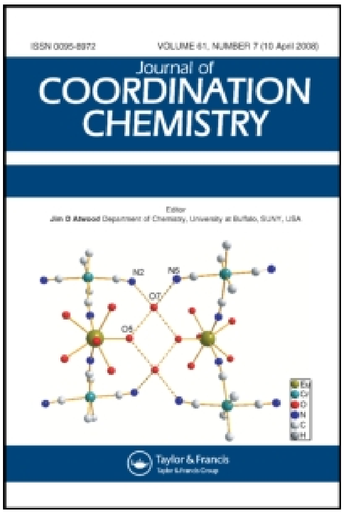

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NMR EXCHANGE STUDIES ON THE COMPLEXES *cis*-[Rh(CO)$_2$(pyridine *N*-oxide)(X)] (X = Cl, Br)

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^{13}C nmr spectra of the complexes *cis*-[Rh(CO))$_2$(pyO)(X)] (X = Cl, Br; pyO = pyridine *N*-oxide) are discussed. Variable temperature ^{13}C nmr spectroscopy has been used to monitor the exchange process occurring in acetone-d_6 solution. Rate constants for the exchange reaction have been determined by complete band shape analysis. The enthalpy of activation for the chloro- and bromo-complexes was found to be 53.3 ± 1.0 kJ mol^{-1} and 48.3 ± 0.8 kJ mol^{-1} respectively. The entropy of activation was found to be 5.5 ± 0.6 J mol^{-1} K^{-1} and -11.0 ± 0.3 J mol^{-1} K^{-1}, for the chloro- and bromo-complexes, respectively. It is suggested that the fluxionality of the molecules results from an *inter*molecular exchange of pyridine *N*-oxide rather than from loss of carbon monoxide. A mechanism for the exchange process is proposed.

KEYWORDS: Nmr, rhodium(I), pyridine *N*-oxide, carbonyl, fluxionality, rate constants

INTRODUCTION

The present work was undertaken to examine the interesting fluxional behaviour occurring in the ^{13}C nmr spectra of the complexes *cis*-[Rh(CO))$_2$(pyridine *N*-oxide)(X)] (X = Cl, Br). Preliminary nmr data[1] for these compounds had indicated that they were suitable for a detailed dynamic nmr (DNMR) study because the coalescence temperature occurs in an accessible temperature range and the pyridine *N*-oxide complexes do not decompose rapidly in solution.

Complete nmr band shape analysis has been applied by various workers[2-6] to the study of fluxional rhodium(I) complexes. The rhodium complexes are particularly amenable to nmr studies because ^{103}Rh has 100% natural abundance and a nuclear spin of 1/2. Thus, the spectra are characterized by the appearance of $^1J(^{103}$Rh-L) coupling. This spin-spin coupling provides an indication of the type of exchange occurring within the complexes. In *intra*molecular exchange processes, nuclear positions in a molecule are permutable without bond-breaking; hence spin-spin coupling may be maintained between the nuclei involved. In *inter*molecular exchange processes, there are bond-breaking and bond-formation steps. Bond-scission necessarily leads to loss of spin-spin coupling between the nuclei in the two fragments generated by the scission process. This loss of spin-spin coupling is a strong nmr test of an *inter*molecular exchange process and is extremely sensitive.[7]

The combined results obtained from the variable temperature ^{1}H, ^{13}C and ^{15}N nmr spectra[1] show that in the temperature range studied, the fluxional process involves the loss of pyO rather than the loss of CO, and the exchange of pyO occurs *via* an *inter*molecular exchange process.

