Qualitative Interpretation of Mössbauer Data for some [1]Ferrocenophanes; Fe–Pd Dative Bonding in $[(SC_5H_4)_2FePd(PPh_3)]$ and Fe–Hg and Fe–H$^+$ Bonding in Ferrocene

Jack Silver
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ

The Mössbauer data for a number of ferrocene complexes in which the Fe is directly bonding to or interacting with an additional atom are discussed. For weak ferrocenyl Fe–X (X = Ge, Si, P, or Pd) interactions in [1]ferrocenophanes or 1,2,3-trithia[3]ferrocenophanes quadrupole splittings (Δ) around 0.4 mm s^{-1} smaller than that of ferrocene are observed. These are explained by the interactions of the ferrocene electrons with the X atom. Exalted Δ values relative to ferrocene are found for ferrocenyl Fe (and substituted ferrocenophanes) bonded to mercury, and for ferrocenyl Fe bonded to H$^+$. These are explained by ring tilt altering the molecular orbital bonding scheme relative to ferrocene, causing the $3d_{z^2}$ orbital to partake in the bonding. This orbital makes a negative contribution to Δ so that if electron density is removed from it then Δ will increase. Compounds of Pd^{II} and Pt^{II} trichalcogeno[*n*]ferrocenophanes (*n* = 7 or 9) which show little variation in quadrupole splitting from ferrocene (but do differ by having higher isomer shifts) are also explained as having metal–iron bonds.

Recently the Mössbauer spectroscopic data for some cyclopentadienyl (cp) and arene iron(II) sandwich compounds provided the key to an overall qualitative rationalisation of their bonding.[1] This approach allowed an understanding of the effects of substituents on the five- and six-membered rings. It was found that backbonding from the iron to the ring orbitals was of great importance, and the Mössbauer quadrupole splitting is twice as sensitive to backbonding from the iron e_2 orbitals than it is to changes in e_1 (ring orbital donation to the iron) forward bonding.

There are now several ferrocene derivatives in which direct iron bonding or interaction (weak or strong) from the ferrocenyl iron to other atoms has been suggested.[2–9] These compounds include ferrocenophanes,[2,3] metal phosphine derivatives of 1,1′-ferrocenedithiol,[4,5] the mercury(II) chloride complex of ferrocene,[6,7] of [2]ferrocenophane,[8] and the Fe–H$^+$ bonded complexes of ferrocene.[9] The Mössbauer parameters for these complexes fall into two distinct groups and interpretation of these has caused some controversy, particularly over the questions: (1) whether or not they are significantly different to those of ferrocene itself[7,9–12] and (2) whether they are able to verify the presence of iron-to-heteroatom interactions.[7,9,11]

The purpose of this paper is to collect together and rationalise, qualitatively, the Mössbauer data for these compounds to give insight into the presence or absence of iron-to-heteroatom interactions.

Experimental

Complex (**10**) of Table 2, $[Fe(C_5H_4SH)_2]$, was kindly donated by Professor J. Dilworth. Mössbauer data were recorded and fitted as previously described.[12]

Table 1. ^{57}Fe Mössbauer parameters for ferrocene complexes

Compound	*T*/K	δ^a/mm s^{-1} (±0.01)	Δ/mm s^{-1} (±0.01)	Ref.
(**1**) $[Fe(cp)_2]$	77	0.52	2.37	*b*
(**2**) $[Fe(cp)_2]\cdot 7HgCl_2$	80	0.53	3.09	7
(**3**) $[Fe(C_5H_4CH_2)_2]\cdot 3HgCl_2$	78	0.49^c	3.29^c	8
(**4**) $[Fe(cp)_2]\cdot CF_3SO_3H^d$	80	0.44	2.59	9
(**5**) $[Fe(cp)_2]\cdot HAlCl_4{}^e$	80	0.46	2.72	9
(**6**) $[\{Fe(cp)_2\}SiPh_2]$	80	0.51	1.97	11
	77	0.51^f	1.97^f	*g*
(**7**) $[\{Fe(cp)_2\}PPh]$	80	0.53	1.98	11
	77	0.52^f	1.97^f	*g*
(**8**) $[\{Fe(cp)_2\}GePh_2]$	77	0.51^f	2.02^f	*g*
(**9**) $[(SC_5H_4)_2FePd(PPh_3)]$	R.t.^{h}	0.48^f	1.99^f	10
	77^h	0.53^f	2.03^f	28
(**10**) $[Fe(C_5H_4SH)_2]$	77	0.53	2.39	This work

