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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

XI *. STABILISATION AND ELECTRON TRANSFER IN DIFERROCENYL MONOCATIONS AND RELATED SPECIES

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Summary

The structures of the diferrocenyl methyl cation (I) and protonated diferrocenyl ketone (II) are discussed in terms of modes of stabilisation. Evidence supporting the involvement of e_1 rather than e_2 orbitals in I is given with particular reference to values of Mössbauer quadrupole splittings (*QS*) which are very much smaller than those of monoferrocenyl carbenium ions. The reaction of Fc_2CO and Fc_2CHOH with $FeCl_3$ was investigated using frozen solutions. For Fc_2CO, a redox reaction occurred resulting in the oxidation of only one iron site even with excess oxidant. These results were confirmed by cyclic voltammetry. For Fc_2CHOH, no redox reaction was observed but the $FeCl_3$ appears to coordinate to the alcoholic oxygen atom resulting in a marked diminution of *QS*. The observed *QS* values are rationalised in terms of electron donation by the ferrocenyl e_1 orbitals. This explanation is extended to cover previously reported Mössbauer spectra for biferrocenium and biferrocenylenium monocations.

Introduction

We have reported the Mössbauer data for ferrocenyl carbenium ions [2,3] and protonation of ferrocenyl ketones [4] as part of our work on Mössbauer studies of ferrocene complexes [2–11]. In these studies we postulated that exalted *QS* values (i.e. greater than that of solid ferrocene itself) in ferrocene systems are due to electron withdrawal from iron-based orbitals e_2, whereas low *QS* values are due to electron withdrawal via ring-based orbitals, e_1. Bridged ferrocenyl carbenium ions and related protonated ketones were found to behave in a similar manner [7].

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In recent years a number of Mössbauer studies [12–17] on biferrocene and other complexes containing two neighbouring ferrocene moieties have been reported. Two distinct types of Mössbauer data have been found for the monocations of these complexes. These are: (1) those that show two distinct Mössbauer sites arising from one Fe^{II} centre and one Fe^{III} centre caused where the rate of thermal intervalence transfer is less than 10^7 s^{-1} (the ^{57}Fe nuclear excited state lifetime is 10^{-7} s) in such compounds as biferricenium triiodide [14], and (2) those that show only one Mössbauer doublet with a much reduced quadrupole splitting such as in biferricenylenium triiodide and related compounds [14,15]. Here the rate of intervalence transfer due both to thermal and tunnelling processes is such that only an average iron environment is seen and hence it would be expected that the rate is greater than 10^7 s^{-1} (for detailed arguments on the apparent rate against the theoretical rate see Refs. 14, 15 and 17). These latter average valence type cations have the odd electron delocalised in a molecular orbital encompassing both iron centres. The main structural difference found in the compounds that display these effects are in the Fe–Fe distances, in the biferricenylenium ions it is safe to assume that the distance is close to that in biferrocenylene [17] (3.98 Å); unfortunately for the Fe^{II}/Fe^{III} biferricenium ions no crystal structure is known, but for diferrocenylselenium iodine triiodide hemi (methylene chloride) the distance is 6.06 Å [17] which is much greater.

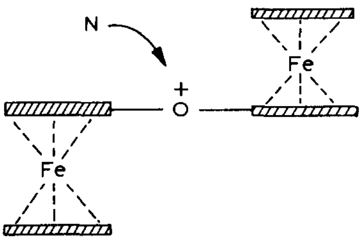
The crystal structure [19] of α,α-diferrocenylmethylium tetrafluoroborate shows that the carbenium ion is in the transoid conformation. The exocyclic carbon is displaced 0.5 Å above the ring of the first ferrocenyl moiety and 0.4 Å below the plane of the other ferrocenyl. As a result the exocyclic carbon atom is closer to the iron atom of the first ferrocenyl (2.69 Å) than to the other Fe atom (2.87 Å). The Mössbauer data QS 2.10 mm s^{-1} for this compound [14] shows evidence for only one iron site, and this was explained by the two iron atoms that have approximately the same charge which does not differ appreciably from that of ferrocene. The latter point is highly questionable as ferrocene in their paper is accredited with a QS of 2.396 mm s^{-1}. However they then state, it is in accord with their results to assume a positive charge on the iron. In the light of our studies [2–4,7] we interpret the data of Gleiter et al. [13] to show that the e_1 orbital overlaps are helping to stabilise the charge on the exocyclic carbon and that though the iron crystallographic environments are not the same the electronic environments are identical. We were especially interested in this diferrocenylmethylium ion as all the carbenium ions we have examined show larger QS values than ferrocene. This stimulated us to carry out studies on the chemistry of both the diferrocenylmethyl alcohol and the corresponding ketone.

