Studies of the Bonding in Iron(II) Cyclopentadienyl and Arene Sandwich Compounds. Part 1. An Interpretation of the Iron-57 Mössbauer Data

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A qualitative approach to the understanding of substituent effects in iron(II) sandwich compounds containing five- and six-membered rings is described. In particular, this approach highlights the differences between the symmetric, bis(arene)- and bis(cyclopentadienyl)-, and the asymmetric, mixed arene–cyclopentadienyl-iron(II) complexes. The results are discussed with respect to their chemical and physical properties and ^{57}Fe Mössbauer spectra.

Three main classes of iron sandwich compound have received attention since the discovery of ferrocene.[1] These are (*a*) ferrocene $[Fe(\eta-C_5H_5)_2]$, and its substituted cyclopentadienyl analogues, (*b*) the bis(arene)iron(II) salts $[Fe(arene)_2]^{2+}$, and (*c*) the mixed arene–cyclopentadienyl derivatives $[Fe(\eta-C_5H_5)(arene)]^+$.

A primary driving force for the many ^{57}Fe Mössbauer spectroscopic studies of these compounds has been the need to increase the understanding of the bonding particularly in the case of the ferrocenes. From studies of ferrocene and its substituted analogues[2–10] [class (*a*)] it is now well established that, although the effects of substitution are relatively small, they are systematic.[9] Electron-donating substituents cause an increase in the quadrupole splitting (q.s.) relative to ferrocene (q.s. ≈ 2.37 mm s^{-1}), whereas electron-withdrawing substituents cause a decrease in q.s.[9,10] It has been shown by magnetic Mössbauer measurements that the quadrupole coupling constants for $[Fe(\eta-C_5H_5)_2]$ and $[Fe(\eta-C_5H_5)(\eta-C_6H_6)]^+$ are positive.[3,11] We assume that coupling constants of all the sandwich compounds are positive. Because of residual doubts about the signs of field gradients, arising from opposing definitions in the literature[3,12] and from unknown shielding and antishielding effects, we prefer to keep discussions of quadrupole splittings in terms of the quadrupole coupling constant; as this is positive and of axial symmetry, for sandwich compounds it is synonymous with quadrupole splitting. The isomer shifts (i.s.) (0.52 mm s^{-1}) are relatively invariant and have been treated[10] as constant in more than one case.*

Mössbauer studies of class (*b*) complexes are much less abundant.[15,16] However we have recently reported[17] on this class of compound and found that we were unable to prepare complexes with arenes bearing electron-withdrawing substituents. This class showed similar substituent effects to those of the class (*a*) compounds although the q.s. values were in a lower range {q.s. = 1.90 mm s^{-1} for $[Fe(\eta-C_6H_6)_2][PF_6]_2$}. One important difference from compounds in class (*a*) is the effect of substitution on the i.s., which becomes more positive with increased methylation.

Several groups have reported Mössbauer parameters for class (*c*) compounds.[11,15,18–23] These compounds exhibit the smallest q.s. {1.68 mm s^{-1} for $[Fe(\eta-C_5H_5)(\eta-C_6H_6)]^+$} of the three classes; also substituent effects change with the nature of the ring, being opposite in sign for the cyclopentadienyl ring compared to the arene ring and to those in compounds of class (*a*) and (*b*). However, attempts to rationalise these facts have been few and those that have appeared are not convincing.[15,18]

The purpose of this paper is to present an overall qualitative understanding of the bonding in these three classes of compound that gives insight into their chemistry and physical properties, particularly ^{13}C n.m.r. spectra, which will be discussed elsewhere.

Table. ^{57}Fe Mössbauer spectroscopic data at 80 K for principal and selected compounds of classes (*a*), (*b*), and (*c*)[a]