^{a} All isomer shifts are relative to iron foil at room temperature. ^{b} A. Houlton, R. M. G. Roberts, J. Silver, P. T. Bishop, and M. Herberhold, *J. Organomet. Chem.*, 1989, **364**, 381. ^{c} Errors 0.02 mm s^{-1}. ^{d} Frozen solution. ^{e} Solid. ^{f} No errors given. ^{g} A. G. Osborne, R. H. Whiteley, and R. E. Meads, *J. Organomet. Chem.*, 1980, **193**, 345. ^{h} Given as room temperature (r.t.) in ref. 10.

Results and Discussion

The Mössbauer data for the relevant ferrocene complexes are presented in Table 1. In order to rationalise these Mössbauer quadrupole splittings (Δ) it is first necessary briefly to recap some of the arguments made previously.[1] Following the suggestions of several groups,[13] it is assumed that the axial orbitals of the iron in the ferrocene moieties ($3d_{z^2}$ and $4p_z$) are essentially non-bonding, because their energies are high relative to those of the ligand orbitals of axial symmetry. It therefore follows that their electron populations are constant and that their negative contributions to Δ are invariant to ligand substitution (or iron–metal bonding providing the essential ferrocene structure is unchanged).

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

The remaining asymmetric orbitals are the two sets of iron 3*d* orbitals, of symmetry e_1 (the $3d_{xz}$ and $3d_{yz}$ orbitals) and e_2 (the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals). The e_2 electron density generates a positive contribution to Δ and e_1 a negative contribution of magnitude one half that of the e_2 set (per electron). The contribution of these orbitals to Δ may be written as in equation (1)

$$\Delta \propto (2p_2 - p_1) \qquad (1)$$

where p_2 and p_1 are the electron populations of e_2 and e_1 respectively; Δ is then twice as sensitive to changes of p_2 than it is to changes of p_1.

Therefore the differences in Δ, δΔ, of a compound relative to $[Fe(cp)_2]$ can be approximated to the changes in p_1 and p_2. Thus Δ will be controlled by changes in the population of the e_2 and e_1 orbitals (*i.e.* changes in the backbonding and forward donation respectively).

The Δ values in Table 1 can be split into two classes. Compounds **(2)**—**(5)** have Δ values larger than that of ferrocene $[Fe(cp)_2]$, whereas for **(6)**—**(9)** the Δ values are smaller. It is convenient to discuss these two classes separately. The structures of complexes **(6)**—**(9)** are all known.[2–4] In **(6)**—**(8)** the ferrocene rings are tilted away from the bridging atom.[2,3] The tilt angles are 16.6, 19.2, and 26.7°, for the Ge, Si, and P structures respectively.[2,3] The Fe–Ge, Fe–Si, and Fe–P distances are 2.74, 2.68, and 2.77 Å respectively and the authors suggested that these clearly showed that no bonding interactions were present.[2] We did not agree with this interpretation[11] pointing out some known Fe–P bond lengths that were pertinent and not too different. In support of our earlier comments, the crystal structures of four bis(diphosphine) complexes of iron(II) have recently appeared.[4] In this work seven other similar known structures are compared. Iron–phosphorus distances between 2.60 and 2.71 Å are found in three complexes (admittedly all high-spin Fe^{II}). However, these long Fe–P bonds are not thought to be solely due to the difference between the high- and low-spin radii for Fe^{II}.[14,15] Thus an Fe–P distance of 2.77 Å may be indicative of a weak interaction. Such an interaction cannot be ruled out simply because the sum of the covalent radii is 2.37 Å.[2] For the Fe–Si distance (2.68 Å) in compound **(6)**, Fe–Si bonds of 2.30,[16] 2.35, and 2.36 Å[17] have been reported, all close to the sum of the covalent radii[2,3] (2.37 Å). Thus can some interaction be ruled out at 2.68 Å? In the case of the Fe–Ge distance 2.74 Å[2] the sum of the covalent radii are 2.47 Å. Bond lengths of 2.377(2)[18] and 2.430(2) Å[19] have been established for Fe–Ge bonds. Thus 2.74 Å may indicate some interaction.

