Journal of Organometallic Chemistry, 326 (1987) 217–228
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AN IRON-57 MÖSSBAUER STUDY OF (η^6-ARENE)(η^5-CYCLOPENTADIENYL)IRON(II) SALTS

A. HOULTON, K.G. OFORI-OKAI, R.M.G. ROBERTS *, J. SILVER * and A.S. WELLS

University of Essex, Department of Chemistry, Wivenhoe Park, Colchester, Essex CO4 3SQ (Great Britain)

(Received November 19th, 1986)

Summary

^{57}Fe Mössbauer spectra have been obtained for a series of (η^6-arene)(η^5-cyclopentadienyl)iron(II) complexes ($\mathrm{Ar\overset{+}{Fe}Cp}$). Simple Hammett plots of quadrupole splittings (Δ) for Ar ring substituents are sigmoidal, indicating limits to electron withdrawal and donation. For these simple plots the data are best fitted by use of σ_R^- constants, in keeping with the proposed ϵ_2–π^* back-bonding in the iron–arene interaction. The correlations are improved by use of a dual parameter approach with a 40% inductive component. A plot of Δ for ($\mathrm{Ar\overset{+}{Fe}Cp}$) complexes versus those of corresponding ferrocenes is approximately linear but with a slope of 2.3, indicating enhanced substituent effects in the former series due to the positive charge on Fe. Substituent effects on the Cp ring are directly opposite to those found in ferrocenes, and Hammett correlations follow σ_R^+ rather than the σ_R^- constants found to apply for the arene substituents. Electron-releasing groups in the arene ring have been shown to cause marked attenuation of the substituent effects on Δ for both arene and Cp substituents. Mössbauer parameters are also presented and discussed for polysubstituted complexes, polycyclic systems, and novel phosphacyclopentadienyl complexes and adducts. Finally, some tetracyanoquinodimethane complexes (TCNQ) have been synthesised and their Mössbauer parameters are discussed in terms of population of a conduction band.

Introduction

In recent years we have conducted extensive structural studies on ferrocene derivatives using Mössbauer and NMR spectroscopy [1]. During this work we confirmed that electron-donor substituents (+I, +M) increased the quadrupole splitting (Δ), whereas −I, −M groups caused marked reductions [2]. In addition, linear plots of Δ against Hammett σ_R^+ and against $E^{\circ}_{1/4}$ (quarter-wave potentials)

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* Addressees for correspondence.

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were found [3]. We have extended these studies to encompass phosphaferrocenes where similar effects were noted [4]. Recently we have turned our attention to (η^6-arene)(η^5-cyclopentadienyl)iron(II) salts (Ar$\overset{+}{\mathrm{Fe}}$Cp). These complexes have also been studied by Gol'danski and co-workers [5], who showed that substituent effects on Δ alter with the nature of the ring. Thus for the arene ring, +I groups increase Δ whereas for the Cp ring the reverse is true. Correlations were obtained using dual parameter Hammett plots. The data used, however, were subject to rather large errors in Δ (± 0.04 mm s^{-1}) and although the correlation coefficients (r) quoted are impressive, these underlying errors render the interpretation of such plots somewhat problematical. There is also the problem of the fluorine-substituted compound $(\mathrm{C_6H_5F})\overset{+}{\mathrm{Fe}}\mathrm{Cp}$, whose Δ value is highly temperature dependent (1.78 at 80 K, 0.00 at 300 K). Fitzsimmons [6] has remeasured Δ for the parent $(\mathrm{C_6H_6}\overset{+}{\mathrm{Fe}}\mathrm{Cp})$ at 308 K and found two splittings (1.45, 0.71 mm s^{-1}). He has discussed these Δ values in terms of molecular rotation in both this and the fluorine analogue [7]. In both compounds the onset of such motion appears to be preceded by a reduction in Δ. We report in this paper the remeasurement of Mössbauer parameters for this series of derivatives, and have extended the measurements to some novel compounds. Additionally, we report on data for the corresponding TCNQ complexes.

