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# MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

# IV *. SUBSTITUENT EFFECTS IN FERROCENYL-CARBENIUM IONS

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## Summary

The structure of secondary ferrocenyl-carbenium ions of the type $C_5H_5Fe\text{-}C_5H_4\overset{+}{C}HR$ have been investigated by $^1H$ NMR spectroscopy in $CF_3CO_2H$ and by $^{57}Fe$ Mössbauer spectroscopy of solid solutions of the same medium. As with primary ions ($R = H$) exalted values of quadrupole splittings (QS) were observed for $R = CH_3$, $C_6H_5$, indicative of iron participation via $\epsilon_2$ orbitals. For the aromatic series ($R = p\text{-}C_6H_4X$), QS values decreased as the electron donating power of the substituent increased, due to increased stabilisation via the phenyl ring at the expense of iron participation. It is 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 $\epsilon_2$, whereas low QS values are due to electron withdrawal via ring-based orbitals $\epsilon_1$. The NMR data is discussed in terms of steric hindrance to coplanarity of the phenyl ring with the vacant $sp^2$ orbital of the carbenium ion. Dialcohols of the type $Fe(C_5H_4CHOHR)_2$ gave only mono-carbenium ions.

## Introduction

The structure of ferrocenyl-carbenium ions has long been a matter of some controversy. The point at issue is the exact mechanism by which such ions are stabilised. Various models have been put forward to account for the strong electron releasing properties of the ferrocenyl group in these ions. These include (a) stabilisation via cyclopentadienyl ring (Cp) orbital overlaps with the empty

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[*] For part III see ref. 1.

[**] Addressees for further correspondence.

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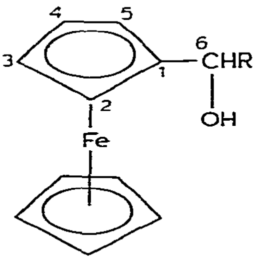
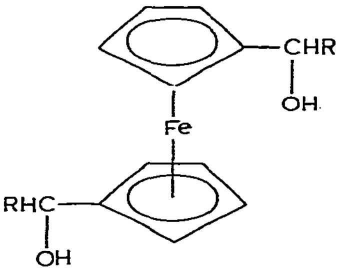
$C_{exo}$ $p$ orbital, (b) iron participation via $\epsilon_{2g}$ metal-based orbitals, (c) ring tilted structures, (d) ring "slip" structures and (e) bent fulvenoid ligands. An excellent summary of the arguments has been recently published [2]. So far only two crystal structures of ferrocenyl-carbenium ions have been reported, that of α,α-diferrocenylmethylium tetrafluoroborate [3] and ferrocenyldiphenylcarbenium tetrafluoroborate [4]. In both cases the exocyclic carbon was bent out of the Cp ring plane towards the central iron atom (angles of 19.9 and 20.7° respectively). The Fe—$C_{exo}$ distances were 2.71, 2.85 and 2.71 Å respectively, which suggest some degree of bonding, though the evidence is not conclusive. Recently $^{57}$Fe NMR has been used to investigate ferrocenyl-carbenium ions [5]. $^{57}$Fe chemical shifts and $^{13}$C—$^{57}$Fe coupling constants support the direct involvement of the iron atom in stabilisation. We have reported [1] some preliminary findings on Mössbauer parameters of frozen solutions of these ions which also indicate iron participation. It is the purpose of this paper to elucidate the extent to which this participation occurs by a systematic variation of substituents on the carbenium carbon ($C_{exo}$).

The corresponding alcohol precursors were synthesised by standard literature methods and the carbenium ions were formed by dissolving these alcohols in strongly acidic media ($CF_3CO_2H$, $CF_3SO_3H$ and $H_2SO_4$). These media have previously been shown to generate the ions almost quantitatively [6]. Solutions of the ions were found to be quite stable over a period of at least two days in $CF_3CO_2H$. The following systems were investigated.



( I )



( II )

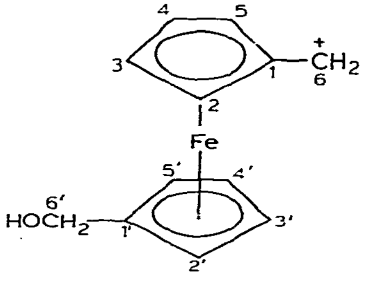
(Ia, R = H;
Ib, R = $CH_3$;
Ic, R = $C_6H_5$;
Id, R = $p$-$C_6H_4CH_3$;
Ie, R = $p$-$C_6H_4OCH_3$;
If, R = $p$-$C_6H_4Cl$;
Ig, R = $p$-$C_6H_4CN$)

(IIa, R = H;
IIb, R = $CH_3$)

The corresponding ions are represented as follows: that from Ia as [I$\overset{+}{a}$] etc.

