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PROTONATION OF METAL CARBONYL COMPLEXES

VI*. PROTONATION OF MANGANESE π-CYCLOPENTADIENYLPHOSPHINE COMPLEXES STUDIED BY ^{13}C AND ^{31}P NMR TECHNIQUES

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Summary

^{13}C and ^{31}P NMR techniques have been applied to the complexes $CpMn(CO)L_2$ and $CpMn(CO)_2L$ (where L_2 is a bidentate tertiary phosphine, L is a monodentate tertiary phosphine, and Cp is cyclopentadienyl). It is shown that the complexes are protonated reversibly, when dissolved in CH_2Cl_2 in the presence of CF_3COOH, with the proton attacking the manganese atom.

Introduction

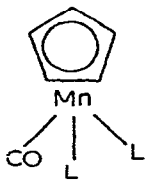
Recently the question of the basicity of transition metal π-complexes has been given considerable attention [1, 2] as a result of the notable relationship that exists between the basicity of the complexes and the reactivity towards electrophiles. In previous communications [3—6] IR and ^1H NMR methods were used to show that in sufficiently acid media there is reversible protonation of π-complexes of chromium [3, 4], manganese [5], vanadium, niobium, and rhenium [6] containing benzene or π-cyclopentadienyl ligands. Whether the proton attacks the metal atom or one of the π-ligand carbon atoms was not clear in some cases. For π-arene complexes of chromium, ^1H NMR data showed that a Cr—H bond was formed between the metal and the proton [4, 7].

Alterations in the sign and magnitude of CO stretching vibrations observed for π-arene complexes of chromium [3] are completely analogous to those observed for π-cyclopentadienyl manganese [5] complexes, and therefore protonation in the latter case may also be assumed to involve the metal atom. This assumption, however, requires experimental verification.

The present paper deals with the protonation of manganese π-cyclopentadienylcarbonylphosphine complexes studied with ^{13}C and ^{31}P NMR techniques.

* For part V, see ref. 23.

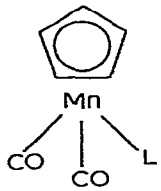
We have studied the spectra of $CpMn(CO)L_2$ (I), $CpMn(CO)_2L$ (II) (where L_2 is a bidentate tertiary phosphine and L is a monodentate tertiary phosphine) and also $Et_5C_5Mn(CO)_2PPh_3$ (III) as a function of L, acidity, temperature and other variables.



(Ia), $L_2 = Ph_2PCH_2CH_2PPh_2$;

(Ib), $L_2 = Ph_2PCH_2CH_2CH_2PPh_2$;

(Ic), $L = PPh_3$



(IIa), $L = P(C_6H_{11})_3$

(IIb), $L = P(iso\text{-}C_3H_7)_3$

(IIc), $L = P(CH_2C_6H_5)_3$

(IId), $L = PPh_3$

Results and discussion

$^{13}C\text{-}\{^1H\}$ NMR spectra of complexes I—III measured in neutral or acidic media (Table 1) demonstrate that addition of the necessary amount of CF_3COO to solutions of the complexes in CH_2Cl_2 lowers the shielding of the π-cyclopentadienyl carbons in all cases. In acid media the ^{13}C signals are shifted downfield by 5—9 ppm. The downfield shift depends on various factors such as acidity (CF_3COOH but not CH_3COOH was effective), amount of acid and temperature. The singlet structure remains unaffected in all cases.

These results may be explained simply by assuming that partial positive charge is built up on the π-complex (on the π-cyclopentadienyl ligand in particular) by the added proton. To test this assumption, we have also studied the cationic complex $[CpMn(CO)(NO)PPh_3]^+$ (IV) in which one of the carbonyl groups is replaced by a nitrosyl ligand, NO*. It is well known for CO and NO that their donor-acceptor properties, ligand bonding modes and the geometry parameters of the linear fragments M—CO and M—NO are very similar [8, 9], therefore the substitution of NO for CO is not expected to cause any alteration in the geometry of the complexes under study. ^{13}C NMR data show that on going from $CpMn(CO)_2PPh_3$ (IId) to the isoelectronic unicharged cation $[CpMn(CO)(NO)PPh_3]^+$ the Cp ligand carbon signals are shifted downfield by 12.9 ppm. Consequently, the unit positive charge built up on IV leads to NMR effects similar to those observed in the protonation of complexes I—III. The

