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THE EFFECT OF DONOR LIGANDS ON THE REACTIVITY OF π-AROMATIC LIGANDS IN MANGANESE AND CHROMIUM COMPLEXES

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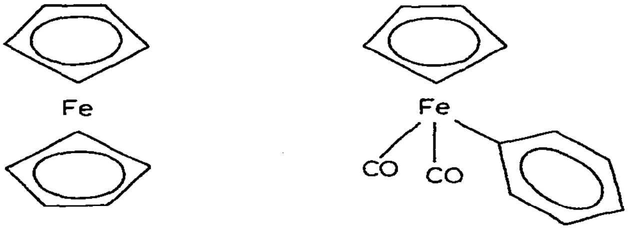
SUMMARY

The effect of ER_3 ligands (where $E=P$, As or Sb and R=alkyl or phenyl) on the reactivity of π-cyclopentadienyl or π-benzene rings in the complexes π-$C_5H_5Mn(CO)_n(ER_3)_{3-n}$ and π-$C_6H_5XCr(CO)_2ER_3$ during hydrogen isotopic exchange reactions with acids is discussed. A reaction mechanism is proposed.

INTRODUCTION

The mutual effect of the ligands coordinated to the same transition metal atom, particularly insofar as the properties of π-aromatic ligands are changed as the nature of the other ligands coordinated to the metal atom is changed, is an important, but virtually unstudied problem in the chemistry of transition metal π-complexes. Cases are known, however, where such effects are clearly distinguishable. Thus, a comparison of the properties of the π-cyclopentadienyl (Cp) ligands in ferrocene (I) and in the σ-phenyliron complex (II) provide a good example. Both complexes are isoelectronic, diamagnetic and uncharged (Fig. 1)

The Cp ligands in ferrocene enter readily into a variety of electrophilic substitution reactions[1,2]. According to Rosenblum[3], Friedel–Crafts' acylation of ferrocene is six orders faster than that of benzene ($K_{rel}=3.3\times10^6$). In contrast, the Cp ligand in

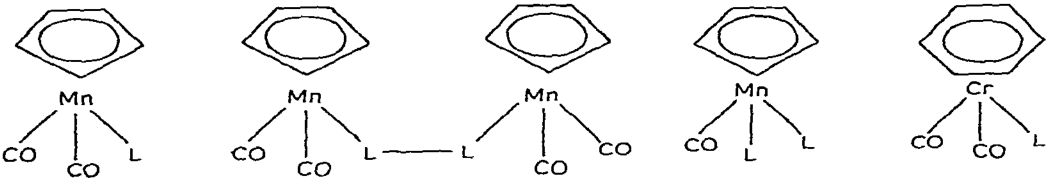


(I) (II)

Fig. 1.

complex (II) has no tendency to undergo electrophilic substitution reactions. On Friedel–Crafts' acylation of (II), the Cp ring is not involved in the reaction, only the σ-bonded phenyl ligand being acylated[4]. However, the Cp ring of (II) undergoes protophilic hydrogen exchange much more readily than those of ferrocene. Thus, (II) exchanges its proton for deuterium quite rapidly in the presence of EtONa in EtOD, whilst under the same conditions ferrocene does not undergo such an exchange reaction[5]. This behaviour shows that the reactivity of the Cp ligand in π-cyclopentadienyliron complexes is determined essentially by the nature of the other ligands coordinated to the same iron atom.

At this point it is relevant to review the data on the dependence of the reactivity of cyclic π-ligands in manganese and chromium complexes on the nature of the other ligands attached to the metal atom. The principal procedure used for investigating such reactivity was to study the isotopic hydrogen exchange of these complexes with various acids[6], a reaction which may be referred to as electrophilic hydrogen isotope exchange (HIE). Measurement of the rate of HIE for cyclic π-ligands (π-cyclopentadienyl and π-benzene) showed that the reactivity of these ligands is very much influenced by the nature of the other ligands (L) coordinated to the same transition metal atom. Two systems were used to study this effect (Fig. 2): (*a*) π-cyclopentadienylmanganese complexes, prepared by the replacement of one [(III) and (IV)] or two CO groups [(V)] in cyclopentadienylmanganese tricarbonyl (cymantrene) with different *n*-donor ligands L; (*b*) π-arenechromium complexes obtained by the replacement of one CO group in benzenechromium tricarbonyl, (VI). Although carbonyl substitution in transition metal π-complexes with different *n*-donor ligands has been investigated some time ago[7,8], virtually no studies have been made of the properties and reactivities of the resulting products.



(III) (IV) (V) (VI)

Fig. 2.