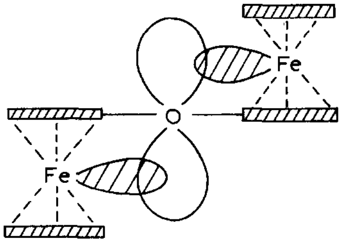
Results and discussion

Protonation of Fc_2CO and stability of Fc_2CH^+

The protonation of diferrocenyl ketone has been investigated by a number of workers. Illuminati et al. [21,22] reported on the use of ferrocenyl ketones as Hammett indicators using UV spectroscopy. The pK_a values of various ketones (FcCOR) were reported. Acetyl ferrocene was found to be some five orders of magnitude stronger a base than acetophenone. However, interestingly the introduction of a second ferrocene substituent (Fc_2CO) caused a further increase in base strength of only 0.38 pK_a units. The authors interpret this surprising result to a "saturation" effect of the first ferrocene group. This explanation is unlikely in that this would result in two different iron environments which is contrary to our Mössbauer findings. Hester and Cais [23] have studied the protonation of Fe_2CO in $CF_3CO_2H/CHCl_3$ mixtures. In pure CF_3CO_2H the Cp resonances were assigned at 4.48 ppm and the H(2,5) and H(3,4) protons at 5.36 and 5.47 ppm respectively. (However see below). We obtained a qualitatively similar spectrum but the above resonances occurred at 3.90, 4.77 and 4.85 ppm using extreme TMS as a reference. The assignment of the substituted ring protons however is probably wrong in view of the work of Olah and Mo [24] on the protonation of acetylferrocene. Hester and Cais also suggests that diprotonation occurs in the more acidic media and postulate structures such as Fc_2C^{2+} and $Fc_2COH_2{}^{2+}$. The former is most unlikely in view of the Mössbauer results discussed later and there is no real evidence for diprotonation from either ^1H NMR or Mössbauer spectroscopy.

Formation of the carbenium ion (or ion pair) from Fc_2CHOH occurs readily. Values for pK_{R^+} for either process range from 4.08 in H_2O [25] to 2.44 in benzene [21]. The corresponding pK_{R^+} value for $FcCH_2{}^+$ is much lower at -1.17 illustrating the enhanced stability of Fc_2CH^+, though in benzene there appears to be relatively little difference in carbenium ion stability for $Fc\overset{+}{C}HMe$, $Fc_2\overset{+}{C}H$ and Fc_3C^+. In a study of nucleophilic attack on carbenium ions by water it was found that $Fc_2\overset{+}{C}H$ reacted considerably slower than monoferrocenyl carbenium ions and as $Fc\overset{+}{C}HPh$, and was explained in terms of steric hindrance of the second ferrocene substituent [25]. It is well established that nucleophiles attack such ions from the *exo* side of the molecule [26], probably due to neighbouring group participation by the iron e_{2g} orbitals.





In the case of $Fc_2\overset{+}{C}H$, attack by a nucleophile N would be *exo* to ferrocenyl substituent Fc1 but must of necessity be *endo* to Fc2 due to the transoid nature of the rings [19,20]. In the case of $Fc_2\overset{+}{C}H$, molecular orbital treatment of the four electron three orbital system shows that there is no net energy gain by participation by the second e_{2g} set. Mixing of the first e_{2g} set and the $2p$ orbital would result in some stabilisation. Interaction between this new MO set and the second e_{2g} orbital produces no net gain, it being a "filled-filled" interaction. Indeed, the two way overlap would resemble the S_N2 transition state and would therefore be unstable. It therefore appears that stabilisation of the ion occurs preferentially via the Cp ring based orbitals. It is interesting in this context to examine the recent ^{57}Fe chemical shift data of Von Philipsborn et al. [27] for these ions and ferrocene derivatives in general. For the carbenium ions, both $Fc\overset{+}{C}H_2$ and $Fc\overset{+}{C}HMe$ show unexpected shielding of the iron nucleus compared with ferrocene. This surprising effect was attributed to the conversion of a Cp ring into a fulvene-type ligand. By contrast

