

# Studies of the bonding in iron(II) cyclopentadienyl and arene sandwich compounds. Part 5. An interpretation of the $^{57}\text{Fe}$ Mössbauer spectroscopic data of dibromoborylferrocenes, and related molecules

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## Abstract

The Mössbauer spectroscopic parameters of three dibromoboryl ferrocenes and of a related dichloroboryl ferrocene are reported. The results are discussed in relation to the known crystal structures, the Mössbauer parameters and the correlation of the latter with Hammett substituent constants. These data are also compared with those of other ferrocenes that form ferrocenyl carbocations ( $-\text{CR}_2^+$  is isoelectronic with  $-\text{BX}_2$  where X = halogen) as well as protonated ferrocenyl ketones. It is concluded that normal ferrocenyl carbocations, though nominally isoelectronic with the similarly substituted dibromoboryl ferrocenes, bond in a very different manner involving a change in structure where the two cyclopentadienyl rings are no longer parallel. However, the protonated ferrocenyl ketones show Mössbauer quadrupole splittings that are similar to those of the dibromoboryl ferrocenes; this is interpreted to suggest that the former cations have significant carbocationic character and parallel cyclopentadienyl rings. The nature of the Fe–B interactions are discussed in terms of the overall C–B bonding, particularly in the case where four dihaloboryl groups are present. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Mössbauer; Iron; Cyclopentadienyl; Arene; Dibromoboryl ferrocenes

## 1. Introduction

Ferrocenyl carbocations ( $\text{FcCR}_2^+$ ) have been shown to be remarkably stable species; the mechanism of carbenium center stabilization has been widely discussed [1–5]. During extensive studies on ferrocene, and its derivatives, using Mössbauer spectroscopy, the  $\text{FcCR}_2^+$  species have been studied [6,7], and the 1,1'-dications have also been investigated [7–10]. During our studies we were not able to find evidence for dications, possibly because of their instability compared to the

monocations. Indeed if it were not for frozen-solution Mössbauer studies, we would not have been able to attempt to study the dications at all [7]. Others have also found extreme difficulty with the isolation of such species [12,13].

Recently a number of crystal structures of ferrocene complexes containing the  $\text{BBr}_2$  substituent (which is isoelectronic with the cationic  $\text{CR}_2^+$  group) have appeared in the literature [14–16]. The availability of these crystal structures has allowed us to carry out a Mössbauer spectroscopic investigation in which we could compare the spectra of these compounds and their geometry to the spectra of the previously studied  $\text{CR}_2^+$  derivatives [6–8], and to the geometry of similar compounds [1–3].

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## 2. Results and discussion

The Mössbauer spectra of dibromoborylferrocene (**1**) and 1,1'-bis(dibromoboryl)ferrocene (**2**) are surprisingly similar. The isomer shift (i.s.) values of these compounds are the same (within experimental error) but this is not surprising in view of our previous findings [17]. However the quadrupole splitting (q.s.) values are also the same within experimental error. The q.s. values of around  $2.14(1) \text{ mm s}^{-1}$  are small compared with that of ferrocene itself ( $2.39(1) \text{ mm s}^{-1}$ ) [17].

We have previously shown that for iron sandwich compounds the q.s. is defined by relationship (1), where  $p_2$  and  $p_1$  represent the electron populations of the  $e_2$  and  $e_1$  orbitals, respectively. The  $e_2$  and  $e_1$  orbitals are the asymmetric orbitals that are made up of combinations of the Fe 3d orbitals and cyclopentadienyl ring (Cp) orbitals. The  $e_2$  orbitals can be thought of as predominantly iron based, and the  $e_1$  predominantly ring based. The  $e_2$  electron density gives a positive contribution to the q.s. and the  $e_1$  a negative contribution of a magnitude one half of that of the  $e_2$  set (per electron) [17]. Both  $p_2$  and  $p_1$  are sensitive to ligand substitution, but the q.s. is twice as sensitive to changes in  $p_2$  as it is to changes in  $p_1$ .