π-CYCLOPENTADIENYLMANGANESE COMPLEXES

The effect of ligand substitution has been studied in greatest detail for cymantrene derivatives π-$C_5H_5Mn(CO)_2L$ (III)[9,10]. Replacement of one carbonyl group in cymantrene by tertiary phosphine, arsine or stibine increases the rate of HIE with acids by between 2–4 orders of magnitude. The quantitative data relating the dependence of the rate of electrophilic HIE in the Cp ring of (III) on the nature of the ligand are listed in Table 1. From these data it follows that replacement of CO with stronger electrondonor ligands leads to an increase in the rate of hydrogen exchange in the cyclopentadienyl ring. In conjunction with this increase in the rate of HIE the CO stretching mode frequencies decrease due to the increased back donation d_π-

TABLE 1

THE RATE OF HIE OF $CpMn(CO)_2L$ COMPLEXES AS A FUNCTION OF THE NATURE OF THE LIGAND L[a]

	K_{rel}	$\nu(CO)$ (cm^{-1})[b]	
CO	1	1939	2023
$P(OPh)_3$	70	1900	1963
$SbPh_3$	750	1875	1935
PPh_3	2000	1875	1937
$AsPh_3$	2500	1874	1936
$P(CH_2Ph)_3$	4800	1865	1929
$P(i\text{-}C_3H_7)_3$	16000	1862	1927
$P(C_6H_{11})_3$	31000	1859	1925

[a] Reaction conditions for HIE; initial ratio of complex/CF_3COOD/CH_2Cl_2 is 1/10/50, temperature 25°C.
[b] In CS_2.

(Mn)–p_π(CO) and the greater contribution of structure (B):

$$\underset{(A)}{\bar{M}-C\equiv\overset{+}{O}} \leftrightarrow \underset{(B)}{M=C=O}$$

It should be pointed out that the donor effect of tertiary phosphine as a ligand is dependent on the nature of the radicals bound to the phosphorus atom and increases with increasing donor properties of the latter according to the series OPh < Ph < CH_2-Ph < i-C_3H_7 < C_6H_{11}. Variation of the donor atom (P, As, Sb) has considerably less effect. The data obtained indicate that the effect of donor ligands is transmitted through the manganese atom to both the carbonyl groups and the cyclopentadienyl ring.

Upon replacement of CO for triphenylphosphine in cymantrene there is a noticeable increase in the nucleophilicity of the Cp ligand which has enabled an electrophilic HIE to be performed with the complex π-$C_5H_4XMn(CO)_2PPh_3$ containing a substituted Cp ligand (where X = donor and acceptor substituents). These compounds are readily prepared in high yield by the irradiation of the corresponding π-$C_5H_4XMn(CO)_3$ complex and PPh_3 in benzene[11]. With π-cyclopentadienylmanganese complexes, only the effect of increasing the number of ethyl groups in the Cp ligand on the rate of electrophilic HIE has been studied[12]. The attempted hydrogen exchange between cymantrenes with the electron-withdrawing substituents and various acids was unsuccessful for no reaction occurred at low acidity of the medium whilst at high acidity decomposition of the complexes occurred at a faster rate than hydrogen exchange. The values of the relative rate constants for HIE (K_{rel}) with trifluoroacetic acid in CH_2Cl_2 for complexes of the type π-$C_5H_4XMn(CO)_2PPh_3$ are listed in Table 2[13,14]. From these data it will be seen that the behaviour of substituents in this system is different from that of the same substituents in the benzene system but similar to the effect in ferrocene[16,17]. Thus, the thiomethyl group, for example, which generates $+C$ and $-I$ effects, increases the rate of HIE in benzene[18] and thiophene[19] considerably but has only a marginal effect on the rate of the acidic HIE discussed above.

The rate of exchange of the α- and β-hydrogens of the Cp ring in these compounds was measured by following the change in the intensities of the proton signals in the

TABLE 2

THE DEPENDENCE OF THE RATE OF HIE IN THE COMPLEXES π-$C_5H_4XMn(CO)_2PPh_3$ ON THE NATURE OF THE SUBSTITUENT X[a]

X	K_{rel}	$\nu(CO)$ (cm^{-1})[b]	
H	1	1891	1951
$PhCH_2$	3.0	1888	1947
Et	12.5	1886	1947
SCH_3	3.3	1892	1950
Cl	0.14	1901	1958
CH_3OOC	0.004	1903	1960

[a] Reaction conditions for HIE: initial ratio of complex/CF_3COOD/CH_2Cl_2 is 1/10/50, temperature 25°C.
[b] In cyclohexane. See ref. 15.

^1H NMR spectrum during the course of hydrogen exchange. The partial rate constants for HIE in the α and β positions in the Cp ring of these complexes are shown in Fig. 3.

