

MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

X *. STERIC AND POLAR FACTORS IN FERROCENYL KETONES AND CARBENIUM IONS

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Summary

A series of new ferrocenyl alcohols of the types $\text{FcCH(OH)-C}_6\text{H}_4\text{X}$ and FcCH(OH)R where R = 1-adamantyl, 9-anthracyl and mesityl have been synthesised. The ^1H NMR spectra of these carbenium ions derived from these alcohols have been measured and discussed, together with those of the ketone precursors in $\text{CF}_3\text{CO}_2\text{H}$. Mössbauer spectra were obtained for the above derivatives in frozen solid solution in $\text{CF}_3\text{CO}_2\text{H}$. For the protonated ketones only small differences in quadrupole splitting (QS) were observed as the structure of the aryl or alkyl groups was varied, all having QS values of 0.23–0.36 mm s^{-1} lower than that of ferrocene. For the aryl carbenium ions the enhanced QS correlated reasonably well with Hammett σ^+ values ($r = 0.953$, 7 points). No systematic trends in QS were observed for the *o*, *m* and *p* series of substituents. The more sterically hindered carbenium ions show a significant lowering of QS due to the Cp rings twisting out of the carbenium ion sp^2 plane. In the case of the anthracyl derivative, no appreciable change in QS occurred on forming the carbenium ion indicative of stabilisation of the ion by the anthracyl rather than the ferrocenyl moiety. The different modes of stabilisation of the protonated ketones and the carbenium ions are discussed.

Introduction

Recent work [2] in these laboratories has shown that substituent effects on the quadrupole splitting (QS) of ferrocenyl ketones is very small but increases significantly on protonation in $\text{CF}_3\text{CO}_2\text{H}$. Both protonated and unprotonated species show a reduction in QS relative to ferrocene, the former generally showing a greater

* For part IX see ref. 1.

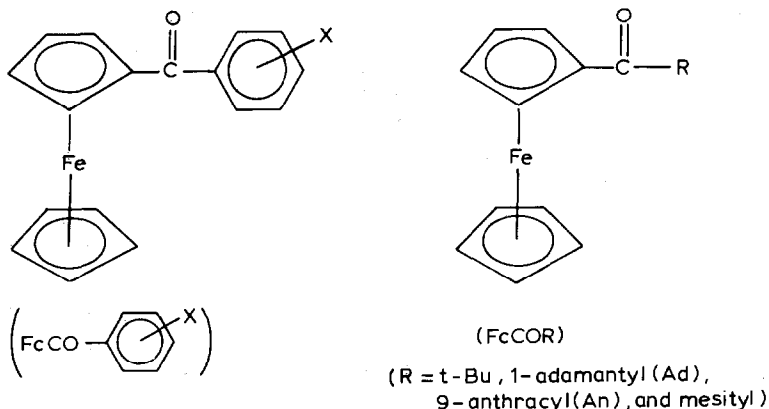
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reduction. These results have been interpreted in terms of electron withdrawal by ligand-based orbitals (e_{1g}). By contrast substituent effects are much more pronounced in the ferrocenyl carbenium ions [3,4] and QS values are generally greater than that of ferrocene. In this case, stabilisation of the carbenium ion is thought to occur using overlaps of e_{2g} orbitals on the iron with the empty p orbital on the carbon atom. More recently [5], we have reported on some bridged ketones and carbenium ions. For the carbenium ion derived from [4]-ferrocenophane-7-ol, a very large QS value of 2.79 mm s^{-1} was found. Since the positive centre is insulated in this case by a methylene group, stabilisation can only occur via participation by e_{2g} orbitals which is known to cause increases in QS [6,7].

This paper deals in more detail with polar and steric effects in a series of ferrocenyl ketones and carbenium ions. A number of new compounds have been synthesised for this purpose. A complimentary study of the structure and ^{13}C and infrared spectroscopy of these compounds [8] has also been undertaken, the results appearing in the preceding paper.

Results and discussion

The ketones used in this work were synthesised by standard methods [8] and reduced to the corresponding alcohols with NaBH_4 in dry MeOH .



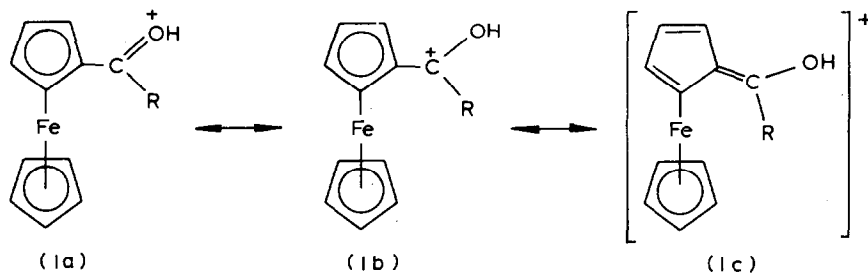
More stringent reduction was required for the sterically hindered derivatives, LiAlH_4 in dry ether being employed.

