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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

XIV *. CARBENIUM IONS AND KETONES OF [3]FERROCENOPHANES

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Summary

A series of [3]ferrocenphane (FcP) derivatives have been investigated using ^{57}Fe Mössbauer and ^{1}H NMR spectroscopy. For the 2- and 3-acetyl-FcP in neutral and acidic media, proton resonances were assigned by analogy with the unbridged species, which themselves were analysed using specifically α deuteriated compounds. 2-Acetyl-FcP exhibited a strongly shielded methyl group due to out of plane deformation of the carbonyl function. The corresponding carbenium ions were produced from the parent alcohols in CF_3CO_2H and their NMR spectra discussed. [3]Ferrocenophan-6,8-dione (A) was unprotonated in CF_3CO_2H, monoprotonated in 80% H_2SO_4 to give the symmetrical carbenium ion. The NMR spectrum of the ion is fully discussed. Mössbauer spectra of 2- and 3-acetyl-FcP revealed the latter to have an anomalously low value of both quadrupole splitting (*QS*) and isomer shift (*IS*).

The *QS* of frozen solutions of A at pH 13 show little change from those of ferrocene indicating that the carbanionic charge creates a symmetrical electron density about the iron atom by repulsion of the e_{2g} electrons.

The carbenium ion generated at the 2 position in [3]FcP showed a higher *QS* than that in the 3-position due to better overlap with e_{2g} orbitals. The symmetrical carbenium ion derived from dehydro-[3]ferrocenophane showed exalted *QS* values indicative of iron e_{2g} orbital overlap. The effect of bridging on Mössbauer parameters is also discussed.

Introduction

Bridged ferrocenes have continued to attract much interest in terms of their physical properties, structures and their reactivity. A useful short review has ap-

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* For part XIII see ref. 1.
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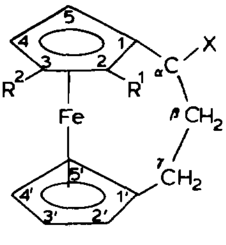
peared [2] together with a survey of recent developments in the field [3]. We have recently reported Mössbauer and NMR data on [3]- and [4]-ferrocenophane ketones and carbenium ions [4]. The results indicate that the carbenium ions are stabilised by Fe–C interactions as shown by very large quadrupole splitting (*QS*) of 2.79 mm s^{-1} for the carbenium ion derived from [4]ferrocenophan-7-ol. In this paper we report on the Mössbauer and ^{1}H NMR spectra of both ring and bridge substituted [3]ferrocenophanes.

It was hoped that detailed study of this system would give an insight into the geometrical factors which governs *QS* and also ^{1}H NMR chemical shifts.

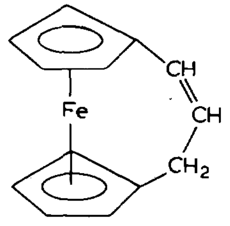
Discussion and results

The series Ia–Ig of [3]ferrocenophanes were used in the study.



(I)

	R^1	R^2	X
Ia	H	H	H, H
Ib	H	H	=O
Ic	CH$_3$CO	H	H,H
Id	H	CH$_3$CO	H,H
*Ie	CH$_3$CH(OH)	H	H,H
If	H	CH$_3$CH(OH)	H,H
Ig	H	H	H,OH



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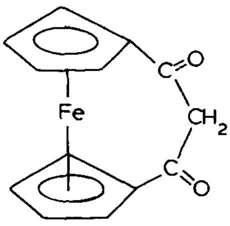

(III)

^{1}H NMR Spectroscopy

Acetyl [3]ferrocenophanes and related derivatives. The proton NMR spectra of these compounds have been analysed by McGuire et al. [5] using shift reagents and computer simulation techniques. From this work, unambiguous assignments were obtained, which corrected earlier assignments [6]. Discrepancies were found between the observed chemical shifts and those calculated from the known anisotropy of the carbonyl group [7].

