Journal of Organometallic Chemistry, 97 (1975) 429—441

CARBON-13 NMR SPECTRA OF FERROCENES AND FERROCENYL-ALKYLIUM IONS

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(Received May 7th, 1975)

Summary

The proton-coupled and proton-decoupled pulsed Fourier-transform ^{13}C NMR spectra of a series of neutral ferrocene derivatives and ferrocenylalkylium ions have been recorded and analysed. The influence of a substituent group upon the ^{13}C shifts of the carbons of the ferrocene rings has been investigated. The spectra of the ferrocenylalkylium ions are discussed in relation to the distribution of positive charge and to the various structural models which have been proposed for such species.

Introduction

The application of pulsed Fourier-transform techniques has produced an upsurge of interest in ^{13}C NMR spectroscopy of organic compounds [1] and it is apparent from work already published that the method offers a valuable probe into the electronic structures and metal—ligand interactions of organometallic complexes [2]. In view of the marked dependence of ^{13}C shieldings upon electron density [1,3], ^{13}C NMR spectroscopy would appear particularly useful for the study of charge distribution in cationic and anionic hydrocarbon—metal complexes. With this possibility in mind, we have carried out a detailed analysis of the spectra of a series of ferrocenylalkylium ions ($FcC^+R^1R^2$), species whose structures have been a topic of interest and controversy for over a decade [4,5a].

In this paper*, we compare the conclusions obtained from these spectral analyses with those formed earlier in complementary investigations [5]. To

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* A preliminary account of some of this work has been published [6].

provide meaningful comparisons of the ^{13}C shieldings for these cations with those for uncharged analogues, we have also recorded and analysed the spectra of a series of neutral ferrocene derivatives. These additional data have enabled us to examine the influence of a substituent group upon the ^{13}C shieldings of the carbon atoms of the ferrocene system.

Experimental

For spectral determinations, solutions of the neutral ferrocenes in $CDCl_3$ were used while the ferrocenylalkylium ions were obtained [5] by dissolving the corresponding alcohols in CF_3CO_2D. The rather unstable primary cation (FcC^+H_2) was more conveniently generated from the ether ($FcCH_2OCH_2Fc$) in CF_3CO_2D. All of the ferrocene derivatives used have been described previously in the literature. Generally, substrate concentrations in the range 0.6-0.8 g/2.5 ml were used for the solutions with TMS as internal standard in all cases.

TABLE 1

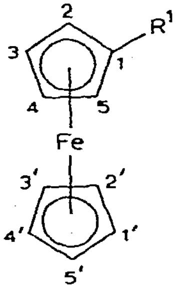
^{13}C NMR CHEMICAL SHIFTS FOR FERROCENE AND ITS DERIVATIVES[a]

Compound	Chemical shifts[b]						
	C(1)	C(2,5)	C(3,4)	C(1'-5')	C(α)	R^1	R^2
Ia	67.9	67.9	67.9	67.9			
Ib	83.7	69.0	67.0	68.5		14.7(Me)	
Ic	79.5	69.6	72.2	69.8		201.3(CO): 27.3(Me)	
Id	76.7	70.9	71.0	69.7		209.8(CO): 44.1(*C*Me$_3$): 28.1(Me$_3$)	
IIa	83.7	69.7	67.8			14.4(Me)	
IIb	80.9	71.0	73.5			200.6(CO): 27.5(Me)	
IIIa	88.0	67.9	68.2	68.2	60.5		
IIIb	94.4	65.9, 66.3	67.6, 67.7	68.2	65.4		23.6(Me)
IIIc	93.1	64.8, 68.7	67.6, 67.7	68.2	75.1		34.9(CH): 18.5,18.6(Me$_2$)
IIId	91.6	65.3, 69.7	67.3, 67.5	68.1	77.9		35.0(*C*Me$_3$): 25.8(Me$_3$)
IIIe	100.0	65.5	67.6	68.2	68.7	30.8(Me)	30.8(Me)
IIIf	99.3	65.3[c], 68.4[c]	67.4[c], 67.7[c]	68.2	73.5	24.2(Me)	39.2(CH); 17.8,18.6(Me$_2$)
IIIg	98.4	66.8, 69.3	66.7. 67.3	68.3	75.3	25.0(Me)	37.4(*C*Me$_3$): 25.8(Me$_3$)
V[d]	99.7	67.4(2), 65.3(5)	83.8(3), 69.7(4)	70.2, 70.5 }(2',5') 67.4, 68.8 }(3',4') 84.2 (1')	69.3	30.8(Me)	30.8(Me)

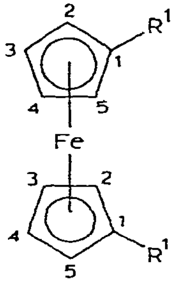
[a] For $CDCl_3$ solutions. [b] Chemical shifts are given as ppm downfield from internal TMS [δ(TMS) = 0] and are considered accurate to ± 0.1 ppm. [c] Tentative assignment. [d] Chemical shifts of the ring methyl carbons are 14.2 (3-Me) and 14.3 ppm (1'-Me).