^1H NMR spectra

The PMR spectra of ferrocenyl ketones and alcohols in strongly acidic media differ markedly at room temperature. This is very clearly exemplified by the simplest derivatives, acetyl ferrocene, FcCOMe (I) and its corresponding alcohol FcCH(OH)Me (II). I in CCl_4 shows the following resonances (δ , ppm):

2.30s (CH_3), 4.10s (Cp), 4.33t (H(3), H(4)) and 4.63t (H(2), H(5)) whereas in $\text{CF}_3\text{CO}_2\text{H}$ the corresponding resonances occur at 2.00s, 4.10s, 5.00 br.s and 4.61 br.s. ppm (see below). Protonation produces a characteristic purple-mauve colour. The salient feature of the protonated form is that H(2) and H(5) remain magnetically equivalent indicating a low rotational barrier about the carbonyl–ring bond. (For a more detailed discussion see ref. 2 and references therein.)

At much lower temperatures -101°C in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ [9]) the protonated ferrocenyl ketones can be "frozen out" resulting in spectra which are very similar to those of the corresponding carbenium ions, the chemical shifts of which were used to assign the resonances of the former system. This led to the interesting conclusion that H(2,5) protons are more shielded than H(3,4) in the protonated ketones, the exact reverse of the case for the unprotonated species. Presumably this is the result of resonance depicted below, which would place positive charge on C(3,4). Contribu-



tions from 1c are quite small for the unprotonated ketones since H(2) and H(5), and H(3) and H(4) are magnetically equivalent in SO_2ClF alone at -20°C [9]. Also, such a structure would seriously weaken the Fe-Cp bonding. The principle factor which determines the chemical shift therefore appears to be the anisotropy of the carbonyl group ($\delta(\text{H}(2,5)) > \delta(\text{H}(3,4))$). It is hoped to verify these assignments shortly in these laboratories making use of specifically deuteriated derivatives [10]. The rotational barriers for protonated ketones are significantly lower than those of the corresponding carbenium ions [11] where H(2), H(3), H(4) and H(5) are each magnetically distinct even at room temperature [12] (see Table 2).

We are thus forced to conclude that the well documented basicity of the ferrocenyl ketones must be due to a direct field effect exerted by the Cp ring electrons. An alternative explanation invoking hydrogen-bonded iron species [13] may be discarded on the following grounds. No Fe-H resonances are observed in the characteristic regions $\delta - 2$ to -2.5 ppm which implies that any such interaction would involve exchange processes which are rapid on the NMR time scale. Such a hydrogen-bonded species would twist the carbonyl out of the Cp plane by about 40° which would result in at best an Fe-H distance of $> 3 \text{ \AA}$ too long for significant interaction. In addition, [4]-ferrocenophan-6-one has its carbonyl group 18° out of the Cp plane [14] which makes such Fe-H interactions more difficult, yet it has almost the same basicity as acetylferrocene [15].

Returning to our current results for protonated ferrocenyl ketones in Table 1, it is instructive to consider the chemical shift differences (Δ) between H(3,4) and H(2,5). Δ should be governed by the anisotropy of the carbonyl and resonance interactions, both of which in turn depend on the angle ϕ between the Cp ring and carbonyl planes. For FcCO-t-Bu and FcCOAd , ϕ is fairly large ($\sim 40^{\circ}$) and results in a Δ value of zero whereas for FcCHO and FcCOMe ($\phi = 0^{\circ}$), Δ values are much larger (0.66 and 0.33 ppm respectively). For the aryl series, Δ is relatively constant at ~ 0.3 ppm, the exceptions being the value for the strongly electron withdrawing *p* cyano derivative and ferrocene carboxaldehyde. The observation that Δ varies little over the *ortho*, *meta* and *para* substituents indicates that the aromatic group exerts a relatively small influence on the ferrocenyl rings which are not forced significantly

TABLE 1
 ^1H NMR CHEMICAL SHIFTS (δ , ppm from TMS) OF PROTONATED FERROCENYL KETONES ($\text{FcC}-\text{R}$) IN $\text{CF}_3\text{CO}_2\text{H}$