Results and discussion

(η^6-Arene)(η^5-cyclopentadienyl)iron(II) derivatives (Ar$\overset{+}{\mathrm{Fe}}$Cp) differ significantly in the nature of the ligand bonding from that for the corresponding ferrocene series. In the latter derivatives, the metal ligand bonds are formed principally by π-electron donation by the Cp to the iron atom. In contrast, the major contribution to arene–iron bonding comes from donation of metal $d_{x^2-y^2}$ and d_{xy} electrons to π^* orbitals of the arene. In these systems the arene ring is electron-rich compared with the free ligand, the reverse being true for the Cp$^-$. This effect is well illustrated by the upfield shift (41 ppm) of the benzene ^{13}C resonance in $[(\mathrm{C_6H_6})\overset{+}{\mathrm{Fe}}\mathrm{C_5H_5}][\mathrm{PF_6^-}]$ relative to free benzene, and the corresponding downfield shift (8 ppm) of the Cp resonance relative to ferrocene. A detailed analysis of these shifts has been given by Sutherland et al. [8]. Recent MO treatment of such sandwich structures [9] has led to the calculation of bond orders (P_{ij}) for the ligand–metal interactions. In ferrocene, the bond order for the ϵ_1–π overlaps (mainly d_{xz}, d_{yz} contributions from iron) is calculated as 0.958, which is greater than the ϵ_2–π bond order (0.696, mainly $d_{x^2-y^2}$, d_{xy} contribution from iron). Reductions in both P_{ij}'s occur when one Cp ligand is replaced by $\mathrm{C_6H_6}$. The P_{ij}'s of the benzene–iron bond are 0.745 and 1.61 for ϵ_1 and ϵ_2 overlaps, respectively. The composition of the ϵ_1 and ϵ_2 orbitals also changes from $\mathrm{MCp_2}$ to $(\mathrm{C_6H_6}\overset{+}{\mathrm{M}}\mathrm{Cp})$, ϵ_2 for the arene–iron interaction, becoming less metal- and more ligand-based, whereas the reverse applies for ϵ_1. The overall picture is one in which iron to arene–ligand back-bonding dominates over Cp ligand to iron π donation. This reversal of the roles of ϵ_1 and ϵ_2 in binding should result in similar substituent effects for both arene substituents in (Ar$\overset{+}{\mathrm{Fe}}$Cp) and for Cp substituents in $\mathrm{FeCp_2}$ derivatives. Table 1 lists ^{57}Fe Mössbauer data for the simple monosubstituted derivates $[(\mathrm{C_6H_5X})\overset{+}{\mathrm{Fe}}\mathrm{Cp}][\mathrm{PF_6^-}]$. As expected, electron-withdrawing groups decrease and electron-releasing groups increase the quadrupole splitting (Δ). A plot of Δ values for these complexes against those for the corresponding ferrocenes is approximately linear with a slope of +2.3. This reflects the enhance-

TABLE 1

^{57}Fe MÖSSBAUER DATA FOR $[(C_6H_5X)\overset{+}{Fe}C_5H_5][PF_6^-]$ COMPLEXES (Isomer shift δ, quadrupole splitting Δ both in mm s^{-1})

X	δ [a]	Δ [a]
NH_2	0.52 [b]	1.83 [b]
NMe_2	0.55(1)	1.79(1)
CH_3	0.51 [b]	1.78 [b]
F	0.54 [c]	1.77 [c]
$NHCOCH_3$	0.54 [b]	1.76 [b]
OCH_3	0.52 [b]	1.76 [b]
OCH_3	0.54(1)	1.75(1)
H	0.52(1)	1.68(2)
Br	0.54 [b]	1.68 [b]
Cl	0.52(1)	1.66(2)
Ph	0.53(1)	1.63(1)
$CONH_2$	0.53 [b]	1.62 [b]
$CO_2^-K^+$	0.53(1) [d]	1.60(1) [d]
Ph_3Sn	0.52(1) [e]	1.58(1) [e]
CO_2H	0.53(1)	1.52(1)
CN	0.53(1)	1.51(1)
NO_2	0.53(1)	1.50(1)

[a] This work except where indicated to the contrary. [b] Ref. 5. [c] Ref. 7. [d] Frozen solid solution in aqueous KOH. [e] Ref. 30.

