

The IR, NMR (^1H , ^{13}C) and electronic spectra of the complexes *cis*-[Rh(CO) $_2$ (pyridine-*N*-oxide)(X)] (X \equiv Cl, Br)

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Abstract

The complexes *cis*-[Rh(CO) $_2$ (pyO)(X)] (X \equiv Cl, Br; pyO, pyridine-*N*-oxide) and their labelled analogues containing ^{13}C O and pyO- d_5 were synthesized. The isotopically labelled species were used to assign the internal ligand modes and the skeletal vibrations in the IR spectra over the range 4000–50 cm^{-1} . The νRhC and νRhO bands occur within the range 400–500 cm^{-1} , while νRhCl and νRhBr occur at 310 and 213 cm^{-1} respectively. The ^1H and ^{13}C nuclear magnetic resonance spectra are discussed. The electronic spectra reveal a strong, broad band at 271 nm which is assigned to the combined $\text{X}^- \rightarrow \text{Rh}^+$, $\pi \rightarrow \pi^*$ (CO) and $\pi \rightarrow \pi^*$ (pyO) transitions, while the somewhat weaker band at 327 nm originates in the $4\text{d}(\text{Rh}) \rightarrow \pi^*(\text{CO})$ transition.

1. Introduction

The familiar bridge-splitting reaction of [Rh(CO) $_2$ (X)] $_2$ by amines and heterocyclic bases [1] has been exploited to synthesize the square planar rhodium(I) complexes of formula *cis*-[Rh(CO) $_2$ (pyO)(X)] (X \equiv Cl, Br; pyO, pyridine-*N*-oxide). Since earlier vibrational studies of related systems have been confined almost entirely to the carbonyl region [2], we have paid particular attention to the full spectral range (4000–50 cm^{-1}) and have employed multiple isotopic labelling (^{13}C , ^2H) for the purpose of reaching reliable IR band assignments. The isotopically enriched ^{13}C species employed for the IR spectra have also proved useful for nuclear magnetic resonance (NMR) studies, enabling the determination of the $^2J(^{13}\text{C}-^{13}\text{C})$ and $^1J(\text{Rh}-\text{CO})$ coupling constants. Further fundamental characterization of the complexes includes elemental analysis and electronic spectroscopy.

2. Experimental details

The complex *cis*-[Rh(CO) $_2$ (pyO)(Cl)] was prepared by the slow addition of pyO (0.50 mmol) in warm benzene (10 ml) to a stirred solution of [Rh(CO) $_2$ (Cl)] $_2$ (0.257 mmol) in benzene (10 ml) [1]. The orange product was precipitated by the addition of hexane (10 ml).

After stirring (5 min), the product was collected by filtration, washed (hexane) and dried over silica gel under reduced pressure. Calculated for $\text{C}_7\text{H}_5\text{ClNO}_3\text{Rh}$: C, 29.04%; H, 1.74%; N, 4.84%. Found: C, 29.1%; H, 1.8%; N, 4.8%. Melting point (m.p.), 118 $^\circ\text{C}$.

The complex *cis*-[Rh(CO) $_2$ (pyO)(Br)] was similarly synthesized from [Rh(CO) $_2$ (Br)] $_2$, prepared by the addition of LiBr (0.50 mmol) to a solution of [Rh(CO) $_2$ (Cl)] $_2$ (0.10 mmol) in dry acetone. After stirring (20 min), the solution was evaporated to dryness on the water bath, dry CH_2Cl_2 was added and the yellow suspension was filtered. The filtrate was again evaporated to dryness and the residue was recrystallized from hot hexane. Calculated for $\text{C}_7\text{H}_5\text{BrNO}_3\text{Rh}$: C, 25.18%; H, 1.51%; N, 4.19%. Found: C, 25.0%; H, 1.5%; N, 4.2%. M.p., 126 $^\circ\text{C}$.