R	θ^a	H(2,5)	H(3,4)	Δ^b	Cp	Aromatic	Others
C_6H_5^c	45	4.77	5.12	0.35	4.00	6.6-7.4m	-
$2\text{-C}_6\text{H}_4\text{Me}$	54	4.62	5.00	0.38	4.10	6.6-7.4	1.95 Me
$4\text{-C}_6\text{H}_4\text{Me}^c$	44	4.83	5.17	0.34	4.05	7.30, 6.90	1.92 Me
$2,4,6\text{-C}_6\text{H}_2\text{Me}_3$	62	4.60	4.93	0.33	4.10	6.52s	2.00 (4-Me) 2.13 (2-Me)
$2\text{-C}_6\text{H}_4\text{Cl}$	45	4.52	4.78	0.26	4.05	7.0 brs	-
$2\text{-C}_6\text{H}_4\text{Cl}^d$	45	-	5.97	-	4.73	7.6 brs	-
$3\text{-C}_6\text{H}_4\text{Cl}$	39	4.60	4.80	0.20	3.88	6.8-7.5 m	-
$4\text{-C}_6\text{H}_4\text{Cl}^c$	42	4.67	4.95	0.28	3.93	7.37-7.05	-
$2\text{-C}_6\text{H}_4\text{Br}$	47	4.47	4.77	0.30	4.01	6.8-7.6 m	-
$3\text{-C}_6\text{H}_4\text{Br}$	41	4.62	4.83	0.21	3.90	6.7-7.7 m	-
$4\text{-C}_6\text{H}_4\text{OMe}^c$	41	4.88	5.13	0.30	4.00	7.55-6.65	3.95 (Me)
$4\text{-C}_6\text{H}_4\text{CN}^c$	42	4.00	4.63	0.63	3.93	7.53 s	-
t-Bu	39 ^e	4.68	4.68	0.00	3.98	-	1.05 (Me)
1-Ad	37 ^e	4.92	4.92	0.00	4.12	-	1.42, 1.70 (Ad)
9-An	58	4.27	4.63	0.36	3.85	6.6-7.5 m	7.73 (C(10) ^f)
H	0	4.52	5.18	0.66	4.28	-	9.10 (CHO)
CH_3^g	0	4.67	5.00	0.33	4.10	-	2.00 (Me)

^a Calculated angle of twist of benzene ring out of carbonyl plane for unprotonated ketones (ref. 8). ^b $\Delta = \delta(\text{H}(2,5)) - \delta(\text{H}(3,4))$. ^c Data from ref. 2. ^d 80% w/v $\text{H}_2\text{SO}_4/\text{D}_2\text{O}$ ($\text{H}(3,4)$ signals masked by aromatics). ^e Calculated angle of twist of Cp ring out of carbonyl plane for unprotonated ketones (ref. 8).

TABLE 2

¹H NMR DATA FOR A SERIES OF SUBSTITUTED PHENYL FERROCENYL CARBENIUM IONS (C₅H₅)Fe(C₅H₄CHAr) IN CF₃CO₂H^a

Ar	H _{exo}	H(Cp)	H(2)	H(5)	H(3)	H(4)	Aromatic	Others
C ₆ H ₅ ^b	7.42	4.17	4.83	4.10	5.71	5.50	7.17 ^c , 6.93 ^d	—
2-C ₆ H ₄ Me	7.78	4.23	4.80	4.23	5.73	5.50	6.7–6.9 m	2.00 (Me)
3-C ₆ H ₄ Me	7.47	4.25	4.90	4.25	5.83	5.60	6.8–7.1 m	1.90 (Me)
4-C ₆ H ₄ Me ^b	7.60	4.23	4.97	4.20	5.83	5.60	7.22 ^c , 6.83 ^d	1.83 (Me)
2-C ₆ H ₄ Cl	7.90	4.53	4.81	4.25	5.81	5.70	6.8–7.1 m	—
3-C ₆ H ₄ Cl	7.50	4.48	5.03	4.33	6.03	5.83	7.2–7.35 m	—
4-C ₆ H ₄ Cl ^b	7.41	4.28	4.88	4.17	5.88	5.65	7.18 ^c , 6.92 ^d	—
2-C ₆ H ₄ Br	7.83	4.53	4.90	4.31	5.86	5.71	6.9–7.2 m	—
4-C ₆ H ₄ OMe ^b	7.73	4.23	5.00	4.23	5.83	5.58	7.40 ^c , 6.60 ^d	3.47 (Me)
4-C ₆ H ₄ CN ^b	7.33	4.35	4.80	4.20	5.88	5.75	7.33 s	—
2,4,6-C ₆ H ₂ Me ₃	8.45	4.50	4.63	4.63	5.87	5.87	6.58 s	2.08 (<i>o</i> -Me) 1.80 (<i>p</i> -Me)

^a ppm from TMS. ^b Data from ref. 4. ^c and ^d Chemical shifts of H_A and H_B protons (*ortho* and *meta* to the carbenium ion substituent, see ref. 4).

out of the CO plane. This supports conclusions drawn from $\nu(\text{CO})$ and ¹³C carbonyl chemical shifts presented in a previous paper [8].