ment of substituent effects due to the overall positive charge on the iron in the $(Ar\overset{+}{Fe}Cp)$ salts. The data in Table 1 comprises a number of remeasured Δ values together with newly available literature values and the older less accurate data obtained by Gol'danskii and his colleagues [5]. The latter group [5] used a dual parameter approach using inductive and resonance constants. The actual nature of the constants used, derived from NMR sources, remain obscure, and it is not clear if the resonance component (σ_c) is related to σ_p or σ_p^+. Their work suggests a 65% contribution from resonance effects to the overall effect on Δ. If true, this represents a marked reduction in this effect at the iron atom compared with that on the arene ligand as measured by ^{13}C NMR spectroscopy (cf. 83%, ref. 8). Plots of Δ for monosubstituted arene complexes against various Hammett substituent constants reveal some interesting trends. Graphs of Δ against σ_p [10], σ_p^+ [10], σ_p° [11] and R [12] yielded plots of varying linearity (correlation coefficients (r) 0.86, 0.92, 0.90 and 0.89, respectively, for 12–14 points). The dual parameter approach using the Swain–Lupton F and R values weighed 30/70 did not improve the correlation. Closer examination of the data reveals that most simple plots are sigmoidal at the extremes of the substituent constant range. This is particularly noticeable for the σ_p^+ plot (Fig. 1). Such an effect was less obvious for Gol'danskii's older, less accurate, data [5]. For strong electron-releasing groups NMe_2, NH_2 and OCH_3 there is little change in Δ even though the σ_p^+ value changes by about 0.8 units. Similarly, for the strongly electron-withdrawing groups CO_2H, CN, and NO_2, Δ does not vary significantly (σ_p^+ range of 0.5 units). There thus appears to be a limit to the amount of electron withdrawal via the arene ring which is controlled by the charge on the iron atom. At the other end of the scale similar saturation effects are observed. Excessive electron donation is presumably prevented by the known charge transfer

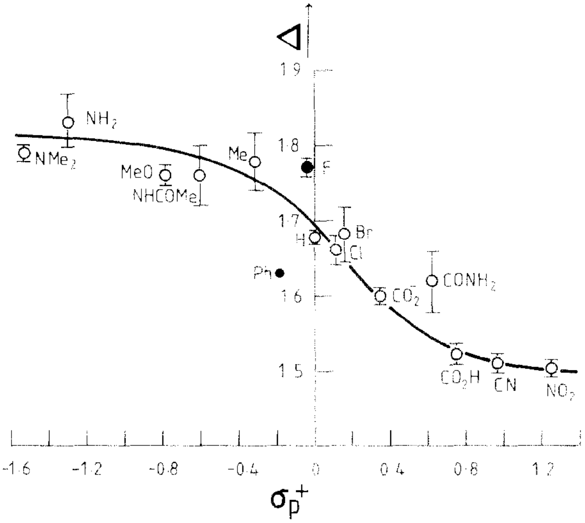


Fig. 1. Plot of quadrupole splitting, Δ (mm s^{-1}) against Hammett σ_p^+ constants for $[(C_6H_5X)\overset{+}{Fe}C_5H_5][PF_6^-]$ complexes.

from the Cp ring to the iron atom. This phenomenon can also be detected for simple ferrocene derivatives, though it is less well defined owing to the much smaller range of Δ values [3]. Such effects are still apparent even when the dual parameter approach is used, particularly for electron-withdrawing groups CO_2H, CN and NO_2 (vide infra). Correlations are also obtained by using the σ_R parameters [13]. It is interesting that σ_R^- gives a substantially better correlation ($r = 0.88$, $N = 13$) than σ_R^+ ($r = 0.78$, $N = 13$). σ_R^+ correlations are found when the site of reaction (or

TABLE 2

^{57}Fe MÖSSBAUER DATA FOR $[C_6H_6Fe^+(C_5H_4X)][PF_6^-]$ SALTS, QUADRUPOLE SPLITTINGS (δ and Δ in mm s^{-1}) FOR CORRESPONDING MONOSUBSTITUTED FERROCENES (Δ_f) AND HAMMETT σ_R VALUES [13]

