Studies of the Bonding in Iron(II) Cyclopentadienyl and Arene Sandwich Compounds. Part 4.[1] A Survey of the Effect of Methyl Substitution on the Bonding in Some Iron Sandwich Complexes

Richard A. Brown, Andrew Houlton, Steven D. Howe, Roger M. G. Roberts* and Jack Silver*
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

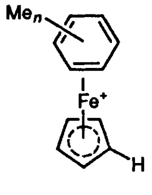
A series of methylated benzene complexes of the type $[Fe(\eta^6\text{-}C_6H_nMe_{6-n})(\eta^5\text{-}C_5H_4X)]PF_6$ (n = 0–6) have been synthesised where X = H, Me or COPh. Iron-57 Mössbauer data are presented and quadrupole splittings (q.s.) correlated with the degree of methylation (n) of the arene moiety. For X = H, a linear correlation between q.s. and n was found. For X = Me, a similar correlation was obtained but with a significantly lower slope whereas for X = COPh the plot showed a minimum at n = 1. These results are discussed in relation to the bonding in other iron sandwich complexes {ferrocenes and $[Fe(\eta^6\text{-arene})_2]^{2+}$ salts}. This has enabled a rationalisation of Mössbauer parameters for a wide range of iron sandwich complexes to be made.

We have recently put forward explanations for the seemingly anomalous ^{57}Fe Mössbauer parameters of substituted (η^6-arene)(η^5-cyclopentadienyl)iron(II) cations.[2,3] Usually electron releasing groups cause an increase in the quadrupole splitting (q.s.) of iron(II) sandwich compounds whereas electron withdrawing groups cause a decrease. For the above complexes similar behaviour is observed when the electron withdrawing or donating substituent is located on the arene ring. However, for substituents on the cyclopentadienyl ring the converse is true.

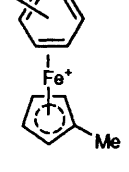
To investigate this phenomenon further, three series of hexafluorophosphate salts have been synthesised: $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)]PF_6$, $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_4Me)]PF_6$ containing an electron donating methyl group and $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_4COPh)]PF_6$ containing an electron withdrawing benzoyl group. In this paper we present the ^{57}Fe Mössbauer spectroscopic data and survey the results together with those of a wide range of iron sandwich structures and their implications for the wider understanding of the bonding in such compounds.

Results and Discussion

The following cations were synthesised (n = 0–6).



Series a



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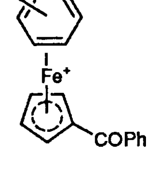

Series c

In all cases the arene was varied from benzene to hexamethylbenzene. The Mössbauer spectroscopic data for the series of complexes a, b and c are contained in Tables 1, 2 and 3 respectively. Fig. 1 is a plot of methyl substitution *vs.* q.s. for these series.

For series a, a plot of q.s. against number (n) of methyl substituents is reasonably linear (r = 0.983, N = 9, standard deviations in parentheses) and results in correlation (1). This

$$\text{q.s.} = 0.066(5)n + 1.66(1) \qquad (1)$$

systematic increase in q.s. with n can be explained using our previous arguments.[2,3] The observed q.s. dependence on the relative populations (p_i) of the e_1 and e_2 molecular orbital sets† is given by equation (2).

$$\text{q.s.} \propto 2p_2 - p_1 \qquad (2)$$

The effect of progressive methyl substitution will be to lessen the need for back bonding *via* e_2 orbitals thus increasing p_2 and hence increasing the q.s. It is interesting to compare the above correlation with that obtained from the only systematic study of q.s. variation with alkyl substitution for ferrocene. A plot of the data of Sano and co-workers[4] reveals a linear dependence of q.s. on n (the number of ethyl groups in this case) up to and including hexaethylferrocene. Thereafter no appreciable change in q.s. is observed. This can be explained by a saturation effect

Table 1 Iron-57 Mössbauer parameters[a] for $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)]PF_6$ salts (series a)

Arene	i.s.	q.s.
Benzene	0.52	1.67
Methylbenzene	0.52	1.74
1,2-Dimethylbenzene	0.52	1.77 (1.81)[b]
1,3-Dimethylbenzene	0.52	1.78
1,4-Dimethylbenzene	0.51	1.76
1,3,5-Trimethylbenzene	0.53	1.89
1,2,4,5-Tetramethylbenzene	0.52	1.91
1,2,3,4-Tetramethylbenzene	0.52	1.92
Pentamethylbenzene	0.50	1.96
Hexamethylbenzene	0.53	2.08

[a] i.s., Isomer shift; q.s., quadrupole splitting all in mm s^{-1} and at 80 K. Tolerances on both 0.01 mm s^{-1}. [b] For BF_4^- salt.

