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NUCLEAR MAGNETIC RESONANCE SPECTRA OF ARENECYCLOPENTADIENYLIRON COMPOUNDS

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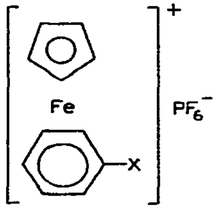
SUMMARY

PMR spectra of arenecyclopentadienyliron compounds $[XC_6H_5FeC_5H_5]^+PF_6^-$, $[p\text{-}XC_6H_4CH_3FeC_5H_5]^+PF_6^-$, $[C_6H_6FeC_5H_4X]^+PF_6^-$ containing various substituents X have been studied. PMR chemical shifts have been correlated with the sets of the Hammett–Taft σ parameters. The results are compared with those obtained for the non-coordinated arenes or with earlier data. Hexafluorophosphates of *p*- or *m*-fluorodiphenylcyclopentadienyliron have been prepared and their ^{19}F NMR spectra are used to determine σ_I and σ_R^0 of the phenyl ring in $[C_5H_5FeC_6H_6]^+PF_6^-$ which differs from the uncoordinated phenyl in that it is a strong electron acceptor.

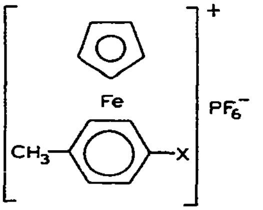
The nature of the metal–ligand bonding is one of the important problems in the chemistry of π-complexes containing cyclopentadienyl or arene ligands. Though physical and/or chemical properties of arene-carbonyl, bis-arene, or arene-cyclopentadienyl complexes were widely investigated, the problem has no definite solution so far. A possible way to resolve it consists in comparing electron system and properties of free and the respective π-bonded ligands.

Some information on the electron structure may be revealed by investigating the electron effect of substituents as transferred by a free and the coordinated ligand or the transfer of the effect from a ligand to the other through a transition metal atom. These effects may be traced by the NMR method.

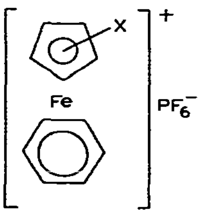
We have studied proton magnetic resonance spectra of hexafluorophosphates of three series of arenecyclopentadienyliron cations (see Tables 1, 2, and 3) containing various substituents.



(I)



(II)



(III)

TABLE 1

PARAMETERS OF PMR SPECTRA OF COMPOUNDS (I), $[XC_6H_5FeC_5H_5]^+PF_6^-$

X	$\delta(C_5H_5)$ (ppm)	$\delta'(C_5H_5)^a$ (ppm)	$\delta(\text{Arene})^b$ (ppm)	$\delta(X)^c$ (ppm)
NH_2	4.95	+0.24	6.01	5.67
CH_3	5.13	+0.06	6.35^d	2.51
C_2H_5	5.15	+0.04	6.38	1.34 $(CH_3)^f$
OCH_3	5.15	+0.04	6.33	4.03
$NHCOCH_3$	5.15	+0.04	6.58	2.17 (CH_3) 9.445 (NH)
Cl	5.31	−0.12	6.64	
F	5.32	−0.13	6.63	
CN	5.47	−0.28	6.86	
H	5.19	0.00	6.44^d	
COOH	5.27	−0.08	6.81	
$COOC_2H_5$	5.24	−0.05	6.82	4.50 (CH_2) 1.44 (CH_3)
$CONH_2$	5.22	−0.03	6.75^e	
OC_6H_5	5.23	−0.04	6.35	7.43

[a] $\delta'(C_5H_5)$ are contributions of substituents to chemical shifts of C_5H_5 ring protons. [b] Approximate centres of multiplets. [c] Chemical shifts of protons of substituents. [d] Singlets. [e] The compound was poorly soluble. [f] The signal of CH_2 protons was obscured by that of the solvent.