X	δ	Δ [a]	Δ_f [b]	σ_R^-	σ_R^+	σ_R
H	0.52(1)	1.68(1)	2.37	0.00	0.00	0.00
COMe	0.52(1)	1.75(1)	2.26	0.20	0.41	0.20
COEt	0.54(1)	1.84(1)	–	0.13 [c]	0.25	0.18
$CO\overset{+}{H}(Et)$	0.54(1)	1.86(1)	–	0.72 [c]	0.61 [c]	0.54 [c]
COPh	0.50(1)	1.76(1)	2.26	0.11	0.18	0.11
$CO\overset{+}{H}(Ph)$	0.54(1)	1.91(1)	2.15	0.72 [c]	0.61 [c]	0.54 [c]
CO-t-Bu	0.54(1)	1.72(1)	2.28	0.12	0.19	0.12
$CO\overset{+}{H}$(t-Bu)	0.54(1)	1.95(1)	2.02	0.72 [c]	0.61 [c]	0.54 [c]
NH_2 [d]	0.58	1.58	2.43	−1.10	−0.55	−0.80
OMe [d]	0.52	1.65	–	−0.66	−0.51	−0.58
Et [d]	0.48	1.74	–	−0.14	−0.07	−0.14
CO_2H	0.52(1)	1.78(2)	2.21	0.11	0.31	0.11
NHCOMe [d]	0.46	1.70	–	−0.47	−0.28	−0.35
CMe_2COMe	0.54(1)	1.84(1)	–	–	–	–

[a] This work. [b] Data from Ref. 3. [c] Calc. values eqs. 1–3. [d] Data from Ref. 5

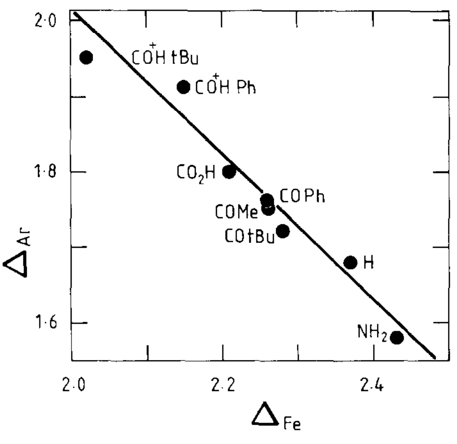


Fig. 2. Plot of quadrupole splittings for $[C_6H_6\overset{+}{Fe}(C_5H_4X)][PF_6^-]$ (Δ_{Ar}) against those for corresponding ferrocenes (Δ_{Fe}).

probe) is a strong π electron acceptor, whereas for strong π donor sites σ_R^- usually applies. As already indicated, the iron site acts as a π donor in the arene ring via overlap of $d_{x^2-y^2}$ and d_{xy} orbitals with π^* ligand orbitals. The best correlation is obtained by using a dual parameter equation with a 60/40 weighting of σ_R^- to σ_I ($r = 0.952$, $N = 13$ points, slope $= -0.47$), close to that obtained by Gol'danskii [5].

The Δ values for Cp ring substituents appear in Table 2 together with those for the corresponding ferrocenes. It is apparent that the spread of values for Cp substituents is approximately 2/3 of that for the arene substituted analogues. As predicted by MO theory, the substituent effect in the Cp ring in $(Ar\overset{+}{Fe}Cp)$ are the reverse of those found in the arene ring. A plot of $\Delta[C_6H_6\overset{+}{Fe}(C_5H_4X)]$ against $\Delta[C_5H_5Fe(C_5H_4X)]$ is linear ($r = 0.975$, $N = 8$) with a slope of -0.92, showing that the substituent effects are of the same magnitude but of opposite sign (Fig. 2). This is due to the overall charge transfer to the arene ring. Unfortunately the σ_R values are not available for many of the substituents quoted [13]. There is, however, a fairly good correlation between ^{13}C NMR shifts relative to benzene of carbons *para* to the substituents ($\delta(C_4)$) and the various σ_R parameters used in this work.

$$\delta(C_4) = 15.5,\ \sigma_R^\circ + 1.5, \qquad r = 0.952,\ N = 25 \tag{1}$$

$$\delta(C_4) = 15.2,\ \sigma_R^- - 0.99, \qquad r = 0.930,\ N = 18 \tag{2}$$

$$\delta(C_4) = 12.0,\ \sigma_R^+ + 1.31, \qquad r = 0.940,\ N = 20 \tag{3}$$

(data for $CHCl_3$ or CCl_4 solution)

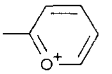
This enables σ_R constants to be estimated. The values for $R{-}C{=}\overset{+}{O}H$ have been calculated using the $\delta(C_4)$ value of +9.9 ppm reported for the oxonium group [14]  since this was obtained in a low dielectric solvent (CF_3CO_2H/ CD_2Cl_2). It is further assumed that the R group has no effect on σ_R values. Plots of σ_R^+, σ_R^- and σ_R° all show correlation with Δ values ($r = 0.911$, 0.811, 0.907 respectively for $N = 14$). Thus in the case of the Cp substituents, not only are the

