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EVIDENCE OF IRON—MERCURY BONDS IN COMPLEXES OF FERROCENE WITH MERCURIC CHLORIDE FROM MÖSSBAUER SPECTROSCOPY

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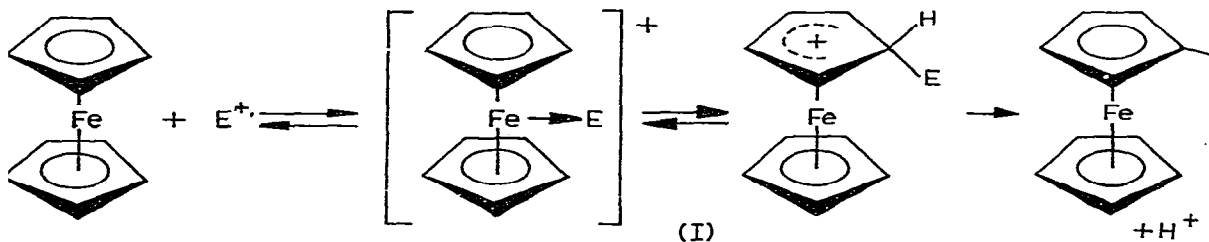
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Summary

Novel Mössbauer spectra of ferrocene/mercuric chloride adducts are reported, displaying anomalously high quadrupole splittings, which are interpreted as strong evidence for Fe—Hg bonding. The results are discussed in conjunction with tilting of the cyclopentadienyl rings.

Introduction

Electrophilic substitution in metallocenes has been the subject of a number of studies during the past two decades. Ferrocene in particular has received much attention, largely due to its thermal stability and ease of synthesis. The role of the central iron atom in these substitutions has been in question for some time. Rosenblum et al. [1] postulated that the electrophilic species bonds initially to the iron before attacking the cyclopentadienyl rings.



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However, no real evidence for such an interaction was found. Studies of protodesilylation of trimethylsilylferrocene [2,6] revealed no evidence for I, as did a subsequent stereochemical investigation of intramolecular ring acylation [3].

Direct evidence for the existence of structures such as I comes from NMR data of ferrocene in boron trifluoride hydrate [4] and trifluoromethanesulphonic acid [5] where very highly shielded protons were observed ($\delta = -2.1$ and -2.25 ppm, respectively). Ferrocene thus displays significant electron-donor properties which have been quantified for some substituted ferrocenes [6]. The characterisation of such complexes, of course, does not prove that they are indeed intermediates in electrophilic processes. Such a proof is not at all straightforward and involves very detailed kinetic measurements, (cf. Diels-Alder reactions [7]). The site of protonation depends on the strength of the acidic species, weak acids forming π hydrogen bonds with the cyclopentadienyl rings and stronger acids forming metal-H bonds. The latter had been ruled out as intermediates in H/D exchange reactions [8].

Reaction of ferrocene and ruthenocene with mercuric halides give various adducts [9]. When a solution of ferrocene in an organic solvent was treated with mercuric chloride (the stoichiometry is not critical) orange-red crystals appeared. These are diamagnetic and on standing, turned dark blue and became paramagnetic. The red compound analysed as $\text{Fe}(\text{cp})_2 \cdot 7 \text{HgCl}_2$, and the blue, on crystallisation, analysed as $\text{Fe}(\text{cp})_2 \cdot 2 \text{HgCl}_2$. Some evidence of Fe-Hg bond formation in the former was presented. X-ray crystal structures on similar ruthenium derivatives $\text{Ru}(\text{cp})_2 \cdot \text{HgBr}_2$ and $\text{Ru}(\text{cp})_2 \cdot 3 \text{HgCl}_2$ indicated the presence of Ru-Hg bonds [10]. Recently, a study of the electronic spectrum of ferrocene and ruthenocene with mercuric halides in acetonitrile revealed the presence of charge-transfer bands at 360 and 280 nm, respectively [11], attributed to $\text{Cp}_2\text{M} \rightarrow \text{HgX}_2$ processes. Irradiation of solutions at these wavelengths resulted in oxidation of the metallocenes to the metallocenium cations and the formation of mercurous ions, and NMR evidence of such complexation together with estimates of the lifetime of the complexes has recently been presented [5]. In this paper we provide evidence for the structure of these interesting species based on Mössbauer isomer shifts and quadrupole splitting.