The ¹H chemical shifts of the carbenium ions are listed in Tables 2 and 3. $\delta(\text{H}_{exo})$ correlates rather better with Hammett σ^+ values ($r = 0.88$) than with σ ($r = 0.78$) though neither is very good. A comparison of the average H(3,4) chemical shifts ($\delta(3,4)$) of the carbenium ion and protonated ketones reveals that $\delta(3,4)$ increases for the former as the electron withdrawing power of the substituent increases whereas the trend is reversed in the latter series. This again points to a different mode of stabilisation of the two ions. Mössbauer and other data indicate iron participation in carbenium ion stabilisation resulting in deshielding of H(3,4) by reducing the shielding effect of the e_{2g} electron pair involved in this participation. Electron withdrawing groups in the aromatic ring would induce a greater participation and hence a greater deshielding. The reasons for the reverse substituent effects for the protonated ketones are not clear. One possible explanation is that electron releasing substituents (+M) increase the π electron density in the carbonyl group

TABLE 3

¹H NMR DATA FOR SOME STERICALLY HINDERED FERROCENYL CARBENIUM IONS C₅H₅Fe(C₅H₄-CHR) IN CF₃CO₂H

R	H _{exo}	H(Cp)	H(2)	H(5)	H(3)	H(4)	Others
<i>t</i> -Bu	6.78	4.67	4.67	3.88	5.78	5.78	0.97 (Me ₃ C)
Ad	6.57	4.73	4.73	3.95	5.82	5.82	1.2–2.0 (Ad)
An	8.17 ^a	4.31	4.75	4.75	5.77	5.77	6.9–7.8 m (6H) (An) 8.05 s (1H) 9.13 s (1H) 8.47 ^a (H(10'))
Me	6.63	4.56	4.56	4.03	5.83	5.83	

^a Assignment tentative.

thus enhancing its anisotropy. In these cases the substituents are complimentary (+M, R, -M). For -M groups the π electrons of the benzene ring are competed for with the result that the carbonyl π electron density remains relatively constant.

For the series of aryl ferrocenyl carbenium ions the difference in chemical shift (2,5) between H(2) and H(5) is generally smaller for the *ortho* and *para* and is probably a consequence of the increased interplanar angle θ which will alter the anisotropic deshielding effect of the phenyl ring. In the case of the mesityl ion, Δ (2,5) is zero. Molecular models suggest that, given the CO and carbonyl planes are coplanar, a θ value of about 60° should be adopted by the phenyl ring and due to steric hindrance of the *ortho* methyl groups the molecule is probably locked in this staggered conformation. At this angle the deshielding effect of the benzene ring will be minimal and the two *ortho* methyl groups would be in almost identical environments close to the Cp rings. For the sterically hindered molecules (Table 3), the t-Bu and 1-adamantyl ferrocenyl carbenium ions have almost identical spectra which are quite similar to that of Fc $\dot{\text{C}}\text{HMe}$. The anthracyl derivatives display some interesting features. FcCH(OH)An (III), unlike the other aromatic members of the series, showed separate signals for the substituted Cp ring protons (H(2-5)). In addition the aromatic protons showed a marked lack of symmetry. H(10') is usually the most deshielded proton in anthracenes but in this instance a one-proton multiplet appears at about 9.2 ppm (H(10') 8.56 ppm). This contrasts with the spectrum of 1-anthracyl ethanol, An-CH(OH)Me (IV), which shows a two proton signal at 8.4 ppm (H(10') 8.10 ppm) indicative of a much more symmetrical molecule. The effect of a neighbouring chiral carbon is apparently small in this case. III dissolves in $\text{CF}_3\text{CO}_2\text{H}$ to give a deep red solution whose PMR spectrum shows that H(2) and H(5) are now magnetically equivalent (see Fig. 1 as are H(3) and H(4)). We assign the downfield singlet at 9.13 ppm as being due to H(10') representing a downfield shift of about 1 ppm on forming the ion and suggesting some charge delocalisation via the anthracyl moiety (see Mössbauer discussion). H_{exo} we tentatively assign to the singlet at 8.17 ppm which is significantly downfield from others in this series. Unfortunately it was not possible to compare the carbenium ion from III with An $\dot{\text{C}}\text{HMe}$ since the latter underwent further reaction to give as yet unidentified products.