The pulsed Fourier-transform spectra were recorded at a frequency of 25.16 MHz using a Varian XL-100-15 spectrometer equipped with VFT-100 pulse unit and a 620L-16k computer, locking on the solvent D-signal. Proton-coupled spectra were taken once with an acquisition time (t_a) of 1.6 s (for sp^2 and sp^3 carbon regions) and once with a t_a of 4.0 s (for sp^2 carbon region only) for the neutral ferrocenes, and with a t_a of 1.0 s for the cations. Proton-noise-decoupled spectra were taken with a t_a of 0.8 or 1.6 s by the conventional method. (The resolutions corresponding to these t_a values were 0.63, 0.13, 1.0, 1.25, and 0.63 Hz/point respectively.)

(continued on p. 434)

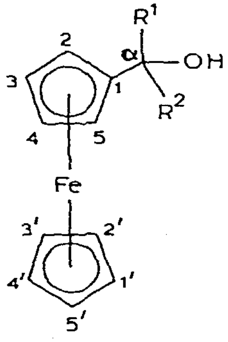


(I)



(II)

(Ia, R^1 = H;
Ib, R^1 = Me;
Ic, R^1 = COMe;
Id, R^1 = $COCMe_3$)
(IIa, R^1 = Me;
IIb, R^1 = COMe)



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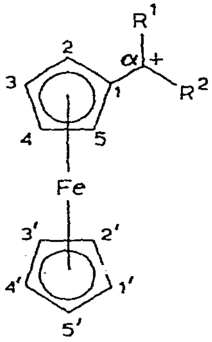
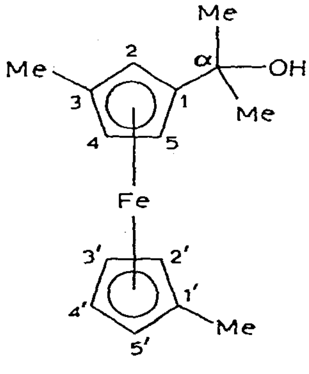


(IV)

(III, IV a, R^1 = R^2 = H;
b, R^1 = H, R^2 = Me;
c, R^1 = H, R^2 = $CHMe_2$;
d, R^1 = H, R^2 = CMe_3;
e, R^1 = R^2 = Me;
f, R^1 = Me, R^2 = $CHMe_2$;
g, R^1 = Me, R^2 = CMe_3)



(V)

TABLE 2

^{13}CH COUPLING CONSTANTS[a]

Structure	C(2,5)				C(3,4)			C(1′-5′)			C(α)[b]	Other carbons
	^1J	^2J	^3J	^3J[CH(α)]	^1J	^2J	^3J	^1J	^2J	^3J	J	J
Ia	175.5	6.8	6.8		175.5	6.8	6.8	175.5	6.8	6.8		
Ib	174.9	6.6	6.6	3.8	173.2	6.1[c]	7.7[c]	175.0	6.8	6.8	126.5(q)	
Ic	178.2	6.4	6.4		176.6	5.9[c]	7.6[c]	176.5	6.8	6.8		Me, 127.1(q)
Id	178.3	6.5	6.5		176.4	*d*	*d*	176.4	6.75	6.75		Me$_3$, 126.7(q), 4.85(sp)
IIa	173.0	6.5	6.5	3.9	174.4	6.5	6.5				127.1(q)	
IIb	179.2	6.4	6.4		177.9	*d*	*d*					Me, 127.5(q)
IIIa	*d*	*d*	*d*	*d*	*d*	*d*	*d*	175.4	6.7	6.7	143.1(t)	
IIIb	174.4	6.5	6.5	2.7	175.5	6.6	6.6	175.4	6.75	6.75	144.0(d),	Me, 125.0(q),
	174.2	6.6	6.6	2.8	175.4	6.5	6.5				4.3(q)	4.6(d)
IIIc	175.3	6.6	6.6	4.5	175.5	6.3	6.3	175.5	6.7	6.7	143(d)	CH, 125.5(d)(bd);
	174.6	6.4	6.4	2.3	175.5	6.3	6.3					Me$_2$, 125(q)(bd)
IIId	175.6	6.6	6.6	4.8	175.0	6.0	7.5	175.6	6.8	6.8	141.8(d)	Me$_3$, 125.0(q), 4.7(sp), 3.1(d)
	174.7	6.5	6.5	2.5	175.5	6.5	6.5					
IIIe	174.4	6.4	6.4		175.5	*d*	*d*	175.4	6.8	6.8		Me, 126.0(bq)
IIIf	175.0	6.6	6.6		175.6	*d*	*d*	175.4	6.8	6.8		Me, 125.9(q), 3.4(d);
	176.1	*d*	*d*		175.7	*d*	*d*					CH, 126.0(d); Me$_2$, 125.7(q)