Compound	Class	i.s.[b]	q.s.[b]	Ref.
(**1**) $[Fe(\eta-C_5H_5)_2]$	(*a*)	0.52	2.37	8
(**2**) $[Fe(\eta-C_5H_5)(\eta-C_5H_4Me)]$		0.53	2.39	4
(**3**) $[Fe(\eta-C_5Me_5)_2]$		0.53	2.50	7
(**4**) $[Fe(\eta-C_5H_4CN)_2]$		0.55	2.29	4
(**5**) $[Fe(\eta-C_5H_4COMe)_2]$		0.52	2.15	4
(**6**) $[Fe(\eta-C_6H_6)_2]^{2+}$	(*b*)	0.53	1.90	15
(**7**) $[Fe(\eta-C_6H_5Me)_2]^{2+}$		0.53	1.93	15
(**8**) $[Fe(\eta-C_6H_3Me_3\text{-}2,4,6)_2]^{2+}$		0.56	2.01	15
(**9**) $[Fe(\eta-C_6Me_6)_2]^{2+}$		0.64	2.10	15
(**10**) $[Fe(\eta-C_5H_5)(\eta-C_6H_6)]^+$	(*c*)	0.52	1.68	21
(**11**) $[Fe(\eta-C_5H_5)(\eta-C_6Me_6)]^+$		0.53	2.08	21
(**12**) $[Fe(\eta-C_5H_5)(\eta-C_6H_5CN)]^+$		0.53	1.51	21
(**13**) $[Fe(\eta-C_5H_5)(\eta-C_6H_5NO_2)]^+$		0.53	1.50	21
(**14**) $[Fe(\eta-C_5H_4NH_2)(\eta-C_6H_6)]^+$		0.58	1.58	21
(**15**) $[Fe(\eta-C_5H_4OMe)(\eta-C_6H_6)]^+$		0.52	1.65	21
(**16**) $[Fe(\eta-C_5Me_5)(\eta-C_6H_6)]^{+\,c}$		0.55	1.40	19
(**17**) $[Fe(\eta-C_5Me_5)(\eta-C_6Me_6)]^{+\,c}$		0.58	1.80	19

[a] For all class (*b*) and (*c*) compounds the anion is PF_6^- except where indicated. [b] Isomer shifts in mm s^{-1} (± 0.01) are referred to natural iron foil at 298 K as zero shift, quadrupole shift in mm s^{-1} (± 0.01). [c] Anion unknown but probably PF_6^-.

Discussion

Typical Mössbauer data for the principal members of each class of compound (*a*)—(*c*) are presented in the Table.

There have been a great many studies and calculations of the bonding in ferrocene and sandwich compounds in general,[22,24–30] and the salient points are summarised below.

The important consequences of the bonding, as far as the ^{57}Fe Mössbauer spectra are concerned, are the contributions of the Fe 3*d* and 4*p* orbitals to the quadrupole splitting and the effects that occur when these contributions are modified by substitution, and also by band formation in the solid state.

Trautwein *et al.*[5] have reported that the Fe 4*p* orbitals, particularly the $4p_z$, contribute to quadrupole splitting. We follow suggestions by other workers[24–30] that axial orbitals,

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* Bridged ferrocenes[13] and metal complexes of 1,1′-bis(diphenylphosphino)ferrocene[14] show correlated changes in both q.s. and i.s. and in these compounds constancy of the i.s. is invalid.

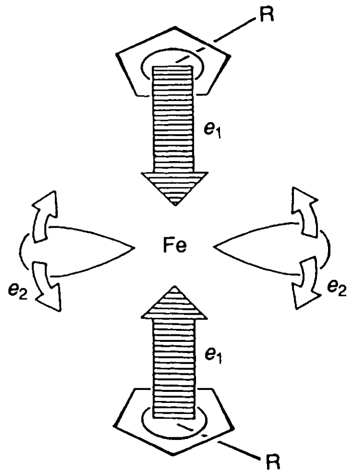

Figure 1. Schematic diagram showing bonding in compounds of class (*a*). When R is electron releasing the e_1 donation will be enhanced lessening the need for e_2 back bonding. Hence q.s. increases. When R is electron withdrawing the e_2 donation will try to compensate for the necessarily reduced e_1 donation. Hence q.s. decreases

$3d_{z^2}$ and $4p_z$, are essentially non-bonding in these systems because their energies are high relative to the ligand orbitals of axial symmetry; it follows that their populations are constant and that their negative contributions to q.s. are invariant to ligand substitution.

The $4p_x$ and $4p_y$ orbitals of Fe are of e_1 symmetry. These are also considered to give a constant (probably zero) contribution to the quadrupole splitting.

The remaining asymmetric orbitals are the two sets of Fe $3d$ orbitals, of symmetry e_1 and e_2. The e_2 electron density gives a positive contribution to q.s. and e_1 a negative contribution of magnitude one half that of the e_2 set (per electron).[31] The contribution of these orbitals to q.s. may be written as in equation (1) where p_2 and p_1 represent the electron populations

$$\text{q.s.} \propto (2p_2 - p_1) \qquad (1)$$

of e_2 and e_1 orbitals respectively. Both these populations are sensitive to ligand substitution, to the type of ring, and to interactions between rings of different types, but q.s. is twice as sensitive to changes of p_2 as it is to changes of p_1.

Hence the difference in q.s., Δ(q.s.), of a given compound relative to the unsubstituted parent {$[Fe(\eta\text{-}C_5H_5)_2]$, $[Fe(\eta\text{-}C_6H_6)_2]^{2+}$, and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ for classes (*a*), (*b*), and (*c*) respectively} can be approximated to the changes in p_1 and p_2.

