

Synthesis and Dynamic Behaviour of Rhodium(I) Complexes containing the Di-2-pyridyl Sulphide Ligand

Giuseppe Tresoldi,* Pasquale Piraino, Enrico Rotondo and Felice Faraone

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, 98166 Messina, Italy

The complex $[\text{Rh}(\text{cod})(\text{dps})]\text{X}$ **1** (cod = cycloocta-1,5-diene; dps = di-2-pyridyl sulphide; X = BF_4 , PF_6 or ClO_4) has been prepared by reaction of dps and AgX with $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$; $[\text{Rh}(\text{CO})_2(\text{dps})]\text{X}$ **2** can be prepared by a similar route but higher yields are obtained by bubbling CO through a CH_2Cl_2 solution of **1**. Triphenyl-phosphine or -arsine easily replaces a molecule of CO in **2** to give $[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{dps})]\text{X}$ **3** or $[\text{Rh}(\text{CO})(\text{AsPh}_3)(\text{dps})]\text{X}$ **4**. These compounds have been characterized by usual spectroscopic techniques which indicate a N,N-inside conformation for the chelate dps ligand. The reaction of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ with dps gives rise to stoichiometry-, concentration-, solvent- and temperature-dependent equilibria in which the starting materials, the binuclear complex $[\{\text{Rh}(\text{cod})\text{Cl}\}_2(\mu\text{-dps})]$ **5a**, $[\text{Rh}(\text{cod})(\text{dps})]^+$, $[\text{Rh}(\text{cod})\text{Cl}_2]^-$ and Cl^- are involved. Complex **5a** and $[\text{Rh}(\text{cod})(\text{dps})][\text{Rh}(\text{cod})\text{Cl}_2]$ **5b** can be isolated as solids whereas $[\text{Rh}(\text{cod})(\text{dps})]\text{Cl}$ is present only in solution. Conductivity measurements and electronic spectra indicate that the ionic species are stabilized in methanol, whereas in CH_2Cl_2 the starting materials and binuclear species dominate at low and higher concentration respectively. Proton and ^{13}C NMR spectra, in CD_2Cl_2 indicate that exchange of the $\text{Rh}(\text{cod})$ unit between the starting materials, binuclear and ionic species occurs rapidly in the NMR time-scale at room temperature. When dps is added to **5a** or **5b** (molar ratio 1:1) the concentration of the binuclear species decreases and an equilibrium occurs between $[\text{Rh}(\text{cod})(\text{dps})]\text{Cl}$ and $[\text{Rh}(\text{cod})\text{Cl}(\text{dps})]$ where the dps ligand is monodentate.

Much attention has recently been paid to the co-ordination chemistry of bipyridine and bipyridine-like ligands which allow some rotation around the axis between the two pyridine rings. This kind of flexibility seems to favour unusual co-ordination modes of bipyridine^{1,2} as well as catalytic activity for chelated rhodium(I) complexes.³ Furthermore 2,2'-bipyridyl complexes of ruthenium(II) have proven to be quite useful for studying phenomena such as luminescence and photoreduction/oxidation, and the degree to which ligand properties can influence the excited-state properties of bipyridineruthenium complexes is of considerable interest.⁴

In this context we have studied the ligating properties of di-2-pyridyl sulphide (dps). Results of theoretical calculations^{5,6} predict the minimum-energy conformation **A** for the free molecule and the maximum-energy conformation **B** (see Fig. 1). The planar conformation **C** and several twisted conformations can be populated with equal probability owing to the small activation energies required for interconversion of these conformers. Di-2-pyridyl sulphide adopts in solution essentially three equally populated twisted conformations similar to **A-C**, with the pyridine-ring plane twisted by *ca.* 36° with respect to the CSC plane.⁵ Each conformer may act as a ligand towards transition-metal substrates, resulting in different stoichiometries and stereochemistries of the reaction products.

Since the co-ordination of the ligand occurs through the nitrogen atoms,⁷⁻⁹ the planar and non-planar conformers **C** in spite of unfavourable orientation of the nitrogen atoms for chelation may be bonded to a metal as unidentate ligands or to two metals as bridging ligands. Conformers **A** and **B** may act as chelating ligands but steric requirements make unlikely such a co-ordination for **B**. As far as we know, few examples of dps chelate complexes have been reported.⁷ These compounds have been characterized by visible spectra, magnetic moments and conductivity measurements. More recently uranyl complexes^{8,9} have been prepared and fully investigated. In this paper, the

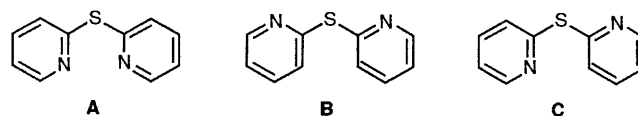
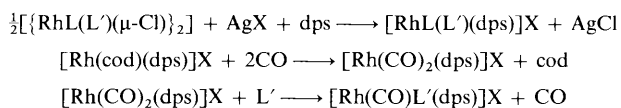


Fig. 1 Planar configurations of dps: N,N inside, **A**; N,N outside, **B**; and N inside, N outside, **C**

synthesis and spectral properties of di-2-pyridyl sulphide complexes of rhodium(I) are reported.