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† In this approach, we assume that the symmetry of the orbitals is not affected when substituents are present, since these orbitals are ring- and iron-based.[2,3]

Table 2 Iron-57 Mössbauer parameters* for $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_4Me)]PF_6$ (series b)

Arene	i.s.	q.s.
Benzene	0.51	1.67
Methylbenzene	0.51	1.67
1,2-Dimethylbenzene	0.50	1.75
1,3,5-Trimethylbenzene	0.53	1.82
1,2,4,5-Tetramethylbenzene	0.52	1.87
Pentamethylbenzene	0.53	1.95
Hexamethylbenzene	0.53	1.96

* i.s., Isomer shift; q.s., quadrupole splitting all in mm s^{-1} and at 80 K. Tolerances on both 0.01 mm s^{-1}.

Table 3 Iron-57 Mössbauer parameters* for $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_4COPh)]PF_6$ (series c)

Arene	i.s.	q.s.
Benzene	0.51	1.77
Methylbenzene	0.52	1.74
1,2-Dimethylbenzene	0.53	1.78
1,3-Dimethylbenzene	0.52	1.75
1,3,5-Trimethylbenzene	0.53	1.80
1,2,4,5-Tetramethylbenzene	0.54	1.88
1,2,3,4-Tetramethylbenzene	0.52	1.92
Pentamethylbenzene	0.54	1.99
Hexamethylbenzene	0.58	2.02

* i.s., Isomer shift; q.s., quadrupole splitting all in mm s^{-1} and at 80 K. Tolerances on both 0.01 mm s^{-1}.

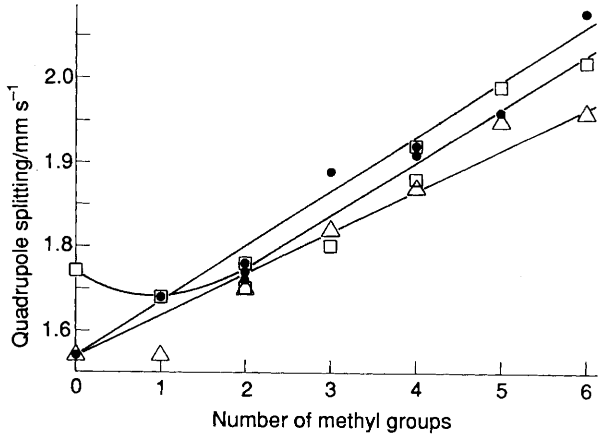

Fig. 1 Plots of quadrupole splitting (mm s^{-1}) against number of methyl substituents for series a (●), b (△) and c (□)

representing the situation where virtually no back bonding is required resulting in a constant population of the e_2 levels. The linear portion of the graph ($r = 0.997$, $N = 4$) gives correlation (3).

$$\text{q.s.} = 0.0130(7)n + 2.39(1) \qquad (3)$$

Clearly the ferrocene system is much less sensitive to substituent effects than the (η^6-arene)(η^5-cyclopentadienyl)-iron(II) sandwich complexes reflecting the much greater donor strength of the cyclopentadienyl rings. Interestingly a similar, albeit less well defined, correlation [equation (4)] is obtained for the bis(arene)iron(II) salts ($r = 0.895$, $N = 11$, see Fig. 1 in ref. 5).

$$\text{q.s.} = 0.028(4)n + 1.92(2) \qquad (4)$$

This system shows a somewhat enhanced sensitivity to alkyl substitution compared to that of ferrocene. However, no saturation effect is noted due to the much weaker donor capacity of the arene ligands. The actual q.s. values are considerably lower than those for ferrocene due to the greater back donation (lowering p_2) required by the arene ligands. Series b (which has a donor substituent on the cyclopentadienyl ring) shows similar trends to series a, with again a fairly good linear correlation ($r = 0.985$, $N = 7$) of q.s. with n according to equation (5). The sensitivity to methyl substitution is, however,

$$\text{q.s.} = 0.055(4)n + 1.65(1) \qquad (5)$$

lower than that for series a, probably reflecting the greater involvement of e_2 orbitals in back bonding to the arene ligand. By contrast series c (which has an acceptor substituent on the cyclopentadienyl ring) shows anomalous behaviour. The plot of q.s. *vs.* n shows a minimum at $n = 1$ followed by a fairly linear increase of q.s. with n ($r = 0.978$, $N = 7$) from $n = 2$ onwards yielding equation (6). It seems probable that such behaviour

$$\text{q.s.} = 0.069(6)n + 1.62(3) \qquad (6)$$

results from competition by the two ring systems for iron back bonding. Electron release to the arene ring by methyl groups causes it to demand less back bonding from the e_2 orbitals resulting in an increased q.s. Electron withdrawal by substituents on the cyclopentadienyl ring would increase back bonding to that ring hence decreasing the q.s. Evidently there comes a point when electron release to the arene ring outweighs electron withdrawal from the cyclopentadienyl ring after which the normal trends observed for series a and b take over.