If the carbon bonds to the P, Si, and Ge atoms are considered in these structures[2,3] then an interesting fact emerges. The (cp)C–P distances are 1.836(9) and 1.849(10) Å and the phenyl C–P distance is 1.825(9) Å. In a recent work we listed cyclopentadienyl (cp)C–P distances for six ferrocene structures (12 different molecules); the largest was 1.836 Å and the average was 1.814 Å. Also for the same molecules the (Ph)C–P distances average 1.824(7) Å.[20] It therefore appears that the two (cp)C–P bonds are long and the (Ph)C–P bond is average so the P atom is in need of electron density which it gains by an Fe–P interaction. Similar findings are apparent for the C–Si distances in compound **(6)** (Table 2), (cp)C–Si 1.881(11), (Ph)C–Si 1.862(15) and 1.881(15) Å respectively.[3] Although the errors are large the distances appear long when compared to similar bonds in other compounds, 1.865(2) Å for (cp)C–Si[21] and 1.852(5), 1.854(5), and 1.846(4) Å for (Ph)C–Si.[22] Thus as for the P case it appears that the Si atom is in need of electron density, hence the long-range Fe–Si interaction.[3] The (cp)C–Ge distances are 1.960(15) Å[2] and the (Ph)C–Ge distances are 1.968(15)[2] and 1.958(15) Å.[2] Again these are long and show the Ge atom needs the long Fe–Ge interaction when compared to (Ph)C–Ge 1.954(1) Å in $GePh_4$[23a] and 1.945(14) Å in $GePh_3(COMe)$.[23b]. These arguments are partially summarised in Table 2.

The crystal structure of complex **(9)**[4] shows that the rings are tilted towards the claimed Fe–Pd dative bond, the tilt angle is 19.6°, and the Fe–Pd distance is 2.878(1) Å. The fact that the tilt angles are relatively small[4] and that for compound **(9)** is in the opposite direction to those of **(6)**—**(8)** shows that this angle is not likely to be important and probably does not affect the ferrocene electronic orbitals significantly. If this assumption is correct, then the arguments outlined above will still apply. It is important to note that: (1) the changes in Δ for compounds **(6)**—**(9)** of around 0.40 relative to ferrocene are large compared to ring-substituted ferrocenes,[1,24] and (2) the parent compound **(10)** (Table 1) has a Δ value slightly larger than that of ferrocene itself. Thus S atoms in the ferrocene plane do not pull electron density from the ferrocene rings, and do not lower Δ. On metal complexation to the S atoms there may be some withdrawal from the ferrocene unit *via* the S atoms but the effect of this is expected to be small, around 0.1—0.15 mm s^{-1} from the Δ values. This would be explained as electron withdrawal from e_1 orbitals.[1] To explain a further decrease in Δ of around 0.3 mm s^{-1} as in compound **(9)** an interaction between the Fe and Pd is necessary. Such an interaction would involve the removal of electron density from the iron $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals (the e_2 set); this would lower Δ [see equation (1)].

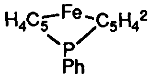
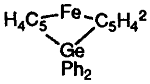
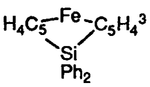
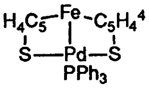
For the [1]ferrocenophanes it is not possible to examine the effect of a bridge substituent (such as Ge, Si, or P) that is too far away from the iron to interact with it, as no such compound has been made. All the compounds **(6)**—**(8)** manifest relatively small Fe–X (X = Ge, Si, or P) distances.[2,3] We have discussed the possibility of these being bonding interactions; all have Δ values around 1.99 mm s^{-1}.[11] They would all be expected to have interactions with the iron e_2 orbitals and lower Δ *via* equation (1). It should also be appreciated that the Pd, Ge, Si, and P atoms could also have some interactions with the iron $3d_{xz}$ and $3d_{yz}$ orbitals (the e_1 orbitals) *via* their empty *d* orbitals and remove some electron density from these. This might be expected from equation (1) to increase Δ, but as Δ is twice as sensitive to the e_2 electron population the latter would dominate. So overall the only consistent way to explain the observed Mössbauer Δ values for compounds **(6)**—**(9)** is the presence of Fe–X (X = Ge, Si, P, or Pd) bonding interactions. However, decreases in Δ of less than 0.20 mm s^{-1} cannot be put down to such interactions, contrary to the findings of others.[10] It must be appreciated that these bonding interactions in compounds **(6)**—**(9)** are weak, as the distances are long.