IIIg	175.1	6.5	6.5		175.0	6.0	7.0	175.5	6.8	6.8		Me, 125.9(q):
	174.3	6.5	6.5		175.2	6.2	7.5					Me$_3$, 125.5(q), 4.7(sp)
IVa	187.0	*d*	*d*	*d*	183.7	*d*	*d*	184.3	6.4	6.4	169(t)	
IVb	187.0	*d*	*d*	*d*	184.0	*d*	*d*	183.5	6.7	6.7	164(d)	Me, 130.3(q), 2.6(d)
IVc	186	*d*	*d*	*d*	184	*d*	*d*	184	6.8	6.8	163.0(d)	CH, 131.5(d)(bd); Me$_2$, 127.6(q)(bd), 128.8(q)(bd)
IVd	187.7	6.1	6.1	*d*	184.0	*d*	*d*	183.1	6.8	6.8	158(d)	Me$_3$, 128.0(q), 4.2(sp), 4.2(d)
	187.7	6.1	6.1	*d*	184.1	*d*	*d*					
IVe	186.4	6.0	6.0		183.3	6.5	6.5	182.3	6.7	6.7		*e*
IVf	186.0	6.1	6.1		183.0	5.1	8.0	182.1	6.7	6.7		*e*
	186.1	6.1	6.1		183.1	5.0	8.1					CH, 130.9(d): Me$_2$, 127.0(q), 4.6(qi): 129.7(q), 5.5(qi)
IVg	186.5	6.2	6.2		183.1	*d*	*d*	182.0	6.6	6.6		*e*
	185.7	6.3	6.3		183.1	*d*	*d*					Me$_3$, 128.2(q), 4.6(sp)

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[a] In Hz: (d) doublet, (t) triplet, (q) quartet, (qi) quintet, (sp) septet: for those structures in which the carbons of the C(2,5) and C(3,4) pairs are anisochronous, the couplings given first refer to the higher-field resonance. Couplings associated with the C(1) resonance could not be evaluated due to the low signal intensity of these quaternary carbon atoms. [b] Although C(α)/H(2,5) couplings were unresolved, linewidths observed suggest ^3J values of 0.5-1 Hz. [c] Evaluated by iterative least-squares analysis. [d] Coupling constant not evaluated. [e] The (Me$\overset{+}{C}$) methyl coupling could not be evaluated due to H/D exchange in CF$_3$CO$_2$D.

Europium-shifted spectra were obtained for $CDCl_3$ solutions (0.32 *M* in substrate) with up to 0.1 mol-equivalent of $Eu(fod)_3$ added. The $\Delta\delta_{Eu}$ values given in Table 3 are extrapolated from the shifts observed by this procedure to those for an equimolar mixture of substrate and shift reagent and are of qualitative significance only. In the spectra of selected ferrocene derivatives, a few signals showing higher-order splittings were analysed by the iterative least-squares method of Castellano and Bothner-By [7] using the improved LAOCN3 procedure.

Results and discussion

Neutral ferrocenes

(a). Chemical-shift assignments. The ^{13}C chemical shifts for ferrocene (Ia) and a number of monosubstituted (Ib-d; IIIa-g) and 1,1'-disubstituted derivatives (IIa,b) are given in Table 1 which also contains the values for the trisubstituted compound V. Associated CH coupling constants are listed in Table 2. Unambiguous identification of the resonances of the various carbons was achieved from selective and off-resonance ^{1}H-decoupling experiments, from europium-shifted spectra in the case of the ketones and alcohols, and most successfully from an analysis of the splittings in the nondecoupled spectra.