It is interesting to note that for all the aromatic ferrocenyl carbenium ion H_{exo} appears substantially downfield from the alkyl analogues. The mesityl ion for example has H_{exo} at 8.45 ppm (cf. 6.63 ppm for Fc $\dot{\text{C}}\text{HMe}$), fairly close to that of Fc $\dot{\text{C}}\text{HAn}$ which would have about the same twist angle θ . H_{exo} for Fc $\dot{\text{C}}\text{H}_2$ is 5.37 ppm. Iron participation (and hence H_{exo} shielding) has been shown to be substantial for this ion. We therefore suggest that the greater δ value for the aromatic series is due at least in part to a reduced involvement of the iron atom. Closer examination of the data in Table 2 offers support for this thesis. Electron releasing substituents (*meta,para*) have higher δ values than electron withdrawing groups, highlighted by the values the *para*-cyano (7.33 ppm) and the *para*-methoxy (7.73 ppm). Further confirmation of this comes from the Mössbauer parameters discussed below.

Mössbauer spectroscopy

Table 4 lists the Mössbauer parameters, quadrupole splittings (QS) and isomer shifts (IS) for the aryl ferrocenyl ketones. The QS of the solids range between 2.23

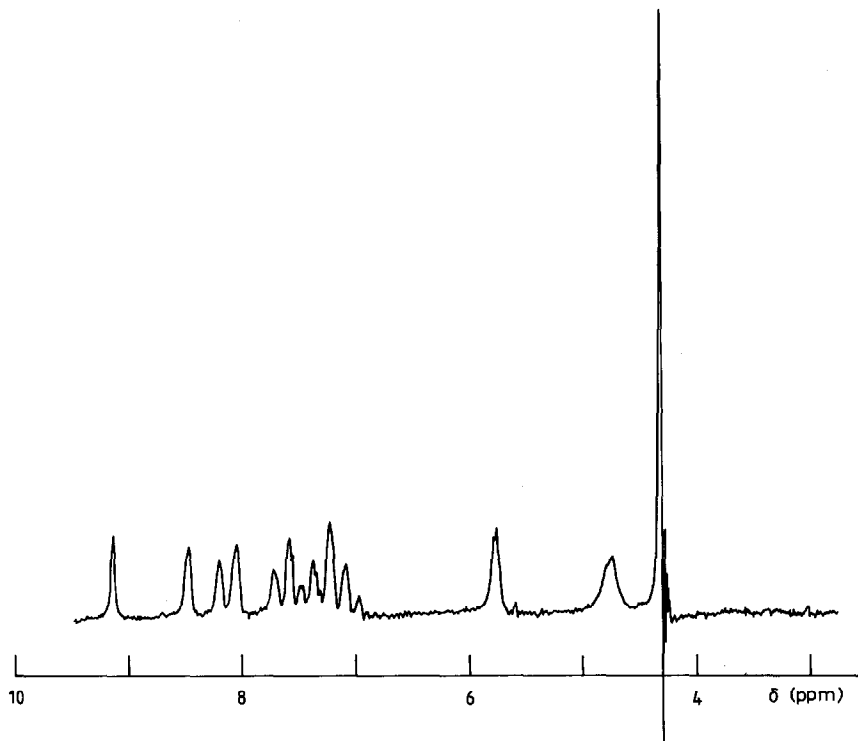
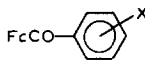


Fig. 1. ^1H NMR spectrum of anthracyl ferrocenyl methanol in $\text{CF}_3\text{CO}_2\text{H}$ (δ ppm from TMS).