TABLE 2

PARAMETERS OF PMR SPECTRA OF COMPOUNDS (II), $[p\text{-}CH_3C_6H_4XFeC_5H_5]^+PF_6^-$

X	$\delta(\text{Arene})$ (ppm)		$J_{AB}+J_{AB'}$ (Hz)	$\delta(CH_3)$ (ppm)	$\delta(C_5H_5)$ (ppm)	$\delta'(C_5H_5)^a$ (ppm)	$\delta(X)^b$ (ppm)
	$\delta(o\text{-H})$	$\delta(m\text{-H})$					
NH_2	5.82	6.05	6.9	2.37	4.89	+0.24	5.58
CH_3	6.28	6.28		2.48	5.08	+0.05	
C_2H_5	6.27	6.27		2.50	5.06	+0.07	1.28 (CH_3) 2.82 (CH_2)
OCH_3	6.25	6.25		2.445	5.09	+0.04	4.03
$NHCOCH_3$	6.77 or 6.30	6.30 or 6.77	6.9	2.47	5.09	+0.04	9.46 (NH) 2.17 $(COCH_3)$
Cl	6.72	6.47	6.7	2.51	5.25	−0.12	
F	6.72	6.435	6.7^c	2.50	5.26	−0.13	
H	6.35	6.35		2.51	5.13	0.00	
CN	6.91	6.70	6.9	2.61	5.41	−0.28	

[a] $\delta'(C_5H_5)$ are contributions of substituents to chemical shifts of C_5H_5 ring protons. [b] Chemical shifts of protons of substituents. [c] $J(o\text{-H–F})$ 4.9 Hz; $J(m\text{-H–F})$ 3.4 Hz.

The results obtained with (I), (II) and (III) were subject to a detailed correlational analysis. The chemical shifts of cyclopentadienyl protons [(I), (II)] or benzene ring and methyl protons [(II), (III)] were correlated with the σ Hammett–Taft parameters or the respective constants obtained from the NMR spectra. The data were processed by a least-square procedure on an M-20 computer.

The spectrum of benzenecyclopentadienyliron hexafluorophosphate consists of two singlets with chemical shifts δ 6.44 and 5.19 ppm, which belong to benzene and

TABLE 3

PARAMETERS OF PMR SPECTRA OF COMPOUNDS (III), $[C_5H_4XFeC_6H_6]^+PF_6^-$

X	$\delta(C_6H_6)$ (ppm)	$\delta'(C_6H_6)^a$ (ppm)	$\delta(C_5H_5)$ (ppm)	
			2-H	3-H
C_2H_5	6.39	+0.05	5.12	5.12
OCH_3	6.45	−0.01	4.94	5.14
H	6.44	0.00	5.19	5.19
Cl	6.51	+0.07	5.53	5.21
NH_2	6.16	+0.28	4.78	4.84
$COCH_3$	6.52	−0.08	5.70	5.46
$COOH^b$	6.55	−0.11	5.65	5.40
$NHCOCH_3$	6.36	+0.09	5.01 or 5.53	5.53 or 5.01
SC_6H_5	6.41	+0.03	5.23 or 5.21	5.21 or 5.23
$N(CH_2)_5$	6.33	+0.11	4.95 or 4.75	4.75 or 4.95
OC_2H_5	6.43	+0.01	4.94	5.14

[a] $\delta'(C_6H_6)$ are contributions of substituents to shielding of arene protons. [b] Poorly soluble.

cyclopentadienyl protons, respectively. The cyclopentadienyl proton signal is shifted downfield by 1.02 ppm as compared with the respective signal of ferrocene. This may be explained by the fact that the cation charge is partially delocalised to the cyclopentadienyl ring. The benzene ring signal is shifted upfield by 0.89 as compared with the signal of the uncomplexed benzene.

Chemical shifts of the unsubstituted cyclopentadienyl ring protons of the cations in (I), where the benzene ring is substituted by NH_2, C_2H_5, CH_3, OCH_3, $NHCOCH_3$, Cl, F, CN (each of the substituents having a complete set of the Hammett parameters), have been treated with the correlational analysis. The shifts correlate linearly with the Taft σ_p^0 according to eqn. (1).

$$\delta'(C_5H_5) = -0.484\,\sigma_p^0 + 0.04 \qquad r=0.969;\ s=0.034 \text{ ppm} \qquad (1)$$

Unfortunately, other compounds of (I) ($X = CONH_2$, OC_6H_5, COOH) were not reported to have a complete set of the Hammett–Taft parameters. The data obtained for all the compounds may be correlated, however, if we use inductive (σ_i) and resonance (σ_r^0) parameters obtained from the NMR spectra:

$$\delta'(C_5H_5) = 0.476\,\sigma_i - 0.309\,\sigma_r^0 + 0.034 \qquad r=0.959;\ s=0.033 \text{ ppm} \qquad (2)$$

In (II) with a methyl group and a substituent in *p*-position in the benzene ring, the cyclopentadienyl proton signals are shifted upfield by about 0.06 ppm as compared with the signals of the respective monosubstituted derivatives of (I).