TABLE 1

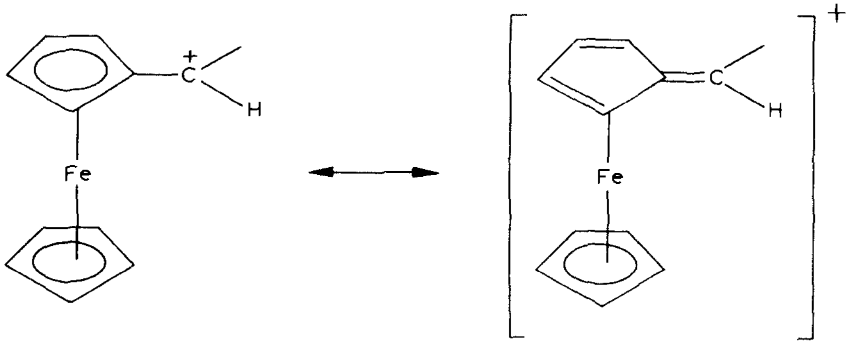
CORRELATION OF ^{57}Fe NMR CHEMICAL SHIFTS ($\delta(^{57}Fe)$) (ppm) from $^{73}GeCl_4$) AND QUADRUPOLE SPLITTINGS (QS (mm s^{-1})) FOR SOME FERROCENES FcR AND FERROCENYL CARBENIUM IONS ($Fc\overset{+}{C}HR$)

Ferrocenes		
R	QS [a]	$\delta(^{57}Fe)$ [b]
H	2.38	1543
COMe	2.27	1766
COPh	2.26	1808
$(COMe)_2$	2.14	1986
Ferrocenyl carbenium ions		
R	QS [c]	$\delta(^{57}Fe)$
H	2.70	1036
Me	2.61	1340
Fc	2.13 [d]	2275

[a] Values from Ref. 4. [b] Average values taken from Ref. 27. [c] Values from Refs. 2 and 3. [d] This work cf. Ref. 12.

Fc_2C^+ showed a large deshielding indicative of a different type of structure. An interesting feature of the ^{57}Fe NMR results is that there is a good correlation of $\delta(^{57}Fe)$ with QS (Table 1). For uncharged ferrocenes a correlation coefficient (r) of 0.994 (4 points) is obtained whereas for carbenium ions $r = 0.996$ (3 points). The two correlations appear to lie on parallel lines though as yet the data is too scanty to be statistically satisfactory. Nevertheless, such correlations if substantiated would be very useful in predicting $\delta(^{57}Fe)$ values which are difficult to measure experimentally.

The PMR spectra of I in CD_2Cl_2 reported by both Cais [19] and Mueller-Westerhoff [28] differ substantially in the assignment of the central methine proton, H_{exo} (δ 5.00 and 8.46 ppm). In this work, the spectrum (external TMS as reference) of a CF_3CO_2H solution of Fc_2CHOH showed a sharp singlet (10H, Cp) at 4.06, two broad triplets at 4.45 and 5.16 ppm (4H each H(2), H(5) and H(3), H(4) respectively) and a sharp singlet at 7.90 ppm for the carbenium methine, the latter being in reasonable agreement with that of Mueller-Westerhoff et al. Thus H_{exo} is very much more deshielded than that of the monoferrocenyl cation $Fc\overset{+}{C}H_2$ (5.37 ppm, Ref. 2) which is probably shielded by the iron e_{2g} electron pair. This is further evidence for e_{1g} orbital stabilisation since, in a structure with fulvenoid character, H_{exo} becomes



pseudo olefinic in character and thus suffers deshielding via the anisotropic effect of the partial double bond.