By comparing the protonated ferrocenyl ketones with the corresponding ferrocenyl carbenium ions [8], Olah and Moh [9] report that unlike the unprotonated species, the α protons are more shielded than the β protons. We have been able to

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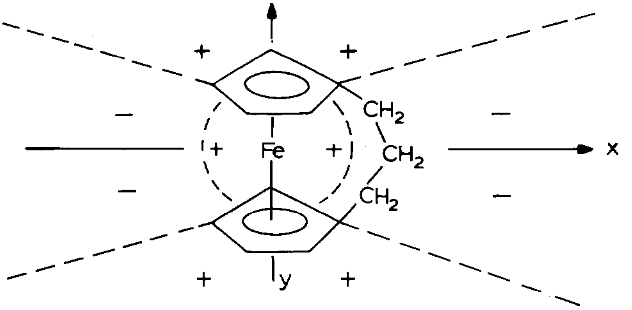
* Carbenium ions produced from alcohols are denoted thus Ie$^+$ etc.

confirm this assignment by using specifically α-deuteriated derivatives [10] (see Experimental) and conclude that this change in shielding is due to polarisation of the C_p and/or the e_{2g} electrons towards the positively charged oxygen atom. The normal carbonyl magnetic anisotropy will be reduced since the π electrons of the CO group are now held in a positive electric field. Similar shielding of H(2) and H(5) occurs in the carbenium ion analogues where iron participation is evident [11] indicating that the e_{2g} electrons contribute to the shielding. The e_{2g} orbitals will be concentrated in an area away from the bridge. The greater ease with which bridged ferrocenes form complexes with $HgCl_2$ compared with ferrocene itself is in keeping with this [12,13].

For [3]ferrocenophane itself, one would therefore expect H(2) and H(5) to be more shielded than H(3), H(5) being closer to the major lobes of the lone pair orbitals (see Fig. 4 in ref. 5). This is the case, though the chemical shift differences are very small (0–0.5 ppm).

The bridged species also appear to fit the shielding scheme (i) [5,14] and is supported by the observations that the methylene protons in [2]ferrocenophane (3.01 ppm) are significantly deshielded compared with those of [3]ferrocenophane (1.95 ppm).



(i)

The change in shielding on approaching the central iron atom along the x axis is also demonstrated by the very low δ values of the iron bound proton in protonated ferrocene [15] and the high field shifts of some ferrocenyl alcohols [16].

^1H NMR chemical shifts for the protonated and unprotonated acetyl-[3]ferrocenophanes (Ic and Id) appear in Table 1. After making the correction for the different references used, it is clear that, as expected, there is a general trend to higher δ values. The assignments were made with reference to the unbridged protonated ketones. The bridge causes a shielding of the ring protons of about 0.2 ppm compared with ferrocene itself, which is almost exactly the same effect as two ethyl groups [17]. The H(2), H(5) protons in protonated acetylferrocene resonate at 4.65 ppm *. Placing a bridge adjacent to it, as in Ic, would decrease this to 4.45 ppm. In the spectrum of Ic the peak at 4.47 ppm is therefore assigned to H(3). Similarly the two-proton resonance at 4.80 ppm is assigned to H(4), H(5) (4.99–0.20 ppm). Assignments in the lower non-acylated ring are much more difficult to make and those listed must be regarded as rather tentative.

The reversal of shielding effects on protonation of ferrocenyl ketones described above leads to the assignments of the non-acylated ring protons.

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* δ values quoted are relative to external TMS.

TABLE 1

^{1}H NMR CHEMICAL SHIFTS (δ ppm) OF PROTONATED AND UNPROTONATED ACETYL-[3]FERROCENOPHANES (CH_3COFcP)

