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 intercon-

vert 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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not appear to be documented. This paper reports the results of a variable-temperature ^{1}H NMR study of this type of exchange in five-coordinate rhodium(I) diene complexes of the type B(pz)$_4$Rh(diene) in which B(pz)$_4$ denotes tetrakis(1-pyrazolyl)borate ion. Three dienes were used: duroquinone (dq), 1,5-cyclooctadiene (cod), and norbornadiene (nbd). For the dq complex, the X-ray structure indicates that the two olefinic groups of the quinone ligand occupy one axial and one equatorial site in the five-coordinate trigonal-bipyramidal molecule. The remaining one axial and two equatorial sites are occupied by the nitrogen atoms of three B(pz)$_4$ pyrazolyl groups. The nbd and cod complexes are four-coordinate square-coplanar species in the solid state.[1] In solution, however, ^{1}H NMR indicates that the dq and cod complexes appear to be five-coordinate and the nbd may well be also. This behavior of the nbd and cod complexes is in contrast to that of RhCl (mbp)$_2$, which is five-coordinate in the solid and four-coordinate in solution,[4] but similar to that of the related pyrazolylborate complex HB(pz)$_3$Pt(CH$_3$)CO.[10] The ^{1}H NMR spectra of the rhodium(I) diene complexes are compatible with two separate dynamic processes occurring in solution:

(i) Free and coordinated pyrazolyl groups exchange. For the dq complex this bond-breaking process is slow at room temperature and the exchange rate increases in the sequence dq, cod, and nbd. For the nbd complex the exchange is too fast to measure at −81 °C in CD$_2$Cl$_2$.
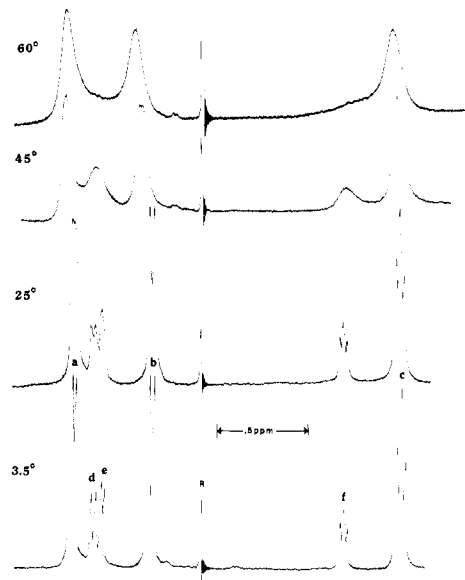
(ii) Coordinated pyrazolyl (and olefin) groups exchange between the axial and equatorial sites of the trigonal bipyramid. For pyrazole exchange this process does not involve bond breaking and is still rapid on the NMR time scale at the lowest temperature reached in these measurements (−89.6 °C for the cod complex). Another possibility is that the absence of any line-width effect is due to accidental magnetic equivalence of the protons. On the other hand, rapid exchange of coordinated pyrazolyl groups in B(pz)$_4$PtCH$_3$(L) has been observed.[10]

The ^{103}Rh NMR spectrum of each complex consists of one signal, and the chemical shifts measured relative (acac)Rh(CO)$_2$ do not appear to correlate with the rate of exchange of the pyrazolyl groups. This appears to be the first direct observation of ^{103}Rh spectra of rhodium(I) olefin complexes in solution. Previous ^{103}Rh NMR measurements of Rh(I) and Rh(III) complexes in solution have had to deal with relatively long T_1 relaxation times.[11,12] This difficulty does not occur with unsymmetrical rhodium(I) olefin complexes as discussed in another paper.[13]

Experimental Section

Chemicals. The preparation of B(pz)$_4$Rh(cod), B(pz)$_4$Rh(nbd), and B(pz)$_4$Rh(dq) is described in the previous paper.[14] (acac)-Rh(CO)$_2$ obtained from Alfa, potassium tetrakis(1-pyrazolyl)borate obtained from Columbia Organic Chemicals, and deuterated solvents obtained from Merck, Sharp and Dohm were used without purification.