The crystal structures of di- and mono-ferrocenyl carbenium ions differ in some important respects. Thus for $[Fc_2CH]^+$ $[BF_4]^-$ the iron atoms are not displaced significantly from a central position between the two Cp rings [20]. However for $[FeCPh_2]^+$ $[BF_4]^-$ the iron atom is displaced 0.08 Å towards the exocyclic carbon atom [29], as might be expected for stabilisation by e_{2g} orbitals. Thus evidence from a variety of sources points towards a different type of stabilisation for the diferrocenyl carbenium ions involving overlap with the ring based orbitals (e_1). Further experimental evidence comes from the Mössbauer data discussed in the next section.

Mössbauer spectroscopy of Fc_2CO, $Fc_2\overset{+}{C}HOH$ and derivatives

The structure of diferrocenyl ketone [30]

Each iron atom is sandwiched between two rings which are planar, parallel, separated by 3.30 Å and rotated 5° from an eclipsed orientation. The ferrocenyl groups are rotated 17° out of the carbonyl plane as a result of intramolecular steric interference between atom H(8) and H(8′). The distance between which would be only about 1.7 Å in a coplanar model, but is increased by 2.5 Å by the rotations from planarity. Because of the rotations, the oxygen atom is displaced from the ring planes by 0.33 Å.

Although the crystal structure of diferrocenyl alcohol is not known in solution it is likely that the molecule has a similar conformation to that found in the tetrafluoroborate salt of its carbenium ion [20,21].

Frozen solution Mössbauer spectroscopic studies were carried out on both the alcohol and ketone using CF_3CO_2H and H_2SO_4 (Table 2).

TABLE 2

^{57}Fe MÖSSBAUER PARAMETERS FROZEN SOLUTIONS OF Fc_2CO AND Fc_2CHOH WITH $FeCl_3$ IN STRONG ACIDIC MEDIA AT 80 K

Complexes/Solvent	*IS* (mm s^{-1})	*QS* (mm s^{-1})	Halfwidth
Fc_2CHOH/solid	0.51(2)	2.45(2)	0.12(2)
Fc_2CHOH/TFA	0.52(2)	2.13(2)	0.18(2)
$[Fc_2\overset{+}{C}H][PF_6^-]$	0.54(2)	2.13(2)	0.15(2)
Fc_2CO/solid	0.53(2)	2.28(2)	0.13(2)
Fc_2CO/H_2SO_4 80%	0.53(2)	2.11(2)	0.13(2)
$Fc_2CHOH + FeCl_3$/[a]	0.57(2)	2.20(2)	0.16(2)
$CH_3COC_2H_5$	0.52(3)	0.78(6)	0.22(5)
$Fc_2CO + FeCl_3$/[a]	0.50(2)	2.24(2)	0.13(2)
$CH_3COC_2H_5$	1.46(4)	3.01(2)	0.19(5)
	0.50(4)	0.00	0.30(6)
$Fc_2CO + FeCl_3$/[b]	0.53(2)	2.22(2)	0.14(2)
$CH_3COC_2H_5$	1.41(3)	3.17(6)	0.22(5)
	0.46(2)	0.00	0.31(3)

[a] The molecular ratio of $FeCl_3$ to ferrocenyl complex is 1/1. [b] The molecular ratio of $FeCl_3$ to ferrocenyl complex is 2/1.

The *QS* value of the solid ketone, Fc_2CO was 2.28 mm s^{-1}, typical of a ferrocenyl ketone. The frozen solution of the protonated ketone in H_2SO_4 80% showed a decrease in *QS* to 2.11 mm s^{-1}. ΔQS (0.17 mm s^{-1}) of this ketone is within the range of other mono-protonated ferrocenyl ketones 0.19–0.04 mm s^{-1} reported previously [4,7].

The quadrupole splitting of the alcohol in the solid state was 2.45 mm s^{-1}, whereas in frozen solution in trifluoroacetic acid it decreased to 2.13 mm s^{-1}. This value was in good agreement with that previously reported for the solid salts of $[Fc_2CH]^+$ $[ClO_4]^-$ [11], $[BF_4]^-$ [13] and the $[PF_6]^-$ (Table 1).