EXPERIMENTAL

The complexes *cis*-[Rh(^{13}CO)$_2$(pyO)(X)] (X = Cl, Br) were prepared as previously described.[1] The level of enrichment of ^{13}CO was kept below ~30% in order to avoid broadening or partial splitting of the carbonyl resonances due to $^2J(^{13}$CO–Rh–^{13}CO) coupling. The variable temperature (+25°C to −55°C) ^{13}C nmr spectra of the complexes were recorded in acetone-d_6 on a Varian VXR-200 Fourier transform spectrometer operating at 50.3 MHz. The chemical shifts were measured relative to the internal solvent resonance (acetone-d_6 = 29.80 ppm). The sample temperature accuracy was verified by measuring the known peak separations in methanol and was within 0.5°C over the entire range. Complete band shape analysis of the carbonyl region (170–190 ppm) of the spectrum was performed using the computer program DNMR5.[8,9]

RESULTS AND DISCUSSION

The temperature-dependent ^{13}C nmr spectra (carbonyl region) of *cis*-[Rh(CO)$_2$(pyO)(X)] (X = Cl, Br) are shown in Figures 1 and 2. At room temperature (~25°C), the spectra show a doublet due to ^1J(Rh-CO) coupling. At low temperature, two doublets are seen. Assignment of the carbonyl resonances was based on ^{15}N-^{13}C coupling, the high field doublet being assigned to the carbonyl *trans* to the halide. This assignment is in agreement with the practice of assigning the carbonyl resonance with largest Rh-C coupling to the carbonyl *trans* to the halogen. As the sample temperature is lowered, the doublet collapses into a broad hump (at ~ −5°C) and then separates into two doublets as a result of the two different carbonyl environments, each doublet having a characteristic ^1J(Rh-CO) value. Figures 1 and 2 also show the computer simulated spectra calculated using the parameters given in Table 1 together with their associated errors. A weighted least-squares analysis of ln K against $1/T$ was performed in order to take into account the variable accuracy of the results, measurements near the coalescence temperature being more precise as the band more sensitive to the rate of exchange.[10] The plots (Fig. 3) yield straight lines, from which the enthalpy and entropy of activation may be obtained using equation (*1*),

$$\ln K_{ex} = -\Delta H^{\ddagger}/RT + [(\Delta S^{\ddagger}/R) + \ln(kT/h)] \qquad (1)$$

where K_{ex} = rate constant, T = temperature, and k, h, R = Boltzmann, Planck and gas constants, respectively.

The results for the exchange in the *cis*-[Rh(CO)$_2$(pyO)(Cl)] complex are $\Delta H^{\ddagger}$ = 53.3 ± 1.0 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 5.5 ± 0.6 J mol^{-1} K^{-1}. Similarly, the results for the *cis*-[Rh(CO)$_2$(pyO)(Br)] complex are: $\Delta H^{\ddagger}$ = 48.3 ± 0.8 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −11.0 ± 0.3 J mol^{-1} K^{-1}.

The activation parameters for the ligand exchange are similar to those found in other square planar rhodium complexes.[11] Infrared studies[1] on the *cis*-