Results and Discussion

The complexes $[\text{RhL}(\text{L}')(\text{dps})]\text{X}$ were prepared according to Scheme 1. The first reaction involves the *in situ* formation of a



Scheme 1 LL' = cod = cycloocta-1,5-diene, **1**; L = L' = CO, **2**; L = CO, L' = PPh_3 , **3**; L = CO, L' = AsPh_3 , **4**; X = ClO_4 , PF_6 or BF_4

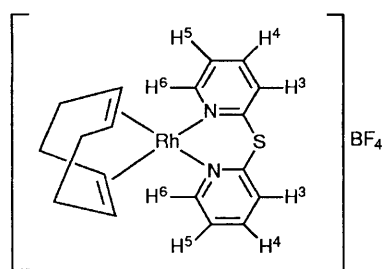
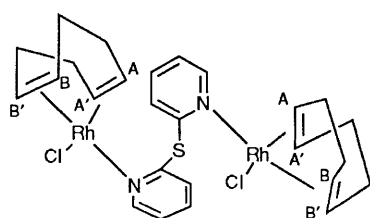
solvento species followed by displacement of the co-ordinated solvent by dps. The reactions proceed smoothly at room temperature and complex **1** is obtained in high yields when an excess of dps is used, whereas the formation of complex **2** is accompanied by some decomposition. Complex **2** can be also obtained, in higher yields, by bubbling CO through a dichloromethane solution of **1**. It undergoes substitution of a molecule of CO in the presence of an equimolar amount of L' giving complexes **3** and **4**. The same reaction carried out with an excess of L' leads to decomposition of the substrate.

The compounds are yellow solids soluble in acetone and moderately soluble in chloroform and dichloromethane. Compound **1** is stable for several months in the solid state and for

Table 1 Analytical^a and characteristic IR data^b

Compound	Analysis (%)				IR/cm ⁻¹		
	C	H	N	S	v(CO)	Selected dps bands	v(Rh-Cl)
dps						1572s, 770vs, 405m	
1 [Rh(cod)(dps)]BF ₄	44.50 (44.45)	4.20 (4.15)	5.70 (5.75)	6.60 (6.60)		1584s, 785vs, 770vs, 445m	
2 [Rh(CO) ₂ (dps)]BF ₄	33.25 (33.20)	1.85 (1.85)	6.50 (6.45)	7.35 (7.40)	2097vs, 2033vs	1592s, 791vs, 789vs, 428m	
3 [Rh(CO)(PPh ₃)(dps)]BF ₄	52.20 (52.10)	3.50 (3.45)	4.15 (4.20)	4.70 (4.80)	2000vs	1584s, 791vs, 772vs, 433m	
4 [Rh(CO)(AsPh ₃)(dps)]BF ₄	48.90 (48.90)	3.30 (3.30)	3.90 (3.95)	4.55 (4.50)	1990vs	1584s, 788vs, 771vs, 435m	
5a [{Rh(cod)Cl} ₂ (μ-dps)] ^c	48.90 (48.70)	5.00 (5.00)	3.75 (3.85)	4.35 (4.40)		1582s, 1555s, 772vs, 760vs, 435m, 418m	282s, 262s
5b [Rh(cod)(dps)][Rh(cod)Cl ₂] ^d	45.75 (45.85)	4.70 (4.75)	4.10 (4.10)	4.65 (4.70)		1583, 780vs, 775vs 438m	275s, 252s

^a Required values are given in parentheses. ^b Nujol mulls. ^c Crystallized with 0.5 molecule C₆H₅Me, Cl 9.80 (9.75)%. ^d Cl 10.50 (10.40)%.

**1****5a**

some days in solution. The other compounds are less stable with respect to air (about 2 weeks in the solid state and some hours in solution). Conductivity measurements in acetone solution indicate that these complexes are 1 : 1 electrolytes.

The study of the multiplicity and shifts of the IR bands associated with internal modes of vibration of the pyridine rings can lead to fairly clear structural conclusions.¹⁰ In the spectra of complexes **1–4** these bands are significantly shifted to higher frequencies from their position in the free-ligand spectrum (Table 1) in accordance with the co-ordination of both pyridine N atoms. Furthermore two bands, in the range 792–770 cm⁻¹, characteristic of the out-of-plane CH deformation suggest non-equivalence of the two pyridine rings in the solid state. These data have been interpreted in terms of conformation **A** of the pyridine rings which are rotated out of the all-planar configuration. The recent synthesis and X-ray analysis of the complex Pd(dps)Cl₂,¹¹ which shows in the pyridine region IR bands similar to those of complexes **1–4**, support the above suggestion.