The difference between the rates of exchange at the α and β positions is relatively small, differing only by a factor of 1.5–2 even when introduction of the carbomethoxylic group led to a decrease in the overall rate of exchange of almost three orders of magnitude[14]. It is interesting to note that a similar effect has been observed in the ferrocene series[17,20]. This could be taken to suggest that levelling out of the differences in the reactivities at non-equivalent positions in the π-bonded aromatic ring is probably a common feature of transition metal complexes.

The products of the substitution of the two CO ligands in cymantrene by phosphines are known[21]. To follow further changes in the reactivity upon substitution of the second CO group, we have studied electrophilic HIE in the Cp ligand of the complex $CpMn(CO)(PPh_3)_2$ (Va) as well as in the chelate complexes $CpMn(CO)[Ph_2P(CH_2)_nPPh_2]$ containing the bidentate ditertiary phosphine ligand $Ph_2P(CH_2)_nPPh_2$ (where $n=3$, (Vb), 2, (Vc) or 1, (Vd). On replacement of the second CO group by a phosphine ligand, the electron density at the Mn atom increases relative to that present in the monophosphine complexes which leads to a decrease in the frequencies of the stretching modes of the remaining carbonyl group by about 70 cm^{-1}.

Coordination of the Mn atom with the second phosphine ligand does not, however, increase the rate of hydrogen exchange. In contrast, in going from the complex $CpMn(CO)_2PPh_3$ to the complex $CpMn(CO)(PPh_3)_2$ the rate of HIE falls sharply (by more than 200–300 times)[22]. The same trend is observed with the diphosphine

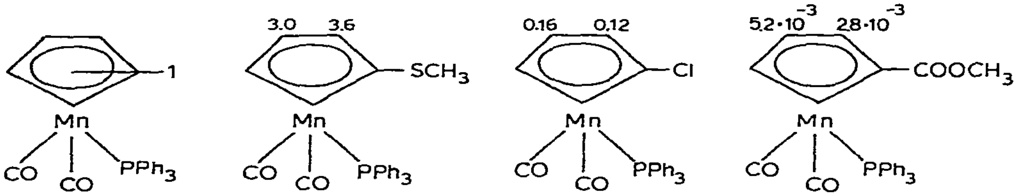


Fig. 3. The partial rate constants for electrophilic HIE at the α- and β-hydrogen atom in the complexes π-$C_5H_4XMn(CO)_2PPh_3$.

chelate complexes. The data on hydrogen exchange with diphosphine complexes is given in Table 3 where for comparison the data on the reactivity of the complex CpMn$(CO)_2PPh_3$ under the same conditions are also included.

The rate of HIE with trifluoroacetic acid in CH_2Cl_2 increases in the series of compounds (Va)–(Vc), but under these conditions the complex (Vd) is unstable which is probably a reflection of the considerable strain present in the four-membered metallocycle $\overline{\text{Mn–P–C–P}}$. The ^{13}C NMR signal of the Cp carbon atoms shifts upfield in the spectra of the same series of compounds, indicating that the electron density at the carbon atoms of the Cp ligand increases which is in agreement with the higher HIE rate.

The differences observed in the rates of HIE and in the values of $\delta^{13}C$ for the complexes (Va)–(Vd) are probably due to variations in the geometry of the diphosphine ligands (the two phosphorus atoms are not linked together nor linked via a polymethylene chain of varying length). Differences do exist in the degree of overlap of the sp^3 hybrid orbitals of the phosphorus atom with the d orbitals of manganese and in the degree of back-donation in the P–Mn bond. As a result, the electron-density distribution in compounds (Va)–(Vd) is not the same. Differences in the geometry of the diphosphine ligands which lead to some differences in the C–O bond orders are also clearly indicated by the change in the ν(CO) frequencies for complexes (Va)–(Vd) from 1825 to 1842 cm^{-1}.

An analysis of the dependence of the rates of these various reactions on the acidity of the medium may provide valuable information on the mechanism of these reactions in the presence of acid. With these two types of manganese complex (the mono- and diphosphines), the dependence of the rate of HIE on the acidity of the medium has been shown to be opposite over the particular range of acidity studied.

For cymantrene and CpMn$(CO)_2PPh_3$, the rate of HIE with CF_3COOD in CH_2Cl_2 increases[23] with increasing acidity on addition of small amounts of D_2SO_4. In contrast, with the diphosphine complexes (Va)–(Vb) a similar addition of D_2-

TABLE 3

HYDROGEN EXCHANGE IN DIPHOSPHINEMANGANESE COMPLEXES[a]