Results and discussion

The red and blue ferrocene/mercuric chloride compounds, as prepared in our laboratory by the method of Morrison and Hendrickson [9], analysed reasonably well for the stoichiometries $\text{Fe}(\text{cp})_2 \cdot 7 \text{HgCl}_2$ and $\text{Fe}(\text{cp})_2 \cdot 2 \text{HgCl}_2$, respectively, as reported previously. The Mössbauer spectra for both these compounds appear in Table 1. The red adduct showed an isomer shift (IS) similar to those of other simple ferrocene derivatives [12] ($0.52 \pm 0.02 \text{ mms}^{-1}$ relative to Fe). However, the quadrupole splitting (QS) (typically $2.3 \pm 0.1 \text{ mms}^{-1}$ for the ferrocene, Fig. 1) was considerably greater in $\text{Fe}(\text{cp})_2 \cdot 7 \text{HgCl}_2$ (3.09 mms^{-1} at 80 K). The variation in QS through a series of ferrocene derivatives is relatively small. This is a consequence of the fact that the electric field gradient at the nucleus arises largely from the π bonding ligands. These are not greatly influenced by changes in the σ bonding of ring substituents. The two previous studies on the red adduct [9,11] indicated the presence of an iron-mercury

TABLE 1
MÖSSBAUER PARAMETERS FOR FERROCENE ADDUCTS HgCl₂

	Temp. (° K)	Isomer shift (mm sec ⁻¹)	Quadrupole splittings (mm sec ⁻¹)	Line width (half-width at half max.) (mm sec ⁻¹)
Fe(Cp) ₂ · 7 HgCl ₂	80	0.53(1)	3.09(1)	0.14(1)
	125	0.52(1)	3.03(2)	0.12(1)
	175	0.52(1)	3.05(2)	0.12(2)
	225	0.47(1)	2.96(2)	0.14(2)
	275	0.45(2)	2.94(3)	0.13(3)
Fe(Cp) ₂ · 2 HgCl ₂ (material aged from above)	80	0.52(4)	2.98(7)	0.15(7)
		0.62(3)	—	0.32(5)
	298	0.42(2)	—	0.15(3)

bond and crystallographic data also suggest similar bonding in ruthenium analogues [10]. Such an iron—mercury bond would clearly result in changes in the electronic environment of the iron in the ferrocene moiety, with concomitant modification of the MO diagram of energy levels. The Mössbauer data for the quadrupole splitting presented here, strongly indicates such an electronic change, though the isomer shift is relatively unaltered.

Important questions arise concerning the disposition of the two cyclopentadienyl rings. The tilting of the rings with respect to one another has received much theoretical consideration [12a,b]. The MO treatment has recently been modified by Green et al. [13] to incorporate features from both previous bonding descriptions. Ring tilt is fairly common in organometallics of the titanocene type, but for ferrocene derivatives data is rather more sparse. Tetrakis-1,1',3,3'-*t*-butylferrocene has its rings inclined at an angle of about 7° [14], whilst X-ray investigation by de Boer et al. [15] of 1,1'-dimethylferrocenium triiodide has shown that the methyl groups are eclipsed and the dihedral angle (ϕ) between the rings is about 6°. Ring tilting has been shown by Watts et al. [16] to lead to a characteristic A₂B₂ spectrum in the NMR, in which the separation of the A₂B₂ pattern is directly dependent on the angle of tilt. This treatment was extended to protonated ferrocenes (ferrocenium ions) by Ling and Bitterwolf [17] who found that for the 1,1'-dimethylferrocenonium ion the α and β protons showed significantly different chemical shifts as compared with the unprotonated parent ferrocene, where α and β proton resonances overlapped. The different proton environments were attributed to hindered ring rotation of the substituted ring, the hindrance resulting from the inability of the substituent to pass through the region of closest ring approach, (the so-called "pinch" position). An order of decreasing tilt

Me > Me₂ > MeEt > Et > Et₂

was established. As anticipated from this series, ring tilt in *t*-butyl derivatives is not very significant. However, it was found that for 1,3 di-*t*-butylferrocenonium ions two Fe—H resonances were observed, being assigned to two non-interconverting rotamers resulting from approaches of the proton to the side closest and the side remote from the substituents [18]. Ring tilt has been unambiguously