Exchange Measurements. CW ^{1}H NMR spectra of 0.3 M Rh(I) complexes in CDCl$_3$ solutions were measured at 100 MHz using a Varian HA-100-15 NMR spectrometer equipped with a variable-temperature probe. Temperatures between −20 and +70

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Figure 1. Temperature dependence of the pyrazolyl ring proton resonances for 0.3 M B(pz)$_4$Rh(dq) in CDCl$_3$ at 100 MHz. For assignments, see text. Temperature is in degrees celcius, and magnetic field increases from left to right.

°C were measured by thermocouple and those between −90 and −40 °C were measured by using the NMR spectrum of methanol. It was possible to supercool the CDCl$_3$ solutions to −90 °C. The NMR signals of the small amount of CHCl$_3$ in CDCl$_3$ solvent and added CH$_2$Cl$_2$ were used as internal line width and chemical shift references. Tetramethylsilane was used as an internal lock.

Because the coupling constants are small and the signals of the doublets overlap, the width at half height could not be measured conveniently, and consequently the exchange lifetime τ was obtained by computer simulation of the line shapes.[15] For these simulations, the line width at half-height $\Delta\nu_0$ and the chemical shift δ between the two averaging lines in the absence of exchange must be provided. To correct for variations in $\Delta\nu_0$ from one measurement to the next, its value at each temperature was determined for each measurement from the line width $\Delta\nu_R$ of an internal reference using a linear relation between $\Delta\nu_0$ and $\Delta\nu_R$ determined at 3.5 °C for dq and at 31 °C for cod. At these temperatures the exchange contributions to the respective signals of dq and cod complexes is negligible.

In the absence of exchange or at very slow exchange, the position of the pyrazolyl proton signals of B(pz)$_4$Rh(dq) depends on temperature in a linear fashion between −20 and +25 °C. This relation was assumed to apply also at higher temperatures and was used to calculate the value δ at each temperature that was used in the computer simulation. For the cod complex, whose coalescence temperature occurs at about −62 °C, a dependence of the chemical shift on temperature could not be established. Therefore δ, which is determined at −89.6 °C for this complex, is treated as independent of temperature.

^{103}**Rh Spectra.** The FT ^{103}Rh NMR spectra of the (acac)-, (nbd)-, (cod)-, and (dq)Rh^I complexes were measured at 25 °C by using a Bruker WH 00 spectrometer operating at 12.65 MHz. This spectrometer is operated by the Southwestern Ontario NMR Centre located in the Department of Chemistry at the University of Guelph. Spectra were obtained by using CDCl$_3$ solutions of 0.2 M nbd, cod, and dq complexes and 0.3 M acac complex in 10-mm sample tubes. For the olefin complexes, the number of scans varied from 300 to 1000, with most spectra requiring typically less than 20 min of signal averaging.

Results and Discussion

^{1}**H NMR Spectra.** The temperature dependence of ^{1}H NMR signals of the pyrazolyl protons is illustrated in

(15) Cocivera, M. Bell Telephone Laboratories Memorandum MM68-1132-1, 1968. This program has been modified by K. W. Woo for use at the University of Guelph.

Table I. Chemical Shifts (Ppm) Relative to Me₄Si for the ¹H NMR Signals of the Protons on the Pyrazolyl Groups in Rhodium(I) Diene Complexes

	chem shift[a]		
complex	H₃ or H₅	H₄	H₃ or H₅
B(pz)₄Rh(dq)			
coordinated[b]	8.04 (2.8)	6.30	7.63 (4.0)
uncoordinated[b]	7.88 (2.8)	6.61	7.93 (4.1)
B(pz)₄Rh(cod)			
coordinated[c]	7.60	6.35	7.23
uncoordinated[c]	7.85	6.28	6.67
B(pz)₄Rh(nbd)			
coalesced signals[d]	7.43 (2.9)	6.29	6.95 (3.7)

[a] Numbers in parentheses are proton–proton coupling constants in Hz. [b] Measured at 3.5 °C. [c] Measured at −81 °C. Signals are too broad to measure coupling constants; see Figure 2. [d] Coalescence of signals due to coordinated and uncoordinated pyrazolyl groups. Measured at 0 °C.