Compound	$10^7 K_{HIE}$ (s^{-1})	K_{rel}	ν(CO) (cm^{-1})[b]	$\delta^{13}C$ Cp ligand (ppm)[c]
CpMn(CO)$(PPh_3)_2$ (Va)	1.9 ± 0.7	0.004	1827	82.17
CpMn(CO)$(PPh_2CH_2CH_2CH_2PPh_2)$(Vb)	25 ± 5	0.03	1825	80.57
CpMn(CO)$(Ph_2PCH_2CH_2PPh_2)$ (Vc)	760 ± 80	1.25	1840	79.66
CpMn(CO)$(Ph_2PCH_2PPh_2)$ (Vd)		[d]	1842	76.71
CpMn$(CO)_2PPh_3$	650 ± 40	1.0	1866 1935	

[a] Reaction conditions for HIE; initial ratio of complex/CH_2Cl_2/CF_3COOD is 1/50/10, temperature 50°C[22]. [b] In CH_2Cl_2. [c] Chemical shift of carbons in the Cp ligand as observed in the ^{13}C NMR spectrum in $CHCl_3$ solution (relative to tetramethylsilane as the internal standard). [d] Complex (Vd) under these conditions decomposed rapidly and no reproducible kinetic data were obtained.

SO_4 leads to a decrease in the rate of reaction. In media of sufficiently high acidity*, the HIE reaction of diphosphine complexes is virtually suppressed[22], whilst in the HIE reaction of complex (Vc) with CF_3COOD (in the absence of CH_2Cl_2 as a solvent) decreasing the acidity of the medium by employing dilute CH_3COOD increases the reaction rate. Thus with cymantrene and the complex $CpMn(CO)_2PPh_3$, the rate of HIE increases as the acidity of the medium increases in a similar manner to classical aromatic systems, *e.g.* derivatives of benzene[24]. For diphosphine complexes, the dependence on acidity is reversed.

Important information on the state of π-cyclopentadienyl complexes of manganese has been obtained by means of IR spectroscopy[25]. Complexes of the type $CpMn(CO)_2L$ exhibit two absorption bands in the region of the CO stretching modes. On introducing CF_3COOH into the system, the IR spectra of solutions of these complexes in CH_2Cl_2 as well as in other solvents ($CHCl_3$, benzene, nitromethane) reveal two new absorption bands shifted to higher frequencies by 100–120 cm^{-1}. The appearance of such bands provides evidence for the reversible protonation of the initial complexes in accordance with the scheme:

$$CpMn(CO)_2L + H^+ \rightleftarrows [CpMn(CO)_2(L)H]^+$$

The position of this equilibrium depends essentially on the nature of the ligand L and on the presence of substituents in the Cp ligand. The formation of such a protonated complex has been observed only for those systems which are capable of HIE under these conditions. In Table 4, data on the protonation[25] and the rate of HIE for monophosphine manganese complexes obtained under the same conditions are compared. The quantity $\Delta\nu$ is equal to the difference between the $\nu(CO)$ values for the corresponding complex in CS_2 and $CH_2Cl_2 + CF_3COOH$; the ratio of the peak intensities of the bands for the protonated and non-protonated forms are also presented. The quantity $D_{prot}/D_{non\text{-}prot}$ is a measure of the relative amount of the protonated form present and this quantity increases as the degree of protonation increases.

TABLE 4

PROTONATION AND HIE OF MONOPHOSPHINE MANGANESE COMPLEXES $CpMn(CO)_2L$[a]

L	$\Delta\nu(CO)$ (cm^{-1})	$D_{prot}/D_{nonprot}$	K_{rel} *of HIE*
CO	0[b]	0	0[c]
$P(OPh)_3$	0[b]	0	0[c]
PPh_3	110	0.018	1.0
$P(CH_2Ph)_3$	113	0.049	2.4
$P(i\text{-}C_3H_7)_3$	111	0.177	8.0
$P(C_6H_{11})_3$	110	0.408	15.5
$AsPh_3$	113		1.2
$SbPh_3$	104		0.4

[a] Employing the ratio compound/CF_3COOH (or CF_3COOD)/CH_2Cl_2 = 1/10/50, temperature 25°C. [b] Not protonated under these conditions. [c] HIE reaction does not occur under these conditions.

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* For example, at a ratio of complex/CF_3COOD/D_2SO_4/CH_2Cl_2 of 1/20/2/20, the H_0 value of the acidic mixture is −7.

From Table 4 it follows that the concentration of the protonated form is determined by the nature of the ligand L, the equilibrium being shifted to the right as the electron-donor character of L increases. When no protonation occurs, hydrogen exchange with the complex is also not possible. The rate of HIE with monophosphine manganese complexes increases as the extent of protonation increases, thus suggesting that protonation of the complex is a necessary condition for the occurrence of the HIE reaction. This problem is considered in more detail below, where an analysis is made of the reactivity of chromium compounds.