Contributions of conjugation and induction shown by correlational eqn. (3) for (II), are close to those obtained with (I) (eqn. 4) containing the same substituents.

$$\delta'(C_5H_5) = -0.456\,\sigma_i - 0.410\,\sigma_r^0 + 0.004 \qquad r=0.980;\ s=0.028 \text{ ppm} \qquad (3)$$

$$\delta'(C_5H_5) = -0.456\,\sigma_i - 0.408\,\sigma_r^0 - 0.001 \qquad r=0.982;\ s=0.026 \text{ ppm} \qquad (4)$$

As for the series (III) with a substituent attached to the cyclopentadienyl ring, a less satisfactory linear correlation is found between the chemical shifts of benzene protons and the same σ_i and σ_r^0 values (eqn. 5).

However, the ratio of the resonance and induction contributions remains approximately the same as in eqns. (3) and (4).

$$\delta'(C_6H_6) = -0.381\ \sigma_i - 0.315\ \sigma_r^0 + 0.026 \qquad r = 0.906;\ s = 0.041\ \text{ppm} \qquad (5)$$

These results demonstrate that electron effects of substituents are transferred through the metal atom in arenecyclopentadienyl cations in the same manner as in substituted ferrocenes. A substituent displays induction and resonance interaction with a ring, the interaction being transferred as induction polarization to the other ring through the metal atom. For ferrocene series, the equation similar to eqn. (6) was reported[1]:

$$\delta'(C_5H_5) = -0.39\ \sigma_i - 0.21\ \sigma_r^0 + 0.08 \qquad (6)$$

The contribution of the resonance effect to chemical shift of the unsubstituted ring is stronger with arenecyclopentadienyliron than with ferrocene.

With the complexes of *p*-substituted toluenes, (II, Table 4), the contributions of the substituents to shielding of CH_3 protons [$S(CH_3)$] vary as the Hammett σ_p parameters, eqn. (7).

TABLE 4

CONTRIBUTIONS OF SUBSTITUENTS TO CHEMICAL SHIFTS OF *o*-, *m*-, OR CH_3 PROTONS IN COMPOUNDS *p*-CH_3-C_6H_4X AND [*p*-$CH_3C_6H_4XFeC_5H_5$]$^+PF_6^-$

X	*p*-$CH_3C_6H_4X$			[*p*-$CH_3C_6H_4XFeC_5H_5$]$^+PF_6^-$		
	S_m (ppm)	S_o (ppm)	$S(CH_3)$ (ppm)	S_m (ppm)	S_o (ppm)	$S(CH_3)$ (ppm)
NH_2	+0.31	+0.61	+0.16	+0.30	+0.53	+0.14
CH_3	+0.13	+0.13	+0.054	+0.07	+0.07	+0.03
C_2H_5	+0.11	+0.11	+0.052	+0.08	+0.08	+0.01
OCH_3	+0.12	+0.38	+0.09	+0.10	+0.10	+0.065
Cl	−0.03	−0.09	−0.01	−0.12	−0.37	0.00
F	0.00	+0.20	+0.03	−0.085	−0.37	+0.01
H	0.00	0.00	0.00	0.00	0.00	0.00
CN	−0.20	−0.43	−0.11	−0.35	−0.56	−0.10

$$\delta(CH_3) = -0.168\ \sigma_p + 0.016 \qquad r = 0.958;\ s = 0.017\ \text{ppm} \qquad (7)$$

A similar equation holds with the non-coordinated toluenes measured under similar conditions:

$$S(CH_3) = -0.20\ \sigma_p + 0.027 \qquad r = 0.983;\ s = 0.012\ \text{ppm} \qquad (8)$$

When comparing this equation with earlier data, it is clear that methyl protons in *p*-substituted toluenes are affected by a substituent weaker than the *p*-hydrogens are in monosubstituted benzenes. Diehl[2] who studied how a substituent contributes to shielding of *p*-protons of the mono-substituted benzenes found the following correlational equation:

$$S_p = -0.49\ \sigma_p + 0.1 \qquad (9)$$

From eqns. (8) and (9) it follows that the transfer factor is about 0.4.