The assignment of the solution structure of compounds **1–4** is based on the following evidence. (a) In accord with N,N' chelation of the dps ligand,^{9,12} the ¹H and ¹³C NMR spectra show downfield shifts of the pyridine protons and carbons. (b) The ¹H NMR spectra of compounds **1** and **2**, in the pyridine region, are consistent with a single ABMX system.^{5,9} (c) The ¹³C NMR spectra show four signals for the pyridine carbons

suggesting that in the complexes the two pyridine rings are in equivalent or averaged equivalent magnetic environments as a result of the interconversion, among the all-planar and the several non-planar conformations **A**. This interconversion is rapid, on the NMR time-scale, even at low temperature as can be inferred from the ¹H spectrum of **1** at 230 K which shows a single ABMX system for the pyridine protons and a single signal for the olefinic protons. (d) The downfield shift of the H⁶ resonance in complex **1**, relatively to the free ligand, is small (0.28 ppm) in comparison with that found for complexes **2–4** (0.58, 0.63 and 0.70 ppm respectively). Downfield shifts are expected for hydrogen atoms closely approaching, above the coordination plane, d⁸ metal atoms, in a square-planar arrangement, and result from magnetic anisotropy of the metal.^{13,14} The transfer of electron density from the ligand to the d⁸ metal can cause a further downfield shift of the above protons. The relatively small downfield shift of the H⁶ proton resonances of compound **1** may result from opposite factors: the deshielding effects previously mentioned and a shielding effect arising from the proximity of H⁶ protons to the C=C double bond of the cycloocta-1,5-diene.

In the NMR spectra of compound **1** the olefinic protons and carbons are observed as an unresolved multiplet at δ 4.30 and as a doublet at δ 85.60 ppm [*J*(Rh–C) 12.8 Hz], respectively. Complexes **3** and **4** give rise at room temperature to a rapid dissociation-association process of L' which broadens all the resonances. At 220 K the dynamic process can be frozen and in the ¹H NMR spectrum the resonances of the two overlapping ABMX system can be observed for the pyridine protons. The ³¹P NMR spectrum of **3** shows at 220 K the expected doublet for the rhodium(I) co-ordinated triphenylphosphine at δ 30.63 ppm [*J*(Rh–P) 129.7 Hz].

The complex [{Rh(μ-Cl)(cod)}₂] reacts with di-2-pyridyl sulphide in toluene to give a yellow compound which, on the basis of analytical, IR, ¹H and ¹³C NMR and conductivity data, was formulated as [{Rh(cod)Cl}₂(μ-dps)] **5a**. This compound generally crystallizes with 0.5 molecule of toluene (see Experimental section).

Comparison of the IR spectra of compounds **5a** and **1** reveals significant differences in the key pyridine bands: (a) doubling of the absorption attributed to the pyridine-ring stretching (1582 and 1555 cm⁻¹); (b) a shift to low frequency of the bands associated with the out-of-plane CH deformations (772 and 760 cm⁻¹); (c) doubling of the band associated with the out-of-plane ring deformations (435 and 418 cm⁻¹). In the far-infrared spectrum of **5a** two strong bands at 282 and 262 cm⁻¹ are assigned to terminal v(Rh–Cl).

Compound **5a** is soluble in dichloromethane and chloroform, and moderately soluble in toluene and benzene. It is also moderately soluble in methanol giving a conductance value in

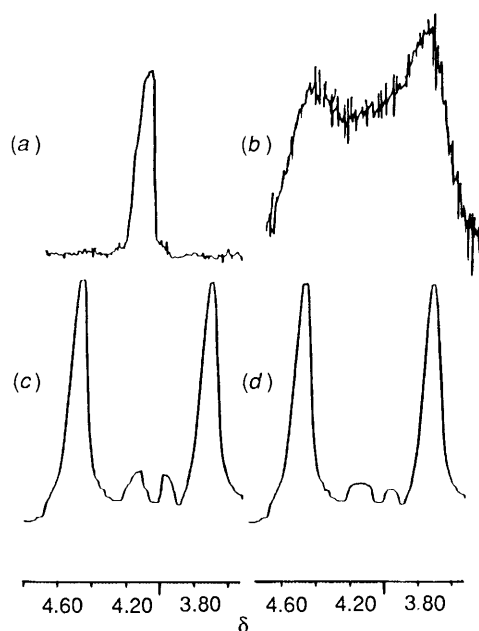


Fig. 2 Proton NMR spectra (olefinic cod region) of compound **5a** or **5b** in CD_2Cl_2 at (a) 310, (b) 267, (c) 230 and (d) 200 K

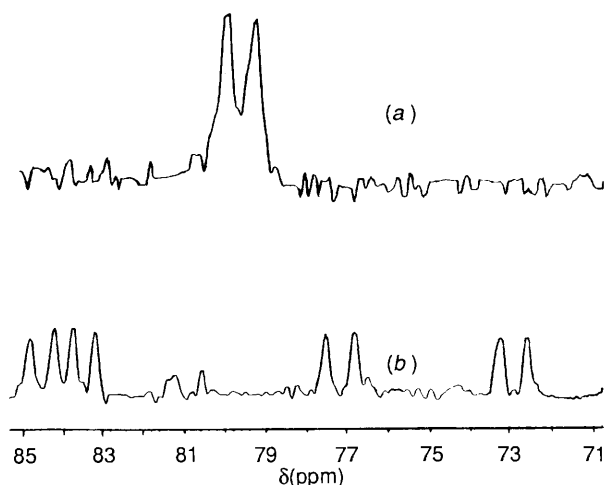


Fig. 3 Carbon-13 NMR spectra (olefinic cod region) of compound **5a** or **5b** in CD_2Cl_2 at (a) 310 and (b) 220 K