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

The first question that must be addressed is from which orbitals do the  $\text{BBr}_2$  groups take their electron density? From previous studies [14,17], it might be expected that the interaction between the empty p orbital of the boron and the filled d-type orbitals at the iron ( $d_{x^2-y^2}$  and  $d_{xy}$ , the  $e_2$  orbitals) [4] is responsible for the observed decrease in q.s. for **1** and **2** relative to ferrocene. According to Eq. (1), a decrease in the electron population of the  $e_2$  orbitals will indeed decrease the q.s., however this is not as straightforward as it may appear as the following alternative mechanism would

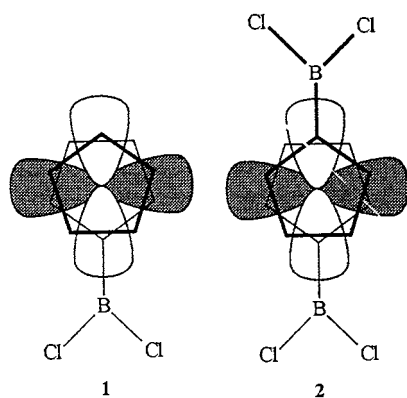


Fig. 1. Views of molecules **1** and **2** showing an Fe  $e_2$  orbital. In **1** the empty p orbital of the boron atom overlaps an  $e_2$  orbital, whereas in **2** the empty p orbitals of both boron atoms overlap with the opposite lobes of the same Fe  $e_2$  orbital.

also lower the q.s. Electron withdrawal via ring-based  $e_1$  orbitals towards boron due to overlap of the  $e_1$  with the empty p orbital at boron would lower the  $e_1$  orbital donation to the iron. This would lower the q.s. due to a greater involvement of  $e_2$  in the back bonding to the rings (to compensate for loss of  $e_1$  forward bonding to iron).

The crystal structures of **1** and **2** should now be considered [14,15]. The dip angle of the exocyclic B–C bond with the cyclopentadienyl ring plane in **1** is around  $18^\circ$ , whereas the two dip angles found in **2** are  $10.2^\circ$ . If it is assumed that the boron atoms need both  $e_2$  and  $e_1$  electron donation to stabilize the compounds, then the fact that the dip angle of **2** is half that of **1** suggests that much of the iron  $e_2$  electron density is used in back bonding to the rings and only a little is available to the boron atom. Thus the boron atoms take most of the electron density they need directly from the rings. A close look at the B–C distances in **1** ( $1.482(8) \text{ \AA}$ ) [14] and **2** ( $1.456(18) \text{ \AA}$ ) [15] supports this as the values are the same (within experimental error), yet in one case there are 2  $\text{BBr}_2$  groups present and in the other only one. The fact that the q.s. data are the same for both compounds suggests that in each case the same total electron density is withdrawn onto the boron atoms directly from the iron. (Though as stated above this is only a minor part of the total electron density the boron atoms need.) For **1** this is by direct interaction of the empty p orbital on the B atom with one lobe of either of the  $e_2$  iron-based orbitals, whereas in **2** the C–B bonds align so that each boron atom, although on a separate cyclopentadienyl ring, interacts with the opposite lobes of the same  $e_2$  orbital, as shown diagrammatically in Fig. 1. The total withdrawal in **2** is equal to that of **1**. This explanation is in accord with the work of Appel et al. [16] and it is emphasized by the Mössbauer spectroscopic data found in previous studies on carbenium ions [6–8]; some of these are presented in Table 1. First, only enhanced q.s. values, relative to ferrocene, were recorded, not reduced values as in the isoelectronic dibromoboryl derivatives. Moreover we suggested from the Mössbauer spectroscopic data [7] that  $[\text{CpFe}(\text{C}_5\text{H}_4\text{CH}_2)]^+$  (**3**) had features in common with protonated ferrocene, in that the structural changes from the parallel rings of ferrocene are large. (In diferrocenylmethyl tetrafluoroborate,  $\text{FcCH}_2^+\text{BF}_4^-$ , the exocyclic dip angle is  $19.9^\circ$  [1], and for ferrocenyldiphenylcarbenium tetrafluoroborate,  $\text{FcCPh}_2^+\text{BF}_4^-$  it is  $20.7^\circ$  [3].) These values are low and not in keeping with the calculations of several groups [14,18], though the calculated values fit for the less sterically hindered ruthenocene and osmocene derivatives, where dip angles of around  $40\text{--}41^\circ$  are found for  $[(\text{C}_5\text{Me}_5)\text{M}(\text{C}_5\text{H}_4\text{CH}_2)]^+$  (M = Ru or Os) [19,20].