The deuterated complexes *cis*-[Rh(CO) $_2$ (pyO- d_5)(X)] (X \equiv Cl, Br) were synthesized as for the unlabelled analogues using pyridine- d_5 -*N*-oxide of 98% isotopic purity obtained from Merck-Frosst (Canada) Ltd. Calculated for $\text{C}_7\text{D}_5\text{ClNO}_3\text{Rh}$: C, 28.55%; H, 1.71%; N, 4.76%. Found: C, 28.5%; H, 1.8%; N, 4.8%. Calculated for $\text{C}_7\text{D}_5\text{BrNO}_3\text{Rh}$: C, 24.81%; H, 1.49%; N, 4.13%. Found: C, 24.90%; H, 1.50%; N, 4.20%.

The ^{13}C -labelled complexes *cis*-[Rh(^{13}C O) $_2$ (pyO)(X)] (X \equiv Cl, Br) were synthesized as for the unlabelled analogues using ^{13}C O of 99% isotopic purity obtained from Merck-Frosst (Canada) Ltd. Calculated for $\text{C}_5^{13}\text{C}_2\text{H}_5\text{ClNO}_3\text{Rh}$: C, 28.84%; H, 1.73%; N, 4.81%. Found: C, 28.8%; H, 1.7%; N, 4.8%. Calculated for

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C₅¹³C₂H₅BrNO₃Rh: C, 25.03%; H, 1.50%; N, 4.17%. Found: C, 24.9%; H, 1.5%; N, 4.2%.

Solid state IR spectra were determined on a dry-nitrogen-purged Perkin-Elmer 983 spectrophotometer from Nujol mulls (or, in the Nujol-masked region, from hexachlorobutadiene mulls) between KBr plates (4000–300 cm⁻¹) and on a Digilab FTS 16B/D interferometer from Nujol mulls between polyethylene plates (500–50 cm⁻¹). Solution IR spectra were obtained from solutions in nitrogen-flushed dichloromethane of spectroscopic grade purity in KBr solution cells on a Perkin-Elmer 983 instrument over the range 2200–1550 cm⁻¹. NMR spectra were obtained on a Varian VXR-200 FT spectrometer operating at 200.0 (¹H) and 50.3 (¹³C) MHz in acetone-*d*₆ or CDCl₃. ¹H and ¹³C chemical shifts were measured relative to the internal solvent references and are reported in parts per million downfield of tetramethylsilane (TMS). Electronic spectra were obtained from nitrogen-flushed spectroscopic grade CH₂Cl₂ solutions in 10 mm quartz cells on a Varian Superscan-3 UV-visible spectrophotometer.

Melting point determinations were made on a Reichert Thermovar instrument. They are uncorrected. Microanalyses were performed by Mr. W. R. T. Hemsted (Chemistry Department, University of Cape Town) on a Heraeus instrument, model CHN-Mikro.

3. Results and discussion

3.1. IR spectra: the 4000–625 cm⁻¹ region

The internal vibrations of pyO have been extensively studied [3–11]. The assignments for the internal ligand modes (Tables 1 and 2) are based on the rigorous study of pyO by Gambi and Ghersetti [11]. The assignments are confirmed by the band shifts induced by ring (*d*_s) deuteration and the results are consistent with those obtained in this laboratory on other metal complexes of pyO [13].

The solution spectra in the region 2200–1800 cm⁻¹ show two bands of almost equal intensity, the anti-symmetric and symmetric CO stretches. The equivalence of their intensities establishes the *cis* square planar structure of these molecules. In the solid state Nujol spectra, the bands are extensively split by lattice interactions. These results are in accord with the *cis* square planar structures established by X-ray crystallographic studies of *cis*-[Rh(CO)₂(pyrazole)(Cl)] [14] and *cis*-[Ir(CO)₂(pyridine)(Cl)] [15].

The assignments of the ν (CO) bands are confirmed by the labelling studies. Substitution of ¹²CO by ¹³CO causes the two ν (CO) bands to shift by about 46 cm⁻¹ towards lower frequencies (theoretical shift, 47 cm⁻¹).