The second group of compounds **(2)**—**(5)** presents a different problem. First there are no known structures of any of these compounds. There is a preliminary report of some ruthenium–mercury(II) halide structures[25] $[Ru(cp)_2]\cdot HgBr_2$ and $[Ru(cp)_2]\cdot 3HgCl_2$ which are likely to have features in common with complexes **(2)** and **(3)**.[6] Unfortunately, although it is pointed out[25] that the Ru–Hg distances are short (2.60 and 2.65 Å), much smaller than the sum (2.81 Å) of the tetrahedral mercury radius (1.48 Å) and the octahedral ruthenium radius (1.33 Å), so that bond formation is demonstrated, there are no details of ring tilt. However, indications of an Fe–Hg interaction and ring tilting in compound **(2)** were found from its i.r. spectrum.[6] Evidence for 'direct' strong interactions between the Fe and Hg atoms in a number of ferrocenophane adducts of mercury(II) salts[8] including compound **(3)** (Table 1) has been found from their electronic absorption and Mössbauer spectra.

There is evidence therefore, including that discussed in ref. 9, for strong interactions, *i.e.* strong chemical bonds in compounds **(2)**—**(5)**. From a comparison of the bond lengths in the similar Ru–Hg compounds,[25] it would be expected that an Fe–Hg bond would be less than the sum of the covalent radii (2.74 Å), probably around 2.52 Å. This would be short and the radius of a covalent Hg atom would be expected to tilt the cp rings very strongly on the ferrocene. Thus a change in the population and the nature of the molecular orbitals would be expected.

This would also be true for the protonated ferrocene complexes **(4)** and **(5)**; again the rings would be tilted. One

Table 2. Bond lengths (Å) for the [1]ferrocenophanes[2–4] compared to typical literature values

Compound				Comments
 2	(cp)C–P 1.836(9) 1.849(10) (cp)C–P[20] 1.814	(Ph)C–P 1.825(9) (Ph)C–P[20] 1.824(7)	Fe–P 2.77 Fe–P[13] 2.60—2.71	Need Fe–P interaction; other bonds around P are all long
 2	(cp)C–Ge 1.960(15)	(Ph)C–Ge 1.958(15) 1.958(15) (Ph)C–Ge[23a] 1.954(1) (Ph)C–Ge[23b] 1.940(14) 1.945(14) 1.950(14)	Fe–Ge 2.74 Fe–Ge[19] 2.430(2)	Need Fe–Ge interaction, other bonds around Ge are long
 3	(cp)C–Si 1.881(11) (cp)C–Si[21] 1.865(2)	(Ph)C–Si 1.862(15) 1.881(15) (Ph)C–Si[22] 1.852(5) 1.854(5) 1.846(4)	Fe–Si 2.68 Fe–Si[16] 2.307(2) Fe–Si[17] 2.350(1) 2.363(1)	Need Fe–Si interactions, other bonds around Si are long
 4	Pd–S 2.302 this is short compared to range quoted[4] 2.284(4)—2.431(3)	Pd–P 2.241(2) this is short compared to typical range[4] 2.230(4)—2.349(2)	Fe–Pd 2.878(1) authors[4] quote Fe–Pd 2.599(1)—2.698(1)	Though Fe–Pd distance is long for a single bond, authors suggested it to be a weak dative bond necessary to give Pd a favourable 16-electron configuration[4]

known structure of the type expected for compounds (**2**)—(**5**) is that of $[Ru(cp)_2I]^+I_3^-$.[26] In this there is an Ru–I bond of 2.73(3) Å which is said to be longer than expected due to steric strain.[26] This is confirmed by the fact that the cyclopentadienyl rings are tilted back to allow the iodine to bond to the Ru atom.[26] The tilt angle between the ring planes is 32.2°. The sum of the covalent radii for Ru and I is 2.66 Å, but obviously from the structural features and the spectral data[26] the bond is lengthened primarily through steric effects.

Compounds (**2**)—(**5**) would be expected to have strong Fe–Hg or Fe–H^+ bonds and angles of tilt similar to that in $[Ru(cp)_2I]^+$.[26] Ring tilt of this magnitude would effect the $3d_{z^2}$ orbital on the Fe atom of the ferrocene moiety. It would now be expected to participate in the molecular bonding, its electron population would be expected to vary, and thus its negative contribution to Δ will vary. Therefore, if electrons are removed from it during bonding, it would be expected to cause a less negative contribution to Δ and thus the latter should increase. Even if the e_2 orbitals bond to the Hg or H^+ atoms, which would lower Δ, the effect of $3d_{z^2}$ becoming active should still increase it.