We previously suggested [21] that the structural change from the normal situation, where the two rings

Table 1  
Mössbauer spectroscopic parameters of FcBBr<sub>2</sub> and related compounds

Compound	i.s. (mm s <sup>-1</sup> )	q.s. (mm s <sup>-1</sup> )	$\Gamma$ (mm s <sup>-1</sup> )	Ref. Mössbauer	Ref. X-ray
1. CpFe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> BBr <sub>2</sub> )	0.52(1) <sup>a</sup>	2.134(10)	0.155(5)	[37]	[14]
2. Fe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> BBr <sub>2</sub> ) <sub>2</sub>	0.52(1)	2.15(1)	0.12(1)	<sup>b</sup>	[15]
3. [CpFe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> )] <sup>+</sup>	0.50(1)	2.70(1)	–	[6]	–
4. [CpFe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> COMe <sub>2</sub> )] <sup>+</sup>	0.52(2)	2.38(1)	–	[6]	–
5. Fe[ $\eta^5$ -C <sub>5</sub> H <sub>3</sub> (BBr <sub>2</sub> )-1,3] <sub>2</sub>	<sup>c</sup>	<sup>c</sup>	–	<sup>b</sup>	[16]
6. Fe[ $\eta^5$ -C <sub>5</sub> H <sub>3</sub> (BCl <sub>2</sub> )-1,3] <sub>2</sub>	0.53(1)	1.85(1)	0.15(1)	<sup>b</sup>	–
CpFe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> COMe)	0.54(1)	2.27(1)	–	[8]	–
[CpFe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> COHMe)] <sup>+</sup>	0.53(1)	2.08(2)	–	[8]	–
Fe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> COMe) <sub>2</sub>	0.54(1)	2.14(5)	–	[8]	–
[Fe( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> COHMe)] <sup>2+</sup>	0.55(1)	1.79(1)	–	[8]	–

<sup>a</sup> Corrected to natural iron as 0.0 mm s<sup>-1</sup>.

<sup>b</sup> This work.

<sup>c</sup> Recording of this Mössbauer spectra prohibited by the high percentage of Br in the molecule (Br absorbs electromagnetic radiation at a similar energy to that of the Mössbauer experiment).

are parallel, must involve dramatic changes in the bonding, and in such cases it is no longer possible to interpret these changes purely in terms of  $e_2$  and  $e_1$  orbitals. We further suggested [21] that though a detailed orbital reorganization was beyond the scope of that work (and indeed this paper), it nevertheless seems clear that it is manifested in a rather large q.s. and an upfield shift of the <sup>57</sup>Fe-NMR resonance. A tentative suggestion was that the iron atom interacts directly with the exocyclic carbon atom and that the cyclopentadienyl rings may be tilted slightly for **3**, whereas for (FcCMe<sub>2</sub>)<sup>+</sup> (**4**) there is no distortion as the Me groups stabilize the positive charge [5]. Thus we expect that direct strong interaction to iron from exocyclic atoms in ferrocene molecules will increase the q.s. only if the two cyclopentadienyl rings are greatly distorted from the parallel arrangement. We therefore conclude that, for the present case of exocyclic boron atoms, the direct interactions to the iron provide the electron density required by the boron atom, but that these interactions are weak when compared to those of atoms forming bonds directly to the iron, such as those in protonated ferrocene [22]. Indeed in **2** the distance of the Fe–B interaction is necessarily longer than that of **1**, as the dip angles are smaller.