and 2.30 mm s^{-1} with no discernible trend in the values as a function of position of substituent. Protonation causes generally a decrease in ΔQS of 0.11 to 0.19 mm s^{-1} *. For the more sterically hindered ketones (Table 5) protonation appears to be more difficult. Thus FeCOAd shows a ΔQS of only 0.09 mm s^{-1} in $\text{CF}_3\text{CO}_2\text{H}$ but a value of 0.24 mm s^{-1} in $80\% \text{ H}_2\text{SO}_4$. The corresponding alcohols (FcCHOHAr) have a range of QS of between 2.33 and 2.41 mm s^{-1} with the *ortho* derivatives having generally the lower values. The carbenium ions generated by dissolving the alcohols in strong acid (Tables 6, 7) show a marked increase in QS as noted previously [4]. We are now able to extend the correlation of ΔQS with Hammett σ^+ values to include the new *meta* derivatives [4]. A correlation coefficient of 0.953 (7 points) is obtained if the *p*-CN derivative is omitted. The justification for the omission is that we believe that iron participation, which causes the large increases in QS by involvement of e_{2g} orbitals in stabilising the carbenium ion, reaches a maximum for the *p*-chloro derivative and any more strongly electron withdrawing substituent would cause no further increase. The above correlation thus establishes a degree of delocalisation via the phenyl ring. For the sterically hindered ions, FcCH-t-Bu , FcCHAd (Table 7), the increase in QS is less than that for FcCHMe . This is probably a reflection of the twisting of the carbenium ion sp^2 plane out of the Cp ring plane ($\sim 40^\circ$ for the corresponding ketones [8]) which would reduce the e_{2g} - p overlaps. The anthracyl derivative shows no significant change in QS on

* $\Delta QS = QS(\text{solid}) - QS(\text{frozen acidic solution})$.

TABLE 4

⁵⁷Fe MÖSSBAUER PARAMETERS (*QS*, *IS* in mm s⁻¹) FOR ARYL FERROCENYL KETONES

 IN SOLID AND FROZEN SOLID SOLUTION PHASE AT 80 K (Fc = ferrocene)

X	Phase	<i>QS</i>	<i>IS</i>	ΔQS^a
H ^b	solid	2.26(2)	0.54(s)	0.11
H ^b	CF ₃ CO ₂ H	2.15(2)	0.55(2)	–
2-Me	solid	2.25(2)	0.52(2)	0.03
2-Me	80% H ₂ SO ₄	2.22(3)	0.54(2)	–
3-Me	solid	2.27(2)	0.52(2)	0.18
3-Me	CF ₃ CO ₂ H	2.09(2)	0.51(2)	–
4-Me ^b	solid	2.23(2)	0.56(2)	0.15
4-Me ^b	CF ₃ CO ₂ H	2.08(2)	0.55(2)	–
4-OMe ^b	solid	2.24(2)	0.53(2)	0.14
4-OMe ^b	CF ₃ CO ₂ H	2.10(2)	0.53(2)	–
2-Cl	solid	2.26(2)	0.53(2)	0.14
2-Cl	80% H ₂ SO ₄	2.12(2)	0.52(2)	–
3-Cl	solid	2.29(2)	0.53(2)	0.19
3-Cl	80% H ₂ SO ₄	2.10(2)	0.49(2)	–
4-Cl ^b	solid	2.25(2)	0.53(2)	0.15
4-Cl ^b	CF ₃ CO ₂ H	2.10(2)	0.56(2)	–
2-Br	solid	2.25(2)	0.52(2)	0.15
2-Br	80% H ₂ SO ₄	2.10(3)	0.45(2)	–
3-Br	solid	2.29(2)	0.55(2)	0.11
3-Br	CF ₃ CO ₂ H	2.18(2)	0.48(2)	–
4-Br	solid	2.30(2)	0.52(2)	0.18
4-Br	CF ₃ CO ₂ H	2.28(3)	0.53(2)	–
4-Br	98% H ₂ SO ₄	2.12(2)	0.50(2)	–
4-CN ^b	solid	2.26(2)	0.52(2)	0.04
4-CN ^b	CF ₃ CO ₂ H	2.22(3)	0.54(2)	–

^a $\Delta QS = QS(\text{solid}) - QS(\text{frozen solid solution})$. ^b Data from ref. 2.

forming the carbenium ion. This is strong evidence that the ion is stabilised by the anthracene moiety rather than the ferrocenyl group which is supported by the greatly deshielded H(10') proton.

TABLE 5

⁵⁷Fe MÖSSBAUER PARAMETERS (*QS*, *IS* in mm s⁻¹) FOR SOME STERICALLY HINDERED FERROCENYL KETONES FcCOR (An = anthracyl, Ad = adamantyl) IN SOLID AND FROZEN SOLID SOLUTION PHASE AT 80 K

R	Phase	<i>QS</i>	<i>IS</i>	ΔQS
An	solid	2.26(1)	0.51(1)	–
An	CF ₃ CO ₂ H	2.15(1)	0.54(1)	0.11
t-Bu	solid	2.28(1)	0.52(1)	–
t-Bu	80% H ₂ SO ₄	2.02(1)	0.53(1)	0.24
Ad	solid	2.22(1)	0.56(1)	–
Ad	CF ₃ CO ₂ H	2.13(2)	0.52(2)	0.09
Ad	80% H ₂ SO ₄	1.98(5)	0.44(4)	0.24
Mesityl	solid	2.34(1)	0.56(1)	–
Mesityl	CF ₃ CO ₂ H	2.14(1)	0.55(1)	0.20