Figure 1 for B(pz)₄Rh(dq). The spectrum at 3.5 °C indicates that there are two types of pyrazolyl groups in the ratio 1:3. In the solid state, three pyrazolyl groups are coordinated to rhodium as in structure 1.[1] Consequently,

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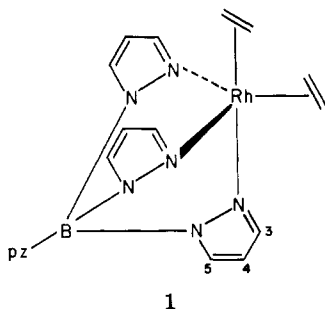
signals a, b, and c are assigned to coordinated pyrazolyl groups. On the basis of line-width behavior and the change in chemical shifts of the signals as the temperature increases, signals a, b, and c exchange with e, d, and f, respectively. Of the three protons on the pyrazolyl group, the resonance of only the H₄ proton can be assigned conclusively without selective deuteration of the ring. Thus signals c and f are assigned to this proton in the coordinated and uncoordinated pyrazolyl groups, respectively, because the closely spaced three lines are probably due to overlap of the two doublets expected for the coupling of this proton with the other two protons. The assignment of the other two resonances is uncertain without appropriate isotopic labeling.

The rate of exchange of the free and coordinated pyrazolyl groups depends on the diene coordinated to rhodium, increasing in the order dq, cod, and nbd. For nbd, the exchange is too fast at −90 °C with use of the HA-100 spectrometer and at −65 °C with use of the WH-400 spectrometer. For cod, the exchange could be slowed sufficiently at −89.6 °C to resolve the signals due to coordinated and uncoordinated pyrazolyl groups at 100 MHz as illustrated in Figure 2 for a solution of 0.2 M B-(pz)₄Rh(cod) in CDCl₃ containing a small amount of CH₂Cl₂ (labeled R) to act as an internal reference. As with dq, there are two types of pyrazolyl groups in the ratio 1:3. The more intense signals are assigned to the coordinated
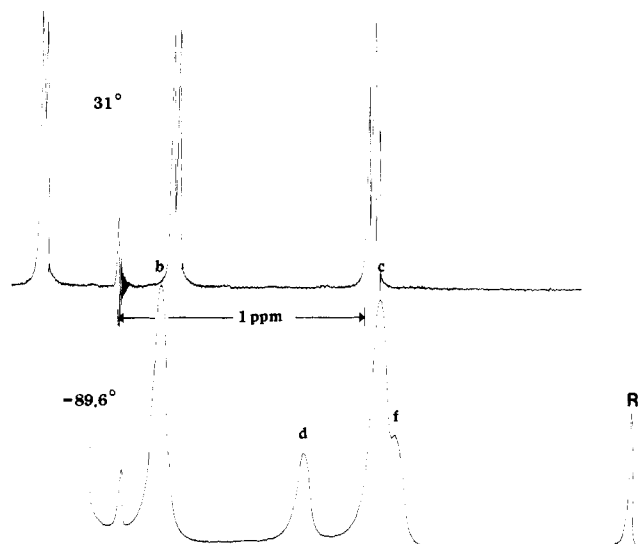

Figure 2. Temperature dependence of part of the pyrazolyl ring proton resonances for 0.3 M B(pz)₄Rh(cod) in CDCl₃ at 100 MHz. Temperature is in degrees Celcius, and the magnetic field increases from left to right. For assignments, see text.

pyrazolyl groups because there is no precedent for three-coordinate rhodium complexes and dimerization seems unlikely. Five-coordination of the cod complex in solution is in contrast with four-coordination observed in the solid state.[1] The opposite change, five-coordinate in solid state and four-coordinate in solution, has been observed for RhCl (mbp₂).[4]

The signal labels in Figure 2 have the same meaning as those in Figure 1. Resonances c and f may safely be assigned to H₄ for the reasons discussed earlier, but again the assignment of the other ring proton resonances to H₃ and H₅ is ambiguous. Proton chemical shifts for coordinated and uncoordinated pyrazolyl groups listed in Table I for the three complexes indicate that the chemical shifts of the protons of uncoordinated pyrazolyl groups are not independent of the nature of the diene in the complex. For the nbd complex, chemical shifts of the coalesced signals at −65 °C are within 0.01 ppm of those listed in Table I.