TABLE 3

^{57}Fe MÖSSBAUER DATA FOR [p-$CH_3C_6H_4X)\overset{+}{Fe}C_5H_5$][$PF_6^-$] SALTS ($\delta$ and Δ in mm s^{-1})

X	δ [a]	Δ [a]
$NHCOCH_3$	0.53	1.90
OCH_3	0.52	1.87
OCH_3	0.52(1) [b]	1.87(1) [b]
NH_2	0.53	1.87
CH_3	0.49	1.81
CH_3	0.55(1) [b]	1.78(1) [b]
Et	0.51	1.78
H	0.51	1.78
F	0.52	1.78
SCH_3	0.53	1.78
Cl	0.52	1.71
Cl	0.51(1) [b]	1.67(1) [b]
CN	0.55	1.66

[a] Data from Ref. 5 unless otherwise stated. [b] This work.

substituent effects in the opposite direction to those in the arene ring but they appear to follow σ_R^+ rather than σ_R^-, which is the result expected for a π donor. The justification for the use of Hammett plots for Cp substituents comes from the observation that the β positions in the substituted Cp ring behave very much like the *para* positions in ^{13}C NMR [15].

Tables 3 and 4 list Mössbauer data for more heavily substituted ($Ar\overset{+}{Fe}Cp$) derivatives. Looked at overall, the substituent effects on the Δ values are broadly additive. The additivity is more striking when only one type of substituent group is considered. Thus for methyl substitution, Δ varies linearly with the number of methyl groups present (Fig. 3). Such a plot does not, however, imply linear correlation with Hammett constants, since it is known that marked deviations occur

TABLE 4

MÖSSBAUER DATA FOR POLYSUBSTITUTED [$Ar\overset{+}{Fe}Cp$][PF_6^-] SALTS (δ and Δ in mm s^{-1})

Arene substitution	Cp substitution	δ [a]	Δ [a]
o-$(OMe)_2$	H	0.54(1)	1.97(1)
m-$(OMe)_2$	H	0.55(1)	1.92(1)
o-Me_2 [b]	H	0.52(1)	1.81(1)
o-Cl_2	H	0.53(1)	1.63(1)
m-Cl_2	H	0.54(1)	1.78(1)
$-(CH_2)_4-$ [b]	H	0.54	1.87
1,3,5-Me_3	H	0.53(1)	1.89(1)
1,3,5-Me_3	Me	0.54(1)	1.79(1)
1,3,5-Me_3	$CH_2\overset{+}{N}Me_2$	0.52(1)	1.77(1)
1,3,5-Me_3	$CH_2\overset{+}{N}Me_2$	0.54(1)	1.88(1)
1,3,5-Me_3	$CH_2\overset{+}{N}Me_3$	0.55(1)	1.85(1)
1,3,5-Me_3	CO_2H	0.55(1)	1.87(1)
1,3,5-Me_3	CO_2^- K^+ [c]	0.52(1)	1.81(1)
Me_6	H	0.53(1)	2.08(1)

[a] This work unless otherwise stated. [b] BF_4^- salt. [c] Frozen solid solution in aqueous KOH.

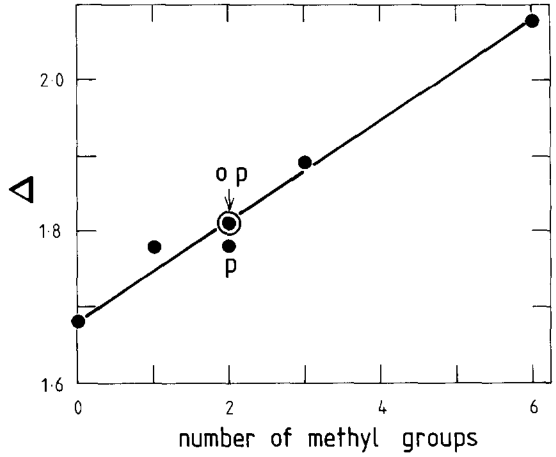
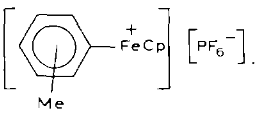