Compound	Solvent	H(2)	H(3)	H(4)	H(5)	H(2′)	H(3′)	H(4′)	H(5′)	Hα	Hβ	Hγ
2-Acetyl FcP	CCl_4 [a]	–	4.44	4.14	4.16	3.60	4.11	3.89	3.81	[b]	–	–
2-Acetyl FcP	CF_3CO_2H [c]	–	4.47	4.80	4.80	3.38	3.67	4.30	3.90	1.69	1.45	1.39
			(4.99) [d]	(5.32)	(5.32)	(3.90)	(4.19)	(4.82)	(4.42)	(2.21)	(1.97)	(1.91)
3-Acetyl FcP	CCl_4 [a]	4.54	–	4.49	4.16	4.16	3.87	4.18	3.83	–	–	–
3-Acetyl FcP	CF_3CO_2H	4.37	–	4.37	4.95	4.22	3.56	4.22	4.00	1.80	1.26	1.26
		(4.89) [d]		(4.89)	(5.47)	(4.74)	(4.08)	(4.74)	(4.52)	(2.32)	(1.78)	(1.78)
Acetyl-ferrocene	CF_3CO_2H	4.65	4.99	4.99	4.65	–	–	–	–	–	–	–
		(5.17)	(5.51)	(5.51)	(5.17)							
FcP	CCl_4	3.92 [e]	–	–	–	–	–	–	–	2.00	2.00	2.00
		(4.44)								(2.52)	–	–

[a] Data from Ref. 5 (internal TMS as reference). [b] Not reported. [c] This work (external TMS as reference). [d] Corrected values to internal TMS as reference appear in parentheses. [e] All ring protons resonate at same frequency.

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ ppm relative to internal TMS) OF [3]FERROCENOPHANE (TMF) CARBENIUM IONS IN CF_3CO_2H

Carbenium ions	H(2)	H(3)	H(4)	H(5)	H(2′)	H(3′)	H(4′)	H(5′)	Bridged protons			
									Hα	Hβ	Hγ	Me
Fc$\overset{+}{\mathrm{C}}$HMe [a]	5.03	6.36	6.21	4.49	5.03	5.03	5.03	5.03	–	–	–	2.25
2-(Me$\overset{+}{\mathrm{C}}$H)TMF (Ie^+)	–	5.05	6.20	5.81	4.63	4.63	5.42	5.05	2.34	1.59	1.33	2.17
3-(Me$\overset{+}{\mathrm{C}}$H)TMF (If^+)	4.98	–	4.38	5.98	4.79	4.53	4.79	5.48	2.27	2.12	2.12	2.12
Ig^+ [b]	4.78	5.77	6.26	4.14	4.78	5.53	5.53	4.78	2.5–3.5	2.5–3.5	2.5–3.5	–
Ig^+ [c]	5.52	6.52	7.05	4.92	5.52	6.32	6.32	5.52	3.2–4.3	3.2–4.3	3.2–4.3	–
II^+ [d]	5.34	5.67	6.69	5.67	5.34	5.67	6.69	5.67	3.65 [e]	5.34	3.65 [e]	–

[a] Data from ref. 9, see also numbering system which differs from that of the [3]ferrocenophanes. [b] Numbered as for Fc$\overset{+}{\mathrm{C}}$HMe. [c] 80% w/w H_2SO_4/D_2O. [d] 85% w/w H_2SO_4/D_2O. [e] Doublet separation 0.27 ppm.

It should be noted that for the 2-acetyl-[3]ferrocenophane (Ic), models indicate steric hindrance to rotation about the Cp–C-*exo* bond due to interaction of the methyl group with the bridge methylenes. The acetyl methyl group in Ic (4.41 ppm) is significantly more shielded than that in the 3-acetyl compound (2.41 cf. 2.30 ppm for acetylferrocene).

It is however likely that the carbonyl is twisted out of the Cp plane. Supporting this is the higher carbonyl stretch of the 2-acetyl (1664 cm^{-1}) compared with that of the 3-acetyl derivative (1642 cm^{-1}). Thus the likely explanation of the anomalous chemical shift of the acetyl methyl group Ic is that the Me group occupies a position above the Cp ring plane (away from the Fe atom) into a shielding area [5] defined in Scheme (i).

For protonated 3-acetyl[3]ferrocenophane, assignments were made in a similar manner with the same reservations concerning the non-acylated ring protons.

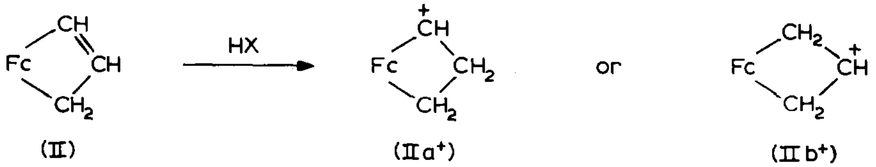
[3]Ferrocenophane-6,8-dione (III) does not protonate in CF_3CO_2H since small spectral changes occur compared with III in $CDCl_3$. In 80% w/w H_2SO_4/D_2O, III shows resonances at 5.63 br.s (2H), H(3), H(4), 5.30 br.s (2H). H(3), H(4); 4.9–5.1 m (4H), H(2), H(5), H(2′), H(5′); 4.56 s. (< 1H).

