Studies of the Bonding in Iron(II) Cyclopentadienyl and Arene Sandwich Compounds. Part 2.[1] Correlations and Interpretations of Carbon-13 and Iron-57 Nuclear Magnetic Resonance and Iron-57 Mössbauer Data

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Carbon-13 NMR data for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4X)]$ and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_5X)]^+$ and ^{57}Fe NMR data for neutral substituted ferrocenes, ferrocenyl carbenium ions and ferrocenophanes have been analysed and correlations between these data sets and those of the ^{57}Fe Mössbauer quadrupole splitting (q.s.) are discussed on the basis of concepts put forward previously. For substituted neutral ferrocenes there is a linear relationship between q.s. and chemical shift $\delta(^{57}Fe)$. For ferrocenyl carbenium ions the relationship suggests a change in structure and bonding from species like $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\overset{+}{C}Me_2)]$ to the more fulvenoid structure $[Fe(\eta\text{-}C_5H_5)(C_5H_4CH_2)]^+$. Bridged ferrocenes (ferrocenophanes) show effects which are associated with ring tilting.

In our recent proposals[1] concerning bonding in the iron sandwich compounds our arguments, based on quadrupole splitting in ^{57}Fe Mössbauer spectra, centred on the important role of back bonding from metal to arene rings which in turn is controlled by the relative populations of the e_1 and e_2 orbitals. Essentially it was suggested that in $[Fe(\eta\text{-arene})_2]^{2+}$ complexes there is competition between the arene rings for the limited availability of metal e_2 electron density; in $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$ complexes the extent of back bonding to the arene is greatly enhanced by the predominantly donor nature of the $\eta\text{-}C_5H_5$ ligand. In this paper we extend this study to include ^{57}Fe NMR data for substituted neutral ferrocenes, ferrocenyl carbenium ions and ferrocenophanes and ^{13}C NMR data for the five- and six-membered ring sandwich compounds.

Results and Discussion

^{13}C NMR Data.—Evidence supporting charge transfer and back bonding comes from a consideration of the ^{13}C NMR chemical shifts (δ) of the parent compounds of classes (*a*), $[Fe(\eta\text{-}C_5H_5)_2]$, (*b*), $[Fe(\eta\text{-arene})_2]^{2+}$ and (*c*), $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$. In such complexes, ring-current anisotropic effects are very much attenuated[2] and are probably negligible. The shifts for ferrocene[3] and bis(η-benzene)iron(II) hexafluorophosphate[4] are 67.9 and 93.4 ppm, respectively. For $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$, the $\eta\text{-}C_5H_5$ resonance is at 75.6 ppm whereas that of the benzene ring is found at 82.3 ppm.[5] It is generally accepted that in a closely related series of arene derivatives the dominant influence on $\delta(^{13}C)$ is that of charge density. The above data show that for the class (*c*) derivative the benzene carbons are about 11 ppm *more* shielded than those in the class (*b*) analogue whereas the $\eta\text{-}C_5H_5$ carbons are about 8 ppm *less* shielded than that in ferrocene [class (*a*)]. If this were due to a simple charge transfer from $\eta\text{-}C_5H_5$ to the arene ring the increase in the arene carbon shielding should be at most $\frac{5}{6}$ of the decrease in $\eta\text{-}C_5H_5$ carbon shielding. The observed figures suggest that there is an additional transfer of electrons directly from iron to the benzene carbons.

Thus the increase in charge density in the arene ring in class (*c*) compounds is in keeping with greater back bonding from the iron which is stimulated by donation from the $\eta\text{-}C_5H_5$ ring.