In the proton-coupled spectrum of ferrocene itself, the ^{13}C resonance appears as a doublet of quintets (dqi), this splitting arising from the large $^{1}J(CH)$ value and the near identity of the much smaller $^{2}J(CH)$ and $^{3}J(CH)$ values*. A dqi resonance was also observed for the carbons of the unsubstituted ring, C(1'-5'), in the spectra of all of the monosubstituted ferrocenes. The C(3,4) signals in the proton-coupled spectra of Ib and Ic showed second-order splittings and were analysed using the LAOCN3 procedure. It was thereby established that in these cases (as well as some others, e.g. in the spectra of IIIg and IVf), the $^{2}J(CH)$ and $^{3}J(CH)$ couplings are markedly different with $^{2}J(CH) < {}^{3}J(CH)$. For the C(2,5) signals, on the other hand, the relation $^{2}J(CH) = {}^{3}J(CH)$ holds in all of the cases studied. Another aid for the differentiation between the C(2,5) and C(3,4) resonances, which is of special interest, is the coupling observed of an α-proton, if present, with C(2,5) but not with C(3,4). This proved the only means of identification of the C(2,5) and C(3,4) signals in the spectra of Ib and IIa where the C(2,5) absorptions show an additional quartet splitting of 3.8 Hz.

Differentiation between the C(2,5) and C(3,4) resonances in the spectra of the ketones Ic, Id and IIb was achieved by selective proton-decoupling. Thus, irradiation of the low-field ^{1}H signal [$\delta(H) = 4.76$] of IIb, which represents the H(2,5) protons [9], caused collapse of the high-field ^{13}C resonance [$\delta(C) = 71.0$] which was thereby identified as the signal of the C(2,5) carbons. These assignments were supported by europium-shifted spectra. Addition of $Eu(fod)_3$ to the $CDCl_3$ solutions of the ketones induced a larger shift of the C(2,5) resonances than of the C(3,4) resonances (see Table 3), in accord with expectation based upon the closer proximity of the C(2,5) carbons to the paramagnetic centre bound to the carbonyl oxygen atom. A corresponding larger shift of the H(2,5)

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* From analysis of the ^{13}CH satellite PMR spectrum of ferrocene, values of 6.30 and 7.22 Hz have been obtained for the $^{2}J(CH)$ and $^{3}J(CH)$ coupling constants respectively [8].

TABLE 3

Eu(fod)$_3$-SHIFTED ^{13}C NMR SPECTRA: $\Delta\delta$(Eu) VALUES[a]

Compound	$\Delta\delta$(Eu) Values[b]				
	C(1)	C(2,5)[c]	C(3,4)[c]	C(1′-5′)	C(α)
Ic	−2.3	+9.6	+6.7	+4.5	
IIb	+1.1	+8.0	+5.6		
IIIa	−7.3	+12.1	+7.9	+6.0	+64
IIIb	−2.8	+10.5, +12.0	+6.4, +6.4	+4.9	+54
IIId	−1.1	+5.4, +2.2	+1.9, +3.4	+1.1	+24
IIIe	+4.2	+9.5	+5.6	+4.2	+54
IIIf	+0.6	+7.8, +4.1	+3.3, +4.1	+2.4	+33
IIIg	+0.7	+1.7, +0.9	+0.8, +0.9	+0.6	+6.5

[a] See Experimental section. [b] Positive values denote a shift to higher field. [c] The value given first refers to the higher-field resonance given in Table 1.

resonances than of the H(3,4) resonances was observed in the europium-shifted proton spectra of these compounds.

A characteristic feature of the ^{13}C spectra of the alcohols IIIb-d,f,g is the presence of five signals for the carbon atoms of the substituted ring, resulting from the asymmetric centre present in the side-chain which renders diastereotopic the carbons of the C(2,5) and C(3,4) pairs. Unambiguous assignment of these resonances was possible from the proton-coupled spectra which revealed the expected (vide supra) additional couplings of C(2,5) with H(α) in the case of the secondary alcohols IIIb-d*. The C(2,5)/H(α) coupling constant for the primary alcohol IIIa could not be evaluated due to the complexity of overlapping signals in the proton-coupled spectrum resulting from very small chemical-shift differences. The C(2,5) resonances in the spectra of the tertiary alcohols IIIe-g, which lack an H(α) proton, were clearly recognisable from their quartet fine structure; the corresponding C(3,4) signals in these spectra were more complex due to the inequality of the associated ^2J(CH) and ^3J(CH) values (vide supra). Some overlapping of signals in the spectrum of IIIg, however, precluded definite assignment of the C(2-5) chemical shifts. It is worth noting here that a qualitative interpretation of the $\Delta\delta$(Eu) values (see Table 3) from the europium-shifted spectra of these alcohols IIIa-g would lead to incorrect chemical-shift assignments in some cases.