The spectrum is best interpreted in terms of a mono-protonated structure in view of the separate signals observed indicating a lack of symmetry. The spectrum also suggests that H/D exchange has occurred in the bridging methylene since its intensity is only 25% of that expected and agrees fairly well with that calculated for statistical exchange in the solvent used.

This exchange is confirmed by the complete absence of the CH_2 signal in CF_3CO_2D/D_2O mixtures. Base-catalysed exchange also occurs and III is soluble in 0.5 *N* NaOD to give a spectrum in which the CH_2 resonances are again absent.

[3]Ferrocenophane carbenium ions. The assignments of the carbenium ions Ie^+ and If^+ appearing in Table 2 were made by comparison with those of the unbridged analogues reported by Hisatome and Yamakawa [9] and present no special feature of note. The chemical shifts of the methyl and methine (^+CH) protons are almost identical and close to the values for the 1-ferrocenylethyl cation [9]. This indicates that the methyl group of Ie^+ lies in the Cp plane unlike the corresponding protonated ketone, a result compatible with Fe participation in the former, not the latter. Ig^+ in 80% H_2SO_4 has an identical spectrum to that in CF_3CO_2H except for a downfield solvent shift of 0.78 ppm.

Dehydro [3]ferrocenophane [18] is not very soluble in CF_3CO_2H in which it is prone to oxidation. It is however reasonably soluble in 85% H_2SO_4. From previous studies it has been shown that no appreciable sulphonation occurs at this acid concentration. The resulting spectrum was completely different from Ig^+. Proton addition to II can occur at either the α or β carbon atom. We conclude that the product is $II_b{}^+$. That a carbenium ion is indeed formed is demonstrated by the typically large *QS* value observed in the Mössbauer spectrum (vide infra). The spectrum of the bridge protons support structure IIb. Unlike the very complex multiplet observed for IIa^+, the protons appear as a sharp doublet (separation 16



(II) (IIa$^+$) (IIb$^+$)

Hz) at 3.65 ppm. The chemical shifts are typical of protons adjacent to a ^+CH group.

The observed doublet is interesting and can only be explained if the bridge remains conformationally rigid. This would occur if there were appreciable interaction between the iron atom and the carbenium ion centre, and would have the effect of freezing the methylene protons to give axial–equatorial pairs.

The remainder of the spectrum is deceptively simple in appearance. It comprises three rather broad singlets at 5.34 (3H); 5.67 (4H) and 6.96 ppm (2H), which we assign as follows H(2), H(2′), ^+CH; H(3), H(3′), H(5), H(5′); and H(4), H(4′) respectively.

Bearing in mind the 0.8 ppm solvent shift between 85% H_2SO_4 and CF_3CO_2H, the ^+CH resonance in IIb is very close to that observed for the cation derived from [4]ferrocenophan-7-ol [19] (4.65 ppm). This is of interest since it shows that the anisotropy of the iron e_{2g} electrons alters considerably if a positive charge is located near the iron atom. Such an effect is apparent from Bitterwolf's work [15] on anisotropy of protonated ferrocenophanes, systems which are rather similar to the bridged carbenium ions.

Thus we conclude that cation IIb^+ is formed in preference to IIa^+ due to direct iron participation. The Mössbauer results discussed below confirm this postulate.

Mössbauer spectroscopy (Table 3)

In the discussion, the quadrupole splittings of the non-bridged ferrocene compounds are referred to ferrocene (Δ 2.40 mm s^{-1}) *, while those of the ferrocenophanes to that of [3]ferrocenophane (2.29 mm s^{-1}). This difference in quadrupole splitting (*QS*) has previously been explained in terms of ring tilting [20]. We suggest that it arises from the geometry of the e_{2g} orbitals which are symmetrically disposed around the iron atom in ferrocene, but in the neutral bridged species are confined to an area remote from the bridge.

