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NMR STUDY OF SOME CYCLOPENTADIENYLIRON CARBONYL DERIVATIVES

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SUMMARY

The PMR spectra of the compounds π-$C_5H_5Fe(CO)_2X$ ($X = CH_3$, C_6H_5, $COCH_3$, I, Br, Cl, CN) and π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* ($R = OCH_3$, CH_3, H, Cl, F, $COOC_2H_5$) have been studied, and the effects of X and R substituents upon the cyclopentadienyl ring chemical shifts have been shown to be predominantly inductive.

From the bais of ^{19}F spectra of the complexes π-$C_5H_5Fe(CO)(L)C_6H_4F$-*m,p* ($L = CO$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$) the inductive (σ_I) and resonance (σ_R^0) constants of the π-$C_5H_5Fe(CO)(L)$ substituents have been determined. An inductive interaction within the iron–aryl bonding has been found to prevail.

The ^{31}P chemical shifts have been measured for π-$C_5H_5Fe(CO)(L')Ar$ complexes (L' = different phosphorus ligands).

INTRODUCTION

In recent years great attention has been paid to the synthesis and study of σ-aryl and σ-alkenyl derivatives of transition metals. The study of the nature of the transition metal–carbon bond and in particular its multiplicity has provided one of the most interesting and complicated problems with such compounds.

From the basis of chemical[1,2], X-ray[3-6] and spectral studies[2,7-9] several workers have assumed that π-interaction caused by a partial metal electron delocalization at the π^*-antibonding orbitals of the aromatic ring is significant in the formation of such bonds. Some earlier studies[10,11], involving IR and polarographic investigations of some iron derivatives of the type π-$C_5H_5Fe(CO)_2X$ ($X = CN$, Cl, Br, I, C_6F_5, C_6H_4Cl-*p*, C_6H_5, CH_3) (series I) and π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* ($R = OCH_3$, CH_3, H, F, Cl, $COOC_2H_5$) (series II), however, has shown that a correlation exists between the CO absorption bands or the half-wave potentials and the inductive constants of substituents for series I whilst no such relationship exists for series II. This result apparently indicates that little π-interaction is involved in the formation of the Fe–Ar σ-bond. Recent IR and ^{19}F NMR studies of a large number of *m*- and *p*-fluoro-substituted metal carbonyl complexes[12] support this latter suggestion and have shown that if such interaction is taking place its contribution is negligible being almost independent of the nature of the metal and its adjacent ligands and of the geometry of the resulting complex. In some ways this result is not altogether unexpected. As carbonyl ligands exhibit much greater π-acceptor properties than aryl groups σ-bonding is however somewhat greater in the case of σ-ketovinyl iron derivatives[13].

In the present study the PMR spectra of the compounds listed above as series I and II (*cf.* Tables 1, 2) and the ^{19}F spectra of complexes π-$C_5H_5Fe(CO)(L)C_6H_4F$-*m,p* (L = various phosphorus ligands) [series III (*cf.* Tables 3 and 4)] have been investigated.

TABLE 1

CHEMICAL SHIFTS OF CYCLOPENTADIENYL RING PROTONS OF π-$C_5H_5Fe(CO)_2X$ COMPOUNDS (SERIES I) IN CHLOROFORM

X	$\delta(C_5H_5)$ *(ppm)*
CH_3	4.616
C_6H_5	4.75
$COCH_3$	4.81
I	4.971
Br	4.972
Cl	4.979
CN	5.10

TABLE 2

CHEMICAL SHIFTS OF CYCLOPENTADIENYL RING PROTONS OF π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* COMPOUNDS (SERIES II) IN CHLOROFORM

R	$\delta(C_5H_5)$ *(ppm)*	*J(P–H) (Hz)*
OCH_3	4.398	0.9
CH_3	4.393	1
H	4.394	1.2
Cl	4.387	1.1
F	4.385	0.9
$COOC_2H_5$	4.40	

TABLE 3

^{19}F CHEMICAL SHIFTS OF π-$C_5H_5Fe(CO)(L)C_6H_4F$-*m* AND -*p* IN CHLOROFORM (SERIES III)[a]

L	$\delta(F_m)$ *(ppm)*	$\delta(F_p)$ *(ppm)*	σ_I[b]	σ°_R[b]
CO	+2.35	+10.95	−0.25	−0.29
$P(OC_6H_5)_3$	+4.29	+13.10	−0.52	−0.30
$P(C_6H_5)_3$	+4.47	+13.84	−0.545	−0.32

[a] Chemical shifts with respect to C_6H_5F signal in the same solvent.