π-ARENE CHROMIUM COMPLEXES

The effect of *n*-donor ligands on the reactivity of the benzene ring π-bonded to the chromium atom has been studied for π-$XC_6H_5Cr(CO)_2PPh_3$ (where $X=H$ or $COOCH_3$)[26]. Replacement of one CO group by PPh_3 in a similar manner to the cymantrene system markedly increases the nucleophilicity of the π-benzene ligand. The rate of HIE with acids increases by more than 3 orders of magnitude. At the same time, the CO stretching frequencies decrease and the ^1H NMR signals of the benzene ring shift by ≈ 0.6 ppm upfield (Table 5) while the ^{13}C signals of the aromatic ligand are displaced upfield by 3–4 ppm[26,27]. A similar effect has also been observed with cyclopentadienylmanganese complexes[28].

Thus substitution of the *n*-donor ligand into arenechromium tricarbonyl, as in cymantrene, increases the electron density at the metal atom and this is transmitted via the chromium atom to both the π-arene and carbonyl ligands.

The effect of substituents on the rate of HIE in π-arenechromium complexes has been studied in greater detail. Introduction of donor substituents into the π-benzene ring has virtually no effect on the rate of HIE in arenechromium tricarbonyl derivatives (Table 6)[29]. This result is somewhat surprising because it is known that intro-

TABLE 5

THE EFFECT OF REPLACEMENT OF CO BY PPh_3 IN π-$XC_6H_5Cr(CO)_3$ ON THE RATE OF HIE AND ON THE SPECTRAL DATA

X	*L*	*ν(CO)*[a] *(cm^{-1})*	*δ arene (ppm)*	*K$_{rel}$ of HIE*[c]
H	CO	1916 1984	5.23	1
H	PPh_3	1861 1911	4.58	2600
CH_3OOC	CO	1923 1991	*o* 6.04[b] *m* 5.22 *p* 5.50	1
CH_3OOC	PPh_3	1876 1926	*o* 5.36[b] $\left.\begin{matrix}m\\ p\end{matrix}\right\}4.47$	2440

[a] For cyclohexane as the solvent. [b] For $CDCl_3$ as the solvent. [c] Reaction condition for HIE; initial ratio of complex/$CF_3COOH = 1/200$, temperature 50°C.

TABLE 6

THE EFFECT OF SUBSTITUTION IN THE π-BENZENE LIGAND ON THE RATE OF HIE IN ARENECHROMIUM TRICARBONYL COMPLEXES π-$XC_6H_5Cr(CO)_3$[a]

Substituent X	*K_{rel} of HIE reaction*	
	For arene ligand in the complex	*For the free ligand*
H	1	1
CH_3	0.9	150
1,3,5-$(CH_3)_3$	1	10^7
CH_3O	2.8	10^5

[a] Reaction conditions for HIE involving the complexes; initial ratio of complex/$CF_3COOD/BF_3 \cdot D_2O$ is 1/30/50, temperature 27.7°C.

duction of three methyl groups into the benzene ring increases the rate of HIE of the aromatic hydrogens by seven orders of magnitude[30], whereas when the benzene ring is π-bonded to a chromium atom the introduction of three methyl groups apparently has no influence on the rate of HIE. The CH_3O group, which increases the rate of hydrogen exchange in benzene by five orders of magnitude[31], causes only a 2–3-fold increase of the reaction rate in arenechromium tricarbonyl complexes.

A study of substituent effects in arenechromium dicarbonyl triphenylphosphine complexes has led to results which are as yet, inexplicable[29,32]. Thus, it has been shown that in this system the effect of substitution in the benzene ring is opposite to that observed in the corresponding benzene series (Table 7). However in this case once more the influence of substituents is somewhat weak, thus donor substituents such as the CH_3O and three methyl groups decrease the rate of the reaction slightly, while electron-withdrawing substituents such as the carbomethoxy group increase the reaction rate by almost an order of magnitude relative to that for the unsubstituted compound. It is interesting that the carbomethoxy group in Cp complexes of transition metals (for example, ferrocene[16] and the cyclopentadienylmanganese dicarbonyl–triphenylphosphine complex[14]) is a strong electron acceptor which leads to a decrease in the rates of HIE in CF_3COOD of about three orders of magnitude. Arene complexes of chromium in various acidic media where they undergo hydrogen exchange have been studied by means of IR[33] and ^1H NMR spectroscopy[34]. IR spectral results have indicated that protonation of arene$Cr(CO)_2PPh_3$ occurs almost completely under conditions of hydrogen exchange (in CF_3COOH) since the CO stretching modes of the initial reactants disappear in the spectra of such solutions and new absorption bands are observed which are shifted by more than 100 cm^{-1} to higher frequencies. It is interesting to note that only with the methylbenzoate complex in CF_3-COOH is a weak band corresponding to the non-protonated complex observed at 1920 cm^{-1}. In Table 8 are listed data relating to the effect of the π-arene ring of the complex π-$XC_6H_5Cr(CO)_2PPh_3$ on the value of $\Delta\nu(CO)$ (*i.e.* the difference between $\nu(CO)$ in cyclohexane as the solvent and in CF_3COOH). In addition, the mole percentage of CF_3COOH in the mixture with CH_2Cl_2 is given at which the ratio of the optical densities of the bands for the protonated and non-protonated forms is equal to unity[33]. This last parameter may be used as a measure of the relative ease of protonation of