3.2. IR spectra: the 625–50 cm⁻¹ region

The skeletal vibrations occur in this region. From symmetry considerations (C_s), the 13 IR-active skeletal modes are depicted in Fig. 1, which also shows the CO stretching modes. Deuteration of pyO enables the ligand modes to be distinguished from the skeletal modes.

For the purpose of assigning the skeletal modes, they may be considered as being of three types: the Rh–X, Rh–O and Rh–CO species. These may be differentiated by X substitution, pyO deuteration and ¹³CO labelling respectively. Bands which are unaffected by either pyO deuteration or ¹³CO labelling are assigned to the Rh–X modes. These bands are, of course, substantially shifted by replacing Cl by Br. The ratio ν (Rh–Br)/ ν (Rh–Cl) is typically about 0.73 which is normal for terminal M–X bonds [16]. The more specific assignments are made from the usual frequency sequence ν (stretch) > δ (in-plane bend) > γ (out-of-plane bend).

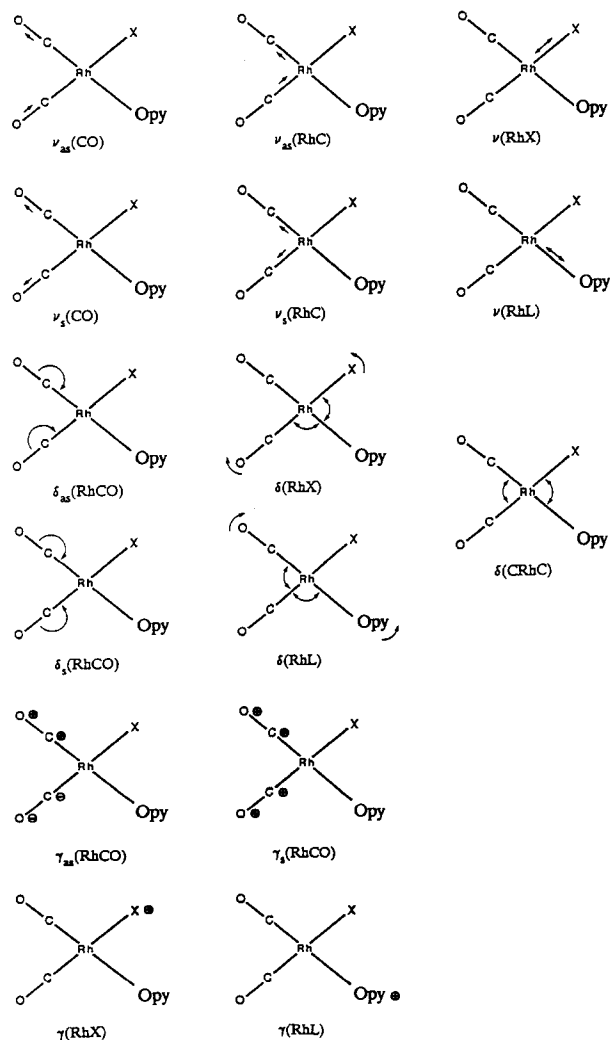


Fig. 1. Carbonyl stretches and IR-active skeletal modes of *cis*-[Rh(CO)₂(pyO)(X)].