* Complex IV contains an unsubstituted cyclopentadienyl ligand of which all carbon atoms are equivalent, and has a chiral centre at the Mn atom bonded to four different ligands. We have also prepared the cationic complex $[\pi\text{-}CH_3CH_2C_5H_4Mn(CO)(NO)L]^+PF_6^-$ (where L is PPh_3). The Cp-ring of this compound contains an ethyl substituent and therefore all the ligand carbons are diastereotopic and have different chemical shifts. $^{13}C\text{—}\{^1H\}$ NMR data for the complex in CH_2Cl_2 solution are as follows: $\delta\,^{13}C$ (TMS): 97.5, 94.0, 93.5, 91.6 and 120.7 ppm, the latter signal belonging to the node carbon. The ^{13}C chemical shift of the substituent are 13.8 (CH_3) and 20.7 ppm (CH_2). Thus, the presence of a chiral centre in the side chain [10] or at the metal atom of the complexes $RC_5H_4Mn(CO)L_1L_2$ makes the Cp ligand carbons diastereotopic.

TABLE 1

^{13}C CHEMICAL SHIFTS OF THE CYCLOPENTADIENYL LIGAND IN π-CYCLOPENTADIENYL-MANGANESE COMPLEXES

Compound		Temp (°C)	^{13}C Chemical shift (δ ppm) downfield from internal TMS			Δδ (protonation) (ppm)
			In CH_2Cl_2	In CH_2Cl_2 / CF_3COOH 4/1	1/1	
Ia	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$	20	79.6	86.8		− 7.4
Ib	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2CH_2Ph_2)$	20	81.8	86.8		− 5.0
Ic	$C_5H_5Mn(CO)(PPh_3)_2$	−20[a]	82.0	90.0		− 8.0
IIa	$C_5H_5Mn(CO)_2P(C_6H_{11})_3$	20	81.3	81.3		0
IIa	$C_5H_5Mn(CO)_2P(C_6H_{11})_3$	−30	81.2		87.4	− 6.2
IIb	$C_5H_5Mn(CO)_2P(i\text{-}C_3H_7)_3$	5	81.0	82.7		− 1.7
IIb	$C_5H_5Mn(CO)_2P(i\text{-}C_3H_7)_3$	−30	81.0		87.4	− 6.4
IId	$C_5H_5Mn(CO)_2PPh_3$	−30	82.4			
III	$C_5Et_5Mn(CO)_2PPh_3$	20	98.8	107.8		− 9.0
IV	$[C_5H_5Mn(CO)(NO)PPh_3]^+PF_6^-$	20	95.8			−12.9[b]

[a] Protonation occurs at room temperature as well but the spectrum was recorded at −20° to suppress the decomposition. [b] Difference between the Cp chemical shifts in IV and the isoelectronic IId.

magnitude of Δδ (Table 1) found for the protonation is slightly lower than the shift quoted when the exchange of the metal-bonded proton with protons of the solvent is suppressed. (At −25 to −30° Δδ for II is 5—9 ppm, whereas at +20° it is lower than 2 ppm.)

$^{31}P-\{^1H\}$ NMR spectra of I—III and the free phosphines recorded in a neutral solvent reveal that coordination with manganese lowers the ^{31}P shielding in the ligand. The sign and magnitude of the effect.(Δδ ^{31}P is −80 to −100 ppm) coincide with the data obtained earlier for other transition metals [11—13] and for the complexes π-$CpMn(CO)_2P(EMe_3)_3$ (E = C, Si, Ge or Sn) [14].