These results show that protonation of the alcohol and the ketone results in each case in a lowering of *QS* values compared to that of ferrocene and their unprotonated precursors (ΔQS 0.32, 0.17 mm s^{-1} respectively). This can be interpreted that in both cases stabilisation takes place through e_{1g} orbitals and conjugation of the two rings adjacent to the centre of positive charge. As already stated in the introduction this means that for the $[BF_4]^-$ salt of $[Fc_2CH]^+$ where the crystal structure is known [11], the iron atoms then have identical electronic environments (seen in the Mössbauer spectra as only one quadrupole doublet) though they have different crystallographic environments as they are different distances from the exocyclic carbon atom. Hence in this case the iron atoms are not directly bonding via e_2 orbitals to the exocyclic carbon atom.

These results support the explanations we have previously given for exalted or reduced ferrocene quadrupole splittings [1–10].

Diferrocene alcohol and ketone were reacted with anhydrous $FeCl_3$ separately. When 1 *M* of Fc_2CHOH was reacted with 1 *M* of $FeCl_3$ in $CH_3CO_2C_2H_5$ two doublets were observed in the Mössbauer spectrum (Table 2). The outer doublet was assigned to diferrocenyl species and the inner doublet to $FeCl_3$, presumably coordinated to the carbinol function. The Mössbauer spectrum of $FeCl_3$ in $CH_3CO_2C_2H_5$ showed only a singlet. When 1 *M* of Fc_2CO was reacted with 1 *M* of $FeCl_3$ in $CH_3CO_2C_2H_5$, the Mössbauer spectrum showed two doublets and one singlet which indicates three different iron environments. One of the doublets is assigned to the iron atom in diferrocene ketone which had not reacted with the $FeCl_3$ (*QS* 2.24 mm s^{-1}). The other doublet with a quadrupole splitting of 3.01 mm s^{-1}, typical of $FeCl_2$ was assigned to the reduced $FeCl_3$ in reaction with one of the two iron atoms in diferrocenyl ketone. Finally the singlet was due to the oxidation of one ferrocenyl iron site to ferricinium. The percentages of the absorption area 62.9, 16.8, 20.3% for Fe^{II} in diferrocenyl ketone (Table 3), Fe^{II} in the $FeCl_2$ complex and Fe^{III} (total) in ferrocinium site in diferrocenyl ketone and a very small amount of unreacted $FeCl_3$ in frozen solution. The experiment was repeated with the ratio of $FeCl_3/Fc_2CO$ of 2/1. The general pattern was different only in the sense of intensities of the absorption peaks. i.e. more unreacted $FeCl_3$ remained in the solution and the corresponding singlet was more intense.

The percentages of the absorption area were 35.5, 22.6 and 41.9%, for Fe^{II} in diferrocenyl ketone, Fe^{II} in $FeCl_2$, Fe^{III} total in $FeCl_3$ and in the ferricinium site respectively.

The fact that less than half of the original iron present in the ketone is oxidised even in the presence of excess $FeCl_3$ can be explained by the first oxidation potential of the ketone being lower than that of the second due to interaction between the two neighbouring iron sites. When the data in Table 3 are compared, it is clear that one

TABLE 3

PERCENTAGES[a] OF Fe^{II} AND Fe^{III} PRESENT IN THE REACTION OF DIFERROCENYL KETONE WITH $FeCl_3$ (FROZEN SOLUTION)

<table>
<tr><th></th><th>Fe^{II} in Fc_2CO</th><th>Fe^{III} ($FeCl_3$)</th><th>Fe^{III} in Fc_2CO</th><th>Fe^{II} ($FeCl_2$)</th></tr>
<tr><td>$Fe_2CO/FeCl_3$ (1/1)</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Initial</td><td>66.6</td><td>33.3</td><td>0</td><td>0</td></tr>
<tr><td>Expected final</td><td>33.3</td><td>0</td><td>33.3</td><td>33.3</td></tr>
<tr><td>Observed</td><td>63</td><td colspan="2">20</td><td>17</td></tr>
<tr><td>$Fe_2CO/FeCl_3$ (1/2)</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Initial</td><td>50</td><td>50</td><td>0</td><td>0</td></tr>
<tr><td>Expected final</td><td>0</td><td>0</td><td>50</td><td>50</td></tr>
<tr><td>Observed</td><td>35</td><td colspan="2">42</td><td>23</td></tr>
</table>

[a] Calculated from % absorption in Mössbauer spectra assuming that the *f* factors for each iron centre are the same at 80 K. However as the *f* factor depends on chemical bonding this may not be strictly true and some error in these figures is to be expected.

