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HYDROGEN ISOTOPIC EXCHANGE AND PROTONATION OF π-CYCLOPENTADIENYLRHENIUM DICARBONYL TRIPHENYLPHOSPHINE

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Summary

An essential difference in reactivity between iso-structural and -electronic rhenium and manganese complexes $CpM(CO)_2L$ (M = Re, Mn; L = CO, PPh_3) was found for their hydrogen isotopic exchange and protonation reactions. PMR established complete protonation of $CpRe(CO)_2PPh_3$ complex in strongly acidic media, the protonated form of the complex being present as a mixture of *cis* and *trans* isomers. A stereochemical structure of the protonated form was determined on the basis of (^1H—^{31}P) spin—spin interaction constants.

Introduction

There are few data in the literature giving quantitative characteristics of the effect of the central metal atom on the reactivity of iso-structural and -electronic π-complexes of Group VII transition metals. Tricarbonylrhenium complexes are known to enter nucleophilic exchange reactions more readily than other analogous Group VII complexes [1,2], and comparison of dissociation constants proved that the carboxylic acid of $CpRe(CO)_3$ is almost twice as strong as its manganese analogue [3]. In addition, it is known that $CpMn(CO)_3$ participates in hydrogen isotopic exchange with a mixture of trifluoroacetic and sulphuric acids (H_0 of the mixture = —7.2) in methylene chloride at a rate ca. 5 times greater than the analogous rhenium complex [4]. However, the dependence of the rate of hydrogen isotopic exchange on the acidity of the medium for both complexes was not established, so their relative reactivities could not be established.

The present work is concerned with the behaviour of rhenium complexes π-$CpRe(CO)_2L$ (I) (Ia, L = CO; Ib, L = PPh_3) in protonation and hydrogen isotopic exchange (HIE) with acids and compares the results with data obtained previously [6,8,11] for manganese complexes π-$CpMn(CO)_2L$ (II) (IIa, L = CO; IIb, L = PPh_3).

Results and discussion

We measured HIE rates of rhenium complexes Ia and Ib with deuteriotrifluoroacetic acid under similar conditions and found rate constants for Ia and Ib to be 1.1×10^{-8} and 9.7×10^{-8} s^{-1}, respectively (Table 1). Table 1 gives, for comparison, the data for HIE of manganese complexes IIa and IIb.

The data imply that in contrast to manganese complexes, in which substitution of the CO ligand by PPh_3 raises the HIE rate of the π-cyclopentadienyl ring more than 500 times, a strong triphenylphosphine ligand in similar rhenium complexes accelerates hydrogen exchange only 9-fold. Moreover, Table 1 shows that the rate of electrophilic HIE for manganese complex IIb is four orders of magnitude greater than that for rhenium complex Ib.

Such a pronounced difference in the effect of the same ligand on the reactivity of rhenium and manganese complexes indicates an essential role of the central metal atom in transfering ligand electronic effects in iso-electronic and -structural complexes of transition metals of the same group of the periodic system. In accordance with this, IR spectroscopy has demonstrated [5] a weaker transfer of electronic effects from R substituents in the cyclopentadienyl ring via the rhenium atom when compared to manganese in complexes of the $R{-}C_5H_4M(CO)_3$ type (M = Re, Mn; R = H, Br, I, $COCH_3$, COC_6H_5).

Bearing in mind that the basicity of rhenium atom (6th period) is higher than that of manganese atom (4th period) one may expect differences in behaviour of similar rhenium and manganese complexes (I and II) in acidic media. To elucidate this, the influence of the acidity of the medium on HIE rate of the rhenium Ib complex was studied (for the manganese IIb complex this dependence has been determined earlier [6]). HIE rate constants of Ib in mixtures of acetic and trifluoroacetic acids with variation in the values of acidity functions [7] were measured. It results that HIE rate of Ib increases with greater acidity of the medium within the H_0' range from +0.5 to −2.6, but further increases in acidity lowers HIE rate (Table 2; Fig. 1, curve Ib). The dependence of HIE rate on the acidity of the medium found for the rhenium Ib complex differs from that of the analogous manganese complex IIb. In the latter case the rate of HIE increases with increased acidity of the medium even at very high acidity levels [6] (Fig. 1, curve IIb). However, when one succeeds in raising the basicity of manganese complexes, e.g. by introducing the second donor phosphine ligand or diphosphine chelate ligand, the dependence of HIE on the acidity of the medium acquires a character similar to that observed with the rhenium Ib complex [6] (Fig. 1, curve IIc).