TABLE 2

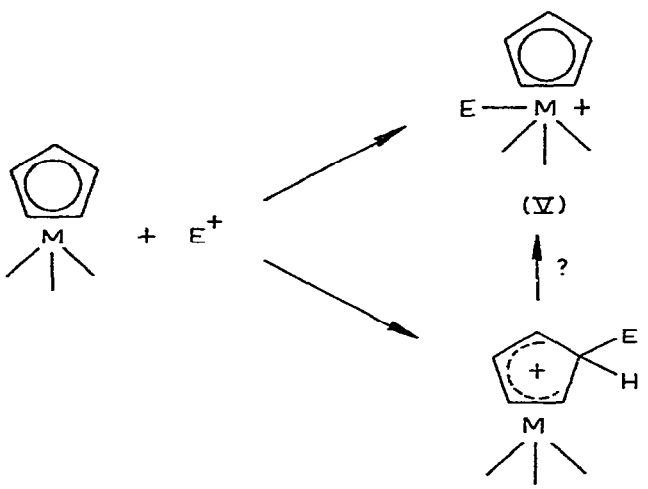
^{31}P CHEMICAL SHIFTS OF PHOSPHINE LIGANDS IN TRANSITION METAL COMPLEXES

Compound		Temp (°C)	^{31}P Chemical shift (δ ppm) downfield from external H_3PO_4			Δδ (protonation) (ppm)
			In CH_2Cl_2	In CH_2Cl_2/CF_3COOH 4/1	1/1	
Ia	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$	20	117.3	100	99.5	+17.3
Ib	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$	20	82.0	74.6		+ 7.4
Ic	$C_5H_5Mn(CO)(PPh_3)_2$	20	92.0	77.5		+14.5
IIa	$C_5H_5Mn(CO)_2P(C_6H_{11})_3$	−25	92.3		79.1	+12.2
IIb	$C_5H_5Mn(CO)_2P(i\text{-}C_3H_7)_3$	−25	98.9		88.0	+10.9
IIc	$C_5H_5Mn(CO)_2P(CH_2C_6H_5)_3$	−25	83.3		71.8	+11.5
IId	$C_5H_5Mn(CO)_2PPh_3$	−25	92.2			
III	$C_5Et_5Mn(CO)_2PPh_3$	20	89.1	64.7		+24.4
IV	$[C_5H_5Mn(CO)(NO)PPh_3]^+PF_6^-$	20	62.9			+29.3[a]
VII	*trans*-$Fe(CO)_3(PPh_3)_2$	20	81.9	55.4		+26.5
VIII	$Ni[P(OEt)_3]_4$	20	159.0	135.0		+16.0[b]

[a] Difference between the phosphine ligands chemical shifts in (IV) and the isoelectronic complex (IId). [b] Data from ref. 16.

The ^{31}P NMR effects of protonation of I—III are of interest (Table 2). When IR and ^{13}C NMR spectra indicate that the compounds are protonated the ^{31}P signal of the phosphine ligand is shifted by 10 to 30 ppm upfield in comparison with the non-protonated compounds, (i.e. those in CH_2Cl_2 with or without added CH_3COOH where the IR spectra showed no protonation). It is important to note that in the ^{31}P NMR spectra also the sign and magnitude of the I—III protonation effect agree with the results obtained for the model compound; in particular for the replacement of the neutral IId by the unicharged cation IV (Table 2). The reason why the positive charge which builds up on the complex should lead to an increase in the ^{31}P phosphine ligand shielding is worth special attention, but the discussion is outside the framework of the present study.

A consideration of the stereochemical aspects of the basicity of transition metal π-complexes shows that there are at least two problems which have no apparent solution and are of interest in terms of the results obtained. First, it is often not clear which is the definitive site of the electrophilic addition, especially when a very small species like a proton is concerned. Second, the structural alterations caused by the electrophilic addition are in some cases not quite clear either.



(V)

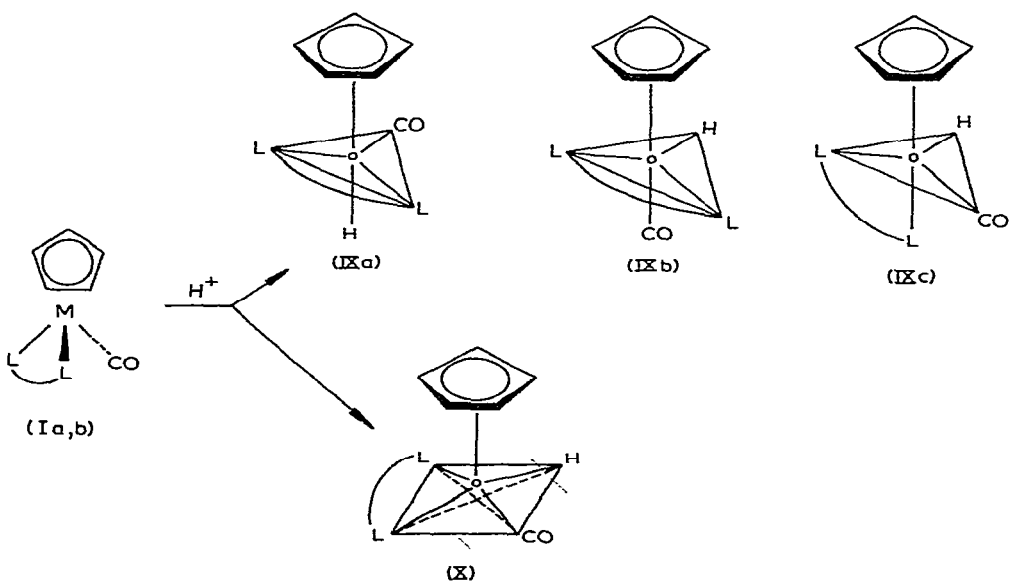
(VI)

In discussing the first point, we may take into account the two possible sites of proton addition to the compounds I—III, viz. the metal atom (V) and/or the cyclopentadienyl ring (VI). We exclude addition at the carbonyl oxygen since this assumption would disagree* with the IR data [3—6] on protonation. In principle both sites may be attacked by an electrophile, but a choice between the two sites cannot be made on the spot since there is not enough data on the relative basicities of these sites in I—III.