Fig. 3. Plot of quadrupole splitting (Δ) versus of methyl groups for



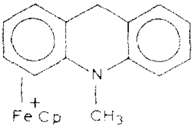
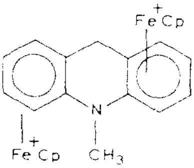
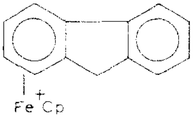
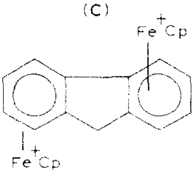
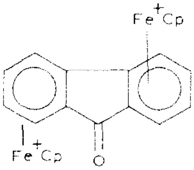
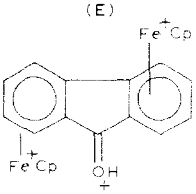
from additivity even for two substituents [16]. For example, when the chlorine substituents are considered, it is evident that no such simple relationship exists. Such behaviour has also been observed in chlorinated ferrocenes [17]. From the data in Table 3 it is clear that the presence of a methyl group on the arene causes a marked reduction in the range of Δ values, reflecting the group's ability to supply electron density as conditions demand. The dominating influence of the arene ring can again be seen in the Δ values of the [(mesitylene)$\overset{+}{\text{Fe}}C_5H_4X$] complexes in Table 4. The most significant effect is the further attenuation of the observed range of Δ values caused by three methyl arene substituents. Thus substituent in the Cp ring exert a much smaller influence on Δ in the mesitylene complexes than in the benzene analogues (of Table 4 and 2). This is particularly noticeable for the charged substituents which in Table 2 show the largest changes in Δ as opposed to the small effects seen in Table 4. We conclude therefore that electron-donating groups such as Me groups can act as electron reservoir supplying as much electron density as the system demands up to a limit.

Data for a series of polycyclic derivatives appears in Table 5. From this it is clear that the presence of a second $\overset{+}{\text{Fe}}$Cp moiety *trans* to the first has little or no effect on Δ. This is in line with the levelling effects noted above for electron-releasing groups such as CH_2 and NMe (compounds **A**–**D**, Table 5). An anomaly is seen when **D** and **E** are compared. The fluorenone derivative has a higher Δ value than that of the fluorene complex itself, which is the reverse of the normal behaviour for ferrocenyl ketones [18]. Protonation of the carbonyl, however, reduces Δ by 0.07 mm s^{-1}, a result which parallels that for the ferrocene series. The reasons for this exceptional behaviour are not easy to see.

Data for some new phosphorus-substituted derivatives [19,20] appear in Table 6. The two phosphacyclopentadienyl (PCp) complexes show a large reduction in Δ compared with [(C_6H_6)$\overset{+}{\text{Fe}}$Cp][PF_6^-]. The PCp moiety is a strong π acceptor, which presumably leads to a reduction in the amount of $\epsilon_2 - \pi^*$ overlap with the benzene ring. It is clear that a methyl substituent on the arene ring now has a much smaller effect than it does in the Cp analogue. The π acceptor properties of the PCp system

TABLE 5

^{57}Fe MÖSSBAUER DATA FOR CpFe^{+} COMPLEXES OF POLYCYCLIC AROMATIC DERIVATIVES (counterions PF$_6^-$ except where stated) (δ and Δ in mm s^{-1})

Polycyclic structure	δ	Δ
 (A)	0.55(1)	1.79(1)
 (B)	0.56(1)	1.78(1)
 (C)	0.53(1)	1.75(1)
 (D)	0.53(1)	1.75(1)
 (E)	0.55(1)	1.80(1)
 (F) [a]	0.55(1)	1.73(1)

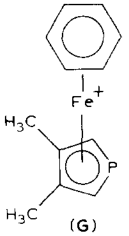
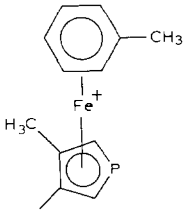
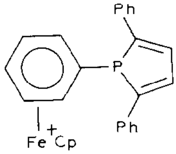
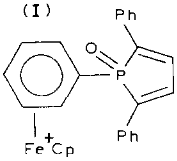
[a] Counterions 2 PF$_6^-$, CF$_3$SO$_3^-$.

are also seen in the σ-bonded complex **I**, where a reduction in Δ of 0.15 mm s^{-1} is observed relative to [(C$_6$H$_6$)Fe$^+$Cp][PF$_6^-$]. Oxidation of this complex to the P^V oxide **J** reduces the π acceptor capacity of the substituent and hence increases Δ to 1.62 mm s^{-1}.