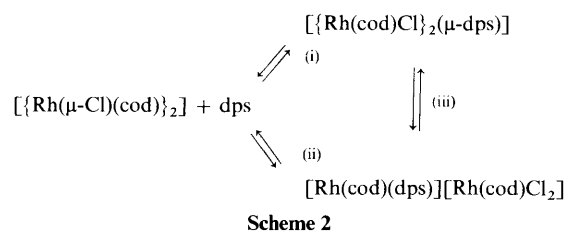
the range expected for 1:1 electrolytes ($80 \text{ S cm}^2 \text{ mol}^{-1}$) while in dichloromethane it is poorly dissociated.

In order to establish the nature of complex **5a** and of the ionic species we attempted the preparation of an ionic product by treating $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ with dps in different molar ratios. After several unsuccessful experiments in methanol or acetone, we were able to isolate a complex which analyzes as $[\{\text{Rh}(\text{cod})\text{Cl}\}_2(\text{dps})]$ **5b** by adding $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ dissolved in CH_2Cl_2 (10 cm^3) to a large excess of dps in diethyl ether (90 cm^3). This compound shows strong IR bands at 1583, 780 and 775 cm^{-1} and a band of medium intensity at 438 cm^{-1} . These data are significantly different from those reported for **5a** but they are closely similar to those of the cationic compounds **1-4** in which the dps ligand is chelated to the metal. Furthermore, in the far-infrared spectrum two strong bands at 275 and 252 cm^{-1} suggest the presence of the *cis* terminal chlorine atoms of $[\text{Rh}(\text{cod})\text{Cl}_2]^-$.¹⁵ On these basis **5b** could be formulated as $[\text{Rh}(\text{cod})(\text{dps})][\text{Rh}(\text{cod})\text{Cl}_2]$.

The UV spectra in CH_2Cl_2 indicate considerable dissociation of compound **5a** and **5b** into the starting materials at low concentrations (the spectra of $5 \times 10^{-5} \text{ mol dm}^{-3}$ solutions are similar to that of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ and some deviations from the Lambert-Beer law are observed in the range $5 \times 10^{-4} -$

$5 \times 10^{-5} \text{ mol dm}^{-3}$). The spectra in methanol suggest the presence of the ionic species $[\text{Rh}(\text{cod})(\text{dps})]^+$ and $[\text{Rh}(\text{cod})\text{Cl}_2]^-$. These spectra obey the Lambert-Beer law in the range $10^{-3} - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ($\lambda_{\text{max}} 420 \text{ nm}$, $\epsilon 1100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

The conductivity measurements in CH_2Cl_2 for $10^{-3} \text{ mol dm}^{-3}$ solutions of compounds **5a** and **5b** suggests that the non-conducting species predominate in this solvent; however the low values of the molar conductance ($4 \text{ S cm}^2 \text{ mol}^{-1}$) could rise from some cation-anion association.^{15,16} These data can be rationalized in terms of the equilibria depicted in Scheme 2.



The ^1H and ^{13}C NMR spectra, in CD_2Cl_2 , of compound **5a** or **5b** are temperature dependent. At room temperature the signal of the olefinic protons is observed at $\delta 4.20$ and those of the pyridine protons H^6 , H^4 , H^3 and H^5 at $\delta 8.67$, 7.63 , 7.53 and 7.24 respectively. In the ^{13}C NMR spectrum the signal of the olefinic carbons is observed as a doublet at $\delta 79.69 \text{ ppm}$ [$J(\text{Rh}-\text{C}) 14.23 \text{ Hz}$] and the signals of pyridine carbons C^2 , C^6 , C^4 , C^3 and C^5 at 158.10 , 151.50 , 137.98 , 128.25 and 123.27 ppm respectively. Taking into account the conductivity measurements, the electronic spectra, the preparative conditions for **5a** and **5b**, and the observation that in the presence of a large excess of dps the ^1H and ^{13}C NMR spectra did not show different signals for the free and the co-ordinated ligand, these spectra are interpreted in terms of rapid equilibria (i)-(iii) between the starting materials, the binuclear and the ionic species. The breaking of the Rh-N and the Rh-Cl bonds makes rapid on the NMR scale exchange of the $\text{Rh}(\text{cod})$ unit. The observation of a Rh-C coupling constant rules out any dissociative mechanism involving breaking of the Rh-cod bond.

At 230 K four signals for the olefinic protons are detected at $\delta 4.55$, 4.18 , 4.02 and 3.78 with relative intensity 5:1:1:5 [Fig. 2(c)]. The small signals at $\delta 4.18$ and 4.02 are assigned to $[\text{Rh}(\text{cod})(\text{dps})]^+$ and $[\text{Rh}(\text{cod})\text{Cl}_2]^-$ respectively. This assignment is confirmed by the spectra of **5a** or **5b** in the presence of dps, molar ratio 5:1, which show the four olefinic proton signals at $\delta 4.55$, 4.25 , 4.02 and 3.78 with relative intensity 4:1:1:4 [see Fig. 5(a)]. The signals at $\delta 4.55$ and 3.78 are assigned to olefinic protons of binuclear species.