It has often been assumed that ring tilt causes a decrease in *QS*. However [2]ferrocenophane has a *QS* value (2.41 mm s^{-1}) [12] greater than that of ferrocene itself which again suggests a non uniform arrangement of the e_{2g} orbitals in bridged ferrocenes.

Dehydro-[3]ferrocenophane has a lower *QS* than [3]ferrocenophane (cf. II vs. Ia). This lowering of *QS* for the dehydro derivative is similar to the lowering observed for conjugated substituents on ferrocene [21], though the magnitude of the effect is smaller. The effect is larger when a carbonyl is present in the bridge (cf. Ib vs. Ia). However, a dicarbonyl bridged substituent has much less of an effect than the unbridged analogue (cf. III vs. diacetylferrocene). III also has a *QS* almost identical to the monocarbonyl bridged derivative Ib.

This result must be a consequence of: (A) the directional properties of the e_{2g} orbitals, and (B) the degree of eclipsing present in the bridged species which itself will be modified by A. Also the bridge will dictate the interplanar angle of the carbonyl and Cp rings. As seen from molecular models, the dicarbonyl bridge imposes the greater strain on the molecule. For Ib the Cp–CO angle, θ, appears to

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* As measured in these laboratories [24].

TABLE 3

^{57}Fe MÖSSBAUER DATA (QS, IS mm s^{-1}) FOR BRIDGED FERROCENE DERIVATIVES AT 80 K IN SOLID (S) AND FROZEN SOLUTIONS (FS)

Compounds	Phase	QS	IS
Ia	S	2.29(2)	0.50(2)
Ib	S	2.22(2)	0.52(2)
Ib	$80\%H_2SO_4$ (FS)	2.14(4)	0.50(2)
Ic	S	2.18(2)	0.50(2)
	S [a]	2.19(2)	0.44(2)
	CF_3CO_2H (FS)	2.05(2)	0.49(2)
Id	S	2.09(2)	0.48(2)
	S [a]	2.07(2)	0.38(2)
	CF_3CO_2H (FS)	2.00(2)	0.49(2)
Ie	S	2.29(2)	0.49(2)
	CF_3CO_2H (FS)	2.58(2)	0.47(2)
If	S	2.27(2)	0.49(1)
	CF_3CO_2H (FS)	2.48(2)	0.47(2)
Ig [4]	S	2.28(2)	0.53(2)
	CF_3CO_2H (FS)	2.53(2)	0.50(1)
II	S	2.24(2)	0.50(1)
	$85\%H_2SO_4$(FS)	2.46(2)	0.45(2)
III	S	2.19(3)	0.50(2)
	$98\%H_2SO_4$ (FS)	1.85(2)	0.46(2)
	0.1N NaOH (FS)	2.23(2)	0.49(2)
FcCOMe [21]	S	2.27(1)	0.54(2)
	CF_3CO_2H (FS)	2.10(2)	0.54(2)
$Fc(COMe)_2$ [21]	S	2.14(5)	0.54(2)
	CF_3CO_2H (FS)	2.09(2)	0.52(1)
	98% H_2SO_4 (FS)	1.79(2)	0.55(2)
FcCH(OH)Me [11]	CH_3CO_2H (FS)	2.36(4)	0.55(2)
	98% H_2SO_4 (FS)	2.61(3)	0.50(2)

[a] At 298 K.

be ~ 20° * and the Cp rings are staggered by 12° [22]. However, the crystal structure of 8-phenyl-[3]ferrocenophan-6-one [23] shows a θ value of 42° and fully eclipsed Cp rings. Thus for 3 carbon bridged ferrocenes θ is maximised when the Cp rings are eclipsed. Models of III show that for the eclipsed conformation the two CO groups are twisted considerably out of the Cp plane, thus drastically reducing conjugation. As a result Ib protonates readily in CF_3CO_2H, whereas III requires a medium of much higher acidity to effect protonation.