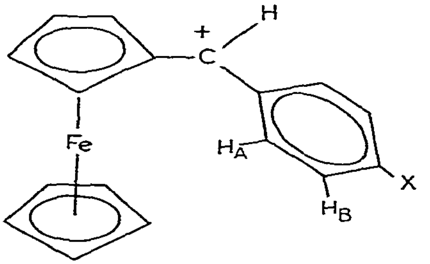
## NMR spectroscopy

The spectrum of [I$\overset{+}{a}$] was reported previously [1]. IIa on solution in $CF_3CO_2H$ gave rise to the mono-carbenium ion



($IIa^+$)

Two sharp proton singlets were observed at 4.65 and 5.68 ppm and assigned to the primary alcohol methylene (C(6')) and carbenium ion methylene (C(6)) respectively. The triplets (*J* 1.6 Hz) at 4.38 and 6.01 ppm were assigned to H(2,5) and H(3,4) respectively by comparison with corresponding protons in the spectrum of [I$\overset{+}{a}$] (4.20, 5.78 ppm). The triplets at 4.85 and 5.20 ppm were therefore assigned to H(2',5') and H(3',4') respectively. The spectrum of [I$\overset{+}{b}$] agreed qualitatively with that reported by Hisatome and Kamakawa [7] but our values of $\delta$ were consistently 0.52 ppm lower. The reason for the discrepancy is not clear. IIb again generated only the mono-carbenium ion. The signals for the methyl groups on the carbenium and alcohol moieties appeared as doublets at 1.83 (*J* 7.0 Hz) and 1.13 (*J* 6.3 Hz) respectively. The corresponding methines were observed as quartets at 6.83 and 5.30 ppm respectively. The two proton multiplet at 5.91 ppm was assigned to H(3) or H(4) and the one proton signal at 4.08 ppm to either H(2) or H(5). The remaining five protons appeared as an overlapping system of peaks at 4.4—5.0 ppm. As with [I$\overset{+}{b}$], due to restricted rotation about the C(1)—C(6) bond [8], protons H(2) and H(5) are magnetically non equivalent. The spectra of the aromatic carbenium ions [I$\overset{+}{c}$—I$\overset{+}{g}$] were remarkably similar differing only in the separation of the H(A) and H(B) protons on the benzene ring and chemical shift of H($\overset{+}{6}$). Table 1 lists the data for the series. It is immediately apparent that as for [I$\overset{+}{b}$] H(2) and H(5), and H(3) and H(4) are no longer magnetically equivalent. Inspection of molecular models shows that for a completely coplanar structure (i.e. Cp ring, empty *p* orbital on $C_{exo}$ and the benzene ring in the same plane), H(A) and H(2) (or H(5)) come within 0.8 Å of one another. This must result in considerable steric strain which can be alleviated by rotation about either C(1)—C(6) or C(6)—C(7) or both *. In order to achieve the optimum H(A)—H(2) distance of



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* Such compressions can also be alleviated to some extent by a deformation of the C(1)—$C_{exo}$ bond toward the iron atom.

TABLE 1

$^1H$ NMR DATA (chemical shifts δ in ppm from TMS) FOR A SERIES OF *para*-SUBSTITUTED PHENYLFERROCENYL CARBENIUM IONS ($C_5H_5FeC_5H_4\overset{+}{C}H$-$C_6H_4X$) AND *para*-SUBSTITUTED ANILINES IN $CF_3CO_2H$

| X | H(5) [a] | H(2) [a] | H(4) [a] | H(3) [a] | H(6) | $C_5H_5$ | H(A) | H(B) | δ(AB) [b] | *J*(AB) | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Ferrocenyl-carbenium ions* | | | | | | | | | | | |
| H | 4,10 | 4,83 | 5,50 | 5,71 | 7,42 | 4,17 | — | — | — | — | — |
| Me | 4,20 | 4,97 | 5,60 | 5,83 | 7,60 | 4,23 | 7,22 | 6,83 | 0,39 | 8 | Me 1,83 |
| OMe | 4,23 | 5,00 | 5,58 | 5,83 | 7,73 | 4,23 | 7,40 | 6,60 | 0,80 | 11 | OMe 3,47 |
| Cl | 4,17 | 4,88 | 5,65 | 5,88 | 7,41 | 4,28 | 7,18 | 6,92 | 0,26 | 8 | |
| CN | 4,20 | 4,80 | 5,75 | 5,88 | 7,33 | 4,35 | 7,33 | 7,33 | 0,00 | — | |
| *Anilines* | | | | | | | | | | | |
| X | — | — | — | — | — | — | — | — | — | — | — |
| OMe | — | — | — | — | — | — | 6,98 | 6,63 | 0,35 | 9 | OMe 3,50 |
| Me | — | — | — | — | — | — | 6,90 | 6,90 | 0,00 | 0 | Me 1,93 |
| Cl | — | — | — | — | — | — | 6,98 | 6,98 | 0,00 | 0 | — |

[a] Assigned by comparison with data of Hisatome and Kamakawa on [$Ic^+$] ref. 7. [b] δ(AB) = δ(A) — δ(B).