The proton-coupled spectrum of the alcohol V proved difficult to analyse due to badly overlapping signals. The assignments given in Table 1 are based, in the main, on a comparison of the observed shifts with those calculated from the spectra of Ia, IIa, and IIIe, assuming that the influence of the C(OH)Me$_2$ and Me substituents upon the chemical shifts of the ring carbons is additive; good agreement between the calculated and observed shifts was found. Further support for the assignments was obtained from europium-shifted spectra which followed a similar pattern to that found for IIIe.

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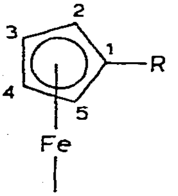
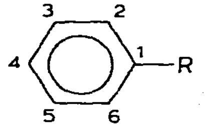
* Our chemical-shift assignments for C(1) and C(α) in the spectra of the alcohols IIIb,c reverse those of other workers [10,11a] which are incorrect. The assignments for IIIc were reversed in a later paper [11b] from this group but the δ_C value given therein for C(α) is incorrect and the C(2-5) resonances were not distinguished.

TABLE 4

SUBSTITUENT EFFECTS ON THE ^{13}C CHEMICAL SHIFTS OF FERROCENE AND BENZENE RING CARBONS[a]





R	Chemical-shift differences (ppm)[b]						
	Ferrocene carbons			Benzene carbons			
	$\Delta\delta(1)$	$\Delta\delta(2,5)$	$\Delta\delta(3,4)$	$\Delta\delta(1)$	$\Delta\delta(2,6)$	$\Delta\delta(3,5)$	$\Delta\delta(4)$
Me	+15.8	+1.1	−0.9	+9.5	+0.8	0.0	−2.9
COMe	+11.6	+1.7	+4.3	+9.0	+0.3	0.0	+4.7
CH_2OH	+20.1	0.0	+0.3	+12.6	−1.3	0.0	−1.0
CH(OH)Me	+26.5	−2.0, −1.6	−0.3, −0.2	+17.7	−2.9	0.0	−1.2
$C(OH)Me_2$	+32.1	−2.4	−0.3	+21.0	−3.8	−0.2	−1.8

[a] Values calculated from the data given in Table 1 (ferrocenes) and from unpublished results (benzenes).
[b] Differences are given relative to the ^{13}C shift for ferrocene (67.9 ppm) and benzene (128.3 ppm); positive values indicate decreased shielding relative to a carbon atom in the reference molecule.

(b). Chemical-shift correlations. The chemical shifts of the carbons of substituent groups in the spectra of all of the compounds studied are unexceptional (see Table 1) and conform to expected values [1]. Several features of the ring-carbon shift patterns through the series merit comment, however. The δ values for the C(1′-5′) carbons in the monosubstituted ferrocenes are relatively insensitive to the nature of the substituent in the other ring and are close to the value for ferrocene itself. The δ values for the substituted ring carbons, on the other hand, respond markedly to the presence of the substituent.

A comparison of the influence of various substituents upon the ^{13}C shifts for ferrocene ring carbons C(1-5) and benzene ring carbons C(1-6) is presented in Table 4. The $\Delta\delta$ values for C(1) of the ferrocenes parallel those for C(1) of the corresponding benzenoid compounds although the magnitude of the substituent effect is greater in the ferrocene series. Furthermore, the substituent effect upon the C(2,5) shifts for the ferrocenes is similar to that observed for the benzenoid C(2,6) shifts. The $\Delta\delta$ values for C(3,4) in the ferrocene series more closely correspond to those for the benzenoid C(4) carbon than to those for C(3,5) which are zero in most cases. In their response to substituent effects, therefore, C(2,5) and C(3,4) of a substituted ferrocene ring may be likened to the *ortho* and *para* positions respectively of a benzene ring, a conclusion similar to that reached earlier by Russian workers in an independent investigation [10].

Ferrocenylalkylium ions

(a). Chemical-shift assignments. The ^{13}C chemical shifts for the ferrocenylalkylium ions IVa-g are given in Table 5 and the associated CH coupling constants

TABLE 5

^{13}C NMR CHEMICAL SHIFTS FOR FERROCENYLALKYLIUM IONS[a]

Cation	Chemical shifts[b]						
	C(1)	C(2,5)	C(3,4)	C(1'-5')	C(α)	R^1	R^2
IVa	111.8	85.5	95.6	83.3	88.6		
IVb	106.9	81.7, 82.8	95.1, 95.4	83.4	119.5		20.1(Me)
IVc	104.3	80.5, 81.3	94.6, 95.1	81.3	133.2		35.1(CH): 21.4, 27.7(Me$_2$)
IVd	101.6	81.1, 82.6	95.1, 95.3	81.2	145.0		41.4(*C*Me$_3$): 31.2(Me$_3$)
IVe	101.2	78.7	94.7	82.9	158.6	27.8(Me)	27.8(Me)
IVf	100.1	76.9, 77.9	94.5 94.9	81.2	178.0	21.7(Me)	40.8(CH): 19.3, 26.3(Me$_2$)
IVg	100.5	79.2, 80.3	95.1, 95.3	81.7	195.6	27.0(Me)	48.4(*C*Me$_3$): 32.8(Me$_3$)