* Formation of the local site M—C=O—H should lower the frequency ν(CO) of the carbonyl and raise the frequencies of the other CO groups. The protonation raises the frequencies of all CO groups.

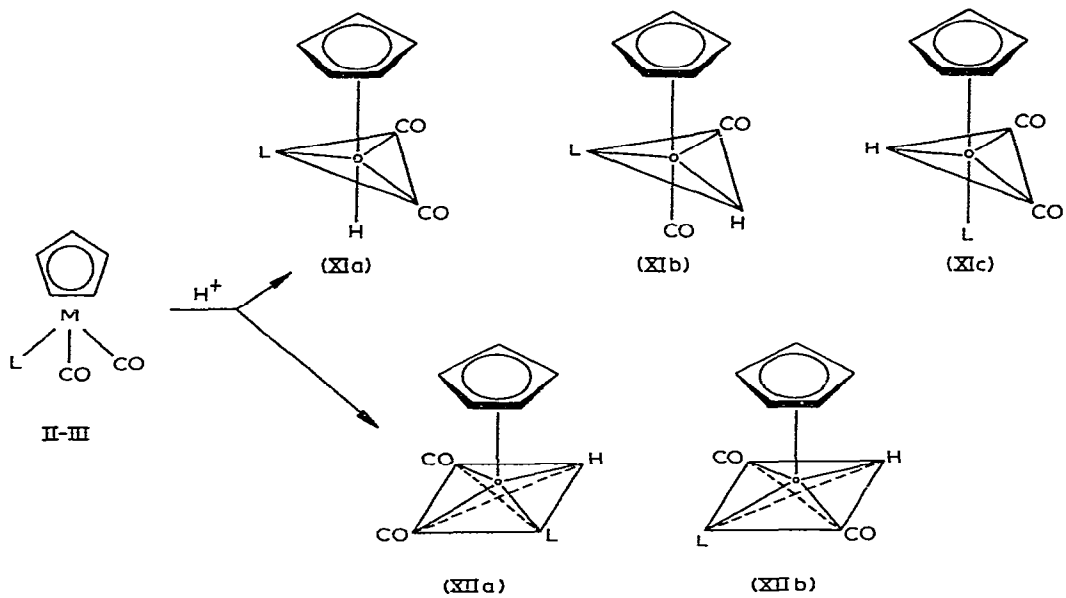
It has already been noted that the ^{13}C Cp signals in the protonated complexes of I—III recorded at —25 to —30° are neither split nor broadened. Consequently, the carbon atoms are equivalent in the protonated species as well, a point which favours the assumption of metal protonation. A similar conclusion follows from comparing the protonation of III with that of compounds containing an unsubstituted Cp ligand, eq. II. Tables 1 and 2 demonstrate that II is protonated as easily as III. The assumption of metal protonation also agrees with data on *trans*-$Fe(CO)_3(PPh_3)_2$ (VII) and $Ni[P(OEt)_3]_4$ (VIII). These complexes have no cyclopentadienyl ligand and are readily protonated; this was observed for VII as early as 1962 by Wilkinson [15]. The ^1H NMR spectrum indicates that the proton in the complex is attached to the iron atom: the protonation results in a Fe—H signal, a triplet with $J(^{31}P—Fe—^1H)$ 30 Hz. The Ni protonation in VII was proved similarly [16], $J(^{31}P—Ni—^1H)$ 26 Hz. Consequently, the effect of protonation on the magnitude and direction of the shift of ^{31}P signals (Table 2) in compounds I—III is similar to that in VII and VIII where metal protonation has been established.

The data discussed above suggest that the metal atom in I—III is the most probable protonation site. Direct proof in the case of Mn is found in the proton-undecoupled ^{31}P spectrum of III. The solution of this compound in CH_2Cl_2 produces a singlet (δ ^{31}P 89.1 ppm, line-width at half height ca. 35 Hz) which by addition of CF_3COOH is transformed to a well-resolved doublet due to $^{31}P—Mn—^1H$ spin-spin coupling (δ ^{31}P 64.7 ppm, J 69 Hz, line-width at half height ca. 40 Hz). Hence, I—III are protonated to give species of the type V containing a Mn—H bond. Note that this does not disagree with the formation of species VI which, if they exist, occur at concentrations and lifetimes below the limit of NMR sensitivity.