The range of chemical shifts obtained with ring protons in *m*-position to substituent X in a disubstituted benzene is by a factor of 1.3 greater in π-complexes than in the respective non-coordinated toluenes (see Table 4). Diehl[2] showed that a substituent contributed to chemical shifts of *m*-protons (S_m) of non-coordinated monosubstituted benzenes according to the following relation using the Hammett σ_p parameters:

$$S_m = -0.30\,\sigma_p + 0.06 \qquad (10)$$

The results reported here for *p*-substituted toluenes are well in agreement with the literature data [*cf.* eqns. (10) and (11)] though they have been obtained by measuring the PMR spectra in another solvent.

We have found a good linear correlation between the Hammett σ_p parameters and contributions given by the substituents to chemical shifts of protons in *m*-position to substituent X.

$$S_m = -0.382\,\sigma_p + 0.041 \qquad r = 0.987;\; s = 0.022 \text{ ppm} \qquad (11)$$

With the respective π-complexes, (III), the contribution of the substituents to chemical shifts of protons in *m*-position to X correlate well with the Hammett σ_p parameters:

$$S_m = -0.49\,\sigma_p - 0.022 \qquad r = 0.996;\; s = 0.016 \text{ ppm} \qquad (12)$$

When comparing reactivity constants ρ from eqns. (11) and (12), it is clear that a substituent affects chemical shifts of *m*-protons stronger in complexed than in the uncomplexed toluenes. With *m*-protons, the combined set σ_i and σ_R^0 gives correlational eqns. (13) and (14) for non-coordinated and complexed toluenes, respectively.

$$S_m = -0.343\,\sigma_i - 0.476\,\sigma_R^0 + 0.033 \qquad r = 0.981;\; s = 0.027 \text{ ppm} \qquad (13)$$

$$S_m = -0.482\,\sigma_i - 0.579\,\sigma_R^0 - 0.016 \qquad r = 0.991;\; s = 0.025 \text{ ppm} \qquad (14)$$

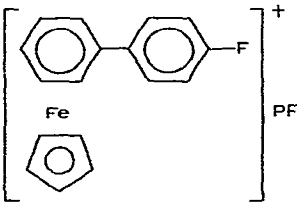
These data show that an increase in the resonance effect transfer is parallelled by an increase in the induction effect transfer when a non-coordinated parasubstituted toluene is replaced by the respective π-complex.

The signals of benzene ring protons in *o*-position to substituent X are shifted markedly downfield in complexed toluenes as compared with the respective uncomplexed *p*-substituted toluenes.

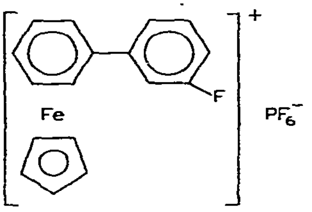
Thus, our results demonstrate that in π-bonded toluenes the substituent affects chemical shifts of the ring protons not weaker than it does so in the free toluenes, unlike the results obtained by Kreiter[3] with *p*-substituted toluenes π-bonded to Cr, W, or Mo carbonyls.

Actually, in arenecyclopentadienyliron cations effects of substituents are transferred even somewhat stronger to the *m*-position. Our results seem to agree with the data obtained by Klopman and Noack though they used no correlational technique[4].

In the ^{19}F NMR spectra of compound $[FC_6H_5FeC_5H_5]^+PF_6^-$ the signal of the fluorine attached to the phenyl ring is shifted upfield by 21.05 ppm from the non-coordinated fluorobenzene. To find resonance or induction parameters of the phenyl group in compound $[C_5H_5FeC_6H_6]^+PF_6^-$, we have synthesized compounds (IV) and (V).



(IV)



(V)

^{19}F shifts as determined for these compounds from a fluorobenzene reference in two solvents are:

(IV)	(V)
$\delta_F = -2.45$ (acetone)	$\delta_F = -2.09$ (acetone)
$\delta_F = -2.53$ (CH_3NO_2)	$\delta_F = -1.71$ (CH_3NO_2)

The Taft equation[5] gives the following values of σ_i and σ_r^0:

$\sigma_i = 0.38$; $\sigma_r^0 = 0.01$ (in acetone)

$\sigma_i = 0.32$; $\sigma_r^0 = 0.028$ (in CH_3NO_2)

Thus, the benzene nucleus in arenecyclopentadienyliron cation differs from phenyl (whose σ_i and σ_r^0 are 0.08 and -0.09 respectively) in that it is a distinct electron acceptor, in other words, it possesses strong negative induction and weak negative conjugation effects. Further, the induction component of the electron influence of phenyl is affected most significantly when an arene is replaced by the arenecyclopentadienyl complex. Strong electron-accepting properties of arenecyclopentadienyliron cation agree with the data obtained earlier[6-8] on ionization constants of arenecyclopentadienyliron acids or amines, or an accelerated nucleophilic exchange of halogen in halogenated compounds of the series.