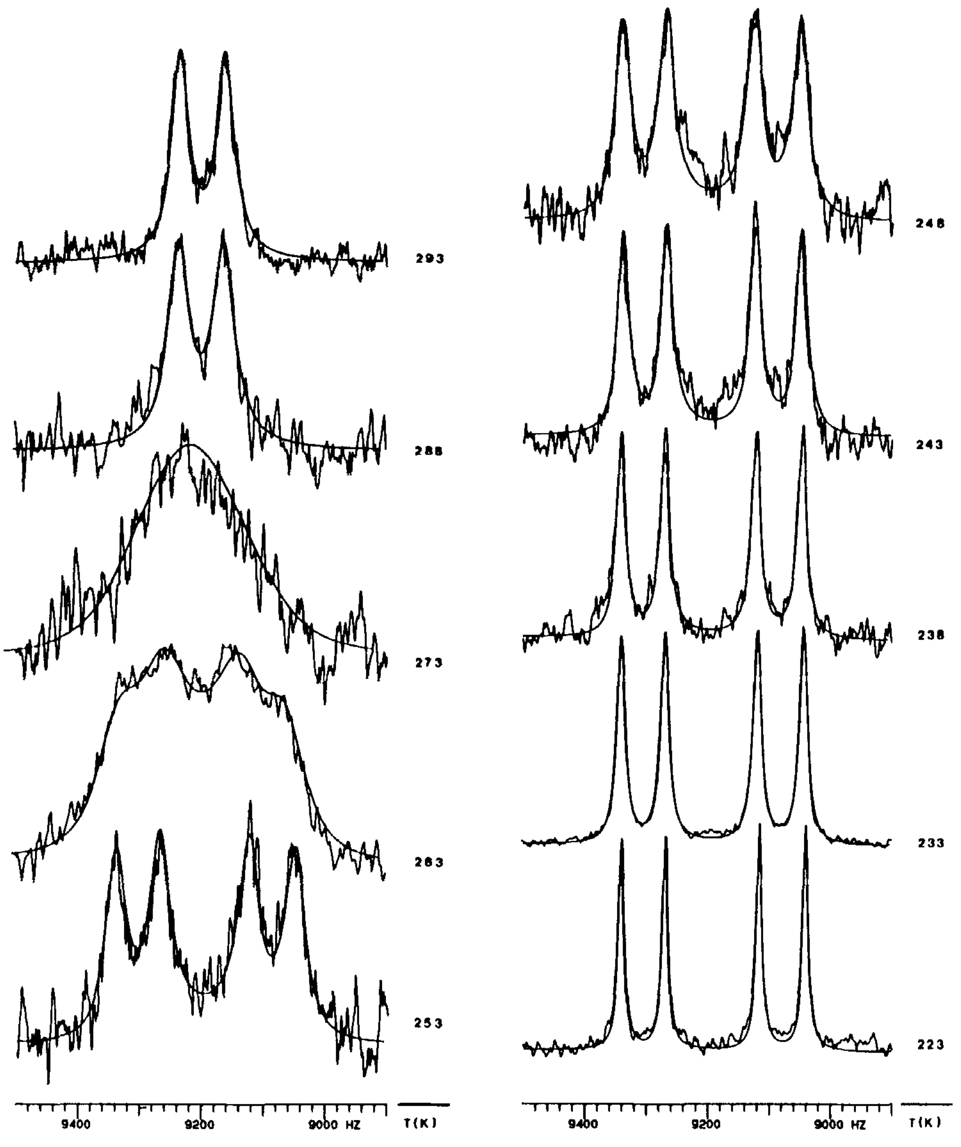

Figure 1 The computer simulated (smooth curve) and variable temperture ^{13}C nmr spectra (carbonyl region) for *cis*-[Rh(CO)$_2$(pyO)(Cl)] (temperatures in Kelvin).

[Rh(CO)$_2$(pyO)(X)] complexes show that the ν(Rh-Opy) band in the chloro complex occurs 8 cm^{-1} higher than in the bromo complex, indicating that the Rh-Opy bond is slightly stronger in the chloro complex than in the bromo complex. In general, the enthalpy of activation depends on the strengths of the bonds that are being broken and formed in getting to the transition state. Thus the slightly higher value of $\Delta H^{\ddagger}$ obtained for the chloro complex, relative to the bromo complex, would be