TABLE 6

^{57}Fe MÖSSBAUER PARAMETERS (QS , IS in mm s^{-1}) FOR ARYL FERROCENYL CARBENIUM IONS, $\text{Fc}\overset{\oplus}{\text{C}}\text{H}-\text{C}_6\text{H}_4\text{X}$ (frozen solid solutions) AND THEIR ALCOHOL PRECURSORS AT 80 K

X	Phase	QS	IS	ΔQS
H ^a	solid	2.39(2)	0.57(2)	-0.16
H ^a	98% H ₂ SO ₄	2.55(2)	0.54(2)	-
2-Me	solid	2.37(2)	0.51(2)	-0.17
2-Me	CF ₃ CO ₂ H	2.54(2)	0.51(2)	-
3-Me	solid	2.39(2)	0.52(2)	-0.17
3-Me	CF ₃ CO ₂ H	2.56(2)	0.50(2)	-
4-Me ^a	solid	2.39(2)	0.56(2)	-0.11
4-Me ^a	CF ₃ CO ₂ H	2.50(2)	0.54(2)	-
4-OMe ^a	solid	2.38(2)	0.55(2)	-0.04
4-OMe ^a	CF ₃ CO ₂ H	2.42(2)	0.53(2)	-
2-Cl	solid	2.35(2)	0.51(2)	-0.21
2-Cl	CF ₃ CO ₂ H	2.56(2)	0.49(2)	-
3-Cl	solid	2.39(2)	0.50(2)	-0.29
3-Cl	CF ₃ CO ₂ H	2.68(2)	0.44(2)	-
4-Cl ^a	solid	2.41(2)	0.56(2)	-0.25
4-Cl ^a	CF ₃ CO ₂ H	2.66(2)	0.56(2)	-
2-Br	solid	2.33(2)	0.51(2)	-0.29
2-Br	CF ₃ CO ₂ H	2.62(2)	0.50(2)	-
3-Br	solid	2.39(2)	0.52(2)	-
4-Br	solid	2.36(1)	0.53(2)	-0.21
4-Br	CF ₃ CO ₂ H	2.57(2)	0.51(2)	-
4-CN ^a	solid	2.39(2)	0.54(2)	-0.25
4-CN ^a	CF ₃ CO ₂ H	2.64(2)	0.56(2)	-

^a Data from ref. 4.

TABLE 7

^{57}Fe MÖSSBAUER DATA (QS , IS in mm s^{-1}) FOR SOME STERICALLY HINDERED FERROCENYL CARBENIUM IONS $\text{Fc}\overset{\oplus}{\text{C}}\text{HR}$ (FROZEN SOLID SOLUTION) AND THEIR ALCOHOL PRECURSORS AT 80 K

R	Phase	QS	IS	ΔQS
An	solid	2.40(2)	0.52(2)	0
An	CF ₃ CO ₂ H	2.42(2)	0.51(2)	-
t-Bu	solid	2.40(2)	0.51(2)	-0.16
t-Bu	CF ₃ CO ₂ H	2.56(2)	0.50(2)	-
Ad	solid	2.40(2)	0.52(2)	-0.17
Ad	CF ₃ CO ₂ H	2.57(2)	0.50(2)	-
H ^a	solid	2.40(2)	0.50(2)	-0.27
H ^a	CF ₃ SO ₂ H	2.67(2)	0.47(2)	-
CH ₃ ^b	CH ₃ CO ₂ H	2.36(4)	0.55(2)	-0.25
CH ₃ ^b	98% H ₂ SO ₄	2.61(3)	0.50(2)	-

^a Data from ref. 3. ^b Data from ref. 4.

Experimental

¹H NMR spectra were run on Varian EM360 instrument and Mössbauer data obtained as previously reported [3].

The syntheses of the ferrocenyl ketones has been reported in a previous paper [8].

The corresponding alcohols were prepared usually by NaBH_4 reduction in MeOH [4] (Method A), though more vigorous conditions (LiAlH_4 in Et_2O) had to be used for some of the sterically hindered derivatives (mesityl, adamantyl) as typified below (Method B) [16].