TABLE 1. IR assignments of *cis*-[Rh(CO)₂(pyO)(Cl)] (cm⁻¹)^a

pyO	pyO- <i>d</i> ₅	¹³ CO	Assignment	Band number	
				Wilson [12]	Gambi and Ghersetti [11]
3106	2312	3107	} ν(C-H)	20b/2	1/12
3075	2299	3076		20a	2
3033	2292	3034		7b	13
2938	2212	2939		7a	3
(2081)	(2080)	(2032)	} ν(C≡O)		
(2006)	(2006)	(1961)			
2076	2077	{ 2055			
		{ 2047			
2061	2060	{ 2022			
2047	2047	{ 1998			
		{ 1993			
1991	1992	{ 1967			
1963	{ 1964	{ 1951			
	{ 1959				
1614	1569	1615	} ν(ring)	8a	4
1571	1539	1572		8b	14
1476	{ 1355	1475		19a/19b	5/15
	{ 1349				
1421	1409	1421	combination/overtone		
1246	1236	1245	} ν(ring)	14	16
1199	1196	1198		3	17
1183	1154	1182	} ν(N-O)	} 13	6
1179	1148	1178			
1157	883	1156	} δ(C-H)	9a	7
1147	870	1147		15	18
1071	820	1070		18b	19
1025	986	1024	ν(ring)	12	9
1010	841	1009	combination/overtone		
953	792	952	γ(C-H)	5/17a	22/25
829	764	827	ν(ring)	1	10
787	563	786	} γ(C-H)	} 11	27
775	546	773			
680	656	679	} γ(ring)	} 4	28
676	649	674			
639	613	638	δ(ring)	6b	20
629	627	610	δ(Rh-C≡O) in-plane		
572	563	571	δ(ring)	6a	11
547	518	545	γ(ring)	16b	29
501	508	491	δ(Rh-C≡O) out-of-plane		
493	} 478	486	ν(Rh-C)/ν(Rh-O)		
486					
461	432	458	β(N-O)	9b	21
448	448	439	ν(Rh-C)		
384	370	383	γ(ring)	16a	24
310	309	310	ν(Rh-Cl)		
299	298	298	δ(Rh-O)		
217	207	216	γ(N-O)	17b	30
139	137	138	δ(Rh-Cl)		
111	111	111	δ(C-Rh-C)		
66	64	66	γ(Rh-Cl)/γ(Rh-O)		

^aRecorded in Nujol, values in parentheses are those recorded in CH₂Cl₂ solution.

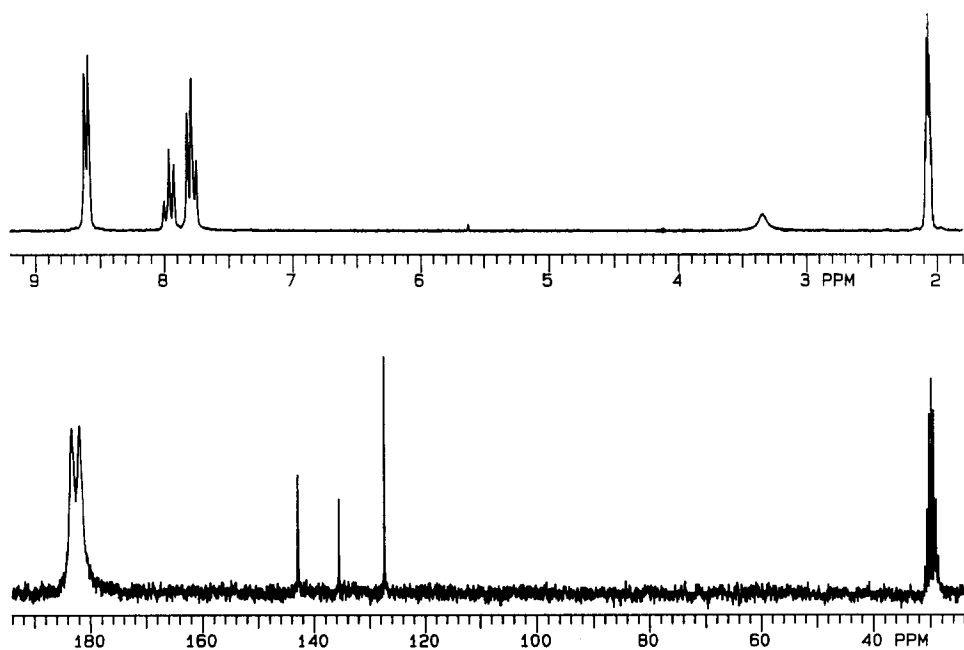
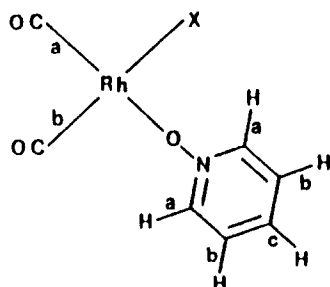
The bands which shift significantly on pyO deuteration, but not on X substitution or ¹³CO labelling, are assigned to the Rh-O modes, while those predominantly affected by ¹³CO labelling are assigned to the Rh-CO