Inspection of molecular models suggests that the dps ligand adopts in the binuclear species the conformation C with a C_2 axis passing through the S atom and perpendicular to a plane containing the two rhodium atoms. In this configuration the olefinic protons and carbons of each C_8H_{12} groups are non-equivalent.^{14,17} In the ^1H NMR spectrum only two of the four olefinic proton signals can be resolved. We assign the signal at $\delta 3.78$ to the protons *trans* to Cl (A,A') which lie in the region shielded by the pyridine-ring current and the signal at $\delta 4.55$ to the protons *trans* to N (B,B'). At 200 K [Fig. 2(d)] the signals of the ionic species ($\delta 4.00$ and 4.18) decrease and the signals at $\delta 4.48$ and 3.76 increase suggesting that the equilibrium (iii) is shifted towards the binuclear species. At 267 K the equilibria depicted in Scheme 2 become rapid on the NMR time-scale and the olefinic proton resonances coalesce into a broad signal [Fig. 2(b)].

In the ^{13}C NMR spectrum at 220 K [Fig. 3(b)] the olefinic carbons give four doublets of approximately equal intensity at $\delta 72.45$ [$J(\text{Rh}-\text{C}) 13.4$], 77.18 [$J(\text{Rh}-\text{C}) 13.2$], 83.48 [$J(\text{Rh}-\text{C}) 11.4$] and 84.55 ppm [$J(\text{Rh}-\text{C}) 12.3 \text{ Hz}$], and a small doublet at 80.97 ppm [$J(\text{Rh}-\text{C}) 14.0 \text{ Hz}$]. The latter signal is assigned to the cationic $[\text{Rh}(\text{cod})(\text{dps})]^+$ which according to the equilibria

Table 2 Selected ^1H NMR data^a

Compound	T/K	Solvent	cod protons ^b		dps protons ^c			
			CH	Olefinic	H ⁶	H ⁴	H ³	H ⁵
dps	310	(CD ₃) ₂ CO			8.50	7.74	7.48	7.26
	310	CD ₂ Cl ₂			8.54	7.62	7.45	7.16
1	310	(CD ₃) ₂ CO	4.30		8.78	8.10	8.07	7.64
	230	(CD ₃) ₂ CO	4.27		8.76	8.10	8.06	7.64
2	310	(CD ₃) ₂ CO			9.08	8.28	8.20	7.78
3	220	(CD ₃) ₂ CO			9.13	<i>d</i>	<i>d</i>	7.22
4	220	(CD ₃) ₂ CO			9.20	<i>d</i>	<i>d</i>	7.18
5a or 5b	310	CD ₂ Cl ₂	4.20		8.67	7.63	7.53	7.24
	230	CD ₂ Cl ₂	4.55 ^e	3.78 ^e	8.73 ^e		7.60 ^f	7.30 ^e
			4.18 ^g	4.02 ^h	8.50 ^g	7.78 ^g	<i>i</i>	7.10 ^g
	200	CD ₂ Cl ₂	4.48 ^e	3.76 ^e	8.70 ^e		7.58 ^f	7.25 ^e
			4.18 ^g	4.00 ^h	8.40 ^g	7.70 ^g	<i>i</i>	<i>i</i>
[Rh(cod)(dps)]Cl ^j	310	CD ₂ Cl ₂	4.13		8.60	7.65	7.48	7.20
	230	CD ₂ Cl ₂	4.10		8.58	7.70	7.45	7.20

^a Recorded at 300 MHz, SiMe₄ as internal standard. ^b The olefinic protons are observed as rather broad singlets. ^c The protons of co-ordinated and free dps give rise to ABMX spectra in which the proton signals appear as multiplets. ^d Masked by broad signals of C₆H₅ protons. ^e Signals of the binuclear species. ^f Broad signals of H³ and H⁴ pyridine protons of the binuclear species. ^g Signals of [Rh(cod)(dps)]⁺. ^h Signals of [Rh(cod)Cl₂]⁻. ⁱ Masked by other signals. ^j Mixture of **5a** or **5b** and dps in molar ratio 1:1.