Generally then changes in q.s. will be controlled by changes in the population of the e_2 and e_1 orbitals (*i.e.* changes in the back bonding and forward donation respectively). Therefore Δ(q.s.) can be expressed in most cases by equation (2), where $p_{2\text{A}}$ and

$$\Delta(\text{q.s.}) \propto [2(p_{2\text{A}} - p_{2\text{B}}) - (p_{1\text{A}} - p_{1\text{B}})] \qquad (2)$$

$p_{2\text{B}}$ are the electronic populations of the e_2 orbitals of the given compound and of the parent of the class concerned, with similar definition of $p_{1\text{A}}$ and $p_{1\text{B}}$.

Figure 1 shows schematically the influence of substituents on the bonding for compounds in class (*a*). The main component in the bonding is the e_1 ring-to-iron donation. As this is large the e_2 back bonding from the iron to the rings is small and hence a large q.s. is observed as the p_2 component of equation (1) is fairly large. As the substituent(s) is varied [Table, compounds (**1**)—(**5**)] the e_1 donation will alter and this as a consequence will change the demand for back bonding. Donor substituents, by increasing p_1, would at first appear to decrease q.s. However the two rings are in competition with each other and the extra donation into e_1 orbitals is to some extent restrained. It appears to be more significant that the reduced acceptor property of the ligand with donor substituents results in an increase in p_2, to which q.s. is twice as sensitive. The increase of q.s. with donor substituents is then primarily due to a reduction of back bonding. This picture is a general one for both class (*a*) and (*b*) compounds.

In class (*b*) [Table, compounds (**6**)—(**9**)] the overall donor–acceptor balance is different. Donation into e_1 orbitals is smaller (p_1 smaller) and back donation from e_2 orbitals greater (p_2 smaller); thus $(2p_2 - p_1)$ should be smaller than for compounds in class (*a*). Another reason, to be discussed elsewhere, is that the larger arene rings give rise to inherently smaller field gradients than do cyclopentadienyl rings [Table, compounds (**6**)—(**9**)].

The class (*c*) compounds show the lowest q.s. values of all [see Table, compounds (**10**)—(**17**)]. This in itself is unusual as from both molecular-orbital calculations[27] and electronic absorption spectra[15] their behaviour is expected to be intermediate between class (*a*) and (*b*) compounds. In addition to the generally low q.s., the effect of substituents on the value of q.s. depends on whether the substituted ring is a cyclopentadienyl or an arene ring. Electron-releasing groups increase the q.s. when present on the arene ring and decrease it when on the cyclopentadienyl ring. The converse is true for electron-withdrawing groups.

Gol'danskii and co-workers[18] attributed these differences to the differing nature of the iron-to-ring bonding. They argued that the greater interaction (*i.e.* back bonding) of the e_2 orbitals of the metal in the case of the arene ring causes substituents to affect these orbitals more strongly. In the bonding to the cyclopentadienyl ring, however, the e_2 orbitals being more localised on the iron atom (*i.e.* less back bonding) will be influenced to a smaller extent and hence substituents will affect the iron *via* the e_1 molecular orbitals. In the light of our studies on compounds in class (*b*),[17] which show similar effects to those of class (*a*), this explanation becomes inconsistent.

A more reasonable explanation can be offered by considering the *intramolecular* charge donor–acceptor system of class (*c*) compounds. Belchenko *et al.*[30] reported calculations suggesting that charge density in the $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ cation resides 65% on the benzene ring, 11% on the cyclopentadienyl ring, and 24% on the iron, but unfortunately the paper did not give a complete set of orbital populations and the model chosen for the calculations treats Fe–C bond lengths to both rings as being equal which is an error.[32] However, this asymmetric charge distribution has important consequences.

Figures 2 and 3 show diagrammatically the charge redistribution due to substitution on the arene and cyclopentadienyl rings respectively. The low q.s. of the parent material $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ can be explained by the fact that the small back bonding necessary to accomplish binding of the cyclopentadienyl ring will enable the electron-deficient benzene to demand and gain more iron back bonding than it can obtain when partnered with another arene. The result is a low q.s. as the p_2 component of equation (1) becomes smaller. The fact that the lowest q.s. is not exhibited for the parent class (*b*) compound $[Fe(\eta\text{-}C_6H_6)_2]^{2+}$ is due to the demands for electron density of the iron itself. The iron cannot satisfy the demands of two arene rings for back bonding in this class of compound. This is also consistent with the inability to synthesize compounds of class (*b*) with arenes bearing electron-withdrawing substituents. A situation is at some point reached with electron withdrawal where the demands of the arene rings for back bonding are more than the iron can supply and hence these compounds are very unstable or do not form at all. Furthermore these are 2+ charged ions and not much electron withdrawal from them is possible.