[a] For CF_3CO_2D solutions. [b] Chemical shifts are given as ppm downfield from internal TMS (δ(TMS) = 0) and are considered accurate to ± 0.1 ppm.

are collected in Table 2. The ^1J(CH) values were found to be significantly larger (by ca. 10 Hz) than those found for the neutral ferrocenes while the ^2J(CH) and ^3J(CH) values are similar in magnitude for both neutral and cationic species. As noted by other groups [11,12], the magnitude of the ^1J[CH(α)] values (range: 158-169 Hz) found for the primary and secondary cations IVa-d are in accord with sp^2 but not sp^3 orbital hybridisation at C(α) of these species.

As for the neutral ferrocenes, the chemical-shift assignments given in Table 5 are securely based upon analyses of the proton-coupled spectra and upon selective proton-decoupling experiments. It is well established [5,13] that, in the ^{1}H NMR spectra of cations of the type IV, the H(3,4) resonances always appear downfield of those of H(2,5). Double-resonance experiments, therefore, readily permitted identification of the C(2,5) and C(3,4) resonances in the ^{13}C spectra. Thus, irradiation of the H(3,4) resonances of the cation IVb caused collapse of the ^{13}C resonances at δ = 95.1 and 95.4 which can therefore be assigned to C(3,4). It is apparent from the proton-coupled spectra that the signals of the C(2,5) and C(3,4) carbons can also be differentiated from the magnitudes of the ^1J(CH) values which, in each case studied, are larger for the former pair by ca. 3 Hz.

From these experiments, it is clear that the chemical-shift assignments given by Sokolov et al. [11a] for C(2,5) and C(3,4) in the spectrum of the cation IVc are incorrect and should be reversed. Furthermore, the δ(C) values cited for these carbons in a later paper [11b] are incomplete and the chemical-shift value (125.3 ppm) given for C(α) in the cation IVe is wrong. Our δ(C) values for the cations IVa,b, however, agree with those reported by Seyferth et al. [12], taking account of the difference between the external TMS reference used by them and the internal TMS used in this work; their one-bond ^{13}CH coupling constants, however, differ from those reported herein by up to 6 Hz. They based their chemical-shift assignments on the larger separation of the C(2)/C(5) reso-

TABLE 6

^{13}C CHEMICAL-SHIFT DIFFERENCES BETWEEN ALCOHOLS AND DERIVED ALKYLIUM IONS[a]

Alcohol	Cation	$\Delta\delta$ Values[b,c]					$\Sigma\Delta\delta$ Values[d]
		C(1)	C(2,5)	C(3,4)	C(1'-5')	C(α)	
IIIa	IVa	23.8	17.6	27.4	15.1	28.1	217.4
IIIb	IVb	12.5	15.8, 16.5	27.5, 27.7	15.2	54.1	226.6
IIIc	IVc	11.2	15.7, 12.6	27.0, 27.4	13.1	58.1	229.7
IIId	IVd	10.0	15.8, 12.9	27.8, 27.8	13.1	67.1	249.5
IIIe	IVe	1.2	13.2	27.1	14.7	89.9	239.2
IIIf	IVf	0.8	11.6, 9.5	27.1, 27.2	13.0	104.5	254.0
IIIg	IVg	2.1	12.4, 11.0	28.4, 28.0	13.4	120.3	303.2

[a] Calculated from the δ values given in Tables 1 and 5. [b] $\Delta\delta = \delta(\text{cation}) - \delta(\text{alcohol})$. [c] For the purpose of calculation of the $\Delta\delta$ values, it has been arbitrarily assumed that the carbon of a diastereotopic C(2,5) or C(3,4) pair which gives the lower-field resonance in the alcohol also gives the lower-field resonance in the corresponding cation. [d] $\Sigma\Delta\delta$ = sum of the $\Delta\delta$ values for all of the carbon atoms of the system, including those of the alkyl substituents.

nances rather than those of the C(3)/C(4) resonances in the spectrum of IVb. Since C(α) in cations of this type is sp^2 hybridised (vide supra), the diastereotopism associated with the carbons of the C(2,5) and C(3,4) pairs in the unsymmetrically substituted systems IVb-d,f,g (see Table 5) must have its origin in the restricted rotation around the C(1)—C(α) bond [5a].