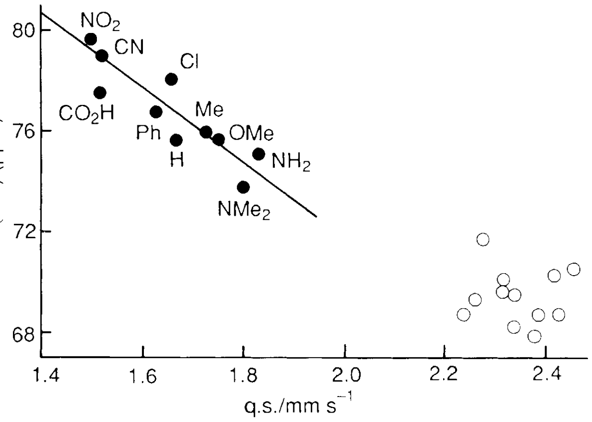

Fig. 1 Plot of $\delta(^{13}C)$ for unsubstituted C_5 rings *vs.* ^{57}Fe Mössbauer quadrupole splitting. ● $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_5X)]^+$; ○ $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4X)]$

^{57}Fe NMR Data.—The above concepts are reinforced when a comparison is made of ^{57}Fe NMR chemical shifts, $\delta(^{57}Fe)$, for typical members of classes (*a*)–(*c*). The shifts relative to ferrocene (0.0 ppm) are 32.9 ppm[6] for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ and 2107.8 ppm for $[Fe(\eta\text{-}C_6H_6)_2][PF_6]_2$. Thus, the effective densities at iron in $[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ are very similar to each other but the very large downfield shift in $[Fe(\eta\text{-}C_6H_6)_2]^{2+}$ is commensurate with a much lower electron density at iron. These facts suggest strongly that in $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ the C_5 ring donates a large amount of electron density (even more than each ring in ferrocene does), some of which is transmitted to the arene ring.

Correlation of ^{13}C and ^{57}Fe NMR with ^{57}Fe Quadrupole Splitting Values.—Greater insight into the effects of substitution can be gained from plots of NMR chemical shifts against ^{57}Fe Mössbauer quadrupole splitting (q.s.) values.[7,8] The data are given in Table 1[9–20] for compounds **1**–**19**. Fig. 1 shows such plots of ^{13}C chemical shifts for the unsubstituted $\eta\text{-}C_5H_5$ ring in ferrocenes[3,21] and in $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_5X)]^+$ derivatives.

Table 1 NMR chemical shifts and quadrupole splitting data (mm s^{-1}) for neutral ferrocenyl compounds, ferrocenyl cations and ferrocenophanes

	1,1′ Substituents				
Compound	R	R′	$\delta(^{57}Fe)$	Solvent	q.s.[a]
Neutral substituted ferrocenes					
1	Br	H	-14.4^b	$CDCl_3$	2.46^c
2	I	H	-20.5^d	CH_2Cl_2	2.44^c
3	Cl	H	-1.2^b	$CDCl_3$	2.42^c
4	Et	Et	69.2^d	$CDCl_3$	2.42
5	CH_2OH	H	11.3^d	CS_2	2.40^e
			-1.2^b	$CDCl_3$	
6	Me	H	44.5^d	CS_2	2.39
			43.6^b	$CDCl_3$	
7	CH(OH)Ph	H	-22.9^d	CH_2Cl_2	2.39^f
8	H	H	0.0	$CDCl_3$	2.37
9	CH(OH)Me	H	7^b	$CDCl_3$	2.36
			0^d	CH_2Cl_2	
10	CN	H	121.3^d	$CDCl_3$	2.32
			113.1^d	CS_2	
11	Ph	H	188.1^d	$CDCl_3$	2.30^g
			188.2^b	$CDCl_3$	
12	CO_2Me	H	194.7^b	$CDCl_3$	2.30
13	COBu	H	257.3^d	CS_2	2.28^h
14	$CO[(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)Fe]$	H	238.5^d	CH_2Cl_2	2.28^i
15	COMe	H	234.2^b	$CDCl_3$	2.26
			215.5^d	CH_2Cl_2	
16	COPh	H	289.1^b	$CDCl_3$	2.26
			269.0^d	CH_2Cl_2	
17	CHO	H	232.5^b	$CDCl_3$	2.24
			217.2^d	CS_2	
			210.0^d	CH_2Cl_2	
18	CO_2Me	CO_2Me	379.8^b	$CDCl_3$	2.16^j
19	COMe	COMe	436.9^b	$CDCl_3$	2.15
			425.6^d	CH_2Cl_2	
Ferrocenyl carbenium ions					
20	$[Fe(\eta\text{-}C_5H_5)_2H]^+$		-1099^d	$BF_3{\cdot}H_2O$	$2.72^{k,l}$
21	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CH_2)]^{+i}$		-523.5^d	H_2SO_4	2.70^f
					2.67^a
22	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CHMe)]^+$		-219.2^d	H_2SO_4	2.61^e
23	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CHPh)]^+$		221.0^d	H_2SO_4	2.55^e
24	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2)]^+$		288.5^d	H_2SO_4	2.40^f
25	$[\{Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)\}_2CH]^+$		712.8^d	CH_2Cl_2	2.13^k
1–1′ Bridged ferrocenes					
	Bridge				
26	$\overset{+}{C}HCH_2CH_2$		-161.0^d	H_2SO_4	2.53^m
27	$CH_2CH_2CH_2CH_2$		-56.5^n	CF_3CO_2H	2.35^o
28	$CH_2CH_2CH_2$		-275.5^d	CH_2Cl_2	2.29^m
			-259.3^b	$CDCl_3$	
29	$CH(OH)CH_2CH_2$		-227.2^d	CH_2Cl_2	2.28^m
30	$COCH_2CH_2$		123.0^d	CH_2Cl_2	2.22^m
			148.1^b	$CDCl_3$	