[b] σ_I and ρ°_R: inductive and resonance constants of π-$C_5H_5Fe(CO)(L)$ estimated using the Taft equation[15]: $\delta(F_m) = 7.1\ \sigma_I + 0.6$ and $\delta(F_p) - \delta(F_m) = -29.5\ \sigma^\circ_R$.

TABLE 4

^{19}F CHEMICAL SHIFTS OF π-$C_5H_5Fe(CO)(L)C_6H_4F$-*p* IN BENZENE (SERIES III)[a]

L	$\delta(F_p)$ *(ppm)*
CO	+10.75
$P(OC_6H_5)_3$	+12.37
$P(C_6H_5)_3$	+13.28
$P(C_6H_5)_2(C_2H_5)$	+13.03
$P(C_6H_5)(C_2H_5)_2$	+13.43
$P(C_6H_4CH_3\text{-}p)_3$	+13.88

[a] Chemical shifts with respect to the C_6H_5F signal in the same solvent.

RESULTS AND DISCUSSION

Most of the proton magnetic resonance spectra of the compounds in series I have already been studied by other authors but under different conditions. For this reason we have recorded the spectra of all the compounds in series I under standard conditions: concentration 0.25 mole/l, solvent $CHCl_3$ and hexamethyldisiloxane as internal standard. The resulting PMR spectral parameters are listed in Table 1. A systematic correlational analysis of the cyclopentadienyl ring proton chemical shifts for the compounds of series I in terms of the Hammett–Taft σ-constants for substituents X[14] (X=CH_3, C_6H_5, $COCH_3$, Cl, Br, I, CN) revealed a linear relationship between $\delta(C_5H_5)$ and the inductive substituent constants:

$$\delta(C_5H_5) = 0.75\,\sigma_I + 4.68 \tag{1}$$

$$S = 0.03 \text{ ppm}, \quad r = 0.98$$

Most of the substituents investigated repel electrons through the type of resonance mechanism involved and only the CN group is a strong acceptor through the involvement of both π and σ mechanisms. The greatest deviation in the experimental chemical shift $\delta(C_5H_5)(\delta(\text{exp}) - \delta(\text{calcd.}) = 0.06$ ppm) occurs in the case when X=CN. Correlational analysis involving the use of both inductive (σ_I) and resonance (σ_R^0) constants results in a much closer correlation *i.e.*,

$$\delta(C_5H_5) = 0.74\,\sigma_I + 0.13\,\sigma_R^0 + 4.69 \tag{2}$$

$$S = 0.02 \text{ ppm}, \quad r = 0.99$$

In the PMR spectra of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* (R=$CH_3$, OCH_3, Cl, F, $COOC_2H_5$) (series II, Table 2) the variation of the cyclopentadienyl ring proton chemical shifts as R changes was found to be of the same order as the experimental error and there was no correlation between the donor–acceptor properties of the substituent and the chemical shifts. This result may be explained by the fact that in these complexes the substituent is quite remote from the reaction center which prevents the occurrence of the inductive effect. In this particular series and also in series IV and V it was in fact observed that the signals of the cyclopentadienyl proton were split into a doublet due to a spin–spin coupling with the phosphorus atom, the doublet components collapsing when the ^{31}P nucleus was irradiated.

^{19}F NMR data provide much more information regarding the electronic effects in these compounds since the ^{19}F shifts are more sensitive to the electronic effect of the substituent.