The exchange lifetimes as a function of temperature given in Table II were obtained on the basis of the following considerations. First, the fact that the pyrazolyl proton signals exhibit an AMX rather than an A₂X pattern indicates the absence of any significant exchange of boron between the two ring nitrogens. Consequently the line-shape changes can be related to exchange between "free" pyrazolyl and rhodium-coordinated pyrazolyl groups, and the position of the ring protons relative to boron is not altered. Second, since the position of the protons is not altered they have the same exchange lifetimes. For this reason, the lifetime determination is based only on an analysis of the b–d resonance pairs. Third, it is assumed that the sign of each proton–proton coupling constant does not change when "free" pyrazolyl becomes coordinated to rhodium. Consequently for dq, the exchange averages the lower field line of b with the lower field line of d and likewise for the higher field lines of b and d. For B-(pz)₄Rh(cod), since the doublets are not resolved at −89.6 °C, b and d (Figure 2) are treated as broad singlets having

Table II. Temperature Dependence of Rates 1/τ for Exchange between Free and Coordinated Pyrazolyl Groups in B(pz)₄Rh(diene)

dq	t, °C	25	35	40	45	50	55.5	60	65
	1/τ, s⁻¹	3	8	17	23	40	55	75	115
cod	t, °C	−88	−87	−83.5	−76.5	−73	−69.5	−66	−62.5
	1/τ, s⁻¹	2.4	2.5	3.5	4.6	12.5	20	35	49

Table III. Transition-State Parameters for
Fluxional B(pz)$_4$Rh(diene)

	$\Delta H^{\ddagger}$, kJ mol^{-1}	$= \Delta S^{\ddagger}$, J mol^{-1} deg^{-1}	$\Delta G^{\ddagger}_{298}$,[a] kJ mol^{-1}	r[b]
dq	73.2 ± 2.8	14.5 ± 8.2	68.9 ± 5.3	0.996
cod	35.9 ± 3.9	-40.3 ± 20.0	47.9 ± 8.9	0.969

[a] Values of $\Delta G^{\ddagger}_{298}$ were calculated from the equation $\Delta G = \Delta H - T\Delta S$. [b] Correlation coefficient of straight line approximation of relation $\ln 1/\tau = f(1/T)$.

line width in the absence of exchange equal to the sum of the line widths and coupling constant of the corresponding doublet in the 30 °C spectrum. Again, this line width is relative to that for an internal standard (CH$_2$Cl$_2$). The solvent CDCl$_3$ was used for each complex. Consequently some of the temperatures used for the cod complex involved super-cooled solutions.

The exchange rates $1/\tau$ given in Table II indicate that the pyrazolyl groups in B(pz)$_4$Rh(dq) exchange more slowly than those in B(pz)$_4$Rh(cod). In turn it appears that the exchange is fastest for B(pz)$_4$Rh(nbd) because it cannot be slowed sufficiently to be measured at -81 °C. This sequence appears to reflect the strength of interaction between rhodium and the diene. Thus, as the diene becomes more electron donating, exchange between "free" and coordinated pyrazolyl groups in the complex becomes faster, indicating that the bond between rhodium and pyrazolyl nitrogen becomes weaker. This conclusion is consistent with the observation that the nbd–Rh bond appears more stable than the cod–Rh bond in reactions of [Rh(diene)$_2$]ClO$_4$ with ligands containing group 5 elements.[16]

The exchange appears to be an intramolecular process because addition of potassium tetrakis(1-pyrazolyl)borate causes no detectable change in the line shape of the signals, indicating that an intermolecular process is unlikely. A plausible mechanism for the intramolecular process involves formation of a four-coordinate intermediate complex (structure 2).