(b). Chemical-shift correlations. Comparison of the chemical-shift data given in Tables 1 and 5 shows that all of the ^{13}C resonances of the ferrocenyl carbon atoms of the cations IV appear downfield of the corresponding resonances of the alcohol precursors III. Since the ^{13}C shift is particularly sensitive to local changes in electron density, this suggests that the positive charge in the

TABLE 7

EFFECT OF ALKYL SUBSTITUTION AT C(α) OF THE FERROCENYLMETHYLIUM ION IVa UPON ^{13}C CHEMICAL SHIFTS

Cation	R^1	R^2	$\Delta\delta^+$ Values[a,b]				
			C(1)	C(2,5)	C(3,4)	C(1'-5')	C(α)
IVb	H	Me	−4.9	−3.25	−0.35	+0.1	+30.9
IVc	H	$CHMe_2$	−7.5	−4.6	−0.75	−2.0	+44.6
IVd	H	CMe_3	−10.2	−3.65	−0.4	−2.1	+56.4
IVe	Me	Me	−10.6	−6.8	−0.9	−0.4	+70.0
			(−9.8)	(−6.5)	(−0.7)	(+0.2)	(+61.8)
IVf	Me	$CHMe_2$	−11.7	−8.1	−0.9	−2.1	+89.4
			(−12.4)	(−7.85)	(−1.1)	(−1.9)	(+75.5)
IVg	Me	CMe_3	−11.3	−5.75	−0.4	−1.6	+107.0
			(−15.1)	(−6.9)	(−0.75)	(−2.0)	(+87.3)

[a] $\Delta\delta^+ = \delta(\text{IVa}) - \delta(\text{substituted cation})$; the values given in parentheses for the tertiary cations IVe-g are calculated from the $\Delta\delta^+$ values for the secondary cations IVb-d, assuming that the effect of C(α) substitution is additive. [b] For those cations where the carbons of the C(2,5) or C(3,4) pairs give different $\Delta\delta^+$ values, the average of these values is given.

former is effectively delocalised throughout the ferrocene system, including the unsubstituted ring. However, the magnitudes of these downfield shifts vary over a considerable range for the carbons of a given system as shown by the spread of $\Delta\delta$ values given in Table 6.

For a particular carbon site through the series IVa-g, the $\Delta\delta$ values for C(2,5), C(3,4), and C(1′-5′) are remarkably consistent (range of values: 14 ± 4, 28 ± 1, and 14 ± 1 ppm respectively). This would suggest that the distribution of positive charge to these nine carbon atoms is relatively insensitive to the presence or otherwise of alkyl substituents at C(α). The corresponding values reported [12a] for FcC^+HPh likewise show that the presence of the C(α)-phenyl group has little effect upon the charge concentrations at these sites. The much wider spread of $\Delta\delta$ values for C(1) (range: 0.8 to 23.8 ppm) of the cations IVa-g, on the other hand, arises from the opposite influence of alkyl substitution at C(α) upon the C(1) chemical shifts for the alcohols (deshielding effect; see δ[C(1)] values in Table 1) and for the cations (shielding effect; see δ[C(1)] values in Table 5). This reversal in influence is understandable if it is assumed that there exists partial double-bond character between C(1) and C(α) of the cations as had been indicated in an earlier investigation [5a]. In this respect, the response of the C(1) shifts for the cations IV to alkyl substitution at C(α) is similar to that observed in the ^{13}C NMR spectra of fulvenes* where α-alkyl substitution also exerts a shielding effect upon the C(1) chemical shift [14].

The $\Delta\delta$ values for C(α) also vary markedly through the series (range: 28.1 to 120.3 ppm) and in the opposite direction to those for C(1) (see Table 6). The extent of this deshielding effect of C(α)-alkyl substitution upon the C(α) shifts is much larger than that evidenced in the spectra of the corresponding uncomplexed fulvenes. For example, the C(α) shift of α-t-butylfulvene (153.9 ppm) occurs 30.5 ppm downfield of that for fulvene itself [14] while the corresponding downfield shift for the ferrocenylalkylium analogues IVa,d is 56.4 ppm. From the variation in the $\Delta\delta$ values given in Table 6, therefore, it appears that the concentration of positive charge at C(α) increases through the carbenium-ion series: primary (IVa) < secondary (IVb-d) < tertiary (IVe-g). Progressive alkyl substitution at C(α) of the parent cation IVa allows this site to sustain a higher proportion of the positive charge with a corresponding reduction in the demand for electron donation from the ferrocenyl system, especially the iron atom. A similar effect has been noted previously with organic alkylium ions [15].