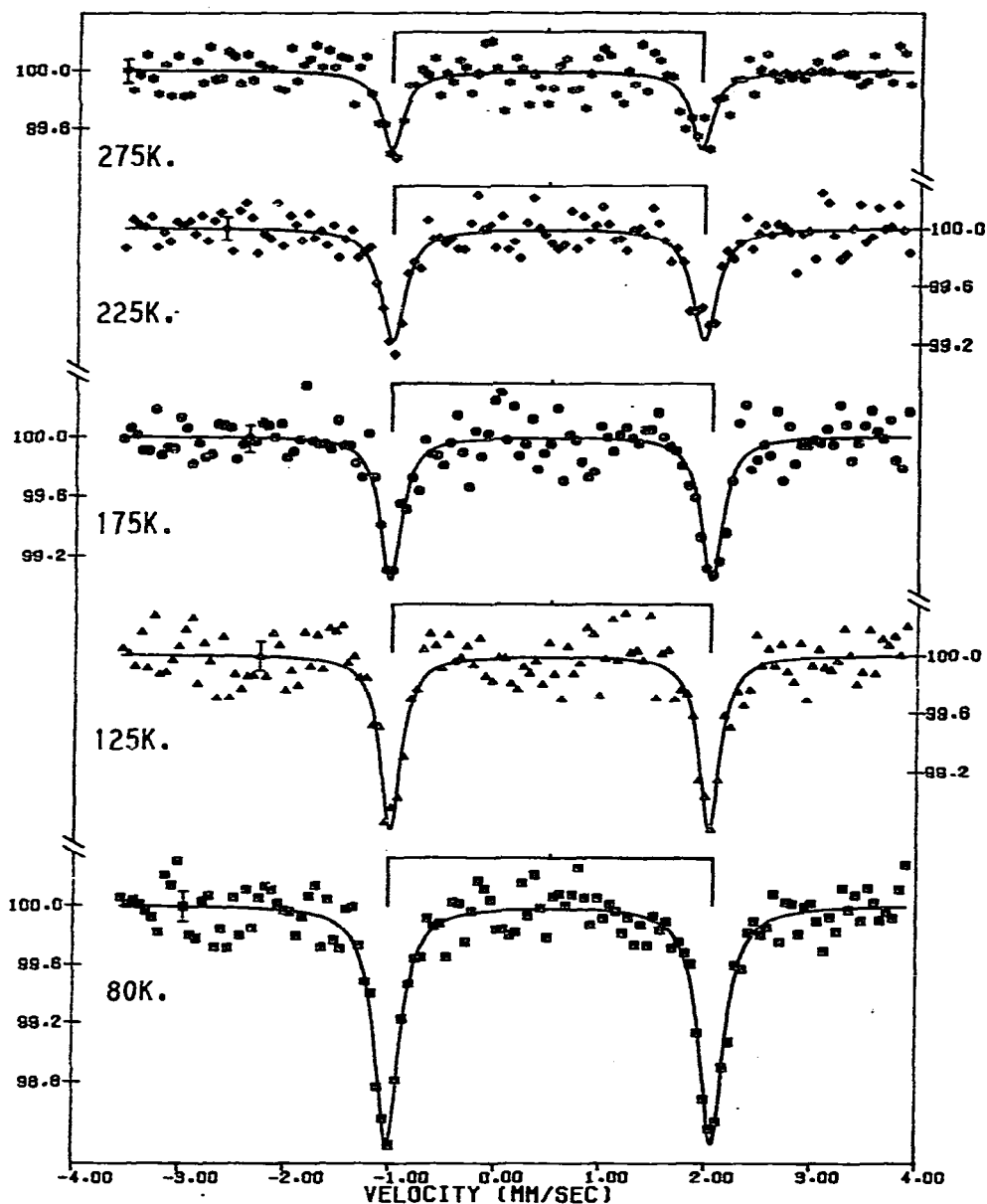
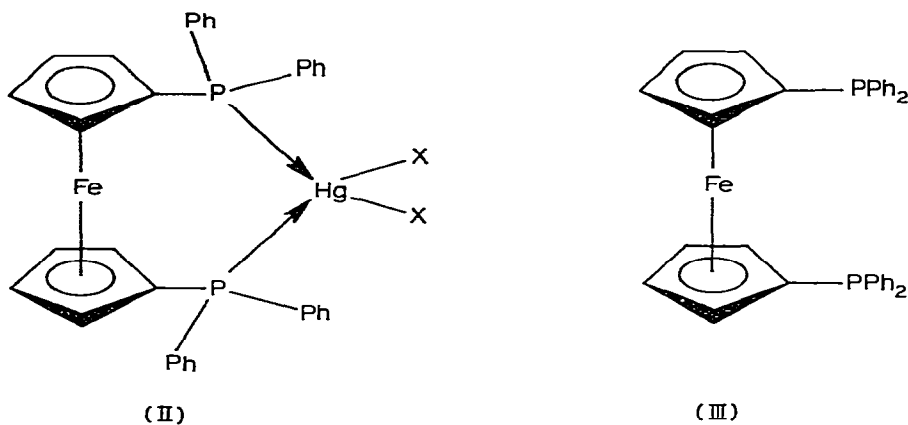