TABLE I

EFFECT OF LIGAND L ON HIE RATE[a] FOR COMPLEXES π-$CpM(CO)_2L$ (M = Re, Mn; L = CO, PPh_3)

Complex	M = Re (I)		M = Mn (II)	
	k(HIE) (s^{-1})	k(Ib)/k(Ia)	k(HIE) (s^{-1})	k(IIb)/k(IIa)
$CpM(CO)_3$ (a)	1.1×10^{-8}	9	2.6×10^{-8}	500
$CpM(CO)_2PPh_3$ (b)	9.7×10^{-8}		1.3×10^{-5}	

[a] Molar ratio complex : CF_3COOD : CH_2Cl_2 = 1 : 200 : 200; temperature 50°C.

TABLE 2

DEPENDENCE OF HIE RATE OF THE COMPLEX $CpRe(CO)_2PPh_3$ (Ib) ON THE ACIDITY OF THE MEDIUM [a]

H'_0	Duration of exchange (min)	Deuterium content (%)		k, (s^{-1})	lg k
		Found [c]	Calculated for equilibrium		
+0.52	14070	0.67	66.68	1.17×10^{-8}	−7.93
−0.02	8200	0.63	66.88	2.01×10^{-8}	−7.70
−0.40	14140	2.20	67.06	3.93×10^{-8}	−7.41
−1.02	8275	2.34	67.39	7.04×10^{-8}	−7.15
−2.05	8380	6.59	67.76	2.04×10^{-7}	−6.69
−2.48	13080	15.52	68.13	3.29×10^{-7}	−6.48
−2.60	8375	10.95	68.26	3.48×10^{-7}	−6.46
−2.80	9805	6.46	68.83	1.68×10^{-7}	−6.78
−3.03	9820	3.84	69.26	9.71×10^{-8}	−7.01
−6.0 [d]	22560	0.56	69.37	5.95×10^{-9}	−8.23

[a] Complex : mixture of acids : CH_2Cl_2 1 : 200 : 200 (methylene chloride added to improve solubility). [b] H'_0 is acidity function of mixtures of CF_3COOD and CH_3COOD in CH_2Cl_2, taken to be numerically equal to H_0 of the mixture of these acids without solvent. [c] Determined by mass spectrometry. [d] H'_0 = −6.0 obtained by adding D_2SO_4, [14].

Thus, a rather considerable difference in the behaviour of iso-electronic and -structural rhenium and manganese π-complexes exists in acidic media, obviously determined by differences in basicity of the complexes and, consequently, by differences in stability of their protonated forms.

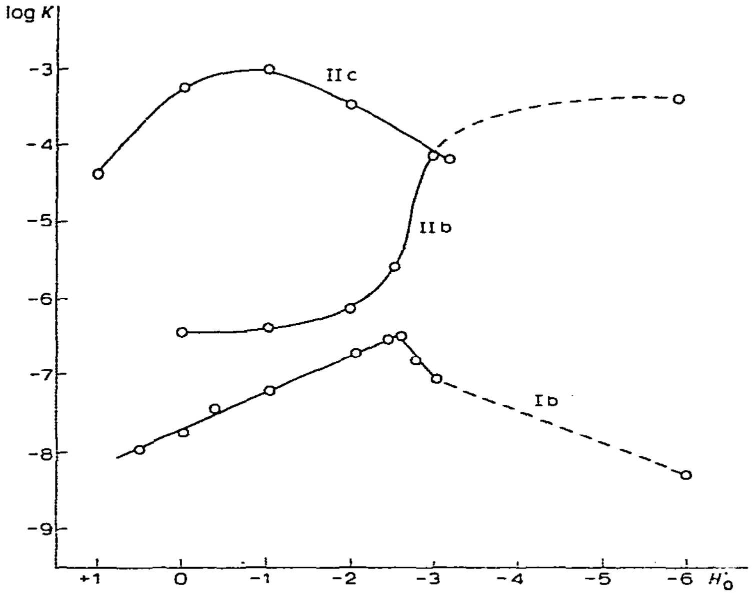

Fig. 1. Dependence of lg k(HIE) on the acidity of the medium: Ib, $CpRe(CO)_2PPh_3$; IIb, $CpMn(CO)_2PPh_3$; IIc, $CpMnCO(Ph_2PCH_2CH_2PPh_2)$. Curves IIb and IIc were obtained under the conditions [6]: complex : mixture of acids : CH_2Cl_2 1 : 10 : 50; temperature 50°C.

