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Preliminary communication

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^{13}C NMR SPECTRA OF FERROCENYLALKYLIUM IONS

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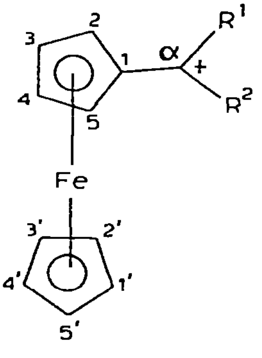
Summary

Pulsed Fourier-transform ^{13}C NMR spectra of a series of ferrocenylalkylium ions have been recorded and analysed.

The mechanism by which a ferrocenyl group delocalises charge from an attached carbenium-ion centre has been a topic of considerable interest and speculation [1]. In view of the marked dependence of ^{13}C shieldings upon electron density [2], we have recorded the ^{13}C NMR spectra of a series of ferrocenylalkylium ions in an attempt to probe the distribution of positive charge to the various ligand carbon atoms of the system.



(Ia) $R^1 = R^2 = H$
(Ib) $R^1 = H; R^2 = Me$
(Ic) $R^1 = H; R^2 = CHMe_2$
(Id) $R^1 = H; R^2 = CMe_3$
(Ie) $R^1 = R^2 = Me$
(If) $R^1 = Me; R^2 = CHMe_2$
(Ig) $R^1 = Me; R^2 = CMe_3$

The ^{13}C NMR spectra of the cations Ia-Ig were obtained for CF_3CO_2D solutions of the corresponding alcohols** using pulsed Fourier-transform techniques.

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[**] These alcohols were prepared by conventional methods and were satisfactorily characterised.

TABLE 1

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

Cation	δ- and Δδ-values [b] (ppm)						
	C(1)	C(2,5)	C(3,4)	C(1'-5')	C(α)	R^1	R^2
Ia	111.8	85.5	95.6	83.3	88.6	—	—
	(23.8)	(17.6)	(27.4)	(15.1)	(28.1)		
Ib [c]	106.9	81.7, 82.8	95.1, 95.4	83.4	119.5	—	20.1 (Me)
	(12.5)	(15.8, 16.5)	(27.5, 27.7)	(16.2)	(54.1)		(−3.5)
Ic [d]	104.3	80.5, 81.3	94.6, 95.1	81.3	133.2	—	35.1 (CH); 21.4, 27.7 (Me_2)
	(11.2)	(15.7, 12.6)	(27.0, 27.4)	(13.1)	(58.1)		(0.2) (2.9, 9.1)
Id	101.6	81 1, 82.6	95.1, 95.3	81.2	145.0	—	41.4 ($\underline{C}Me_3$); 31.2 (Me_3)
	(10.0)	(15.8, 12.9)	(27.8, 27.8)	(13.1)	(67.1)		(0.4) (5 4)
Ie	101.2	78.7	94.7	82.9	158.6	27.8 (Me)	27.8 (Me)
	(1.2)	(13.2)	(27.1)	(14.7)	(89.9)	(−3.0)	(−3.0)
If	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)
	(0.8)	(11 6, 9.5)	(27.1, 27.2)	(13.0)	(104.5)	(−2.5)	(1.6) (1.5, 7.7)
Ig	100.5	79.2, 80.3	95.1, 95.3	81.7	195.6	27.0 (Me)	48.4 ($\underline{C}Me_3$); 32 8 (Me_3)
	(2.1)	(12.4, 11.0)	(28.4, 28.0)	(13.4)	(120.3)	(2.0)	(11.0) (7.0)

[a] For CF_3CO_2D solutions with TMS as internal standard (δ(TMS) = 0); spectra were recorded using a Varian XL-100-15 spectrometer equipped with a VFT-100 pulsed Fourier-transform system. [b] Δδ-values (in parentheses) = δ(cation) − δ(alcohol); the alcohol spectra were obtained for $CDCl_3$ solutions with TMS as internal standard. [c] The ^{13}C chemical shifts of the alcohol precursor of this cation given by Russian workers [4c, 4d, 10] are incorrect. [d] The chemical shifts given for this cation by Sokolov et al. [4c, 4d] are incorrect.