The isomer shift (i.s.) changes in the benzoyl series (series c) are worth commenting on. As the arene becomes more heavily methylated, the i.s. increases. We have previously documented a similar effect in the methylated bis(η-arene)iron(II) salts.[5] An increase in i.s. for ^{57}Fe can arise either from a decrease in s electron density at the nucleus or an increase in p and/or d electron shielding. Electron donation by the methyl substituents would reduce back bonding of iron d orbitals thus enhancing d orbital shielding effects at the iron nucleus. This effect is, however, not apparent in series a and b. The difference is that, for series c, the cyclopentadienyl ring has an electron withdrawing substituent and is thus more like an arene than a cyclopentadienyl ring in its need for back bonding. We have previously shown that back-bonding effects dominate the bonding in iron sandwich compounds, electron deficient ligated rings demanding more back donation from the iron atom.[2,3] There is a limit, however, to the amount of stabilisation available by this route, since (η^6-arene)(η^5-cyclopentadienyl)-iron(II) complexes where the arene has three or more electron withdrawing substituents, such as chlorine, cannot be prepared.

The benzoyl complexes are more weakly bonded than the other derivatives in series a and b and need more iron d-electron participation in the bonding to hold them together. The increasing i.s. values in the latter part of series c are thus readily understood in terms of increased d electron shielding at the ^{57}Fe nucleus. This change in the bonding takes place at a q.s. of 1.88 mm s^{-1}, the value for $[Fe(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(\eta^5\text{-}C_5H_4COPh)]PF_6$, which interestingly is close to the q.s. of $[Fe(\eta^6\text{-}C_6H_6)_2][PF_6]_2$ of 1.90 mm s^{-1}.[5] Indeed the Mössbauer parameters of these two complexes are almost identical indicating that the electron field asymmetries and the electron densities at the iron nuclei are very similar. This in turn suggests that the different ligand sets generate similar metal–ligand bonding. Following on from this, we can now list a wide range of iron sandwich compounds that have hitherto been studied by ourselves and others in an order that is derived from Mössbauer spectroscopy. These appear in Table 4.[1,2,5–10] Table 4 has been arranged in order of descending q.s. values of the iron(II) sandwich complexes {see for example the values (set in bold) of the symmetrical species which lie along the diagonal from $[Fe(C_5Me_5)_2]$ to $[Fe(C_5H_7)_2]$ (C_5H_7 = pentadienyl)}. This

Table 4 Correlation of quadrupole splittings[a] for iron sandwich complexes $[Fe(\eta\text{-}L^1)(\eta\text{-}L^2)]^{n+}$ [b]

Column (ligand)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1 C_5Me_5	**2.50**						1.80						1.40			
2 C_5H_4Me		**(2.42)**[c]	2.39				1.96	1.97	1.90	1.87	1.82	1.67	1.67			
3 C_5H_5		2.39	**2.37**	2.26	2.26	2.21	2.08	1.94	1.93	1.91	1.89	1.74	1.68	2.11	2.00	
4 C_5H_4COPh			2.26	**2.17**						1.88	1.80	1.74	1.77			
5 C_5H_4COMe			2.26		**2.15**							1.74	1.76			
6 $C_5H_4CO_2H$			2.21			**2.16**					1.87		1.78			
7 C_6Me_6	1.80	1.96	2.08	2.02			**2.10**	1.67	1.97							
8 C_6HMe_6		1.97	1.94				1.67									
9 C_6H_7		1.90	1.93				1.97									
10 $C_6H_2Me_4$-1,2,4,5		1.87	1.91	1.88						**2.00**						
11 $C_6H_3Me_3$-1,3,5		1.82	1.89	1.80		1.87					**2.01**					
12 C_6H_5Me		1.67	1.74	1.74								**1.93**		1.52		
13 C_6H_6	1.40	1.67	1.68	1.77	1.76	1.78							**1.90**	1.50		
14 $PC_4H_2Me_2$-3,4[d]			2.11									1.53	1.50	**1.82**		
15 $PC_4H_2Ph_2$-2,5[e]			2.00												**1.52**	
16 C_5H_7																**1.40**

[a] In mm s^{-1} at 80 K. Tolerances on quadrupole splittings ± 0.01 mm s^{-1} or ± 0.02 mm s^{-1}. [b] Data taken from refs. 1, 2, 5–10 and this work. $n = 0\text{–}2$ (PF_6^- salts for $n = 1$ or 2). [c] Refers to 1,1′-diethylferrocene which is expected to have an almost identical value to that of the methyl analogue. [d] 3,4-Dimethylphosphaferrocene. [e] 2,5-Diphenylphosphaferrocene.

order agrees well with the known thermodynamic stabilities of these compounds[9] and reflects the decrease in metal–ligand bonding as the diagonal is traversed.