We have also synthesised some tetracyanoquinodimethane (TCNQ) complexes of the monosubstituted (ArFe$^+$Cp) series. As seen from Table 7, the complexes isolated contain a varying number of TCNQ molecules probably because of co-crystallisa-

TABLE 6

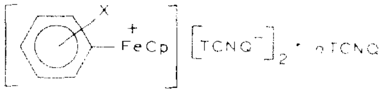
^{57}Fe MÖSSBAUER DATA FOR ($\mathrm{Ar\overset{+}{Fe}Cp}$) DERIVATIVES CONTAINING PHOSPHORUS ATOMS AS SUBSTITUENTS OR AS RING COMPONENTS (δ and Δ in mm s^{-1})

Derivatives	δ	Δ
 (G)	0.52(1)	1.50(1)
 (H)	0.48(1)	1.53(1)
 (I)	0.53(1)	1.53(1)
 (J)	0.55(1)	1.62(1)

tion of the TCNQ. The appearance of the γ(CH) mode of TCNQ at 860 cm^{-1} in the IR spectra confirm this. The analytical data are surprisingly consistent since, for example, all three dichloro derivatives have the stoichiometry $[\mathrm{Ar\overset{+}{Fe}Cp}][\mathrm{TCNQ}]_2^{-}\cdot$ 3TCNQ. The crystal structure of one of these complexes $[(\mathrm{C_6Me_6})\mathrm{\overset{+}{Fe}Cp}][(\mathrm{TCNQ})_2]^{-}$ has been reported [21]. The iron sandwiches were found to form a stack with an intra-annular distance (r_a) of 3.211 Å and an intermolecular ring–ring distance (r_e) of 3.36 Å. These materials exhibit dc conduction typical of TCNQ^{-} salts. The r_e is the expected thickness of the aromatic rings which bring the rings closer than in the pseudo-stack in $[(\mathrm{C_5H_4Me})_2\mathrm{\overset{+}{Fe}}][(\mathrm{TCNQ})_2^{-}]$ [22] (3.63 Å). The carbon atoms are thus at Van der Waals distances, and while the overlap of the rings is not optimum, the structural requirements for developing a one-dimensional band structure out of vacant $\pi^{\star}$ ligand orbitals of the individual metallocenes are met. No hard evidence for iron electron participation in the band structure was presented. Mössbauer data for the $(\mathrm{TCNQ})_2^{-}$ complexes appears in Table 8. The Δ values for those complexes

TABLE 7

YIELDS AND ANALYTICAL DATA FOR



X	n	Yield (%)	Analysis (Found (calc) (%))		
			C	H	N
H	1	12	69.3 (69.5)	2.7 (2.8)	20.4 (20.7)
Cl	1	12	67.1 (66.7)	2.6 (2.6)	19.5 (19.8)
o-Cl_2	4	9	67.2 (66.8)	2.1 (2.2)	23.1 (22.5)
m-Cl_2	4	14	66.7 (66.8)	2.1 (2.2)	22.5 (22.5)
p-Cl_2	4	19	67.4 (66.8)	2.2 (2.2)	23.0 (22.5)
o-$(OMe)_2$	8	7	69.8 (69.4)	2.2 (2.4)	25.5 (24.3)
1,3,5-Me_3	6	19	70.1 (70.5)	2.5 (2.6)	24.3 (23.9)
Me_6	0	30	71.2 (71.2)	4.5 (4.5)	16.2 (16.2)

with electron-donating substituents on the arene ligand are all lower than those for the parent arene complexes. There is some evidence that the nature of the counter-ion has a small though irregular effect on Δ [5]. The reduction in Δ however is more likely to be due to intermolecular transfer of electrons between the metallocenes in the stack forming the conduction band. The change in Δ is that expected for electron-withdrawal in the benzene ring (or electron donation in the Cp ring). Band structure is considered to involve π^* molecular orbitals of ligands. These are normally empty, and require electrons from other sources to form the conduction band. The back-bonding from the iron atom to the arene π^* orbitals fulfils this