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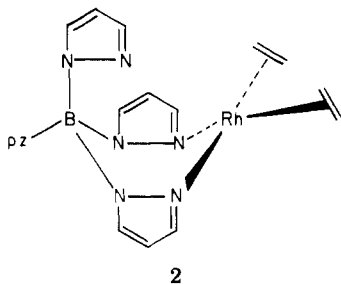
Although the pyrazolyl groups occupy axial and equatorial sites in the complexes, the NMR spectra give no indication that these sites provide different magnetic environments for the protons. A possible explanation is that the pyrazolyl groups exchange rapidly between the axial and equatorial sites on the NMR time scale at the lowest temperature reached in these measurements (-89.6 °C for the cod complex). This process cannot involve rupture of the rhodium–nitrogen bond because bond breaking is not fast on the NMR time scale. An alternative explanation may be that the magnetic environments for the protons are accidentally equivalent; however they are not equivalent in B(pz)$_4$PtCH$_3$(L).[10]
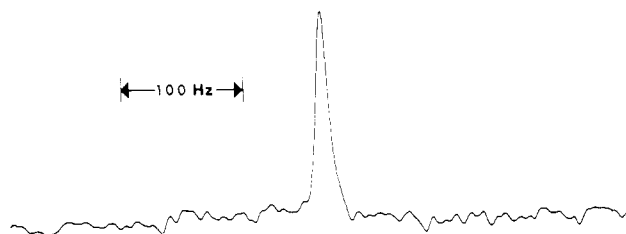
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Figure 3. Rhodium 103 resonance at 12.65 MHz for 0.3 M B(pz)$_4$Rh(cod) in CD$_2$Cl$_2$ at 25 °C obtained by Fourier transform of time-averaged FIDs (1000 scans) over a period of 14 min.

Table III indicates that the errors in $\Delta S^{\ddagger}$ are fairly large so that interpretation of magnitude and sign would not be meaningful. On the other hand, the errors for $\Delta H^{\ddagger}$ are substantially smaller, and this parameter makes the major contribution to $\Delta G^{\ddagger}_{298}$. The fact that the dq complex has a larger $\Delta H^{\ddagger}$ than the cod complex is consistent with the interpretation that rhodium–pyrazolyl nitrogen bonding in solution is stronger in B(pz)$_4$Rh(dq) than in B(pz)$_4$Rh-(cod). By means of comparison, rotation of olefins in Rh(I) complexes have $\Delta H^{\ddagger}$ values around 54 kJ mol^{-1}.[3b,6]

^{103}Rhodium Spectra. The first direct observation of ^{103}Rh NMR of rhodium(I) and -(III) complexes in solution was made by Gansow and co-workers[11] by means of FT NMR using a Bruker WH-180 and highly concentrated samples (about 2 M) in 20-mm tubes. Even under these conditions, about 10 h of time averaging was required, and in the case of the Rh(I) complex a paramagnetic agent was added to reduce the T_1 relaxation time. More recently Gruninger, Schwenk, and Mann report the observation of the ^{103}Rh resonance of 0.19 M (acac)$_3$Rh in CHCl$_3$ using the Quadriga–Fourier transform technique.[12] This approach required a total measuring time of 2 h.

The direct observation of the ^{103}Rh resonances for the dq, cod, and nbd Rh(I) complexes reported here were measured by the standard FT NMR technique using a Bruker WH-400 and 10-mm sample tubes containing 0.2 M complex in CDCl$_3$. The signal illustrated in Figure 3 for the cod complex required 14 min of time averaging at 25 °C. Although the higher field of the WH-400 provides some increase in sensitivity relative to the previous studies, the most important factor probably is the substantially shorter T_1 relaxation times for the rhodium in the present complexes allowing short acquisition times. Total acquisition time for one scan is 0.82 s at 25 °C for the cod complex. A detailed study of the relaxation times of the complexes has been reported in another paper.[13]

The absolute frequency of the ^{103}Rh resonance of (acac)Rh(CO)$_2$ is 12.626 913 MHz at 25 °C when the ^{1}H resonance of Me$_4$Si occurs at 400.13 MHz. Chemical shifts of the ^{103}Rh resonances at 25 °C relative to (acac)Rh(CO)$_2$ are 392.4, 453.8, and 1855.9 ppm downfield for the cod, nbd, and dq complexes, respectively. This sequence does not correspond to the sequence of exchange rates observed for these complexes. It is possible that carbonyl groups of dq have a strong effect on the ^{103}Rh resonance chemical shift. The chemical shifts and T_1 relaxation times are temperature dependent.[13]