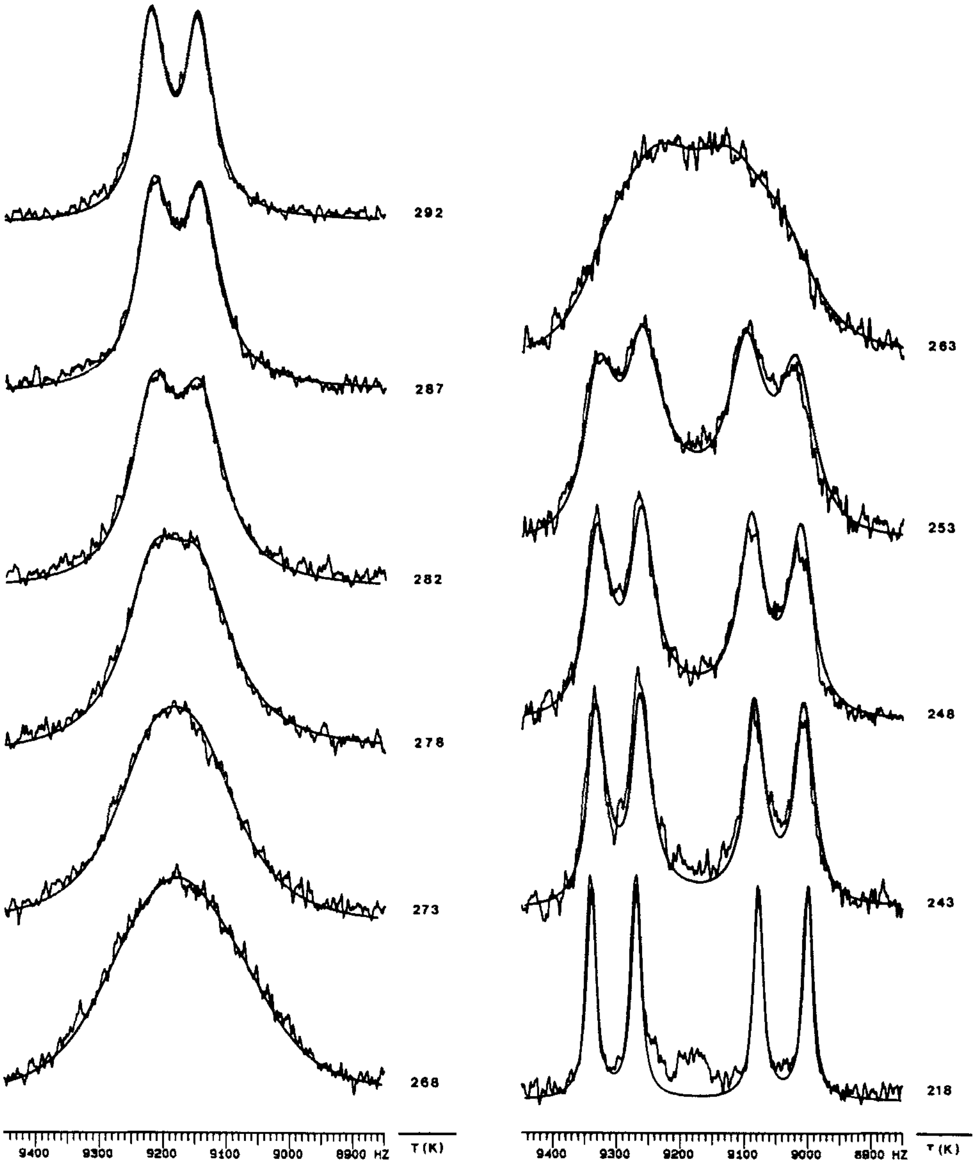

Figure 2 The computer simulated (smooth curve) and variable temperature ^{13}C nmr spectra (carbonyl region) for *cis*-[Rh(CO)(pyO)(Br)] (temperatures in Kelvin).

consistent with Rh-Opy bond fission being involved in the formation of the transition state. If the exchange reaction occurred *via* an associative mechanism, steric strain would predict a reverse order for the enthalpy of activation.

Based on our previous nmr results[1] it is possible to postulate two possible

Table 1 ^{13}C nmr data (carbonyl region) for *cis*-[Rh($^{13}CO)_2$(pyO)(X)] (X = Cl, Br) and their exchange rate constants as a function of temperature.