TABLE 7

THE EFFECT OF SUBSTITUTION IN THE π-BENZENE RING ON THE RATE OF HIE IN ARENECHROMIUM DICARBONYL-TRIPHENYLPHOSPHINE COMPLEXES π-$C_6H_5XCr(CO)_2PPH_3$[a]

Substituent X	K_{rel} *of HIE*	$\nu(CO)$ (cm^{-1})[b]
H	1	1861 1911
CH_3	0.7	1855 1105
1,3,5-$(CH_3)_3$	0.4	1847 1896
CH_3O	0.4	1852 1905
CH_3OOC	9.4	1876 1923

[a] Reaction conditions for HIE; initial ratio of complex/CF_3COOD is 1/130, temperature 27.7°C. [b] For cyclohexane as the solvent.

TABLE 8

IR SPECTRAL DATA RELATING TO THE PROTONATION OF COMPLEXES OF THE TYPE π-$XC_6H_5Cr(CO)_2PPh_3$ IN TRIFLUOROACETIC ACID

Substituent X	$\Delta\nu(CO)$ (cm^{-1})	*Percentage of CF_3COOH which leads to 50% protonation of the complex*
H	103	9.5
CH_3	108	5.6
CH_3O	97	3.5
1,3,5-$(CH_3)_3$	104	2.8
CH_3OOC	91[a]	

[a] The non-protonated form is present in addition to the protonated form in CF_3COOH.

these complexes. As may be seen from Table 8, the presence of electron-releasing groups (CH_3, CH_3O) in the π-arene ring enhances protonation whilst electron-withdrawing groups (CH_3OOC) hinder protonation. Complexes of the type arene-$Cr(CO)_2PPh_3$ in CF_3COOH ($H_0 = -3$) are protonated and undergo electrophilic HIE (Table 7), while complexes such as arene$Cr(CO)_3$ in CF_3COOH are not protonated and do not undergo HIE. Thus, introduction of a PPh_3 ligand leads to a considerable increase in the nucleophilicity of the arene ligand and to a corresponding increase in the basicity of the complex. Protonation and HIE of complexes of the type arene$Cr(CO)_3$ with a lower basicity will occur in a medium of much higher acidity (*i.e.* a mixture of $CF_3COOH + BF_3 \cdot H_2O$, $H_0 \approx -7$) (Table 6).

Use of ^1H NMR spectroscopy has established[34] that protonation of arene chromium complexes under HIE conditions occurs at the metal atom with the formation of a Cr–H bond* (Fig. 4). This is confirmed by the following facts: (*a*) The appearance of a proton signal at $\delta = -4$ ppm upfield which is specific to a hydrogen atom bound to the metal. (*b*) Doublet splitting of the Cr–H proton signal due to spin–spin coupling with ^{31}P. The large spin–spin coupling constant $J(^1H-^{31}P)$ 63–69 Hz

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* The protonation of arene$Cr(CO)_3$ complexes was reported earlier by Wilkinson[35].

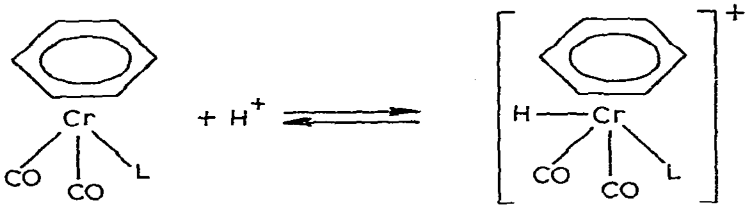

Fig. 4.

indicates that the proton is bound to the chromium atom rather than to the aromatic ring. From an estimate of the intensity of the upfield signal it is possible to show that only one proton adds to the chromium atom. Protonation shifts the aromatic ring proton signals downfield in agreement with the appearance of a positive charge in the complex upon proton addition. The position of the signal of the proton bound to the Cr atom δ(Cr–H), the downfield shift of the proton signals in the benzene ring and the side chain relative to CS_2 as well as the $J(^1H-^{31}P)$ values observed on protonation are given in Table 9.

The absence of a Cr–H proton signal in CF_3COOH in the case of benzene and methylbenzoate triphenylphosphine complexes (Table 9) may be due to rapid exchange between such protons and the medium(the exchange being rapid on the NMR time-scale), since IR spectral studies have shown that in the same medium protonation of the benzene complex is complete and that of the methyl benzoate complex virtually complete.