[a] Ref. 7 unless otherwise stated. [b] Ref. 9 and refs. therein. [c] Ref. 10. [d] Ref. 11 and refs. therein. [e] Ref. 12. [f] Ref. 13. [g] Ref. 14. [h] ref. 15. [i] Ref. 16. [j] The ^{57}Fe Mössbauer datum for compound **18** is not known so the value[7] for R = R′ = CO_2H was taken. [k] Mössbauer and NMR on different anions. [l] Ref. 17. [m] Ref. 18. [n] Ref. 19. [o] Ref. 20.

The ferrocenes do not show any particular correlation, indicating that the effect of substituting one ring is not transmitted to the other ring. For the substituted arene compounds, however, there is a reasonably good linear correlation between $\delta(\eta\text{-}C_5H_5)$ and the q.s. This is entirely consistent with the behaviour of the arenes as electron-acceptor ligands, this behaviour being enhanced by the donor property of the C_5 ring. As the arene becomes more strongly electron withdrawing, taking electrons from the iron e_2 orbitals and decreasing the q.s., so also does the C_5 ring donate more electron density into the metal e_1 orbitals, its carbon atoms becoming relatively deshielded. The $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$ derivatives show much greater sensitivity to substitution of both q.s. and ^{13}C NMR values than do the ferrocenes.

Fig. 2 shows a plot of iron-57 NMR shifts *vs.* iron-57 Mössbauer q.s. for the neutral ferrocenes. Data for the ferrocenophanes are also included. A good linear correlation is observed [Fig 2(*a*)] with acceptor substituents appearing at low q.s. values and downfield shift values. The downfield shifts correspond to loss of electron density on the iron atom. It is noteworthy that the effects of neutral substituents, as detected by NMR shifts, are seen at the iron nucleus, but not at the carbon atoms of the unsubstituted $\eta\text{-}C_5H_5$ ring, adding support to the discussion in the previous paragraph.