2.5 Å the phenyl ring must be rotated about 70° out of plane. Thus the sum of the dihedral angles between the Cp ring and the $sp^2$ plane of $C_{exo}$ ($\phi$) and between this plane and the phenyl ring ($\theta$) should be close to 70°. Evidence of such effects is quite clear from the crystal structure of ferrocenyldiphenylcarbenium tetrafluoroborate [4] where $\phi = 18.3°$ and $\theta$ for the two phenyl rings is 38.2 and 56.8°. One consequence of such an effect in [I$\overset{+}{c}$] is that rotation about both C(1)—C(6) and C(6)—C(7) will be restricted to a "tick tock" motion. Also H(2) and H(5) will move into the shielding cone of the phenyl ring and correspondingly H(A) will experience some shielding from the Cp orbitals. It has been noted that H(2) and H(5) in [I$\overset{+}{c}$] appear at a markedly higher field than those in 6-phenylfulvene [7] an anomaly which can be explained at least in part by the above type of increased shielding. The assignments of the substituted ring protons has been made by double resonance experiments and by comparing coupling constants $J(6,3)$, $J(6,2)$ with those from similar geometries in substituted indenes and benzofurans [7]. Protons in a "zig-zag" relationship have characteristic long range coupling constants of 0.6—0.8 Hz.

An interesting trend is seen in the $\delta$ values for the carbenium ion methine (H(6)) *. For electron releasing substituents H(6) is deshielded relative to the unsubstituted ion whereas electron-withdrawing groups cause shielding. For the latter substituents the ion can gain little in stability via resonance with the phenyl ring which could therefore, without detriment, rotate by $\theta = 70°$ leaving the Cp—$C_{exo}$ system almost coplanar. The ion would then be stabilised by either overlap with the Cp ring orbitals or by direct overlap with $\epsilon_{2g}$ orbitals on the iron atom, a point which will be discussed later. In this situation, the phenyl ring would be close to orthogonal to the $sp^2$ plane of the carbenium ion with the result that H(6) now will be more shielded being close to the shielding cone of the benzene ring. For electron-releasing substituents much stability can be gained by making $\theta$ as small as possible with concomitant increases in $\phi$. Evidence supporting this concept comes from an examination of the chemical shifts and coupling constants of the H(A) and H(B) protons. If $\theta$ were large this would drastically reduce all mesomeric effects and thus the positive charge would not be delocalised to any great extent. This situation would then be similar to that of the corresponding anilinum ions where the charge on the $\overset{+}{N}H_3$ group is localised. The $^1$H NMR of those ions has been investigated [5] and it is found that values of $J$(AB) are generally zero except where strong electron releasing substituents are present (e.g. OMe $J$(AB) 9 Hz) see Table 1. The magnetic equivalence of H(A) and H(B) has been accounted for in terms of ions pairs formed between the $\overset{+}{N}H_3$ group and the trifluoroacetate counter ion [10]. The close proximity of $CF_3CO_2^-$ apparently counteracts the normally strong

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[*] Such a trend has previously been commented upon [20], and explained by greater participation (and hence shielding) by the $\epsilon_{2g}$ orbitals of the central iron atom when *para* electron withdrawing substituents are present. Our results (excluding the *p*-CN) derivative) show poor Hammett correlations of $\delta$(H(6)) with $\sigma_p$ and $\sigma_m$ constants but a reasonable correlation with $\sigma_p^+$ ($r = 0.985$, 4 points). This again is evidence that some resonance stabilisation via the phenyl ring is occurring. The $\delta$(H(6)) value for the *p*-CN derivative is much larger than that predicted by the Hammett plot. The *p*-CN group is so strongly electron withdrawing that the ion is probably stabilised by the ferrocenyl moiety only.

inductive withdrawal of charge by the positive pole. In all cases except that of X = CN, AB spectra are found for the ferrocenyl-carbenium ions and the difference in chemical shift $\delta(AB)$ (= $\delta(A) - \delta(B)$) is commensurate with resonance effects of the substituents used. Thus resonance via the phenyl ring is still significant. The Mössbauer data, now to be discussed, further supports this view.