It has been found previously [8] by an IR method that the rhenium in the $CpRe(CO)_2PPh_3$ complex type is much more basic than the manganese in analogous derivatives. Thus, the Ib complex was practically completely protonated in the mixture $CF_3COOH : CH_2Cl_2$ of mole ratio 1 : 10, while complete protonation of the IIb complex was not observed [8] even in pure CF_3COOH. Therefore, it was considered to be of interest to study the protonation reaction of the complex π-$CpRe(CO)_2PPh_3$ (Ib) by ^1H and ^{13}C NMR and to compare the results with those already available for its manganese analogue [11].

PMR provided us with direct evidence that in acidic media the protonation of the Ib complex involves the rhenium atom. In low acidity media the simultaneous presence of protonated and non-protonated forms of the complex can be observed (Fig. 2a). The PMR spectrum shows two signals in the form of sharp singlets, δ 5.27 and 5.44 ppm (protons of cyclopentadienyl rings of the non-protonated and protonated species, respectively), and a doublet signal due to the hydride hydrogen Re—H in the strong field (δ —7.58 ppm, $J\ {}^1H—Re—{}^{31}P$ = 39 Hz). The ratio of integral intensities of signals with chemical shifts δ 5.44 and —7.58 ppm is 5 : 1 thus testifying to the monoprotonation of the Ib complex.

In high acidity media the character of PMR spectrum of the Ib complex undergoes considerable change. Thus, dissolving the complex in chloroform in a mixture of trifluoroacetic acid and boron trifluoride monohydrate gives in a strong field two doublet signals instead of one, with chemical shifts δ —7.54 ppm

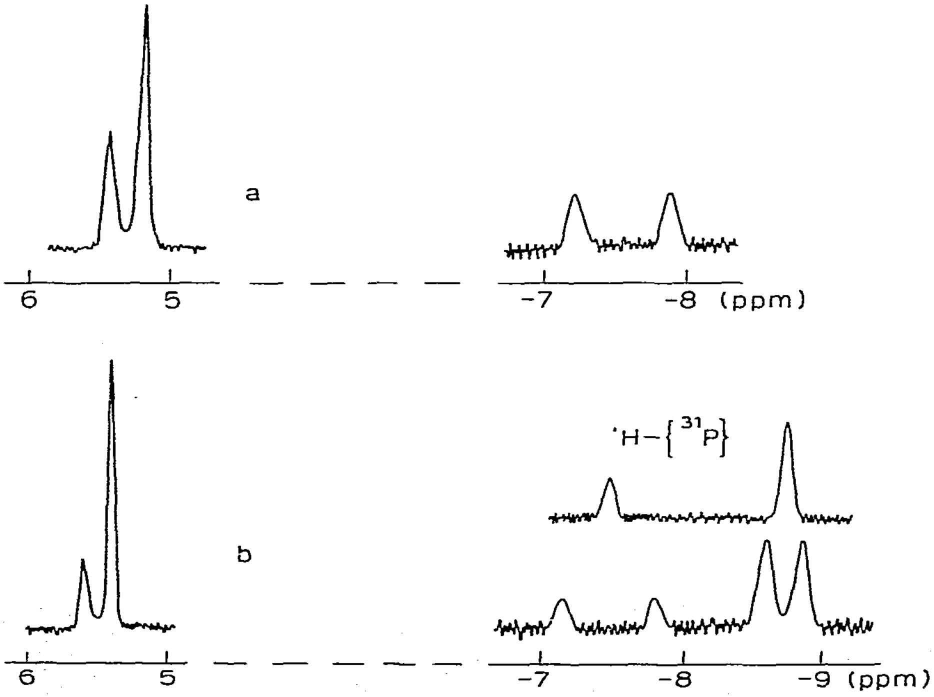

Fig. 2. PMR spectrum of π-$CpRe(CO)_2PPh_3$: a, in chloroform with trifluoroacetic acid ($CF_3COOH : CHCl_3 \approx 1 : 4$, V : V, temperature 10°C); b, in chloroform with trifluoroacetic acid and boron trifluoride monohydrate ($CF_3COOH : BF_3 \cdot H_2O : CHCl_3 \approx 1 : 0.5 : 4$, V : V; temperature 20°C).