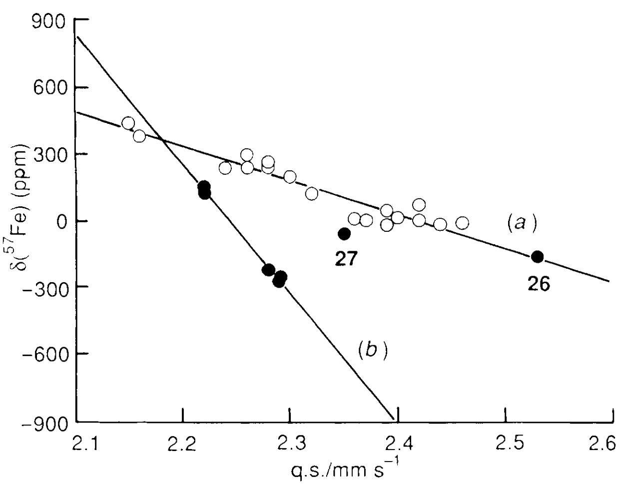

Fig. 2 Plot of $\delta(^{57}Fe)$ *vs.* ^{57}Fe Mössbauer quadrupole splitting for (*a*) neutral substituted ferrocenes and (*b*) ferrocenophanes

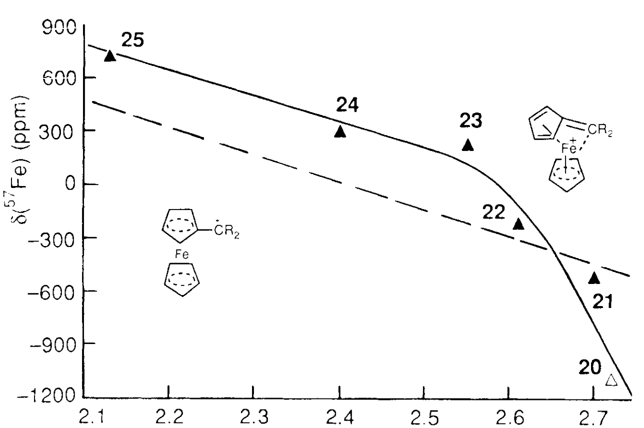

Fig. 3 Plot of $\delta(^{57}Fe)$ *vs.* ^{57}Fe Mössbauer quadrupole splitting for carbenium ions (▲) and protonated ferrocene ion (△). The dashed line is the correlation line, (*a*), for neutral ferrocenes transposed from Fig. 2

Ferrocenyl cations. Fig. 3 includes points for some ferrocenyl cations and also the protonated ferrocene ion, $[Fe(\eta-C_5H_5)_2H]^+$ (compounds **20**–**25** in Table 1). In general terms, separate interpretations of the q.s. values and of the ^{57}Fe NMR shifts are extremely difficult but we demonstrate that the correlation of the two properties, taken in conjunction with the data previously discussed for neutral ferrocenes, is very revealing.

The ions $[Fe(\eta-C_5H_5)(\eta-C_5H_4CHPh)]^+$ $[Fe(\eta-C_5H_5)(\eta-C_5H_4CMe_2)]^+$ and $[\{Fe(\eta-C_5H_5)(\eta-C_5H_4)\}_2CH]^+$, (compounds **23**–**25**) lie on a line parallel to that of the ferrocenes, but with ^{57}Fe NMR shifts about 300 ppm downfield. We associate this shift with the cationic nature of the species; the substituent trend is otherwise very similar to that of the ferrocenes. However, the ions $[Fe(\eta-C_5H_5)(\eta-C_5H_4CH_2)]^+$ and $[Fe(\eta-C_5H_5)(\eta-C_5H_4CHMe)]^+$ (compounds **21** and **22**) show a marked deviation from the trend, giving rise to a rather sudden upfield ^{57}Fe NMR shift as the q.s. continues to increase. The protonated ferrocene ion **20** lies on an extrapolation of the new trend.