If we now compare on the basis of the q.s. values the electron withdrawal of **1** and **2** to that of ferrocenyl carboxylic acids [23], and to acyl ferrocenes [23], it can be seen that the q.s. values for the bis-substituted compounds are similar to that of **2**, but those of the mono-substituted are less than those of **1**. It appears that for direct overlap with the  $e_1$  orbitals for two good electron-withdrawing groups, q.s. values as low as 2.14(2) mm s<sup>-1</sup> are the limit. Thus **1**, which has this value, must clearly be interacting via boron with an Fe  $e_2$  orbital more significantly than each of the two boron atoms in **2**.

We have previously found [8] that monoprotonated ions prepared from ferrocenyl ketones have q.s. values around 2.10 mm s<sup>-1</sup> and diprotonated ions prepared from diketones have values around 1.80 mm s<sup>-1</sup>. Although previously we believed these involved electron withdrawal only from the ring-based rather than the iron-based orbitals [8], in light of this work it appears that these complexes must have some carbenium ion character so that the C<sup>+</sup> atom in **II** (Fig. 2) interacts via its p orbital with the iron  $e_2$  orbitals. This interaction may be stabilized via an extended interaction with the p orbital of the oxygen of the hydroxyl group. We note in **3** that such extended stabilization cannot occur with the H atoms. Further, from this work it is possible to suggest that not only do the protonated ferrocenyl ketones have significant carbocation character but in addition the cyclopentadienyl rings are parallel [21].

In view of the q.s. values for the latter protonated diketones, it is perhaps an oversimplification to consider that **1** and **2**, though apparently isoelectronic with carbenium ions, mimic their properties. The halogen atoms themselves may help to stabilize the boron through electron donation, just as the methyl groups do in the case of **4** (the latter needs no electron density from the ferrocene at all). However in **1** and **2** this might take place via  $\sigma$  donation as the Br–B  $\pi$  bonding is possibly weak [24], although this is a matter of debate [25]. Moreover the B–Br distances in the dibromoboryl-substituted ferrocenes (which range between 1.916 (6) and 1.947(6) Å in **1** [14], and between 1.954(8) and 1.912(8) Å in **2** [15]) are longer than those reported for

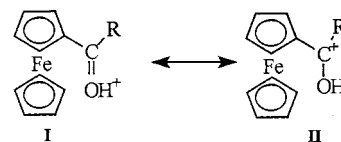


Fig. 2. Carbenium ion character of protonated ferrocenyl ketones.

Table 2

Correlations of q.s. at 80 K and Hammett constants,  $\sigma_F$  and  $\sigma_R$ , for mono-, bis-, and poly-substituted ferrocenes

		q.s. (mm s <sup>-1</sup> )	$\sigma_F$ [31]	$\sigma_R$ [31]	Mössbauer Reference
CpFeC <sub>5</sub> H <sub>4</sub> X, X =	H	2.39(1)	0.0	0.0	[23]
	COOMe	2.30(1)	0.19	0.16	[23]
	COPh	2.26(1)	0.29	0.16	[23]
	COMe	2.27(1)	0.25	0.16	[23]
	BF <sub>2</sub>	2.27(1)	0.23	0.28	[37]
	COC <sub>6</sub> H <sub>4</sub> Cl	2.25(1)	0.34	0.16	[11]
	CHO	2.24(1)	0.35	0.23	[23]
	COOH	2.21(1)	0.37	–	[23]
	BCl <sub>2</sub>	2.20(1)	0.19	0.34	[37]
Fe(C <sub>5</sub> H <sub>4</sub> X) <sub>2</sub> , X =	COMe	2.15(1)	0.50	0.32	[23]
	CHO	2.16(1)	0.70	0.46	[23]
	COOH	2.16(1)	0.74	–	[23]
Fe(C <sub>5</sub> H <sub>3</sub> X <sub>2</sub> ) <sub>2</sub> , X =	BCl <sub>2</sub>	1.85(1)	0.78	1.36	<sup>a</sup>

<sup>a</sup> This work.

BBr<sub>3</sub> in the gas phase (1.8932(54) Å) [26]. Thus, stabilization of the boron by the bromo substituents is unlikely to be a significant factor; apparently the boron atoms take more electron density from the ferrocene sandwich than from the bromine atoms.