Table 3 Selected ^{13}C NMR data^a

Compound	cod carbons		dps				
	Olefinic	CH ₂	C ²	C ⁶	C ⁴	C ³	C ⁵
dps ^b			157.80 (s)	150.94 (s)	138.10 (s)	126.57 (s)	122.77 (s)
dps			155.99 (s)	149.25 (s)	136.30 (s)	125.02 (s)	121.02 (s)
1 ^b	85.60 (d, 12.8)	30.52 (s)	n.o.	153.81 (s)	141.29 (s)	131.46 (s)	127.00 (s)
2 ^b			n.o.	157.17 (s)	143.22 (s)	132.35 (s)	127.10 (s)
5a or 5b	79.69 (d, 14.3)	31.29 (s)	158.10 (s)	151.50 (s)	137.98 (s)	128.25 (s)	123.27 (s)
5a or 5b ^c	72.20 (d, 13.6) ^d	31.45 (s) ^d	159.25 (s) ^d	150.86 (s) ^d	138.00 (s) ^d	130.30 (s) ^d	123.56 (s) ^d
	79.40 (d, 13.4) ^d	30.50 (s) ^d					
	81.50 (d, 13.9) ^e	29.52 (s) ^d					
	83.20 (d, 11.4) ^d						
	84.00 (d, 12.0) ^d						
5a or 5b ^f	72.45 (d, 13.4) ^d	31.58 (s) ^d	159.40 (s) ^d	151.49 (s) ^d	138.19 (s) ^d	130.40 (s) ^d	123.71 (s) ^d
	77.18 (d, 13.2) ^d	30.60 (s) ^d					
	80.97 (d, 14.0) ^e	29.62 (s) ^d					
	83.48 (d, 11.4) ^d						
	84.55 (d, 12.3) ^d						
[Rh(cod)(dps)]Cl ^g	80.05 (br)	31.10 (s)	n.o.	151.38 (s)	137.97 (s)	127.50 (br)	123.00 (s)
[Rh(cod)(dps)]Cl ^{g,h}	81.02 (d, 13.8) ^e	31.78 (s) ^e	n.o.	152.36 (s) ^e	138.70 (s) ^e	127.91 (s) ^e	123.55 (s) ^e
	79.66 (d, 13.1) ⁱ	30.39 (s) ⁱ	n.o.	151.01 (s) ^j	137.53 (s) ^d	127.18 (s) ^j	122.88 (s) ^j
			n.o.	149.97 (s) ^k	137.15 (s) ^k	125.53 (s) ^k	121.76 (s) ^k

^a Recorded at 20.15 MHz and 310 K in CD₂Cl₂ unless stated otherwise; chemical shift in ppm and with multiplicity and $J(\text{Rh}-\text{C})/\text{Hz}$ in parentheses; SiMe₄ as internal standard. n.o. = Not observed, s = singlet, d = doublet and br = broad. ^b In (CD₃)₂CO. ^c At 240 K. ^d Signals of binuclear species. ^e Signals of [Rh(cod)(dps)]⁺. ^f At 220 K. ^g Mixture of **5a** or **5b** and dps in molar ratio 1:1. ^h At 230 K. ⁱ Signals of the monodentate species. ^j Signals of the pyridine co-ordinated to the metal (monodentate species). ^k Signals of the pyridine not co-ordinated to the metal (monodentate species).

in Scheme 2 becomes the main species in the presence of dps (see next experiment). The olefinic carbon resonances of the anionic species [Rh(cod)Cl₂]⁻ are probably obscured by the doublet at δ 77.18 ppm. The four signals of equal intensity are assigned to the binuclear species. The doublets at δ 72.45 and 77.18 ppm are assigned to olefinic carbons *trans* to Cl (A,A') which are shielded by the pyridine-ring current and the signals at δ 83.48 and 84.55 ppm to the olefinic carbons *trans* to N (B,B'). The presence of four doublets in the olefinic region and five resonances in the pyridine region (Table 2) is consistent with the structure depicted in which the C₂ axis makes equivalent the two pyridine rings and the two cod ligands. Furthermore, no appreciable change in the relative intensity of the olefinic carbon signals of the binuclear species can be detected at 240 K.

Upon addition of dps to compound **5a** or **5b**, in molar ratio 1:1, a species formulated as [Rh(cod)(dps)]Cl is formed. This could be characterized only in solution, although a cationic

complex [Rh(cod)(dps)]BPh₄ can be isolated from the solution by addition of NaBPh₄. Furthermore, the molar conductance of **5a** or **5b** in the presence of dps, molar ratio 1:1, is 16 S cm² mol⁻¹.

The ^1H and ^{13}C NMR spectra of [Rh(cod)(dps)]Cl are, also, temperature dependent. The ^1H NMR spectrum at room temperature shows the olefinic proton signal at δ 4.13 [Fig. 4(c)]. The ^{13}C NMR spectrum shows the signal for the olefinic carbons δ 80.05 ppm [Fig. 5(a)] and those for the pyridine carbons C⁵, C³, C⁴ and C⁶ at 123.00, 127.50, 137.97 and 151.38 ppm respectively. The signals at δ 80.05 and 127.50 ppm are broad suggesting an equilibrium between the cationic complex [Rh(cod)(dps)]Cl and a neutral species with monodentate dps.¹ The latter co-ordination is deduced by the low-temperature ^{13}C NMR spectrum which shows signals attributable to co-ordinated and non-co-ordinated pyridine rings (Table 2). The olefinic carbons of the cationic and neutral species give signals