modes. In accordance with earlier studies [17, 18], δ(RhCO) exceeds δ(CRhC) in frequency. The differentiation between ν(RhC) and δ(RhCO) is based on (a) earlier work [18-22] which shows that

TABLE 2. IR assignments of *cis*-Rh(CO)₂(pyO)(Br)] (cm⁻¹)^a

pyO	pyO- <i>d</i> ₅	¹³ CO	Assignment	Band number	
				Wilson [12]	Gambi and Ghersetti [11]
3107	2312	3106	} ν(C-H)	20b/2	1/12
3076	2299	3075		20a	2
3033	2293	3032		7b	13
2938	2211	2938		7a	3
(2080)	(2080)	(2031)	} ν(C≡O)		
(2007)	(2007)	(1961)			
2077	2076	{ 2055			
		2049			
2062	2062	2067			
2047	2047	{ 2000			
		1996			
-	2001	1949			
1996	1996	1924			
1970	1970	1921			
1966	1966	1915			
1960	1960	1906			
1615	1569	1615	} ν(ring)	8a	4
1571	1539	1571		8b	14
1474	{ 1355	1473		19a/19b	5/15
	1347				
1419	1409	1418	combination/overtone		
1244	1235	1244	ν(ring)	14	16
1219	1210	-	combination/overtone		
1196	1190	1196	ν(ring)	3	17
1180	1154	1180	} ν(N-O)	} 13	6
1176	1143	1176			
1155	867	1155	} δ(C-H)	9a	7
1147	839	1147		15	18
1071	819	1071		18b	19
1052	1042	1051	combination/overtone		
1023	982	1023	ν(ring)	12	9
1007	-	1007	combination/overtone		
949	789	949	γ(C-H)	5/17a	22/25
827	761	827	ν(ring)	1	10
783	563	783	} γ(C-H)	} 11	27
771	545	771			
678	653	678	} γ(ring)	} 4	28
674	646	674			
638	613	638	δ(ring)	6b	20
620	618	604	δ(Rh-C≡O) in-plane		
570	561	570	δ(ring)	6a	11
546	515	544	γ(ring)	16b	29
505	505	496	δ(Rh-C≡O) out-of-plane		
484	} 472	} 483	ν(Rh-C)/ν(Rh-O)		
479					
458	432	454	β(N-O)	9b	21
449	445	439	ν(Rh-C)		
376	362	375	γ(ring)	16a	24
219	222	219	γ(N-O)	17b	30
213	213	212	ν(Rh-Br)		
156	153	-	δ(Rh-O)		
121	121	121	δ(Rh-Br)		
112	110	112	δ(C-Rh-C)		
95	88	95	γ(Rh-O)		
65	65	65	γ(Rh-Br)		

^aRecorded in Nujol, values in parentheses are those recorded in CH₂Cl₂ solution.

Fig. 2. ¹H and ¹³C NMR spectra of *cis*-[Rh(CO)₂(pyO)(Br)] (acetone-*d*₆; temperature, 25 °C).TABLE 3. ¹H and ¹³C NMR data of *cis*-[Rh(CO)₂(pyO)(X)] (X is Cl or Br)^a