It is worth noting that both these classes, *i.e.* compounds (**2**) and (**3**) and (**6**)—(**9**), have similar isomer shifts at 77 K. This perhaps would suggest that such iron interactions do not affect the isomer shifts of the ferrocene. However, compounds (**4**) and (**5**) do have lower isomer shifts and we have discussed this previously.[9] If the Δ values are plotted against the isomer shifts for compounds (**2**)—(**6**) of Table 1 along with the 78 K Mössbauer data for the other mercuryferrocenophanes given in ref. 8, then excluding compound (**3**) the other seven compounds lie relatively close to a linear correlation. Thus, as stated,[9] the '*s*' electron density at the nucleus is being affected in a linear fashion by subtle changes in ring tilt in Fe–H^+ or Fe–Hg bonding.

It is interesting to speculate whether there could be a third class of ferrocene compounds where the iron bonds directly to other elements and the bond is of moderate strength. That is in an intermediate way between the two classes discussed above, so that the ring tilt is between 26 and 30°. If so, it might be expected that the $3d_{z^2}$ orbital begins to be affected and this increases Δ, but this is offset by e_2 ($3d_{x^2-y^2}$ and $3d_{xy}$) electron density being donated to the bonding element and decreasing Δ. Thus the overall Δ value may be close to that of ferrocene itself [compound (**1**)]; however, as all the $3d$ orbitals would be taking part in the bonding, there would be less shielding of the *s*-electron density and a smaller (less-positive) isomer shift would be expected. This could only be offset if iron *s*-electron density was also involved in the Fe–X (X = bonding atom) bonding. Recently reports[10,27] have appeared in which a group of palladium(II) and platinum(II) complexes of trichalcogeno[*n*]-ferrocenophanes (*n* = 7 and 9) have been studied; spectral data (^1H and ^{13}C n.m.r., i.r. and visible) suggest that many contain dative Fe–Pd or Fe–Pt bonds. The Mössbauer data for five of these [other than complex (**9**) of Table 1] all have Δ values between 2.10 and 2.44 mm s^{-1}, however all have isomer shift values at liquid-nitrogen or room temperatures that are higher than usual for ferrocene.[10,27] As explained above, such Δ values close to that of ferrocene arising from molecules containing Fe–X dative bonds would be expected to have smaller isomer shifts [as do compounds (**4**) and (**5**), Table 1] unless '*s*'-electron density was being used in the bonding. The conclusion must therefore be (*a*) the Mössbauer parameters can be interpreted to indicate the presence of a metal–iron bond and (*b*) that Fe '*s*'-electron density is used in the bonding in these complexes more than in normal ferrocenes.

One point that has been totally ignored by us[7,9,11] and others[8,10,27] is the fact that the ferrocene moieties in all the compounds (**2**)—(**9**) (Table 1) and others[10,27] are asymmetric molecules. Only one work[28] on ferrocene Mössbauer spectroscopy has considered this. This asymmetry might have been expected to cause the field gradient to be non-axially symmetric and the Mössbauer asymmetry parameter (η) to be non-zero. This, depending on the size, would have an effect on Δ, increasing its magnitude. However, all these compounds are asymmetric in the same sense and might either (1) all be expected to have similar η values and thus would all be affected to almost the same extent (hence the above arguments would still hold), or (2) η may be close to or equal to zero and can therefore be neglected, so all the above would again still hold. It is worth noting that where η was calculated for eight bridged ferrocene systems it was always small in the range 0.04—0.26.[28] An η value of 0.26 would increase Δ by about 1%.

Conclusion

It has been shown on a qualitative basis that two kinds of effective interactions direct to iron exist and have opposite effects on the Δ value. These are: (1) weak interactions to the iron from an external atom such as P,[2] Ge,[2] Si,[3] and Pd[4] that cause ring tilting of 27° or less (these are found to lower Δ by around 0.4 mm s^{-1}); and (2) strong interactions such as those found for Fe–Hg and Fe–H^+ bonding that cause ring tilt in excess of 30° (these change the molecular orbital bonding scheme and are manifest in the Mössbauer spectra as Δ values greater than for ferrocene; for the Fe–Hg compounds the increase in Δ is around 0.7—0.9 mm s^{-1}).

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