	X = Cl	X = Br
Temperature (°C)	- 50	- 55
δCO_a	184.95 ppm	184.97 ppm
$^1J(Rh\text{-}CO_a)^a$	71.59 Hz	73.70 Hz
δCO_b	180.45 ppm	179.68 ppm
$^1J(Rh\text{-}CO_b)^b$	75.06 Hz	77.63 Hz
Relaxation time, T_2	0.017 s	0.017 s

X = Cl		X = Br	
T(K)	$K_{ex}(s^{-1})$	T(K)	$K_{ex}(s^{-1})$
223	~0	218	~0
233	13 ± 3	243	55 ± 5
238	20 ± 5	248	95 ± 10
243	35 ± 10	253	150 ± 10
248	60 ± 10	263	400 ± 20
253	90 ± 10	268	600 ± 50
263	250 ± 25	273	850 ± 50
273	600 ± 100	278	1100 ± 100
288	2600 ± 200	282	1600 ± 100
293	3400 ± 200	287	2200 ± 200
		292	3000 ± 200

[a] CO_a *trans* to pyridine-*N*-oxide. [b] CO_b *trans* to the halogen.

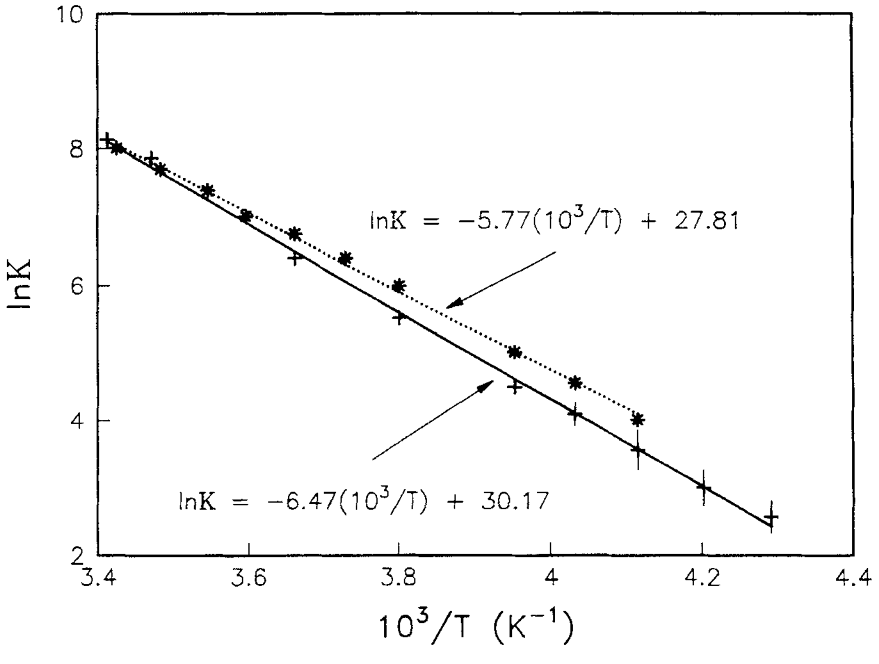

Figure 3 Plots of ln K *vs* $1/T$ for (+) *cis*-[Rh(CO)$_2$(pyO)(Cl)] and (*) *cis*-[Rh(CO)$_2$(pyO)(Br)]. Errors bars are included.

pathways with regard to the mechanism of the exchange process, and these are briefly described below.

1) Attack at the square planar centre by a solvent molecule occurs to give a five-coordinate, square pyramidal intermediate which then isomerizes to a trigonal bipyramidal intermediate. The intermediate then undergoes a Berry pseudorotation[12] for interchange of axial and equatorial ligands, followed by loss of the solvent molecule to yield the stereospecific product (Fig. 4).
2) The complexes *cis*-[Rh(CO)$_2$(L)(X)] can undergo loss of ligand L, either *via* formation of a solvated five-coordinate intermediate as described above, or by the formation of a solvated three-coordinated intermediate, which can subsequently undergo attack by free ligand, L (Fig. 5).