Fig. 1. Mössbauer spectra for the red $\text{Fe}(\text{Cp})_2 \cdot 7 \text{HgCl}_2$ adduct.

identified in bridged ferrocenes [16], also [3]ferrocenophan-1-one [19] and 1,1,2,2-tetramethyl-[2]-ferrocenophane [20] have $\phi = 9^\circ$ and 27° , respectively. More recently, in a Mössbauer study of trimethylene-bridged ferrocene derivatives [21], marked decreases in both the QS and IS were observed as the number of bridges (n) increases. This effect, especially for higher values of n was interpreted not only by ring tilt but also in terms of non planarity of the cyclopentadienyl rings causing a weakening of the metal-ring bonds. For the 1,1'-

trimethylene- and 1,1',2,2'-bistrimethyleneferrocenes, such ring distortion is unlikely to be very severe and the dominant effect will be that due to ring tilt. Thus it seems likely that ring tilt causes a lowering of both QS and IS though in these compounds there is no bonding to the iron other than that of the two rings.

In our case, the incoming mercury atom would cause a large distortion of the e_{2g} orbitals. In addition, the bulk of the Hg atom would necessitate a large value of ϕ . Molecular models suggest very severe hindrance between the ring protons and the Hg atom in the absence of such ring tilt. Supporting this is the observation that ferrocenes with bulky ring substituents fail to produce the orange product [22]. Results obtained in these laboratories using 1,1'-bis-chloromercuriferrocene confirm this finding. Interestingly, substituents capable of complexation with the Hg atom result in no Fe—Hg bond formation but rather in bridged species such as II [22].



The QS and IS for II and its parent III are very close, (2.264, 2.286, and 0.436, 0.437, respectively [22]), proving the absence of any Fe—Hg interaction. The QS value in particular is a great deal lower than our observed value for $\text{Fe}(\text{cp})_2 \cdot 7 \text{HgCl}_2$.

The isomer shift of the blue adduct $\text{Fe}(\text{Cp})_2 \cdot 2 \text{HgCl}_2$ ($0.62 \pm 0.3 \text{ mms}^{-1}$ at 80 K) (Table 1, Fig. 2), is typical of those found for other ferrocinium salts [23,24], while the isomer shift of $\text{Fe}(\text{Cp})_2 \cdot 2 \text{HgCl}_2$ is only a little more negative than that of ferrocene itself [23–26]; the absence of a quadrupole splitting in the blue complex shows that oxidation of the red complex has taken place to form the $\text{Fe}(\text{Cp})_2^+$ ion. Molecular orbital calculations by Shustorovich and Djatkina [27] show that the ferrocinium cation is formed by removal of an electron from the e_{2g} molecular orbital of ferrocene itself. For the oxidation of $\text{Fe}(\text{Cp})_2 \cdot 7 \text{HgCl}_2$ to $\text{Fe}(\text{Cp})_2 \cdot 2 \text{HgCl}_2$ it is likely that the covalent Fe—Hg bond splits photolytically so that the electron passes to the Hg_2^+ reducing it to Hg_2^{2+} with the release of most of the “lattice” HgCl_2 .