## Mössbauer spectroscopy

Mössbauer spectra of the alcohols were run either in the solid state or in frozen acetic acid solutions. The carbenium ions were generated from these alcohols by solution in either sulphuric or trifluoroacetic acid. The parameters (isomer shift, IS and quadrupole splittings, QS both in mm $s^{-1}$) appear in Table 2. We have already established that these parameters are independent of the nature of the acidic solvent, provided that the acid is strong enough to dehydrate the alcohol [1]. We have also presented evidence for iron participation in the primary carbenium ion $[\mathrm{I\overset{+}{a}}]$ which has an exalted QS value of 2.70 mm $s^{-1}$ compared with the normal value of 2.40 mm $s^{-1}$ of the parent alcohol. Tertiary ions such as $[C_5H_5FeC_5H_4\overset{+}{C}Me_2]$ show similar QS values to the precursor alcohol (2.39 and 2.40 mm $s^{-1}$ respectively [1] which we have interpreted as evidence against any iron involvement in stabilisation of the ion. Consequently, it was of some interest to investigate the secondary ions. $[\mathrm{I\overset{+}{b}}]$ shows an exalted QS (2.61 mm $s^{-1}$) though somewhat lower than that of $[\mathrm{I\overset{+}{a}}]$. In the former, the extra methyl group contributes to ion stabilisation at the expense of some iron participation. In these alkyl systems there appears to be little

TABLE 2

$^{57}$FE MÖSSBAUER PARAMETERS FOR SOME FERROCENYL-CARBENIUM IONS IN SOLID SOLUTION AND FOR THEIR ALCOHOL PRECURSORS AT 80°K.

| Compound | Solvent | QS (mm $s^{-1}$) | IS (mm $s^{-1}$) |
|---|---|---|---|
| Ia [a] | $CH_3CO_2H$ | 2.40(1) | 0.50(1) |
| Ib | $CH_3CO_2H$ | 2.36(4) | 0.55(2) |
| Ic | $CH_3CO_2H$ | 2.39(1) | 0.57(1) |
| Id | solid | 2.39(1) | 0.56(1) |
| Ie | solid | 2.38(1) | 0.55(1) |
| If | neat oil | 2.41(1) | 0.56(1) |
| Ig | solid | 2.39(2) | 0.54(1) |
| $[Ia^+]$ [a] | $H_2SO_4$ [b] | 2.70(2) | 0.48(2) |
| | $CF_3CO_2H$ | 2.67(2) | 0.47(2) |
| $[Ib^+]$ | $H_2SO_4$ | 2.61(3) | 0.50(2) |
| $[Ic^+]$ | $H_2SO_4$ | 2.55(1) | 0.54(1) |
| $[Id^+]$ | $CF_3CO_2H$ | 2.50(1) | 0.54(1) |
| $[Ie^+]$ | $CF_3CO_2H$ | 2.42(1) | 0.53(1) |
| $[If^+]$ | $CF_3CO_2H$ | 2.66(1) | 0.56(1) |
| $[Ig^+]$ | $CF_3CO_2H$ | 2.64(1) | 0.56(1) |
| IIa | $CH_3CO_2H$ | 2.36(1) | 0.55(1) |
| IIb | $CH_3CO_2H$ | 2.38(1) | 0.54(1) |
| $[IIa^+]$ | $H_2SO_4$ | 2.67(3) | 0.52(2) |
| $[IIb^+]$ | $H_2SO_4$ | 2.58(1) | 0.52(1) |

[a] Previously reported ref. 1. [b] 98% Analar sulphuric acid.

hindrance to coplanarity of Cp and the empty carbenium ion *p* orbital. In view of this evidence of significant iron participation, we embarked on a study of substituent effects in these secondary systems using *para* substituted phenyl derivatives. The results in Table 2 show that all the alcohols have QS values in the normal ferrocene range (2.38—2.41 mm s$^{-1}$). The QS values of the ions however show a systematic trend, lower QS values being observed for those ions with electron-releasing substituents. For electron-withdrawing substituents such as *para* Cl, large QS values were obtained comparable with those observed for the iron-protonated complexes recently reported [11]. Thus the above variations in QS can be explained by maximal participation by iron in cases of extreme electron withdrawal. We are now of the opinion that such exalted QS values are due to overlaps of iron based orbitals $\epsilon_2$ ($d_{x^2-y^2}$, $d_{xy}$) with the empty *p* orbital on $C_{exo}$. It is clear from studies of ferrocenes containing conjugated electron-withdrawing groups (e.g. C=O, C≡N) that QS values lower than that of ferrocene itself are always found [12—14]. These substituents will mainly affect the ring based orbitals $\epsilon_1$ ($d_{xz}$, $d_{yz}$). Therefore we conclude that electron withdrawal via the Cp ring system results in lower QS values, whereas withdrawal via the iron atom gives high QS values. Extreme examples of the latter affect are to be found in the ferrocene—mercury complexes where a QS value of 3.09 mm s$^{-1}$ has recently been found [15].