Preparation of 1-adamantyl ferrocenyl methanol (Method B)

1-Adamantyl ferrocenyl ketone (3 g, 8.6 mmol) was dissolved in warm dry ether (150 ml) and LiAlH_4 (1 g, 26 mmol) added portionwise over 5 min. The mixture changed from red to yellow indicating that reduction had occurred. After stirring for a further 15 min, methyl acetate was added dropwise until effervescence ceases. The mixture was washed with 3×100 ml portions of water and the ethereal layer separated and dried. On removal of the solvent, a yellow solid remained (2.7 g, 90%) which was recrystallised from EtOH m.p. 146°C (nc). Found: C, 72.4; H, 7.8; Fe, 15.9. $\text{C}_{21}\text{H}_{26}\text{FeO}$ calcd.: C, 72.0; H, 7.5; Fe, 15.9%.

^1H NMR (CCl_4) δ (ppm) 1.5–2.2 m (15H); 3.88s (1H); 4.20 t (2H); 4.25 ppm s (7H).

9-Anthracyl ferrocenyl methanol (nc) (Method B). Yield after chromatography on neutral alumina 26%, m.p. 145°C . Found: C, 77.2; H, 5.3; Fe, 13.7. $\text{C}_{25}\text{H}_{20}\text{FeO}$ calcd.: C, 76.6; H, 5.1; Fe, 14.2%.

^1H NMR δ (ppm) (CCl_4) 3.33s (5H); 3.77 brs (1H); 4.03m (2H); 4.83 brs (1H); 6.72 (1H); 7.0–9.2 m (8H); 8.57s (1H).

t-Butyl ferrocenyl methanol (nc) (Method A). 95%, m.p. 92°C . Found: C, 66.0; H, 7.6; Fe, 20.7. $\text{C}_{15}\text{H}_{20}\text{FeO}$ calcd.: C, 66.2; H, 7.4; Fe, 20.5%.

^1H NMR δ (ppm) (CCl_4) 0.88s (9H); 2.17 brs (1H); 4.03 brs (1H); 4.18s (2H); 4.23s (7H).

2-Chlorophenyl ferrocenyl methanol (nc) (Method A). 75%, m.p. 105 – 106°C . Found: C, 63.6; H, 5.0. $\text{C}_{17}\text{H}_{13}\text{ClFeO}$ calcd.: C, 62.5; H, 4.7%.

^1H NMR δ (ppm) (CCl_4) 2.27 brs (1H); 4.13 brs (9H); 5.70s (1H); 7.20 brs (4H).

3-Chlorophenyl ferrocenyl methanol (nc) (Method A). 60%, m.p. 93 – 95°C . Found: C, 61.2; H, 4.5; Cl, 10.2. $\text{C}_{17}\text{H}_{15}\text{ClFeO}$ calcd.: C, 62.5; H, 4.6; Cl, 10.8%.

^1H NMR δ (ppm) (CCl_4) 2.10 brs (1H); 4.10 brs (9H); 5.26s (1H); 7.13 brs (4H).

2-Bromophenyl ferrocenyl methanol (nc) (Method A). 70%, m.p. 97 – 100°C . Found: C, 55.0; H, 4.4. $\text{C}_{17}\text{H}_{13}\text{BrFeO}$ calcd.: C, 55.0; H, 4.1%.

^1H NMR δ (ppm) (CCl_4) 2.33 brs (1H); 4.13 brs (9H); 5.66s (1H); 7.20d (2H); 7.47d (2H).

3-Bromophenyl ferrocenyl methanol (nc) (Method A). 50%, m.p. 85 – 87°C . Found: C, 55.5; H, 4.6. $\text{C}_{17}\text{H}_{13}\text{BrFeO}$ calcd.: C, 55.0; H, 4.1%.

^1H NMR δ (ppm) (CCl_4) 2.08 brs (1H); 4.01 brs (9H); 5.26s (1H); 7.18d (2H); 7.45d (2H).

2-Tolyl ferrocenyl methanol (nc) (Method A). 67%, m.p. 103 – 105°C . Found: C, 70.7; H, 6.1. $\text{C}_{18}\text{H}_{16}\text{FeO}$ calcd.: C, 70.6; H, 5.9%.

^1H NMR δ (ppm) (CCl_4) 1.25 brs (1H); 2.26s (3H); 4.10s (9H); 5.43s (1H); 7.00s (4H).

3-Tolyl ferrocenyl methanol (nc) (Method A). 80%, m.p. 70 – 72°C . Found: C, 71.2; H, 6.1. $\text{C}_{18}\text{H}_{16}\text{FeO}$ calcd.: C, 70.6; H, 5.9%.

^1H NMR δ (CCl_4) 2.06 brs (1H); 2.30s (3H); 4.03 brs (9H); 5.23s (1H); 7.0s (4H).

1-Anthracenyl ethanol was prepared as described previously [16]. Analyses were performed by the Analytical Department of Manchester University.

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