From the basis of the ^{19}F chemical shifts of *m*- and *p*-substituted phenyl complexes π-$C_5H_5Fe(CO)_2C_6H_4F$ and using the Taft equation[15], values of σ_I and σ_R^0 have been obtained for the π-$C_5H_5Fe(CO)_2$ substituent which are very close to the data reported in ref. 12*, *i.e.*, $\sigma_I = -0.24$, $\sigma_R = -0.29$ (*cf.* Table 3), indicating that the organometallic group in this particular instance is a strong σ- and π-donor. Thus the degree of $d_\pi \rightarrow p_\pi$ bonding in this compound is determined by the π-acceptor ability of the aryl radicals. This group is however a weak π-donor (σ_R^0 for $C_6H_5 = -0.09$)[14], and for this reason this effect is quite small.

In σ-complexes, such as π-$C_5H_5Fe(CO)LC_6H_4F$-*m,p* where $L = P(C_6H_5)_3$ or $P(OC_6H_5)_3$ (series III, Table 3), substitution of one CO group by a phosphorus ligand, which is a better σ-donor but a weaker π-acceptor, causes an upfield shift in the ^{19}F signal in the spectrum. This shift is somewhat greater with the triphenylphosphine complex. The σ_I and σ_R^0 values for π-$C_5H_5Fe(CO)[P(C_6H_5)_3]$ and π-$C_5H_5Fe(CO)$-$[P(OC_6H_5)_3]$ groups, as found from Taft equation (Table 3), indicate that the phosphorus ligand enhances the σ- and π-donor ability of the organometallic group. The inductive constant increases sharply whilst the resonance constant is hardly affected. The small contribution of $d_\pi \rightarrow p_\pi$ bonding in σ-aryl complexes may also be attributed to this cause. In σ-ketovinyl derivatives, where in our opinion the π-bonding is even more pronounced, substitution of a CO group by a triphenylphosphine group leads to even greater multiple σ-bonding[16].

The ^{19}F chemical shifts for some *p*-fluoro-substituted σ-phenyliron compounds measured in benzene are listed in Table 4. The fluorine signal for the compound with a $P(C_6H_4CH_3$-$p)_3$ ligand is located upfield from that for the triphenylphosphine complex which may be attributed to the donor ability of the methyl group. For the same reason the ^{19}F signal of the diethylphenylphosphine complex is even further upfield.

An examination of the character of the iron metal-phosphorus ligand bond and an investigation of the transmission of ligand effects via the metal atom to the cyclopentadienyl ring have been undertaken for compounds of the general formula π-$C_5H_5Fe(CO)(L)C_6H_5$ (series IV) where L = phosphorus ligand. The ^{31}P chemical shifts as well as values of $\Delta\delta$ *i.e.*, the change of phosphorus chemical shift in passing from the free ligand** to its complex, are listed in Table 5. The phosphorus chemical shifts change as the properties of the adjacent groups change. The furthest upfield signal occurs with the diethylphenylphosphine ligand. Substitution of one ethyl by a phenyl group causes an average downfield shift of over 3.6 ppm, which may be associated with the inductive and resonance effects as well as the ring current effect of the phenyl. A similar result has been observed in the ^{31}P spectra of Ni^0 complexes[17]. The signal of the triphenylphosphite complex is located at a much lower field value which may be attributed to the high electronegativity of the oxygens combined to the phosphorus. Bonding of the ligand to the metal results in a significant deshielding of the phosphorus atoms due to the displacement of electron density from the phos-

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* Our measurements were carried out in $CHCl_3$ while those reported in ref. 12 refer to CH_2Cl_2 as a solvent.

** The ^{31}P chemical shifts of the uncoordinated phosphorus groups have been taken from ref. 17.

phorus atoms to the metal atom and this effect is not completely compensated for by a back-donation from the metal to the phosphorus. The extent of this deshielding effect, however, probably depends on the π-attractive ability of the ligand. Thus, after complex formation the change of ^{31}P shift for phenylphosphite is half the value observed for phosphine since the $P(OC_6H_5)_3$ ligand is a more powerful π-acceptor.