The effects revealed by NMR may be attributed to various phenomena. Our data show explicitly that the electron system of the π-bonded benzene ring is essentially perturbed as compared with the free aromatic. The upfield shifts of ring protons or fluorine atom may be related to the fact that the hybridization of carbon atoms changes from sp^2 to sp. Lautenbur and King[9] who studied ^{13}C NMR spectra of a number of π-cyclopentadienyl compounds arrived at a similar conclusion. The PMR signals may shift upfield through sp^2–sp^3 rehybridization as well, which was actually the case with olefinic complexes[10,11]. In arenecyclopentadienyl complexes, however, such a rehybridization should enable substituents to a weaker contribution of their conjugation effect towards the shielding of ring protons, which is not observed experimentally. It is highly probable that σ-electrons of an arene participate in its bonding to a central metal atom much more actively than they are usually thought to be. This problem will be discussed elsewhere in more detail.

EXPERIMENTAL

NMR spectra were recorded with JNM-4H 100 or C60HL instruments in acetone or deuteroacetone at concentrations of 0.2 mole/l with hexamethyldisiloxane as an internal reference. Chemical shifts in the Tables are in δ-scale [according to

$\delta = \delta(\text{HMDS}) + 0.07]$ with an accuracy of ±0.005 ppm. ^{19}F shifts were measured on a unit using external lock. The accuracy is not worse than ±0.08 ppm. The compounds (I), (II), and (III) were synthesized as reported earlier[12].

Synthesis of $[p\text{-}FC_6H_4C_6H_5FeC_5H_5]^+PF_6^-$

Ferrocene (2.5 g, 13.5 mmole), *p*-fluorobiphenyl (4.5 g, 26 mmole), and sublimed $AlCl_3$ (3.6 g, 27 mmole) were stirred in 40 ml of octane at 120° for 4 h. The mixture was cooled to 0° and decomposed by 20 ml of water. The aqueous layer was washed several times with ether, and treated with a saturated solution of $NaPF_6$. The precipitated $[p\text{-}FC_6H_4C_6H_5FeC_5H_5]^+PF_6^-$ was chromatographed on alumina (dichloroethane and acetone) and crystallised from abs. alcohol. The yield is 25% of the theoretical; m.p. 131–132°. (Found: C, 46.58, 46.73; H, 3.12, 3.17; F, 30.57, 30.07. $C_{17}H_{14}F_7FeP$ calcd.: C, 46.60; H, 3.22; F, 30.36%.)

The structure of (*p*-fluorobiphenyl)cyclopentadienyliron was confirmed by its PMR spectrum. The spectrum contains three groups of signals. The AA′BB′ multiplet centred at δ 7.78 ppm (each of its components is split at the fluorine atom) relates to protons of the *p*-substituted benzene ring containing a fluorine substituent.

The second group of signals centred at 6.98 ppm is a complex multiplet of a monosubstituted benzene ring. Since the arene ring bonded to the metal [(I) and (II)] gives a signal at higher field than the non-coordinated arene does, fluorine-substituted arene is thought not to be bonded with the metal. The singlet at 5.20 ppm relates to cyclopentadienyl ring protons. $[m\text{-}FC_6H_4C_6H_5FeC_5H_5]^+PF_6^-$ was synthesized in a similar manner; yield 27%; m.p. 170–171° (dec.). (Found: C, 46.77, 46.62; H, 3.27, 3.12; F, 30.64, 31.00. $C_{17}H_{14}FePF_7$ calcd.: C, 46.60; H, 3.22; F, 30.36%.)

The PMR spectrum of (*m*-fluorobiphenyl)cyclopentadienyliron confirms its structure. The spectrum contains three groups of signals. The downfield signal (a multiplet centred at 7.70 ppm) relates to protons of the *m*-fluorinated benzene ring which does not take part in the complex formation. The benzene ring bonded to iron gives a multiplet centred at 6.84 ppm. The signal at 5.20 ppm relates to cyclopentadienyl ring protons.

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