A more revealing analysis of the effect of alkyl substitution at C(α) upon the ^{13}C shifts of the ligand carbons is provided in Table 7 in which the differences ($\Delta\delta^+$) between the chemical shifts of the individual carbons of the cations IVb-g and those for the corresponding carbons of the parent cation IVa are presented. These data show that, on proceeding from the primary cation IVa to a secondary cation IVb-d and thence to a tertiary cation IVe-g, the effect of progressive alkyl substitution at C(α) upon the ring-carbon shifts is almost additive. Thus, the ring-carbon shifts calculated for the tertiary cations IVe-g from the $\Delta\delta^+$ values for the secondary cations IVb-d correspond closely to the observed

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* Cations of the type IV can be considered as fulvenes π-complexed with a $(CpFe)^+$ residue.

values (see Table 7; largest discrepancy between observed and calculated values: 3.8 ppm for C(1) of IV g). The agreement between the observed shifts for C(α) and those similarly calculated is poor, this again underlining the variation in charge concentration at this site through the series. The enhanced deshielding of the C(α) resonances of the tertiary ions over that calculated assuming an additive influence of alkyl substituents (see Table 7) reflects the greater accumulation of positive charge at C(α) of these species.

For every cation studied, the resonances of the C(3,4) carbons appear at lower field than those of the corresponding C(2,5) carbons (see Tables 5 and 6), a situation similar to that found with the ^{1}H NMR spectra in which the H(3,4) protons resonate at lower field [5,13]. If the ^{13}C shifts meaningfully reflect differences in charge density, this would require that C(3,4) in cations of the type IV bear a higher positive charge than C(2,5). However, other effects may also be important. The greater deshielding of the C(3,4) resonances was previously noted by Seyferth et al. [12a] and interpreted in favour of a structure, originally proposed by Richards et al. [16], in which the iron atom and its attendant cyclopentadienyl ligand are displaced in the direction of C(α) of the fulvene ligand. However, strong evidence against such ring-slip distortion in structures of cations of the type IV in solution has been presented [5,17], and crystallographic studies [18,19] of two ferrocenylalkylium salts have shown that the normal sandwich geometry of the ferrocene system is relatively undistorted in the solid state.

The ^{13}C NMR data obtained in this study are in accord with the structural model proposed by Gleiter and Seeger [20a] for the parent ferrocenylmethylium ion IVa on the basis of Extended Hückel (S.C.C.) calculations. In this structure, one half of the total positive charge resides on the iron atom with the remainder distributed uniformly over the eleven carbon atoms of the ligands*. The fulvene ligand is folded such that the exocyclic C(1)—C(α) bond is bent from the plane of the adjacent cyclopentadienyl ring towards the iron atom. Structural deformation of this nature, which arises from mixing of the metal $3d_{z^2}$ orbital with a fulvene π^* orbital, has been found in the crystal structures of ferrocenylcarbenium salts [18,19] and, recently, for the fulvene ligand of the neutral tricarbonylchromium complex of α,α-diphenylfulvene [21]. Indirect evidence supporting a folded fulvene ligand in cations of the type IV has also been inferred from a ^{1}H NMR study of the species in solution [5a,22]. A consequence of the Gleiter—Seeger structure is that the electron distribution around the iron atom is no longer symmetrical, as with neutral ferrocenes, which would lead to a differential magnetic anisotropic effect of the iron atom upon C(2,5) and C(3,4) of the fulvene ligand. The former pair of carbons, which are located closer to the inclined axis of the anisotropy cylinder, would experience a greater shielding influence than C(3,4) in accord with the results presented earlier. The proton shifts in the ^{1}H NMR spectra of cations of the type IV have been interpreted on this basis [20c] and the argument is equally applicable to an understanding of the ^{13}C shifts.

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* Minor variations in the charges calculated for the individual carbon atoms of the cation IVa are not significant [20b].

Finally, we wish to comment on the $\Sigma\Delta\delta$ values given in Table 6. It is clear from data now available that the corresponding values for metal-free organic carbenium ions vary over a wide range and that there is no "normal" value for a cationic all-carbon framework. For example, the values calculated from published ^{13}C shift values [15] for the diphenyl-, triphenyl-, trimethyl-, and tricyclopropyl-carbenium ions are 230, 259, 309, and 410 ppm respectively. It would appear unjustified, therefore, to use these $\Sigma\Delta\delta$ values (range: 217.4 to 303.2 ppm) for the cations IV to form conclusions concerning the extent of charge delocalisation to the iron atom of the system (cf. ref. 12a).

Acknowledgements

The authors thank Professors R. Gleiter and G.A. Olah for helpful comments and the Northern Ireland Department of Education for a maintenance grant (to T.S.A.).

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