The C_5H_5 proton chemical shifts of compounds in series IV and V (Tables 6 and 7) also depend upon the type of phosphorus ligand attached to the iron atom.

TABLE 5

^{31}P CHEMICAL SHIFTS OF π-$C_5H_5Fe(CO)(L)C_6H_5$ IN CHLOROFORM (SERIES IV)[a]

L	*$\delta(^{31}P)$ (ppm)*	*$\Delta\delta$ (ppm)*
$P(C_2H_5)_2(C_6H_5)$	−63.0	−79.2
$P(C_2H_5)(C_6H_5)_2$	−67.0	−79
$P(C_6H_5)_3$	−70.3	−78.3
$P(C_6H_4CH_3\text{-}p)_3$	−70.1	
$P(OC_6H_5)_3$	−165	−37

[a] Chemical shifts with respect to H_3PO_4.

TABLE 6

CHEMICAL SHIFTS OF CYCLOPENTADIENYL RING PROTONS OF π-$C_5H_5Fe(CO)(L)C_6H_5$ IN CHLOROFORM (SERIES IV)

L	*$\delta(C_5H_5)$ (ppm)*
CO	4.75
$P(C_6H_5)_3$	4.394
$P(C_6H_4CH_3\text{-}p)_3$	4.387
$P(C_6H_5)(C_2H_5)_2$	4.337
$P(C_6H_5)_2(C_2H_5)$	4.313
$P(OC_6H_5)_3$	4.238

TABLE 7

CHEMICAL SHIFTS OF CYCLOPENTADIENYL RING PROTONS OF π-$C_5H_5Fe(CO)(L)COC_6H_5$ IN CHLOROFORM (SERIES V)

L	*$\delta(C_5H_5)$ (ppm)*	*Note*
$P(C_6H_5)_3$	4.473	$\delta(^{31}P) = 70.5$ ppm $\Delta\delta = -78.5$ ppm
$P(C_2H_5)_2(C_6H_5)$	4.393	
$P(C_2H_5)(C_6H_5)_2$	4.37	
CO	4.79[a]	
$P(C_6H_5)_3$	4.45	$COC_6H_4CH_3\text{-}p$ is σ-ligand $\delta(^{31}P) = -70.3$ ppm $\Delta\delta = -78.3$ ppm

[a] Data taken from ref. 19.

However since in these cases there is no longer a direct correlation between the electronic properties of the ligand and the $\delta(C_5H_5)$ chemical shift changes, it must be assumed that the latter are influenced by purely magnetic effects in these cases.

EXPERIMENTAL

The compounds investigated were synthesized using known procedures.

Series I: π-$C_5H_5Fe(CO)_2X$ (X=CH_3[18], C_6H_5[11], $COCH_3$[19], I[20], Cl[21], Br[21], CN[18]).

Series II: π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-$p$[11] (R=$OCH_3$, CH_3, H, Cl, F, $COOC_2H_5$).

Series III: π-$C_5H_5Fe(CO)(L)C_6H_4R$-m,p[22,23] (L=CO, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $P(C_6H_5)(C_2H_5)_2$, $P(C_6H_4CH_3$-$p)_3$).

Series IV: π-$C_5H_5Fe(CO)(L)C_6H_5$[24] (L=CO, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $P(C_6H_5)(C_2H_5)_2$, $P(C_6H_4CH_3$-$p)_3$).

Series V: π-$C_5H_5Fe(CO)(L)COC_6H_5$[24] (L=$P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $P(C_6H_5)(C_2H_5)_2$).

PMR spectra were measured on JNM 4H-100 and C60HL JEOL instruments with hexamethyldisiloxane as internal standard. The ^{19}F spectra were recorded on a JNM 4H-100 spectrometer at 94 MHz with the use of an external proton lock and C_6H_5F as internal standard. The ^{31}P spectra were recorded on a JNM 4H-100 spectrometer at 40 MHz with H_3PO_4 as an external standard.

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