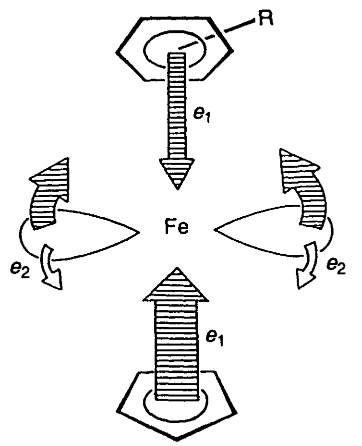

Figure 2. Schematic diagram showing bonding in compounds of class (*c*) upon substitution on the arene ring. The resultant effects are similar to those in compounds of class (*a*) and (*b*)

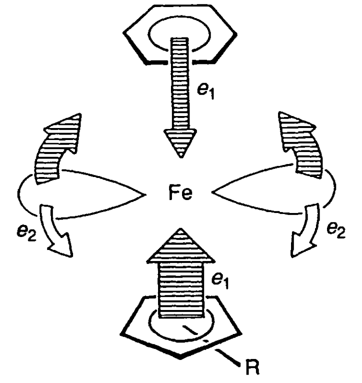

Figure 3. Schematic diagram showing bonding in compounds of class (*c*) upon substitution of the cyclopentadienyl ring. When R is electron releasing the e_2 back bonding to the arene ring will increase. Hence the q.s. decreases. When R is electron withdrawing the e_2 back bonding to the arene ring is inhibited by the reduced e_1 donation from the cyclopentadienyl ring and hence the q.s. increases

Destabilisation by electron withdrawal appears to be a general phenomenon for the three classes of complex. Such a case has recently been highlighted for compounds in class (*a*) in work on various metal derivatives of 1,1′-bis(diphenylphosphino)ferrocene and other ferrocenyl phosphines.[33,34] Corain *et al.*[33] reported the decomposition of 1,1′-bis(diphenylphosphino)ferrocene complexes on oxidation to the corresponding ferrocenium complexes, with only the platinum and palladium complexes being moderately stable, although pure materials could not be isolated. The above argument provides an explanation as to why such ferrocenium complexes are unstable and difficult to isolate, as oxidation corresponds to an extreme form of electron withdrawal.

When electron-donating groups are present on the cyclopentadienyl ring in compounds of class (*c*) (Figure 3) a decrease in the q.s. is seen. The effects of substitution of class (*c*) materials are striking in that substitution of the cyclopentadienyl ring has the reverse effect on q.s. (donors cause reduction of q.s.) whereas arene substituents behave normally. This apparent anomaly confirms the complementary nature of the two ring systems, *i.e.* that cyclopentadienyl rings are primarily donors and arene rings have a much higher acceptor capacity. Thus when a donor on a cyclopentadienyl ring enhances donation to the metal, thereby increasing p_1, charge accumulation at iron is readily dispersed by enhanced back donation from e_2 orbitals to the arene ring (see Figure 3). Thus p_2 is readily reduced and $(2p_2 - p_1)$ clearly becomes smaller. Donor substitution on the arene ring (Figure 2) opposes this cyclopentadienyl-to-arene electron flow and therefore increases the q.s. in the 'normal' way.

The asymmetric charge distribution detected in this way is manifested in other derivatives of the $[Fe(\eta-C_5H_5)(\eta-C_6H_6)]^+$ ion, reported by Lequan *et al.*[35] These studies are based on $[Fe(\eta-C_5H_5)(arene)][(tcnq)_2]$ (arene = C_6Me_6 or $C_6H_3Me_3$-2,4,6, tcnq = tetracyanoquinodimethane) which have pseudo-metallic conducting properties. The salt $[Fe(\eta-C_5H_5)(\eta-C_6Me_6)][(tcnq)_2]$ consists of monomolecular anionic and cationic stacks. From the above explanation it is easy to see why this material can form stacks and may contribute to conducting properties.

Conclusion

This idea of charge redistribution enables the influence of substituents in the three classes of iron sandwich compounds to be understood. Qualitative rationalisation of the response of the quadrupole splitting to changes of ring type and to substituents is possible in terms of changes in back bonding alone; however, this is partly due to the fact that the q.s. is twice as sensitive to back-bonding changes as it is to changes in e_1 (forward) bonding. We therefore think that considerations of e_1 bonding must be included in a general treatment.

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