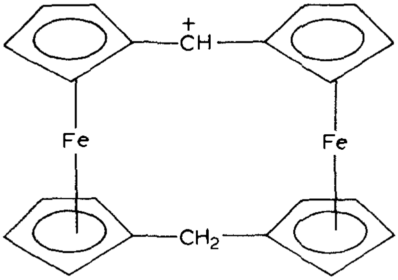
out of every two ferrocenyl iron centres is oxidised even in the presence of excess oxidant.

$E_{1/2}$ values obtained from cyclic voltammetry measurements on Fc_2CO gave two oxidation potentials at 890 and 725 mV compared with a value of 690 mV for $FeCl_3$. As the second oxidation potential of Fc_2CO is so close to that of $FeCl_3$ then no redox reaction would be expected. One other interesting feature of the results is the slight decrease in *QS* of the remaining iron(II) site when the other site becomes iron(III). An insight into this problem comes from a consideration of work on biferrocenium and biferrocenylenium mono-cations conducted by other workers [14–19]. As discussed earlier, the Mössbauer spectra of these cations are rationalised either as being due to average valence type species (Mössbauer spectra show only one iron site) or mixed valence type showing the presence of both Fe^{II} and Fe^{III}. In both types however, the *QS* is less than that of the parent material. The ferricinium sites are unique in showing a small *QS*. Previously no attempt was made to explain these observations. We offer the following solution. Firstly, for the mixed valence cations, oxidation yields a ferrocene and ferricinium site. The latter should result in a single line spectrum. However, in this system both sites are linked via the Cp rings. The ferrocene moiety should have the same *QS* as the original neutral species but in this case can act as an electron rich donor to the neighbouring ferricinium site via e_1 ring-based orbitals. An extra electric field gradient is thus generated at the ferricinium site to give an observable *QS*. The ferrocene site, as a result of electron withdrawal via e_1 orbitals, now has a reduced *QS* [2,3].

The average valence case is explained in an analogous manner, except that now the electron is rapidly and reversibly exchanging at a rate in excess of 10^7 sec^{-1}. Both Fe centres therefore experience the same partial electron density, and hence only one Mössbauer signal is observed with a *QS* substantially lower than that of the original neutral molecule.

In the case of frozen solutions of $Fc_2CO/FeCl_3$, the Mössbauer spectrum exhibits a slightly reduced *QS* of the unoxidised ferrocene site compared with Fe_2CO itself which donates some electron density of the ferricinium moiety. But because the

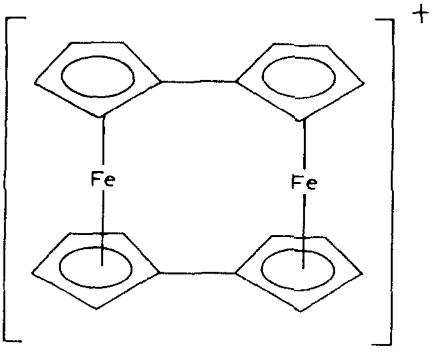
$FeCl_3$ absorbs in the same region as ferrocinium the resulting small *QS* that should be visible in the ferricinium spectra is masked.



(III)

In the case of the reaction of Fe_2CHOH and $FeCl_3$ (1/1) no oxidation is observed as indicated by the absence of high-spin Fe^{II} in the Mössbauer spectrum. The *QS* values of the ferrocene can be explained by coordination of $FeCl_3$ with the oxygen atom. This coordination inductively withdraws electron density from the ring system, causing a marked reduction of 0.25 mm s^{-1} for each ferrocenyl moiety. The presence of the coordinated oxygen to the $FeCl_3$ (which may also be solvent coordinated) causes an observable *QS* (0.78 mm s^{-1}).