We now discuss the stereochemical behaviour of protonated forms of I—III*. For Ia and Ib which contain a chelate diphosphine ligand, the protonated species may have a trigonal-bipyramidal (IXa-c) or a square-pyramidal (X) structure. No splitting of ^{31}P signals consistent with IXc or X has been observed for Ia and Ib under the conditions applied, but the distinction cannot be made without additional evidence.

The protonation of II and III, which contain an $M(CO)_2L$ group, and the protonation of Ic, may involve the formation of five isomers: three trigonal bipyramids (XIa—XIc) and two square pyramids (XIIa, b). X-ray data show that crystals of the structurally related molybdenum complexes $CpMo(CO)_2(L)R$ (where L is a tertiary phosphine or phosphite and R is a one-electron ligand, e.g. alkyl, acetyl, halogen, NCO, etc.) indeed have somewhat distorted square pyramidal geometry, with Cp at the apex and CO at the base in the *trans*-position, structure XIIb [17, 18]. The ^1H NMR data showed that in solution these and similar compounds are mixture of *cis*- and *trans*-isomers of the type XIIa



of XIIb, the *cis/trans* ratio being sharply dependent on R, L, and temperature [19, 20]. For hydride complexes (R = H) of this type the structure may be assigned in some cases on the basis of the $^{31}P—M—^1H$ coupling constant. It has been shown [21] that in hydride transition metal phosphine complexes the constant is 5—30 Hz for square planar and octahedral complexes in which ^1H and ^{31}P nuclei are in the *cis*-position. For the *trans*-isomers, in contrast, J is much higher (60—180 Hz). However, significant deviations from the regular octahedral structure may reverse the *cis/trans* ratio: e.g. for the heptacoordinate complexes $CpMo(CO)_2(L)H$ which may be considered as neutral models of the protonated II and III, J was found to be 64—73 Hz for the *cis*-isomers

* For simplicity, here and later the π-cyclopentadienyl ligand is considered to have one instead of three coordination sites. This does not break the consistency of the discussion.

and 21—29 Hz for the *trans*-isomers [19]. Our value of $J(^{31}P—Mn—^{1}H)$ 69 Hz may be an argument in favour of the *cis*-structure XIIa for protonated III. Similar structures may be valid for the benzenechromium π-complexes studied earlier [4], which had $J(^{31}P—Cr—^{1}H)$ values of 63—69 Hz.

The results obtained here allow a comparison of the stability of the protonated species V with the data reported on the basicity of the compounds. It may be remembered that protonation of the monophosphine complexes (II) can be observed by NMR spectroscopy only at low temperatures and high acid concentrations (the molar ratio of complex/CF_3COOH/CH_2Cl_2 is ca. 1/20/20). On the other hand, the diphosphine complexes (I) are protonated even at room temperature and low acid concentrations (the ratio is ca. 1/8/40). A natural assumption to make is that the Mn basicity in the diphosphine complexes is much higher than that in the monophosphine complexes and that the stability of the protonated species increases with the basicity. Note that the monophosphine complex (III) containing the fully substituted cyclopentadienyl is readily protonated under conditions of complex protonation. Apparently, the basicity of Mn in the complex is increased markedly owing to the concerted donor effects of the phosphine ligand and the ethyl substitutent. In contrast, no protonated species was recorded for IId which contains the unsubstituted cyclopentadienyl, apparently owing to the low basicity of the metal and the small lifetime of the protonated species. Protonation becomes easier with IIa—IIc because tertiary phosphines containing alkyl groups such as C_6H_{11}, i-C_3H_7, and CH_2Ph are stronger donors, and thus have a more marked effect on the Mn basicity compared with triphenylphosphine.

Conclusion

To summarise, ^{13}C and ^{31}P NMR study of cyclopentadienylcarbonylphosphine complexes of manganese demonstrates that the compounds are subject to rapid reversible protonation at the metal atom in the presence of CF_3COOH. The protonation is governed by the basicity of the manganese atom which in turn depends on the number of phosphine ligands, the group attached to phosphorus, and the presence of substituents in the cyclopentadienyl. The data obtained are in excellent agreement with the conclusions made by us previously in an IR study of the protonation of these compounds [5], and allow the structure of the protonated species to be outlined more rigorously.

Experimental

NMR Fourier Transform proton-decoupled spectra were recorded on a Brucker HX-90 instrument. Compounds I—III were prepared by literature methods [5]; complex IV and its ethyl analogue were obtained via a procedure described by Brunner [22].

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