There are no reports of ferrocenyl carbocations where the total charge is greater than two. However ferrocenyl compounds containing more than two BX<sub>2</sub> substituents are known [16,27]. We were unable to obtain Mössbauer spectra from 1,1',3,3'-tetrakis(dibromoboryl)ferrocene (**5**) due to the bromine absorption edge ruining the Mössbauer spectral statistics. This was particularly disappointing in the light of the structural characterization of **5** [16]. The latter compound has four BBr<sub>2</sub> units, two bent in towards the iron atom at angles of 6.9° and the other two of only 1.5°. We were able to obtain the Mössbauer spectra of the analogous 1,1'-3,3'-tetrakis(dichloroboryl)ferrocene (**6**), which unfortunately has not been structurally characterized. This compound has a q.s. of 1.85(2) mm s<sup>-1</sup>. Previously such small values have only been found for very distorted ferrocene molecules where the two rings are significantly tilted against one another [22,28,29]. However, there is no reason to believe that **6** has tilted rings, and it is much more likely that electron withdrawal from both the ferrocene e<sub>2</sub> and e<sub>1</sub> orbitals is the cause of the very low q.s. value. If we tentatively assume that **5** and **6** have the same structure, then the differences in the bending angles can be readily explained. One BBr<sub>2</sub> unit on each ring interacts with one lobe of an e<sub>2</sub> orbital (one BBr<sub>2</sub> with each e<sub>2</sub> orbital). The second BBr<sub>2</sub> substituent on each ring is at an angle of about 144° from the first, and there are no e<sub>2</sub> orbital lobes at this angle; the closest are at 135°, so any interaction is weak and the angle of bending is therefore small. It is significant that the BBr<sub>2</sub> group with the smallest bending angle is the one manifesting the longer B–C distance

(1.56(2) Å compared to 1.48(3) Å) [16]. In addition this is the boron atom with the shortest B–Br bond lengths (1.90(2) and 1.88(2) Å) close to those found in BBr<sub>3</sub> [26], whereas the B–Br distances in the BBr<sub>2</sub> substituent that bends closer to the iron are 1.92(2) and 1.93(2) Å. Thus, although Fe–B interactions are apparently small in 1,1'-3,3'-tetrakis(dihaloboryl)ferrocenes {Fe[η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-(BX<sub>2</sub>)<sub>2</sub>]}, they have a direct effect on both the B–C and B–Br bond lengths and the <sup>57</sup>Fe Mössbauer spectra (in **6**).

Support for the above arguments comes from an analysis of the Mössbauer parameters using Hammett substituent constant correlations. Substituent effects are generally additive for Mössbauer q.s. data. This is illustrated by the data for ferrocene {FcH} (2.39 mm s<sup>-1</sup>), FcBCl<sub>2</sub> (2.20 mm s<sup>-1</sup>), and {[C<sub>5</sub>H<sub>3</sub>(BCl<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Fe} (1.85 mm s<sup>-1</sup>) in Table 2. There are exceptions, however, as saturation effects have been observed both with electron-releasing and -withdrawing substituents, as in the q.s. values for (η<sup>6</sup>-arene)(η<sup>5</sup>-cyclopentadienyl)iron(II) salts [30]. We have used  $\sigma_F$  and  $\sigma_R$  values [31] derived from <sup>19</sup>F-NMR chemical shifts since this compilation includes most of the common substituents as well as the BX<sub>2</sub> groups. The  $\sigma_F$  value of the –COOH was calculated from,

$$F = 0.924\sigma_F - 0.006$$

where *F* is the Swan–Lupton inductive parameter [32]. Where two substituents are present, additivity is assumed. The q.s. values for the carbonyl-substituted ferrocenes in Table 2 show a good linear correlation (*r* = 0.990, *N* = 8) with the inductive parameter,  $\sigma_F$ , up to a value of about 0.5 (see Fig. 3). Thereafter, a saturation effect is apparent with the 1,1'-bis-substituted ferrocenes ({[C<sub>5</sub>H<sub>4</sub>(X)]<sub>2</sub>Fe} where X = CHO, COOH, COC<sub>6</sub>H<sub>4</sub>-*p*-Me, COC<sub>6</sub>H<sub>4</sub>-*p*-Cl). This analysis yields the following relationship for the linear portion of the plot:

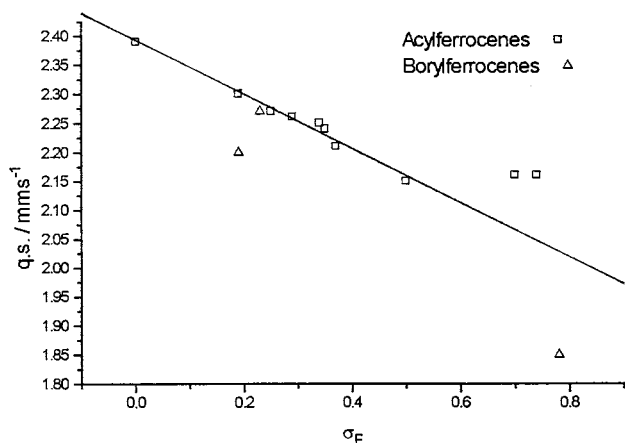


Fig. 3. Plot of q.s. against  $\sigma_F$  values from Table 2.

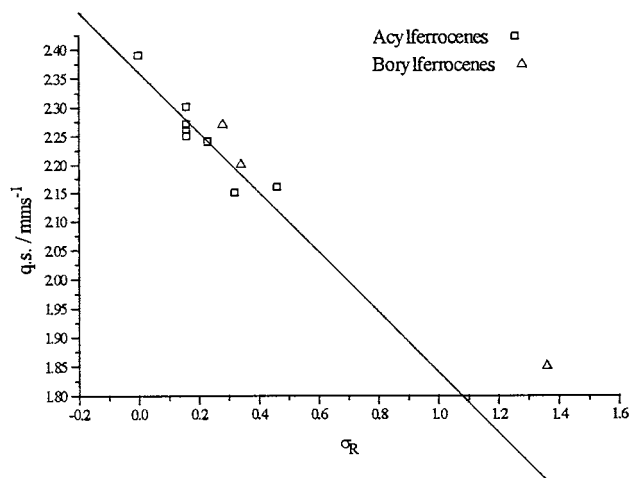


Fig. 4. Plot of q.s. against  $\sigma_R$  values from Table 2.

$$\text{q.s.} = -0.47\sigma_F + 2.39 \quad (3)$$

The boron substituents lie generally well below the line, i.e. the q.s. values are lower than predicted based on the inductive effects, which suggests other causes for the reduced q.s. values.

A similar plot (Fig. 4) using the resonance parameter,  $\sigma_R$ , shows a poor correlation to linear ( $r = 0.924$ ,  $N = 8$ ) giving:

$$\text{q.s.} = -0.52\sigma_R + 2.36 \quad (4)$$

In this case, no saturation effects were observed. The boryl substituents lie somewhat above the correlation line, indicating that full resonance with the cyclopentadienyl ring is not occurring. This is consistent with the dip angle present, which would bend the empty p orbital on the boron away from the cyclopentadienyl ring system. Overall the above analysis suggests that an effect other than polar resonance is present, namely a direct iron–boron interaction.

### 3. Experimental

All compounds were prepared and characterized by the previously reported methods (1 [33], 2 [34], 5 [35]). Mössbauer spectra were recorded at 80 K using the previously reported apparatus [36]. The Hammett substituent constants,  $\sigma_R$  and  $\sigma_F$ , were taken from Table IV of Ref. [31] and derive from  $^{19}\text{F}$ -NMR chemical shifts of *m* and *p* fluorobenzenes. Where more than one substituent is present, the substituent effect is treated as additive (Table 2).  $\sigma_R$  and  $\sigma_F$  values for the COOMe group were taken to be identical to the values for COOEt. This is fully justified by the identical Swan–Lupton parameters, *F* and *R*, for these two substituents.

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