The structure of protonated ferrocene involves direct bonding of hydrogen to the iron atom and the two $\eta-C_5H_5$ rings are tilted to make room for the hydrogen. Clearly this structural change from the normal situation, where the two rings are parallel, must involve dramatic changes in the bonding; it is no longer possible to interpret changes purely in terms of e_2 and e_1 iron orbitals. The detailed orbital reorganisation[22] is beyond the scope of this paper, but it seems clear that it is manifested in a rather large q.s. and an upfield shift in the ^{57}Fe NMR. If this hypothesis is accepted, the plot in Fig. 3 immediately suggests that the ion $[Fe(\eta-C_5H_5)(\eta-C_5H_4CH_2)]^+$ has some features in common with protonated ferrocene. A tentative suggestion is that the iron atom interacts *directly* with the exocyclic carbon atom and that the C_5 rings may be tilted slightly. In other words, the substituted ring now has a structure markedly different from that in, say, $[Fe(\eta-C_5H_5)(\eta-C_5H_4CMe_2)]^+$ and could be represented as a distorted fulvene structure. A similar, but lesser, structural change is indicated for $[Fe(\eta-C_5H_5)(\eta-C_5H_4CHMe)]^+$.

Possible reasons for such structural changes can be sought in the means by which a carbenium ion may be stabilised. Usually it is necessary for the positive charge formally located on the central carbon atom to be delocalised on to the electron-donating substituents such as methyl groups, or by conjugation on to aromatic groups, the central carbon atom having planar trigonal symmetry. Thus in $[Fe(\eta-C_5H_5)(\eta-C_5H_4CMe_2)]^+$ it is entirely reasonable for the positive charge to be stabilised by the two methyl groups, with some help from the C_5 ring of the attached ferrocene. From this standpoint the CMe_2 group acts on the ferrocene like an almost normal, mildly electron-withdrawing substituent, as does CHPh. In $[\{Fe(\eta-C_5H_5)(\eta-C_5H_4)\}_2CH]^+$, carbenium-ion stabilisation is shared between two ferrocenyl groups; the position of this compound in Fig. 3 suggests this to be possible without involving direct interaction with iron atoms.

At the other end of the plot the CH_2 substituent has no intrinsic means of delocalising the positive charge and the data indicate that simple conjugation with the C_5 ring is not sufficient; however, by bending the CH_2 group towards the iron atom the empty p orbital on the carbon can interact with several occupied metal orbitals, probably most efficiently with one lobe of $d_{x^2-y^2}$, the central belt of d_{z^2}, or one lobe of d_{zx}. Such an interaction would automatically disrupt the normal bonding scheme of the ferrocene system, as suggested above. The CHMe substituent can achieve limited stabilisation from its single methyl group, but may also involve a weaker direct interaction between the iron atom and the CHMe central carbon atom.

The general interpretation of the data for the carbenium ions is that where the carbon atom carries substituents which can stabilise a positive charge (Me, Ph, or a second ferrocenyl) the carbon is trigonal planar and behaves almost like a conventional neutral substituent on one C_5 ring; there is a 'field effect' which shifts the ^{57}Fe NMR signal about 300 ppm downfield. As the substituents on the positive carbon become less able to sustain the charge, the exocyclic carbon atom attracts electron density directly from the iron atom, with an accompanying structural change. The effect is manifested particularly by an upfield shift of the ^{57}Fe NMR signal and also by an increased q.s. (an ordinary acceptor group would decrease the q.s.).

Ferrocenophanes. Of the five bridged species considered three are neutral [3]ferrocenophanes (**28**–**30**), one a [3]ferrocenophanyl cation (**26**) and one a [4]ferrocenophane (**27**). There are two known crystal structures[23,24] of [3]ferrocenophanes including **30**. In both, the carbon bridges pull the ring edges together giving a ring tilt of about 10°. Thus it is reasonable to assume that structures **28**–**30** all have similar ring tilts. Both experimental data[25] and calculations[20] have shown there to be a decrease in q.s. with increasing number of [3] bridges, due to changes in both valence and lattice-overlap contributions to the field gradients. However, ring tilt was not invoked as being responsible for these reductions and, in the calculations, a non-tilting model was used. Justification for such a model came from the fact that a ring tilt of 6° on ferrocene caused a negligible effect on the calculated q.s. as 'the contribution to ΔE_Q of carbons closer to the iron is balanced by different contributions of more remote carbons'.[20] This implies that the $\eta-C_5H_5$ rings were tilted about their centres. While the excellent agreement between calculated and experimental data suggests that the actual model used has much to commend it, this particular type of tilt is unlikely to appear in a mono [3]-bridged ferrocenyl derivative and the tilt angles are also greater than 6° (see above).