It is interesting in the context of the two types of stabilisation that MO—LCAO—SCF calculations show that small but significant changes occur in the number of electrons in the *d* orbitals of the central iron when the Cp ring is substituted with a $COCH_3$ or a $CO_2H$ group [16,17]. In each case electron density is depleted in the $\epsilon_2$ orbitals and correspondingly increased in the $\epsilon_1$ orbitals.

The fact that $[\mathrm{I}\overset{+}{\mathrm{e}}]$, where the substituent X = OMe, shows a normal QS value (2.42) in strong evidence that resonance effects are still operating since if the phenyl ring were orthogonal to the $sp^2$ plane ($\theta$ 90°), the methoxy group would act solely as inductive substituent resulting in a large QS value of ~2.6. Thus $\theta$ must be significantly less than 90° with the result that some increase in $\phi$ is likely. It is difficult to quantify the changes in the angles, and it is likely that both $\theta$ and $\phi$ will vary with the nature of the substituent X. One consequence of increasing $\phi$ would be that overlap between the $\epsilon_2$ orbitals and the vacant 2*p* on $C_{exo}$ would decrease but that overlaps with $\epsilon_1$ would increase. This in itself would cause a decrease in QS and the observed value of 2.42 probably is due in part to this effect.

Hammett plots of $\Delta$QS* against $\sigma^+$ show some correlation (excluding X = CN) with a correlation coefficient of 0.967 (4 points) which again supports the existence of resonance contributions from the phenyl ring. It is possible that a QS value of about 2.6—2.7 represents a maximal iron participation for such a system since a full Fe—$C_{exo}$ bond is unlikely to be formed in view of the rather large Fe—$C_{exo}$ distances already observed in the crystal structures previously quoted [3,4].

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* $\Delta$QS = QS ion — QS alcohol.

For the 1,1′-disubstituted alcohols, only the mono-carbenium ions are formed in $H_2SO_4$ and the QS values for [IIa$^+$] and [IIb$^+$] (2.67 and 2.58 respectively) are very close to those of the monosubstituted species ([Ia$^+$], 2.70; [Ib$^+$], 2.61).

## Experimental

Trifluoroacetic acid was purified as previously described [1]. Analar grades of sulphuric acid (98%) and glacial acetic acid were used without further purification. The alcohols were prepared by Friedel—Crafts reaction of the appropriate acyl chloride with ferrocene [18] and reduction of the product ketone with $NaBH_4$. The following typical procedure describes the preparation of *p*-cyanophenyl ferrocenyl ketone. *p*-Cyanobenzoyl chloride (10 g, 0.06 mol), prepared from reaction of thionyl chloride with the corresponding carboxylic acid, and $AlCl_3$ (9 g, 0.067 mol) were dissolved in $CH_2Cl_2$. The solution added dropwise to ferrocene (11 g, 0.059 mol) in $CH_2Cl_2$ and the mixture stirred for 2.5 h. After the usual work up [18], the crude product was purified by column chromatography to give 8 g (43%) *p*-cyanophenyl ferrocenyl ketone, m.p. 136—137°K. Found: C, 68.19; H, 4.27; N, 4.26. $C_{18}H_{13}FeNO$ calcd.: C, 68.60; H, 4.16; N, 4.45%. NMR ($\delta$, ppm, $CCl_4$) 7.82q, 4H; 4.77t, 2H; 4.52t, 2H; 4.08s, 5H.

The product was dissolved in a minimum volume of methanol and an excess of solid $NaBH_4$ added. An immediate colour change occurred from red to yellow. After effervescence had ceased, the mixture was poured into ice water whereupon a yellow precipitate of the product alcohol occurred, (crude yield 85%). It was recrystallised from a small quantity of methanol, m.p. 97—100°C. NMR ($\delta$, ppm, $CCl_4$) 7.47s, br, 4H; 5.33s, 1H; 4.15s, 4.10s, 9H. The Mössbauer spectrometer has been previously described [19] and spectra fitted as previously reported [15].

$^1H$ NMR spectra were run on a Varian EM-360 spectrophotometer.

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