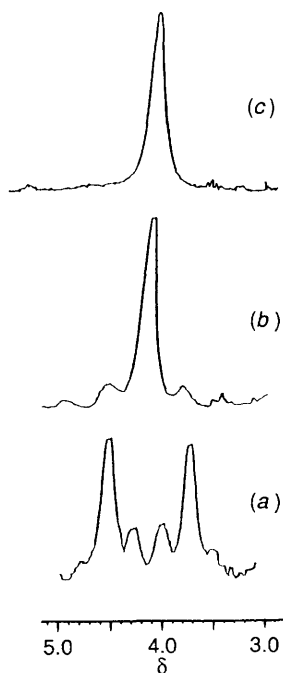


Fig. 4 Proton NMR spectra of a mixture of compound **5a** or **5b** and dps in CD_2Cl_2 at (a) 230 (5:1), (b) 230 (1:1) and (c) 310 K (molar ratio 1:1)

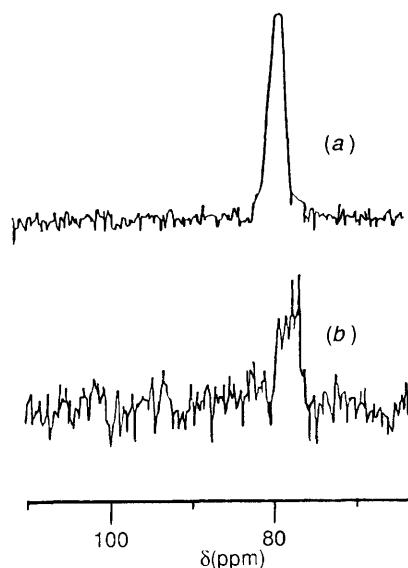


Fig. 5 Carbon-13 NMR spectra (olefinic cod region) of a mixture of compound **5a** or **5b** and dps, molar ratio 1:1, in CD_2Cl_2 at (a) 310 and (b) 230 K

at δ 81.02 [$J(\text{Rh}-\text{C})$ 13.8] and 79.66 ppm [$J(\text{Rh}-\text{C})$ 13.1 Hz] respectively [Fig. 5(b)] whereas the olefinic protons give a broad signal at δ 4.10. In the latter spectrum weak signals due to olefinic protons of binuclear species are also observed at δ 4.55 and 3.78 [Fig. 4(b)].

These spectra are interpreted in terms of the equilibria depicted in Scheme 3. The dynamic behaviour of $[\text{Rh}(\text{cod})(\text{dps})]\text{Cl}$ suggests a mechanism involving an association equilibrium of the cationic substrate with Cl^- through a five-coordinate intermediate to form a neutral species with a monodentate dps ligand.¹⁵



Scheme 3

Experimental

The compounds $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$,¹⁸ $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ ¹⁹ and di-2-pyridyl sulphide⁵ were prepared by published

methods. All the other reagents and solvents were used as supplied. Elemental analyses were carried by the Micro-analytical Laboratory of the Organic Chemistry Institute of Milan and by Analytische Laboratorien Malissa and Reuter, Elbach, Germany. Conductivity measurements were done on a Radiometer CDM3 conductivity meter. Infrared spectra were recorded with a Perkin-Elmer 1720X FT-IR spectrometer, using CsI plates, electronic spectra on a Perkin-Elmer Lambda 5 spectrophotometer, and ^1H , ^{13}C and ^{31}P NMR spectra on Bruker Sy 80 and Varian Gemini 300 spectrometers.

Analytical and characteristic IR data are given in Table 1. ^1H and ^{13}C NMR data in Tables 2 and 3 respectively.

Preparations.— $[\text{Rh}(\text{cod})(\text{dps})]\text{BF}_4$ **1** and $[\text{Rh}(\text{CO})_2(\text{dps})]\text{BF}_4$ **2**. To a stirred acetone solution (10 cm^3) of the appropriate chloro-bridged complex (0.5 mmol) was added solid AgBF_4 (195 mg, 1 mmol). Silver chloride was separated by filtration and the resulting solution of the solvento species added with stirring to a diethyl ether solution (*ca.* 70 cm^3) of dps (376 mg, 2 mmol). The yellow precipitate obtained was collected, washed with diethyl ether, and dried *in vacuo* over P_4O_{10} . Yields: 416 mg, 90%, **1**; 220 mg, 50%, **2**. Complex **2** was more conveniently obtained by bubbling CO through a dichloromethane solution (30 cm^3) of **1** (486 mg, 1 mmol). Addition of hexane (*ca.* 70 cm^3) gave a yellow solid, which was collected, washed with diethyl ether, and dried. Yield 347 mg, 80%. Molar conductivities of $5 \times 10^{-4} \text{ mol dm}^{-3}$ acetone solutions at 20°C : 154, **1**; 150 $\text{S cm}^2 \text{ mol}^{-1}$, **2**.

$[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{dps})]\text{BF}_4$ **3** and $[\text{Rh}(\text{CO})(\text{AsPh}_3)(\text{dps})]\text{BF}_4$ **4**. To a dichloromethane solution (20 cm^3) of compound **2** (217 mg, 0.5 mmol) was added with stirring PPh_3 (131 mg, 0.5 mmol) or AsPh_3 (153 mg, 0.5 mmol). The reaction was monitored by IR spectroscopy and allowed to proceed at room temperature until $\nu(\text{CO})$ due to **2** had disappeared. Addition of hexane (50 cm^3) gave a yellow precipitate which was collected, washed with diethyl ether, and dried. Yields: 568 mg, 85%, **3**; 569 mg, 80%, **4**. Conductivities for $5 \times 10^{-4} \text{ mol dm}^{-3}$ acetone solutions at 20°C : 142, **3**; 140 $\text{S cm}^2 \text{ mol}^{-1}$, **4**.