Experimental

$\text{Fe}(\text{Cp})_2 \cdot 7 \text{HgCl}_2$ and $\text{Fe}(\text{Cp})_2 \cdot 2 \text{HgCl}_2$ were prepared by the methods reported by Morrison and Hendrickson [9]. Both compounds analysed reason-

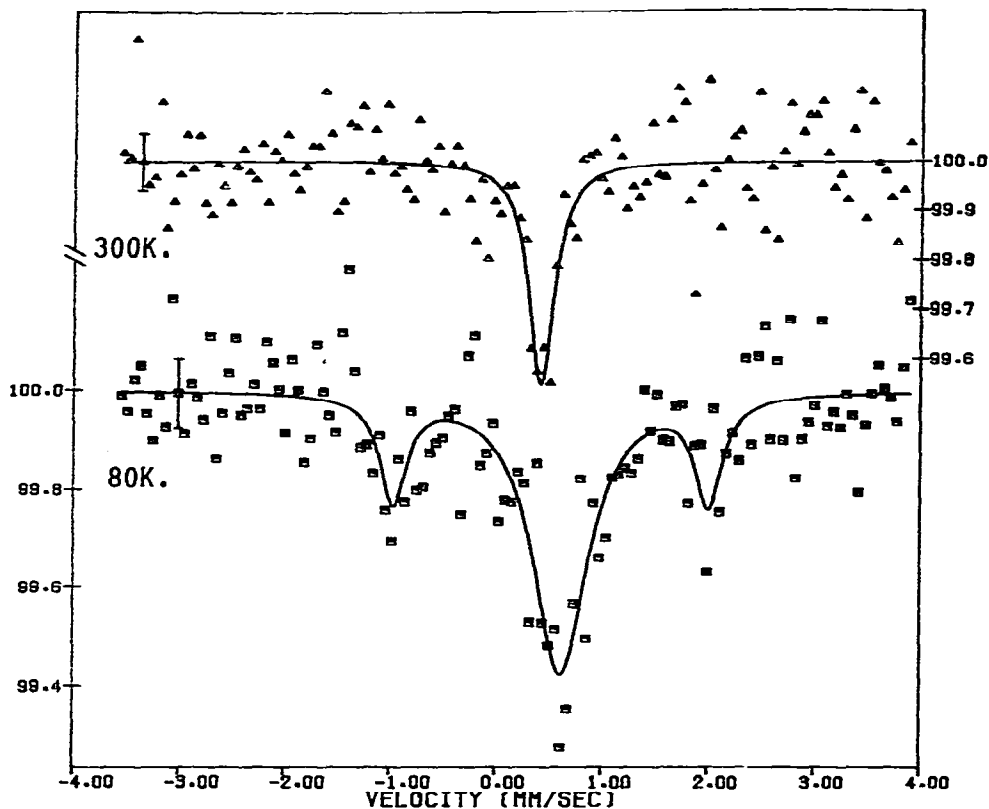


Fig. 2. Mössbauer spectra for the blue-grey $\text{Fe}(\text{Cp})_2 \cdot 2 \text{HgCl}_2$ adduct (aged from the red adduct used for spectra shown in Fig. 1).

ably well for the above stoichiometry. Typical analyses for the orange-red complex are: Found C, 6.10, H, 0.50, Cl, 22.7, Hg, 67.6. Calcd. for $(\text{Cp})_2\text{Fe} \cdot 7 \text{HgCl}_2$, C, 5.76, H, 0.48, Cl, 23.8, Hg, 67.3%. The chlorine analysis of both Hendrickson and our own product was consistently 1% low. This is probably due to the fact that the mercury has to be removed by precipitation as HgS prior to chloride analysis, some of the chloride being entrained in the HgS .

The Mössbauer absorbers had to be very thin to be transparent to 14.4 keV γ -radiation. The freshly prepared powdered solid was pressed between two thin sheets of "Melinex" polyester sheet separated by an annulus of the same material. This, clamped between lead washers, was loaded into a vacuum cryostat, as described previously [28] and the spectra of the red adduct were obtained.

The blue-grey material was prepared by ageing the red adduct in light and air, with no further separation, and was mounted in the same manner; this accounts for the small residual signal from the unoxidised material in these spectra.

Spectra were fitted as described previously [28]; the velocity scale was calibrated using iron foils of 10 mg cm^{-2} thickness to which isomer shifts are referred.

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