($J(^1H—Re—^{31}P) = 39$ Hz) and —8.70 ppm ($J(^1H—Re—^{31}P) = 15$ Hz), the ratio of integral intensities being 1 : 4. Two singlets are also observed due to the cyclopentadienyl protons, with the same ratio of integral intensities and chemical shifts δ 5.63 and 5.46 ppm (Fig. 2b). The integral intensities of these signals and of the signals of two doublets in strong field infers that in the highly acidic conditions specified a practically complete protonation of the Ib complex takes place. Two signals due to protons of the cyclopentadienyl ring and two doublets in strong field result from the formation of two isomers of the protonated Ib complex. The formation of two isomers by addition of hydrogen to the rhenium in Ib can easily be conceived when assuming the structural transformation from trigonal to rectangular pyramidal with a cyclopentadienyl ligand at the apex (Fig. 3).

According to the experimental data on hydride complexes of transition metals with phosphine ligands [9], complexes with square planar or octahedron geometry with ^1H and ^{31}P nuclei in *cis* positions have a spin—spin interaction constant $J(^{31}P—M—^1H) = 5—30$ Hz. *Trans* isomers are distinguished by distinctly higher J values: 60—180 Hz. Therefore, in a number of cases a choice between structures can be made on the basis of the value of this constant. However, a strong deviation from the ideal octahedral structure may result in the ratio between *cis* and *trans* constants to be reversed. Thus, it was found [10] for the heptacoordinated complexes $CpMo(CO)_2LH$, which can be regarded as neutral models of the protonated form of the Ib complex, that J for *cis* isomers equals 64—73 Hz while for *trans* isomers it ranges from 21—29 Hz. In addition, it was demonstrated that in PMR spectra of protonated forms of manganese diphosphine complexes [11] spin—spin interaction constants $J(^1H—^{31}P)$ of *cis* isomers are 2.5—3 times higher than those of *trans* isomers. Analogously, we assigned the doublet with $J = 39$ Hz to the *cis* isomer of the protonated Ib form and the doublet with $J = 15$ Hz to the *trans* isomer. Thus, the rhenium Ib complex is protonated in low acid media giving rise only to the *cis* isomer. The increase in acidity leads to a predominance of the *trans* isomer of the protonated Ib form.

^{13}C NMR studies corroborate the PMR data. A ^{13}C NMR spectrum of the complex Ib in acidic medium where, according to PMR, complete protonation takes place is shown in Fig. 4. This shows that the spectrum has two signals due to carbon atoms in cyclopentadienyl rings at δ 89.11 and 90.15 ppm with relative intensities ca. 4 : 1, similar to PMR spectra of protons in cyclopentadienyl rings. Unfortunately, in the region of the spectrum where the carbonyl carbons bound to the metal resonate only a multiplet (δ 189.02 ppm) is observed with insufficiently high signal : noise ratio, thus precluding any sort of reliable assign-

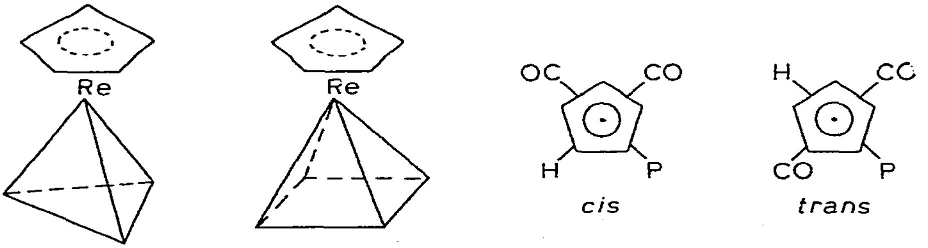

Fig. 3. Possible configurations of the protonated form of the Ib complex.