Perchlorate and hexafluorophosphate salts of complexes **1–4** were prepared similarly.

$[\{\text{Rh}(\text{cod})\text{Cl}\}_2(\mu\text{-dps})]$ **5a**. At -5°C a toluene solution (*ca.* 5 cm^3) of dps (376 mg, 2 mmol) was added to a solution of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ (493 mg, 1 mmol) in the same solvent (*ca.* 20 cm^3). The yellow precipitate obtained was washed with toluene and diethyl ether. The mother-liquor and the washing liquids were cooled overnight in a freezer to complete the precipitation. In most cases the first solid separated crystallizes with 0.5 molecule of toluene. Both the precipitates were dried *in vacuo* over P_4O_{10} . Yields of a typical experiment: $[\{\text{Rh}(\text{cod})\text{Cl}\}_2(\mu\text{-dps})]\cdot 0.5\text{C}_6\text{H}_5\text{Me}$ (355 mg, 50%); $[\{\text{Rh}(\text{cod})\text{Cl}\}_2(\mu\text{-dps})]$ (272 mg, 40%).

$[\text{Rh}(\text{cod})(\text{dps})][\text{Rh}(\text{cod})\text{Cl}_2]$ **5b**. A dichloromethane solution (*ca.* 10 cm^3) of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ (246 mg, 0.5 mmol) was added to a diethyl ether solution (*ca.* 90 cm^3) of dps (564 mg, 3 mmol). The yellow precipitate obtained was collected, washed with diethyl ether, and dried. Yield 300 mg, 88%. Molar conductivities of $1 \times 10^{-3} \text{ mol dm}^{-3}$ solutions of complex **5a** or **5b** at 20°C in CH_2Cl_2 and in methanol are 4 and 80 $\text{S cm}^2 \text{ mol}^{-1}$ respectively.

Acknowledgements

We thank the Public Ministry of Education for financial support.

References

- D. E. Marx and A. J. Lees, *Organometallics*, 1986, **5**, 2072.
- B. S. Creaven, F. W. Grevels and C. Long, *Inorg. Chem.*, 1988, **28**, 2231; B. S. Creaven, C. Long, R. A. Howie, G. P. McQuillan and J. Low, *Inorg. Chim. Acta*, 1989, **157**, 151.

- 3 Y. Guoqing and C. Rongyao, *Organometallic Compounds*, 1983, **1**, 244.
- 4 A. Basu, T. G. Kasar and N. Y. Sapre, *Inorg. Chem.*, 1988, **27**, 4539; T. C. Streckas, H. D. Gafney, S. A. Tysoe, R. P. Thummel and F. Lefoulon, *Inorg. Chem.*, 1989, **28**, 2964.
- 5 C. Chachaty, G. C. Pappalardo and G. Scarlata, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1234.
- 6 P. Colonna, G. Distefano, V. Galasso, G. C. Pappalardo and G. Scarlata, *J. Chem. Soc., Faraday Trans. 2*, 1976, 822.
- 7 D. St. C. Black, *Aust. J. Chem.*, 1967, **20**, 2101; D. Driver and W. R. Walker, *Aust. J. Chem.*, 1968, **21**, 331; M. E. Bridson and W. R. Walker, *Aust. J. Chem.*, 1970, **23**, 1191.
- 8 G. C. Pappalardo and A. Seminara, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1993.
- 9 A. Forchioni, V. Librando and G. C. Pappalardo, *J. Chem. Soc., Dalton Trans.*, 1977, 638.
- 10 D. A. Baldwin, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, 1969, **8**, 107; R. Grzeskowiak and M. Goldstein, *Inorg. Chim. Acta*, 1979, **33**, L153; N. Nonoyama, *J. Inorg. Nucl. Chem.*, 1975, **37**, 59; R. Grzeskowiak, C. Whatley and M. Goldstein, *Spectrochim. Acta, Part A*, 1975, **31**, 1577.
- 11 G. Tresoldi and A. Tiripicchio, unpublished work.
- 12 B. Crociani, F. Di Bianca, A. Giovenco and T. Boschi, *Inorg. Chim. Acta*, 1987, **127**, 169.
- 13 B. Crociani, M. Sala, A. Polo and G. Bombieri, *Organometallics*, 1986, **5**, 1369.
- 14 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1979, 1899.
- 15 B. Crociani, F. Di Bianca, M. Paci and T. Boschi, *Inorg. Chim. Acta*, 1988, **145**, 253.
- 16 T. M. Bockmann and J. K. Kochi, *J. Am. Chem. Soc.*, 1989, **111**, 4669.
- 17 G. S. Rodman and K. R. Mann, *J. Organomet. Chem.*, 1989, **378**, 255.
- 18 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.
- 19 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.

Received 26th September 1990; Paper 0/04345A