An inspection of the off-diagonal data reveals some interesting trends many of which we have previously discussed. For example column 3 contains data for $Fe(C_5H_5)$ species with a variety of other rings and shows a trend to lower q.s. values down the column. The exceptions are the two phospholyl complexes which will be referred to later. As the other ring becomes more electron deficient, the q.s. decreases. This holds true for the ferrocenes (the first group of compounds in column 3), the (η^6-arene)(η^5-cyclopentadienyl)iron(II) salts[2,3] and the (η^5-cyclohexadienyl)(η^5-cyclopentadienyl)iron(II) complexes.[1] The other complexes having five-membered rings (columns 1, 2, 4, 5 and 6) all show the same effect.

From the systematic array of data in Table 4 it is clear that the seemingly rather anomalous q.s. for $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5Me_5)]PF_6$, the magnitude of which we were previously unable to explain,[1] is, in fact, predictable. Thus ordering the column data in the same sense as the diagonal data results in a rationalisation of most of the data in the first six columns. Columns 7 and 10–13 all contain at least one six-membered aromatic ring. Here q.s. values generally increase as each column is descended (except for the last two compounds in column 7 and the phospholyl derivatives in columns 12 and 13, and these anomalies are discussed later).

We have previously explained these q.s. values by assuming that arene ligands act primarily as electron acceptors whereas the cyclopentadienyl rings are strong electron donors.[2,3] As the donor power of the cyclopentadienyl ring is increased (by methyl substitution), the arene ring can accept more e_2 back bonding from the iron resulting in a lowering of q.s.[2] The data in Table 4 show that this is not only true but very systematic.

Columns 8 and 9 contain compounds having cyclohexadienyl ligands.[1] The C_6Me_6 compounds are out of line. For example, $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6H_7)]PF_6$ has a rather small q.s. compared with $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_5H_5)]PF_6$. The salt $[Fe(\eta^5\text{-}C_6HMe_6)(\eta^6\text{-}C_6Me_6)]PF_6$ is reported to have a q.s. of 1.38 mm s^{-1} at both 78 and 293 K.[11] This result appeared to us to be highly anomalous. Accordingly we synthesised the complex as part of this work and found that, whilst the q.s. at 293 K [1.34(1) mm s^{-1}] was reasonably close to the value quoted above, our value at 78 K was considerably higher at 1.67 mm s^{-1}. The q.s. is therefore temperature dependent. Such behaviour is still relatively rare in iron sandwich compounds. We cannot as yet identify the cause of this behaviour though we think it unlikely to be due to tumbling, since the appearance of the Mössbauer spectra (Fig. 1) does not fit in terms of the known kinds of motion. One possibility is that it is due to a change in the asymmetry parameter (η). To account for the size of the observed q.s. change, η would have to vary from 1 to 0 between 78 and 293 K which would seem unlikely. The reason for the somewhat anomalous data for the cyclohexadienyl complexes probably lies in the asymmetric nature of the ligand. This causes a marked change in bonding and the relative population of the e_1 and e_2 molecular orbitals. We have recently addressed this problem using both ^{57}Fe Mössbauer and ^{13}C NMR spectroscopies.[1] The phosphaferrocenes are also anomalous, probably for the same reason, since it is known that the presence of a phosphorus atom in the ring greatly modifies the bonding of these sandwich compounds.[12,13]

Finally, we note that bis(pentadienyl)iron(II)[9] has a q.s. of 1.40(2) mm s^{-1} which, according to our table, classifies pentadienyl as a weak ligand, and is compatible with the known instability of this and similar complexes.

Experimental

(η^6-Arene)(η^5-cyclopentadienyl)iron(II)hexafluorophosphate salts were prepared by the standard method described by Sutherland and co-workers[14] and were characterised by ^1H and ^{13}C NMR spectroscopy. The benzoyl substituted complexes (series c) were obtained by $AlCl_3$ catalysed ligand exchange of benzoylferrocene with the required arene.[15] The members of series b were similarly prepared from 1,1′-dimethylferrocene. The hexamethylcyclohexadienyl complex $[Fe(\eta^5\text{-}C_6HMe_6)(\eta^6\text{-}C_6Me_6)]PF_6$ was made according to the method of Astruc and Dabard[15] by treating $[Fe(\eta^6\text{-}C_6Me_6)_2][PF_6]_2$ with $NaBH_4$ in tetrahydrofuran at 0 °C.

Mössbauer spectra were obtained and fitted as previously described.[16]

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