ΔQS (relative to ferrocene) for acetyl ferrocene is 0.13 mm s^{-1}. Referred to [3]ferrocenophane, the 2- and 3-acetyl derivatives have ΔQS values of 0.11 and 0.20 mm s^{-1}. ΔQS for the 2-acetyl derivative (Ic) is similar to that of acetylferrocene relative to ferrocene, but the 3-acetyl derivative Id shows a lower QS than expected. The reasons for this apparent anomaly are not obvious, since it is not clear what effect homosubstitution would have on the QS, particularly when one of the substituents is a methylene bridge. There is little data available in the literature on this point [25,26]. All that can be concluded from the nonbridged compound data is that they have large QS values relative to ferrocene, and that the effects of the

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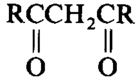
* The interplanar angle was not reported in the crystal structure determination of Ib [22].

t-C_4H_9 groups appear to be additive. The data for the polychlorinated ferrocenes have been discussed in terms of steric factors and we refer the reader to it [25].

There is also little Mössbauer data available in the literature for bridged ferrocene that contain other substituents on the rings. Unfortunately the known data is on multibridged ferrocenes and shows no obvious trends [27]. The homobridged $(CH_2)_3$ substituent would be expected to donate electron density to the rings and increase the *QS*, this is not evident from the data [27]. Thus, as yet there is no explanation for the magnitude of the *QS* for the 3 acetyl derivative Id.

Of the two acetyl derivatives the 2 isomer would be expected to be anomalous due to the likely out-of-plane configuration of the carbonyl group. Interestingly the *QS* values of the 2-isomer and [3]ferrocenophane-6-one (Ib) are very similar. In the latter, the three-carbon bridge causes the carbonyl group to lie at an angle of ~ 20° [22] to the Cp rings.

The *QS* of the protonated 2- and 3-acetyl derivatives are similar (2.05 and 2.00 mm s^{-1}) and both are somewhat lower than that of protonated acetylferrocene (2.1 mm s^{-1}).

A comparison of data for [3]ferrocenophane-6,8-dione (III) in 98% H_2SO_4 with those of diacetylferrocene (in CF_3CO_2H (II)) clearly shows that both carbonyls are protonated in this medium. As reported above, III undergoes H/D exchange. Since the pK_a of structures of type  $R\underset{\underset{O}{\|}}{C}CH_2\underset{\underset{O}{\|}}{C}R$ is about 9 [28] then in 0.1 *N* NaOH, III should be wholly in the carbanionic form. The *QS* of frozen solutions of III at this pH showed no great change from the value for the solid. Thus unlike positive charges, negative charges have little effect on *QS*.

The carbanionic charge would drive electron density in the e_{2g} orbitals to the side remote from the bridge which would cause a more symmetrical overall charge distribution about the iron. This should result in an increase in *QS* (towards that of ferrocene). A small increase in *QS* does occur.

Alcohols and carbenium ions. Alcohol substituents, whether in side chains (Ie, If) or the bridge (Ig), have no effecet on *QS*. On forming the carbenium ion in CF_3CO_2H, significant changes in *QS* occur. Iron participation has already been shown for Ig, being manifest in the large value of $\Delta QS = QS$(carbenium ion) − *Qs*(alcohol) of 0.25 mm s^{-1}. The ΔQS values for Ie/Ie$^+$ and If/If$^+$ are 0.28 and 0.21 mm s^{-1} respectively and compare with the value of 0.25 mm s^{-1} for the 1-ferrocenylethanol system. These results are interpreted as a better overlap of the e_{2g} and empty *p* orbitals for the 2- than the 3-position on account of the ring tilt which directs the *p* orbitals further away from the e_{2g} plane at the latter position.

Finally II undergoes protonation in 85% H_2SO_4 to give the symmetrical carbenium ion IIb$^+$. The ΔQS for this is 0.22 mm s^{-1} and is characteristic of iron participation. This value is much lower than that of the carbenium ion derived from [4]ferrocenophane-7-ol (ΔQS 0.40 mm s^{-1}). The four-carbon bridge in the latter is much more flexible; models show that only minor distortions of this bridge need occur to effect optimum overlap of e_{2g} an *p* orbitals. The three-carbon bridge restricts this phenomenon, as a result the *p* orbital is not orientated for optimum overlap.