TABLE 9

^{1}H NMR DATA RELATING TO THE PROTONATION OF ARENECHROMIUM COMPLEXES[a]

Compound	*δ(Cr–H) (ppm)*	*$\Delta\delta$(ppm)*		*$J(^1H-^{31}P)$ (Hz)*
		Benzene ring	*Substituent*	
$C_6H_6Cr(CO)_3$	−4.05	1.56		
$CH_3C_6H_5Cr(CO)_3$	−4.08	1.37[b]	0.30	
$CH_3OC_6H_5Cr(CO)_3$	−4.12	1.32[b]	0.44	
1,3,5-$(CH_3)_3C_6H_3Cr(CO)_3$	−4.16	1.61	0.31	
$C_6H_6Cr(CO)_2PPh_3$		1.62		
$CH_3C_6H_5Cr(CO)_2PPh_3$	−4.27	1.58[b]	0.38	63
$CH_3OC_6H_5Cr(CO)_2PPh_3$	−4.56	1.37[b]	0.43	69
1,3,5-$(CH_3)_3C_6H_3Cr(CO)_2PPh_3$	−4.08	1.64	0.35	67
$CH_3OOCC_6H_5Cr(CO)_2PPh_3$		0.52 (*m*+*p*) 0.61 (*o*)	0.32	

[a] The spectra of the areneCr$(CO)_3$ complexes were measured in the mixed solvent $CF_3COOH+BF_3\cdot H_2O$ (1/1) while those for areneCr$(CO)_2PPh_3$ were measured in pure CF_3COOH. [b] Difference between the multiplet centres.

MECHANISM OF ACIDIC HYDROGEN EXCHANGE INVOLVING THE π-AROMATIC LIGANDS OF CHROMIUM AND MANGANESE COMPLEXES

As shown above, the initial manganese and chromium π-complexes are rapidly and reversibly protonated in acidic media:

$$QM(CO)_{3-n}L_n + H^+ \rightleftarrows [QM(CO)_{3-n}(L_n)H]^+$$

The position of this equilibrium depends on the nature of the transition metal (M), of the cyclic ligand (Q) and of any other ligands (L) coordinated to the same transition metal atom. Proton addition obviously occurs at the transition metal atom. With chromium complexes, this has been confirmed by means of ^{1}H NMR spectroscopy which has demonstrated the presence of an upfield Cr–H signal and enabled a measurement of the spin–spin coupling between the added proton and the ^{31}P nucleus of the phosphinic ligand. With manganese complexes, a corresponding Mn–H signal is not observed in the upfield region of the ^{1}H NMR spectrum. This can be explained either in terms of fast exchange with the solvent protons at room temperature, or by strong signal broadening due to the high quadrupole moment and high spin ($I = 5/2$) of ^{55}Mn. Unlike the manganese atom, the ^{52}Cr nucleus has no magnetic moment.

The data presented above regarding hydrogen exchange and protonation enable the problem of the mechanism of the HIE reaction involving chromium and manganese π-complexes and various acids (Fig. 5) to be discussed.

The first step in the mechanism probably involves the fast reversible protonation of the complex at the metal atom [step(A)] which is normally the most basic point in such complexes*. Although such protonation is necessary it is insufficient to enable HIE to occur immediately. Hydrogen transfer should therefore occur between the metal atom and the ring [step (B)]** but at present there is insufficient information