X	T (°C)	Chemical shifts (ppm)			Coupling constants (Hz)			
		H _a	H _b	H _c	CO _a	CO _b	¹ J(Rh-CO _a)	¹ J(Rh-CO _b)
¹ H NMR		H _a	H _b	H _c				
Cl	25	8.61	7.78	8.00				
Cl(CDCl ₃)	25	8.45	7.38	7.70				
Br	25	8.58	7.77	7.95				
¹³ C NMR		C _a	C _b	C _c	CO _a	CO _b	¹ J(Rh-CO _a)	¹ J(Rh-CO _b)
Cl	-50	142.92	127.31	136.29	184.95	180.45	71.59 ² J(¹³ C- ¹³ C) ≈ 6.9	75.06
Br	-55	142.86	127.31	135.61	184.97	179.65	73.70 ² J(¹³ C- ¹³ C) ≈ 7.0	77.63

^aAll spectra recorded in acetone-*d*₆ unless otherwise specified. Chemical shifts of ¹H and ¹³C relative to TMS.

$\nu(\text{RhC}) < \delta(\text{RhCO})$, (b) the fact that $\nu(\text{MC})$ bands usually have lower intensity than those of $\delta(\text{MCO})$ [17, 23, 24], (c) the observation that ¹³CO labelling induces a smaller low-frequency shift in $\nu(\text{MC})$ than in $\delta(\text{MCO})$ [25, 26] and (d) the observation that $\nu(\text{MC})$ is generally

more sensitive than $\delta(\text{MCO})$ towards substitution of pyO by another ligand L [25].

With respect to differentiation between the in-plane and out-of-plane $\delta(\text{RhCO})$ and $\gamma(\text{RhCO})$ modes, the earlier confusion in the literature [21–23, 25, 27] has

recently been resolved, unequivocally placing the in-plane δ (RhCO) modes at a higher frequency than the out-of-plane γ (RhCO) modes [28].

3.3. NMR spectra

The room temperature (25 °C) ¹H and ¹³C NMR spectra of the bromo complex in acetone-*d*₆ are depicted in Fig. 2 and the data are given in Table 3. Complexation of pyO to rhodium leads to the anticipated upfield shift of the ligand resonances in the ¹H NMR spectra. Replacement of Cl by Br does not significantly affect the proton chemical shifts and no *J*(¹⁰³Rh–H) coupling is observed. Substitution of a less polar solvent (CDCl₃) for acetone-*d*₆ leads to smaller proton chemical shifts, as expected.

The ¹³C spectra were obtained from approximately 30% ¹³C-enriched samples. Besides the obvious advantage of ease of data acquisition, coupling constants could be obtained and problems arising from the slow decomposition of the solutions above 0 °C were obviated using the enriched samples. The ¹³C NMR spectra show that the complexes undergo some exchange process. A variable temperature study of the dynamics of this process will be reported in a later paper [29].

3.4. Electronic spectra

The solution spectra (in CH₂Cl₂) reveal only two broad bands in the UV–visible region. We anticipate the following transitions: $\pi \rightarrow \pi^*$ (CO), $\pi \rightarrow \pi^*$ (pyO), 4d(Rh) $\rightarrow \pi^*$ (CO) and X[–] \rightarrow Rh⁺. In earlier studies of the electronic spectra of complexes such as *trans*-[Pt(CO)(aniline)(Br)₂] [30], we observed bands at 201 nm (Br[–] \rightarrow Pt²⁺), 234 nm ($\pi \rightarrow \pi^*$ (CO) + $\pi \rightarrow \pi^*$ (aniline)) and a weaker band at 278 nm (5d(Pt) $\rightarrow \pi^*$ (CO)). In the rhodium complexes studied here, the X[–] \rightarrow Rh⁺ band has apparently merged with the $\pi \rightarrow \pi^*$ bands, yielding one very broad band centred at 271 nm ($\epsilon \approx 11800 \text{ m}^2 \text{ mol}^{-1}$) and a weaker band at 327 nm ($\epsilon \approx 400 \text{ m}^2 \text{ mol}^{-1}$) which is assigned to the 4d(Rh) $\rightarrow \pi^*$ (CO) transition. Substitution of Cl by Br does not significantly affect the spectrum.

Acknowledgments

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