Experimental

Preparation of deuteriated ferrocenes

2,5-(Dimethyaminomethyl)ferrocene-d_2 was prepared in 86% yield by the method of Rausch and Siegel [10]. This was converted to the methiodide in high yield by treatment with MeI in dry ether. The deuteriated methiodide was converted to 2,5-hydroxymethylferrocene-d_2 by standard methods [29] (79%). The latter was oxidised with activated MnO_2 in $CHCl_3$ to give 2,5-formylferrocene-d_2 which was purified by sublimation (80%).

2,5-Hydroxyethylferrocene-d_2 was obtained by treatment 2,5-formylferrocene-d_2 with MeMgI in dry ether (67%). Oxidation of 2,5-hydroxyethylferrocene-d_2 with MnO_2 yielded 2,5-acetylferrocene-d_2 (76%). The deuterium content at the 2,5 position was 35 ± 3% which was sufficient to distinguish between the H(2,5) and the H(3,4) resonances in the ^1H NMR spectra of the above derivatives.

Assignments of the H(2,5) and H(3,4) resonances of ketones (FcCOR) and carbenium ions (FcCHR)

For both cases R = H, R = Me in CCl_4 the downfield triplet was significantly smaller than the upfield triplet confirming the tentative assignments previously made [8]. In CF_3CO_2H, however, the reverse situation obtained which enables a clear distinction to be made between the H(2,5) and H(3,4) protons in the protonated ketones. In each case the H(2,5) protons are markedly more shielded than the H(3,4) set. For R = H the difference in shift between the two sets is 0.63 ppm whereas for R = Me it is 0.34 ppm. The assignments for the carbenium ions were made in a similar manner and confirm previous results [9]. The complete data appears in Table 4.

Preparation of ferrocenophanes

[3]Ferrocenophane-6-one was prepared as described by Turbitt and Watts [30]. This was reduced to [3]ferrocenophane in 91% yield by $LiAlH_4/AlCl_3$ in dry ether (3–5 h reflux). Acetylation of [3]ferrocenophane was accomplished using the method of Rinehart et al. [32].

The 2- and 3-acetyl derivatives were separated on neutral alumina eluting successively with cyclohexane 95/5 cyclohexane/ether, and 85/15 cyclohexane/ether.

TABLE 4

^1H NMR CHEMICAL SHIFTS FOR FERROCENYL KETONES (FcCOR) AND CARBENIUM IONS (Fc$\overset{+}{C}$HR) IN CF_3CO_2H (A) AND 80% w/w H_2SO_4/D_2O (B) AS DEDUCED FROM THE 2,5-d_2 ANALOGUES

R	Acid	H(2)	H(5)	H(3)	H(4)	Cp	Others	$\Delta\delta$ [b]
Ketones								
H	A	4.42	4.42	5.05	5.05	4.12	CHO 9.10	0.63
CH_3	A	4.65	4.65	4.99	4.99	4.06	CH_3 2.04	0.34
CH_3	B	5.12	5.12	5.63	5.63	4.55	CH_3 2.47	0.51
Carbenium ions								
H	A	4.16	4.16	5.76	5.76	4.73	CH_2 5.38	1.60
CH_3	A	4.47	3.90	5.80	5.64	4.47	CH_3 1.65 J 7 Hz	–
CH_3	B	4.94	4.40	6.25	6.13	4.94	CH_3 2.14 J 6 Hz	–

[a] Shifts in δ ppm relative to external TMS. [b] $\Delta\delta = \delta(H(3), H(4)) - \delta(H(2), H(5))$.

Both acetyl derivatives were reduced to the corresponding alcohol by $NaBH_4$ in warm methanol and purified by chromatography on neutral Al_2O_3. Yields were 75–85% and the products were low melting solids.

Dehydroferrocenophane was synthesised by standard methods [32]. [3]Ferrocenophane-6-ol was prepared by $NaBH_4$ reduction of [3]ferrocenophan-6-one in MeOH (75%).

NMR and Mössbauer spectroscopy

^1H NMR spectra were run on an EM-360 spectrometer housed in a constant temperature room with a probe head temperature of 28°C. Mössbauer spectra were obtained and fitted as described in previous publications [14,22,25].

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