Loss of CO is not considered to occur since the ^1J(Rh-CO) coupling is maintained over the temperature range employed. Either mechanism would account for the solvent dependence of the reaction kinetics of the related complexes *trans*-[Pt(ethylene)(imidazole)X$_2$](X = Cl, Br).[13] On the other hand mechanism (1) does not account for the observed loss of ^1J(Rh-^{15}N) coupling. One method of determining the relative importance of these two pathways would be to study the kinetics of ligand exchange *via* ^{15}N nmr. Unfortunately, the stability of the complexes and the time necessary to record the ^{15}N spectra precluded this experiment being carried out in detail. Nevertheless, from the coalescence temperature (-35°C) of a ^{15}N nmr study of the *cis*-[Rh(CO)$_2$(aniline)(Cl)] complex,[14] we are able to estimate that the rate of exchange of the aniline ligand is ~25 s^{-1}. At this temperature, the corresponding rate for carbonyl equilibration in the ^{13}C nmr spectra is 20 s^{-1}. This suggests that the second pathway is important, if not

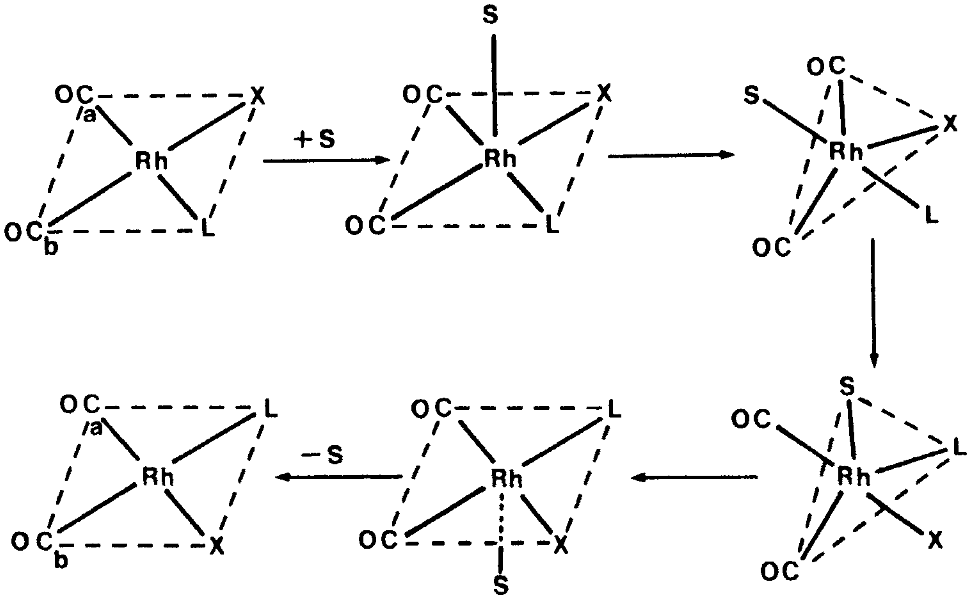

Figure 4 The five-coordinate intermediate pathway.

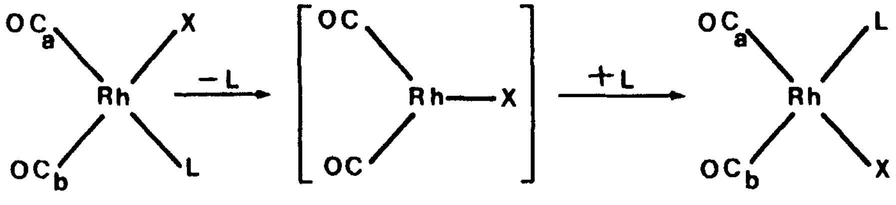

Figure 5 The three-coordinate intermediate pathway.

dominant for this aniline complex, and hence, by analogy, we conclude for the pyridine *N*-oxide complexes also.

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