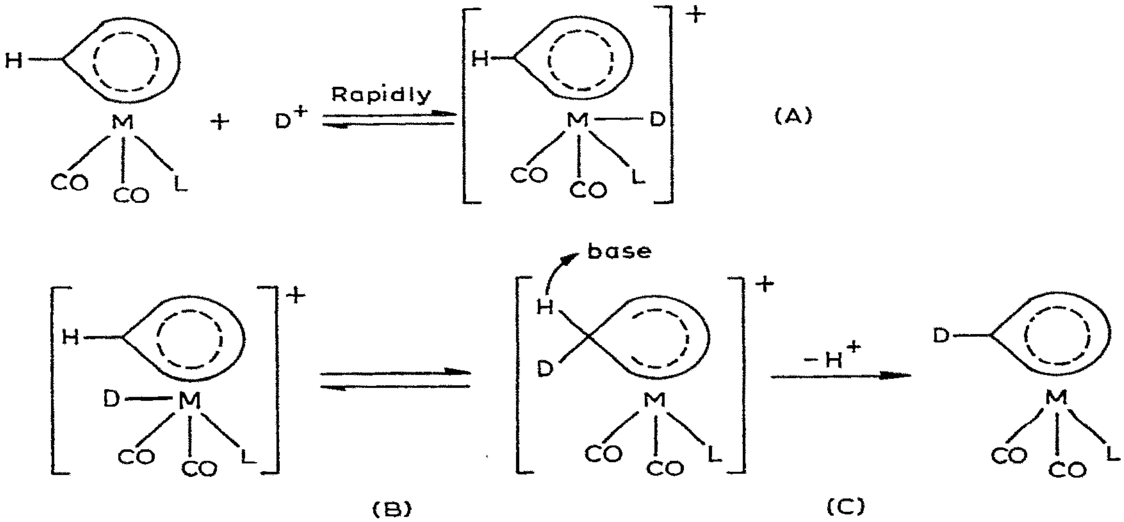

Fig. 5. The proposed mechanism for the acidic hydrogen exchange reaction involving chromium and manganese complexes with cyclic ligands.

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* The suggestion that an electrophile (in particular the proton) first attacks the metal atom in substituting a sandwich compound was advanced some ten years ago by several authors[2,36,37] and is now the subject of considerable discussion (see, for example, ref. 38).

** With transition metal π-complexes, transfer of hydrogen and other ligands from the metal to the π-ligands has been reported on numerous occasions[39–41].

available to indicate the exact nature of this step, *i.e.* whether it occurs via a homolytic or heterolytic mechanism. The final step (C) probably involves proton abstraction by the base present in the system, *e.g.* by the trifluoroacetate ion. It is probable that steps (B) and (C) proceed simultaneously.

Step (A) is usually fast (according to IR spectral data the protonation equilibrium is set up virtually instantaneously) and is reversible. However, if the basicity of the metal is sharply increased the protonation equilibrium may be shifted almost completely towards the formation of a stable protonated form which may hinder (or completely suppress) steps (B) and (C). This apparently occurs during HIE involving manganese diphosphine complexes.

Introduction of two phosphine ligands into cymantrene sharply increases the basicity of the metal and facilitates protonation. IR spectral data indicate that at the same acidity of the medium only partial protonation occurs in the case of the monophosphine complexes whereas the diphosphine complexes are completely protonated[25]. The rate of HIE decreases with increasing acidity for the manganese diphosphine complexes and is entirely suppressed at high acidity of the medium[22]. A similar trend has been observed for the complexes π-$XC_6H_5Cr(CO)_2PPh_3$ where introduction of donor substituents (CH_3O, CH_3, 1,3,5-$(CH_3)_3$ into the π-benzene ring increases the basicity of the chromium atom and leads to the formation of completely protonated complexes containing stable Cr–H bonds. The rate of HIE is less for such complexes relative to the unsubstituted $C_6H_6Cr(CO)_2PPh_3$. Electron-withdrawing substituents decrease the basicity of the chromium atom and lower the strength of the Cr–H bond thus increasing the rate of HIE. This leads to an "abnormal" substituent effect for HIE in such chromium complexes which is opposite to the effect that these substituents have on the rate of similar reactions involving the uncomplexed benzene compounds. It is interesting to note that substitution of the CO ligands by phosphine and other ligands has a much greater influence on the basicity of the metal than substitution in the benzene or cyclopentadienyl rings.

From this it follows that the observed rate of HIE probably depends on the rates of steps (B) and (C). Information on the ratio of these rates may be obtained from measurements of the kinetic isotope effect (KIE) in hydrogen exchange. Recently, in collaboration with Yakushin and Shatenshtein, we have determined values of the KIE[42] in electrophilic HIE in the complexes $CpMn(CO)_3$, $CpMn(CO)_2PPh_3$ and $CpMn(CO)(Ph_2PCH_2CH_2PPh_2)$ labelled with deuterium and tritium in the cyclopentadienyl ring, using CF_3COOH in methylene chloride as the solvent. In all cases the value of K_D/K_T was equal to 1.6–1.7. Existence of a KIE may be taken as proof that proton abstraction by the base [step (C)] is the rate-determining step in the hydrogen exchange of π-cyclopentadienylmanganese complexes. It is interesting to note that the value of KIE in the exchange of benzenechromium dicarbonyl–triphenylphosphine with CF_3COOH is close to unity (1.0 ± 0.1). This absence of KIE on hydrogen exchange with acid when taken together with the above data agrees with the assumption that hydrogen transfer from the metal to the π-aromatic ligand is the slowest step in the case of chromium complexes [step (B)].

Thus all the data obtained to date are in agreement and confirm the mechanism of HIE presented above. In our opinion the correlation observed between the tendency of complexes to undergo protonation at the metal atom and the case with which these complexes undergo HIE reactions is most convincing. This mechanism has, in fact, been found useful in explaining the unexpectedly abnormal behaviour of substituents in a series of arenechromium dicarbonyl–triphenylphosphines.

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