Chemical-shift assignments, given in Table 1, are securely based upon analyses of proton-decoupled and proton-coupled spectra and upon double-resonance experiments*. To provide comparison of these ^{13}C shifts with those for uncharged analogues, we also determined the spectra of the alcohol precursors using $CDCl_3$ solutions. These spectra were analysed using the same methods as those adopted for the cation spectra, proton-coupled spectra being particularly helpful in this respect. The differences ($\Delta\delta$) between the δ-values of the individual carbon atoms of the cations and the corresponding values for the alcohol precursors are included in Table 1.

Several conclusions can be drawn from the results obtained.

(a) The magnitude of the $^1J(CH(\alpha))$-values (range, 158-169 Hz) found for the cations Ia-Id are more in accord with sp^2 than with sp^3 hybridisation at C(α) of these systems, as noted previously by other groups [4].

(b) All of the ^{13}C resonances of the ferrocenyl carbon atoms of the cations appear downfield of the corresponding resonances of the alcohol precursors (see $\Delta\delta$-values in Table 1), revealing that positive charge is effectively delocalised throughout the ferrocenyl system including the unsubstituted ring.

(c) The variation in the $\Delta\delta$-values for C(α) shows that the concentration of positive charge at this centre increases through the carbenium-ion series: primary (Ia) < secondary (Ib-Id) < tertiary (Ie-Ig). Progressive alkyl substitution at C(α) of the parent cation Ia, therefore, allows this centre to sustain a higher proportion of the positive charge with a corresponding reduction in the demand for electron donation from the ferrocenyl system, especially from the iron atom (see (d)).

(d) The narrow range of $\Delta\delta$-values associated with the sets of C(2,5), C(3,4) and C(1′-5′) carbons of the series of cations (14 ± 4, 28 ± 1, and 14 ± 1 ppm, respectively) suggests that the distribution of charge to these nine carbon atoms is relatively insensitive to alkyl substitution at C(α). The wider spread of $\Delta\delta$-values found for the C(1) carbons (12 ± 12 ppm), on the other hand, arises from the opposite effect of β-alkyl substitution at C(α) of the cations (shielding) compared with that for the alcohols (deshielding). This reversal can be rationalised assuming that there exists partial double-bond character between C(1) and C(α) of the cations (cf. (a)), as indicated by an earlier investigation [1b]. The observed diastereotopism of the carbons of the C(2,5) and C(3,4) pairs in the unsymmetrically substituted cations (see Table 1) also has its origin in hindered rotation about the exocyclic C(1)—C(α) bond.

(e) For every cation studied, the resonances of the C(3,4) carbons occur at significantly lower field than that associated with the resonances of the other ferrocenyl carbons, a situation which parallels that found for the ^{1}H resonances in the proton spectra [3]. If the $\Delta\delta$-values meaningfully reflect differences in charge density [5], this would mean that C(3,4) bear a higher positive charge than the other ferrocenyl carbons, in contrast to a recent theoretical prediction [6] but in accord with the results of an earlier study [1c]. On the other hand**, the

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*The ^{1}H NMR spectra of ferrocenylalkylium ions have been thoroughly investigated (see ref. 3).

**Alternatively, it has been suggested by Seyferth et al. (ref. 4a) that this effect results from displacement of the iron atom away from C(3,4) towards C(α) in the structure of these cations as originally proposed by Hill and Richards (ref. 7). However, strong evidence against such ring-slip displacement has been presented (see refs. 1c and 8) and distortion of this nature is not present in the solid state (ref. 9).

lower shielding of the C(3,4) carbons may be a consequence of rehybridisation of the orbitals of the iron atom in order to maximise interaction with C(α). Such a structure in which C(α) is displaced from the plane of the adjacent ring towards the metal atom has been predicted for the cation Ia from s.c.c. extended Hückel calculations [6] and structural distortion of this nature has been found in the crystal structure of a simple ferrocenylalkylium salt [9b].

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