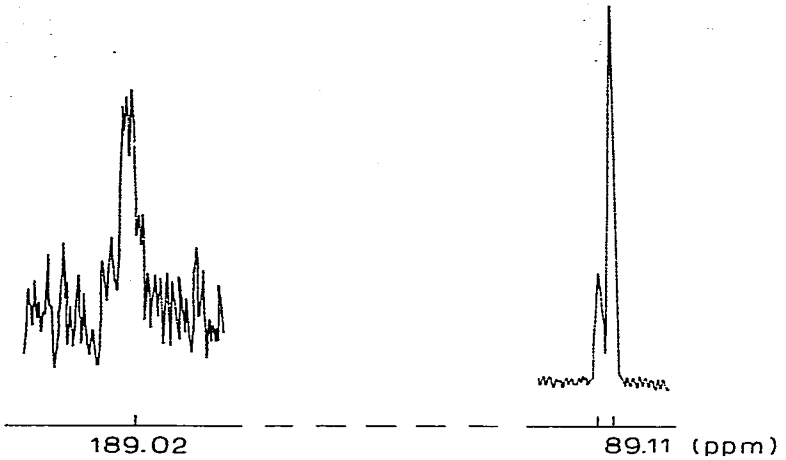

Fig. 4. NMR ^{13}C spectrum of π-CpRe(CO)$_2$PPh$_3$ in methylene chloride with trifluoroacetic acid and boron trifluoride monohydrate ($CF_3COOH : BF_3 \cdot H_2O : CH_2Cl_2 \approx 2:1:4$, V : V; temperature —20°C).

ment of the signals for *cis* and *trans* isomers. Therefore, we carry out the assignment of the ^{13}C NMR signals by analogy with the PMR spectrum making use of the differences in the percentage of each protonated isomer form at the predetermined acidity of the medium. Thus, the signals with δ 89.11 and 90.15 ppm are assigned to the carbon atoms of cyclopentadienyl rings in *trans* and *cis* isomers, respectively.

For the analogous manganese complexes π-CpMn(CO)$_2$PR$_3$ (IId R = i-C_3H_7; IIe R = C_6H_{11}) protonation also occurred on the metal, and the PMR spectra [11] gave doublet signals of hydride protons Mn—H at δ —5.6 and —5.7 ppm, respectively, with J = 51 Hz. However, the separation of signals of the protonated and non-protonated forms of the complexes was not detected in the region of signals due to cyclopentadienyl ring protons. Only one broad proton signal, shifted 0.5—0.6 ppm downfield from the signal due to the protons of the neutral complex, was observed. An attempt to establish the presence of two isomeric forms of these complexes also failed. The basicity of a complex plays an essential role in protonation, and as manganese complexes IId and IIe possess lower basicity, a smaller stability of their protonated forms compared to the rhenium analogue Ib is to be expected. Possibly for this very reason, one cannot detect cyclopentadienyl protons in the PMR spectra of protonated and non-protonated IId and IIe. The protonation of the IIb complex, under the experimental conditions, is undetected by the PMR method.

The studies described allowed us to ascertain an essential difference in the reactivity of iso-structural and -electronic complexes of rhenium and manganese, CpM(CO)$_2$L (M = Re, Mn; L = CO, PPh$_3$), in HIE and protonation reactions and to characterize the difference quantitatively. Thus, the rhenium Ib complex forms a considerably more stable system when protonated at the metal which allows isomeric *cis* and *trans* forms to be observed. The HIE rate of this complex increases with increased acidity of the medium until a certain acidity is reached, after which it decreases. A strong donor ligand, PPh$_3$, exerts a relatively small influence on the HIE rate. The differences in reactivity of iso-structural and -electronic rhenium and manganese complexes result, basically, from the differences in basicities of the central metal atoms and in their abilities to transfer electronic effects from bound ligands. These differences should similarly be expected in other reactions with electrophilic reagents.

Experimental

Cyclopentadienylrhenium dicarbonyl triphenylphosphine (Ib) was obtained according to a known technique [12].

All experiments on hydrogen isotopic exchange of Ib in mixtures of CF_3COOD, CH_3COOD and CH_2Cl_2 were carried out at 50°C in an argon atmosphere. The reaction product was isolated in a way similar to that described previously [13].

The deuterium contents were determined by mass spectrometry using a MX-1303 spectrometer and rate constants were calculated from a first order equation. The results of hydrogen isotopic exchange are summarized in Table 2.

PMR spectra of Ib were obtained on a RYa-2305 spectrometer (frequency 60 MHz) as chloroform solutions with additives of trifluoroacetic acid and boron trifluoride monohydrate. A Fourier spectrometer, Bruker HX-90 (frequency 22.635 MHz), was used for taking NMR $^{13}C-\{^1H\}$ spectra. Chemical shifts were measured against δ scale, cyclohexane was used as an internal standard.

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