From a study of ferrocene and ferrocenium derivatives, including **28**, Duggan and Hendrickson[26] have stated there to be an increase in ($d_{x^2-y^2}$, d_{xy})-ring overlap with ring tilt. Such an increase would result in a decrease in q.s., which is observed. It would be convenient to propose this to be the explanation, however we feel it is not the complete picture.

There are therefore two somewhat different interpretations for the decrease in q.s. observed in the neutral [3]ferrocenophanes.

The [4]ferrocenophane **27** has a q.s. only slightly different from that of ferrocene and its ^{57}Fe NMR is slightly upfield. These data place the substance near to the neutral ferrocene correlation line and this is in keeping with the fact that it has parallel C_5 rings and behaves in a normal way with a small substitution effect.[27]

The [3]ferrocenophanes do not show correlation with the other neutral ferrocenes, and their ^{57}Fe NMR shifts are noticeably upfield and much more sensitive to substitution than are those of the neutral ferrocenes. The data are sparse but these materials appear to create a new correlation line of much greater slope than that of the neutral ferrocenes. This slope [Fig. 2(*b*)] is of the same order as that at the right-hand end of the correlation for the ferrocenyl cations; the distinguishing feature is in the lower q.s. values of the [3]ferrocenophanes rather than in the ^{57}Fe NMR shifts.

Although the data cannot distinguish the two interpreations of low q.s. values mentioned above, we feel that no satisfactory interpretation can be achieved which neglects the effects of ring tilting.

The last compound to discuss (**26**) is both a carbenium ion and a [3]ferrocenophane. The exact position of the trigonal carbon atom has not been established, the proton NMR spectrum being too poorly resolved[18] to allow distinction between the α- and β-carbons of the bridge. However, protonation of dehydro[3]ferrocenophane, which has a double bond between the α- and β-carbons, produces a different cation from the one discussed here, as indicated by its lower q.s. of 2.46 mm s^{-1} and its ^{1}H NMR spectrum, which is consistent with the trigonal carbon atom being in the β position.[18] Compound **26** is produced by protonation and removal of water from the α-substituted alcohol **29**, and is therefore most likely to contain the α-carbon in a trigonal environment.*

Model building shows that there is considerable strain in compound **26**, which may be partly relieved by a combination of ring tilt, staggering of rings and twisting of the bond between the trigonal α-carbon and the C_5 ring. This twisting reduces the conjugation between the ring and the out-of-plane p orbital on the α-carbon, and it becomes difficult to see how the positive charge can be stabilised. The actual structure remains an interesting unknown. It is therefore surprising to find its position in the ^{57}Fe NMR *vs.* q.s. plot to be on a small extrapolation of the line for neutral ferrocenes, behaving as if it were substituted by one or two strong *donor* groups. This position may be accidental for it also lies between the neutral [3]ferrocenophane line and the region where the cations **20**–**22** lie; it is perhaps not so surprising and would be consistent with our combined comments about ring tilt and the possibility of direct interaction of iron with the carbenium group when this group does not have other means of stabilisation.

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* There is no evidence for the commonly encountered α,β hydride shifts in this carbenium ion which would lead to what is presumably the more stable β cation. Hydride shifts may be inhibited by the formation of tight ion pairs, a phenomenon which is characteristic of solvent trifluoroacetic acid. The q.s. value of 2.46 mm s^{-1} suggests very weak interaction with iron-based orbitals whereas in **26** (q.s. 2.53 mm s^{-1}) the empty p orbital is better placed for such an interaction, albeit weak. Iron-57 NMR data are not available for the β cation.