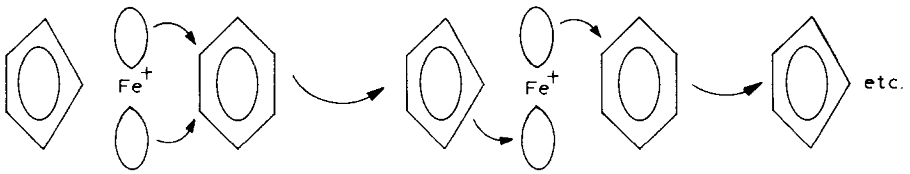
TABLE 8

^{57}Fe MÖSSBAUER DATA FOR TCNQ SALTS OF $(ArF\overset{+}{e}Cp)$ COMPLEXES (δ and Δ in mm s^{-1})

Arene substituent	Anion	δ	Δ	$\delta\Delta$ [a]
H	PF_6	0.52(1)	1.68(2)	
H	$(TCNQ)_2$	0.54(1)	1.65(2)	0.03
1,3,5-Me_3	PF_6	0.53(1)	1.89(1)	
1,3,5-Me_3	$(TCNQ)_2$	0.51(1)	1.77(1)	0.12
Me_6	PF_6	0.53(1)	2.08(1)	
Me_6	$(TCNQ)_2$	0.53(1)	1.97(1)	0.11
1,2-$(OMe)_2$	PF_6	0.54(1)	1.97(1)	
1,2-$(OMe)_2$	$(TCNQ)_2$	0.57(1)	1.89(3)	0.08
Cl	PF_6	0.52(1)	1.66(2)	
Cl	$(TCNQ)_2$	0.54(1)	1.67(2)	−0.01
1,2-Cl_2	PF_6	0.53(1)	1.63(1)	
1,2-Cl_2	$(TCNQ)_2$	0.54(1)	1.66(1)	−0.03

[a] $\delta\Delta = \Delta(PF_6) - \Delta(TCNQ)_2$.

requirement. A likely structure for the band is depicted.



The conduction band is completed by the interaction of the π orbitals of the arene of one complex molecule with the π^* orbitals of the Cp of an adjacent member of the stack. The situation is thus one in which electron density is withdrawn from the arene ligand and donated to the Cp ligand. In both cases the value of Δ will decrease, thus accounting for the observed reductions in Δ in the TCNQ complexes. Where electron-withdrawing chlorine substituents are present on the arene ligand, there are no significant changes in Δ when PF_6^- is replaced by $(TCNQ)_2^-$. Presumably charge is transferred to the chlorine atoms rather than to the neighbouring Cp rings. Indeed it is debatable whether such complexes ever form a stacked structure.

Experimental

The $[(\text{arene})\overset{+}{\text{Fe}}\text{Cp}][PF_6^-]$ salts were prepared by published methods [8,23]. Polycyclic arene derivatives were made as described by Sutherland et al. [24,25]. Details of the synthesis of the phosphorus derivatives listed in Table 6 appear elsewhere [19,20]. The methoxy complexes were prepared by nucleophilic displacement of chlorine by methoxide [26] as follows. Sodium (0.22 g, 10 mg atom) was dissolved in MeOH (30 ml) and $[o\text{-}C_6H_4Cl_2\overset{+}{Fe}C_5H_5][PF_6^-]$ [19] (2 g, 5 mmol) was added. The mixture was refluxed for 2 h under N_2 then cooled, and the solvent was removed. The residue was dissolved in CH_2Cl_2 (50 ml) and extracted with 3 × 30 ml H_2O. The CH_2Cl_2 layer was dried then reduced to about 5 ml and added to ether (60 ml). The resulting precipitate was filtered off and air-dried. Yield 1.2 g (60%). Found: C, 39.4; H, 3.9. $C_{13}H_{15}F_6FeO_2P$ calc.: C, 38.6; H, 3.7%. The *meta-* and *para-*dimethoxy derivatives were prepared as above in 67 and 57% yields, respectively.

Preparation of TCNQ complexes

A solution of Li TCNQ [28] (0.21 g, 1.0 mmol) and TCNQ (0.20 g, 1.0 mmol) in MeCN (10 ml) was refluxed for 30 min. One equivalent of $[Ar\overset{+}{Fe}Cp][PF_6^-]$ was added to the boiling solution and the mixture refluxed for 1 h then filtered hot. The filtrate was left overnight at −20 °C to crystallise. The deep green crystals were filtered off and washed rapidly with cold MeCN followed by ether, and then sucked dry. Table 7 lists yields and analyses.

Mössbauer data were obtained and fitted as described previously [29].

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