five-coordinate in solution and that **1** may also be.

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[14] "CRYSTOR", The Cambridge Crystallographic Data Base at the National Research Council of Canada Laboratories, Ottawa, 1982.

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Supplementary Material Available: Tables II, III, and IV and tables of thermal parameters, calculated hydrogen coordinates, and structure factor for 1, 2, and 3 (65 pages). Ordering information is given on any current masthead page.

Stereochemically Nonrigid Bis(olefin)rhodium Poly(1-pyrazolyl)borato Complexes. 3. ^{1}H and ^{103}Rh Nuclear Magnetic Resonance Studies[1]

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^{1}H and ^{103}Rh NMR spectra have been measured for solutions of Rh(I) complexes of the type RhB(pz$_4$)(diene) in which B(pz)$_4$ signifies tetrakis(1-pyrazolyl)borate ion and diene signifies duroquinone (dp), 1,5-cyclooctadiene (cod), and norbornadiene (nbd). The ^{1}H spectra indicate that the dq and cod complexes are pentacoordinate; i.e., three of the pyrazolyl groups of B(pz)$_4$ are bound to Rh via nitrogen. The dq complex is also pentacoordinate in the solid state whereas the cod and nbd complexes are four-coordinate. ^{1}H spectra at various temperatures and in the presence and absence of potassium tetrakis(1-pyrazolyl)borate indicate that the free and coordinated pyrazolyl groups undergo intramolecular exchange with the relative rates increasing in the sequence dq, cod, and nbd. Activation parameters for this process were determined for dq and cod complexes but not for the nbd complex for which the exchange rate is too fast to measure by ^{1}H NMR. ^{103}Rh NMR was measured for these complexes and the ^{103}Rh chemical shift relative to that for (acac)Rh(CO)$_2$ increases in the order cod, nbd, and dq, which differs from the order for the relative exchange rates. The ease of ^{103}Rh NMR measurements in comparison with previous studies appears to be due to the shorter T_1 relaxation for these diene complexes.

Introduction

A fairly large number of fluxional four- and five-coordinate rhodium(I) complexes have been reported. The fluxional behavior of these complexes is usually related to a reorientation of either an olefin or a diene coordinated to the rhodium. Thus, the ^{1}H NMR spectra of cyclopentadienylrhodium complexes containing one or two ethylene groups indicate that the ethylene group rotates with activation energies between 12 and 15 kcal/mol.[3] When 3-butenyldiphenylphosphine (mbp) is used, RhCl(mbp)$_2$ is four-coordinate in solution with exchange between free and coordinated olefins rapid on the NMR time scale at room temperature.[4] *o*-Styryldiphenylphosphine (ssp) and *o*-styryldiphenylarsine (spas) form five-coordinate rhodium(I) complexes of the formula RhCl(spp)$_2$ and RhCl(spas)$_2$, which are believed to be trigonal bipyramidal with the vinyl groups in equatorial sites. ^{1}H and ^{31}P NMR indicate that there are two isomers, one of which has inequivalent vinyl groups, and that these isomers interconvert rapidly on the NMR time scale around room temperature.[5]

Dienes in four- and five-coordinate rhodium(I) have also been found to reorient. Thus, by ^{1}H NMR [8](1,4)-7-oxanorbornadiene (onbd) groups in Rh(onbd)$_2$Cl and [Rh(onbd)Cl]$_2$ have been found to rotate around the axis through the center of the onbd group. For the former $\Delta H^{\ddagger}$ is 12.4 kcal/mol and $\Delta S^{\ddagger}$ is 3.0 eu.[6] Restricted rotation of norbornadiene (nbd) groups has been observed in [Rh(nbd)(OAc)]$_2$ with an activation energy of about 7 kcal/mol.[7] Other four-coordinate Rh(I) complexes having rotating ethylene groups also appear to undergo intermolecular exchange with free ethylene.[8] In addition to these examples, a brief review presents a number of other four-coordinate square-planar diene complexes of Rh(I) that show temperature-dependent ^{1}H NMR spectra, indicating intramolecular exchange of alkene protons between nonequivalent sites.[9] This exchange appears to be enhanced by donor ligands.

While there is a great deal of information concerning fluxional four- and five-coordinate Rh(I) complexes in which an olefin or diene changes its orientation or position in the complex, exchange involving other ligands, which usually complex via group 5 atoms in these complexes, does

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