Returning to question of carbenium ion stability in the diferrocenyl series, Mössbauer data for the fixed *cis* carbenium ion are of relevance to the above arguments.



(IV)

Being a rigid fixed cisoid structure, there will be less likelihood of iron participation due to mutual repulsion of the two sets of e_{2g} orbitals. Thus stabilisation via ring-based orbitals should be even more dominant. Such stabilisation should be greater for the *cisoid* (III) than the *transoid* ion (I), since in the latter the carbenium ion is displaced further from the Cp ring planes (~ 0.5 and 0.2 Å for I and III respectively). This postulate is confirmed by the *QS* values for the two ions of 2.13 mm s^{-1} for I and 1.80 mm s^{-1} for III [28]. The data for III can be compared with that of the biferricenylenium cation (IV), which has a *QS* value of 1.72 mm s^{-1} at 300 K [14]. Since only one Mössbauer doublet is observed for this ion it is concluded that intervalence transfer is more rapid than 10^7 s^{-1}.

The Fe–Fe distance is 3.98 Å in biferrocenylene itself [18] and is likely to be the same for the ion. This compares with a value of about 5.2 Å for cation III which is still close enough for a rapid intervalence transfer via ring-based orbitals.

The ideas propounded in this paper will be developed in a future paper in this series.

Experimental

Diferrocenyl ketone [31]

To a mixture of aluminium chloride (13.3 g, 0.1 mol) in ethylene chloride (100 ml) under nitrogen was added a solution of diphenylcarbamyl chloride (23.1 g, 0.1 mol) in ethylene chloride (100 ml) with subsequent dropwise addition of a solution of ferrocene (18.6 g, 0.1 mol) in the same solvent (50 ml) over a 10 min period. The reaction mixture was held at reflux for 14 h under N_2. The solvent was removed and the residue was taken up in 20% ethanolic potassium hydroxide and was allowed to reflux for 18 h. After evaporation of the solvent, the reaction mixture was dissolved in water and was acidified with concentrated hydrochloric acid. The crude acid precipitated on cooling. The acid was stirred with phosphorus pentachloride (13.7 g, 0.066 mol) in dry benzene (15 ml) for 2 h at room temperature. The reaction mixture was filtered and the filtrate concentrated in vacuo at 100°C to remove the benzene and phosphorus oxychloride. The resulting FcCOCl (5.2 g, 0.02 mol) was treated with $AlCl_3$ (3.1 g, 0.023 mol) and added to ferrocene (4.2 g, 0.022 mol) in ethylene chloride and stirred for 2 h at room temperature. The complex was decomposed in ice water and worked up in the usual manner for a Friedel-Crafts acylation reaction. 3 g Fc_2CO was collected after separation on an Al_2O_3 column (38%).

Diferrocenyl methanol [32]

Diferrocenyl ketone (4 g, 0.01 mol) was dissolved in dry ether (500 ml) and the solution refluxed for 0.5 h with lithium aluminium hydride (4.0 g, 0.1 mol). The excess of hydride was decomposed with ethylacetate, the mixture filtered, and the filtrate evaporated. The residue (2.5 g, 62%) was recrystallized from cyclohexane to give pure diferrocenylmethanol, m.p. 174–176°C. Mössbauer spectra were obtained and fitted as previously described [33].

Cyclic voltammetry

Half point potentials for $FeCl_3$, ferrocene and diferrocenyl ketone were determined from their reversible redox reactions in anhydrous, nitrogen-saturated 2-butanone, using both gold and carbon working electrodes. The auxilliary electrode was platinum and the reference electrode an Ag/AgCl electrode in aqueous LiCl (2 *M*) with 1% agar. The tip of the reference electrode was approximately 0.1 mm in diameter. The supporting electrolyte was 0.2 *M* $[(n\text{-Bu})_4N]^+$ $[ClO_4]^-$ prepared according to House et al. [34]. Instrumentation was provided by C.W. Anderson, Duke University, Durham, N. Carolina, U.S.A.

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