

THE ^{13}C NMR SPECTRA AND STRUCTURE OF FERROCENYL CARBENIUM IONS

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Summary

The ^{13}C NMR spectra of the series of α, α' -dideuterated ferrocenylcarbenium ions and their precursors, ferrocenylcarbinols as well as other ferrocene derivatives have been measured. The structure of ferrocenylcarbenium ions is discussed.

Introduction

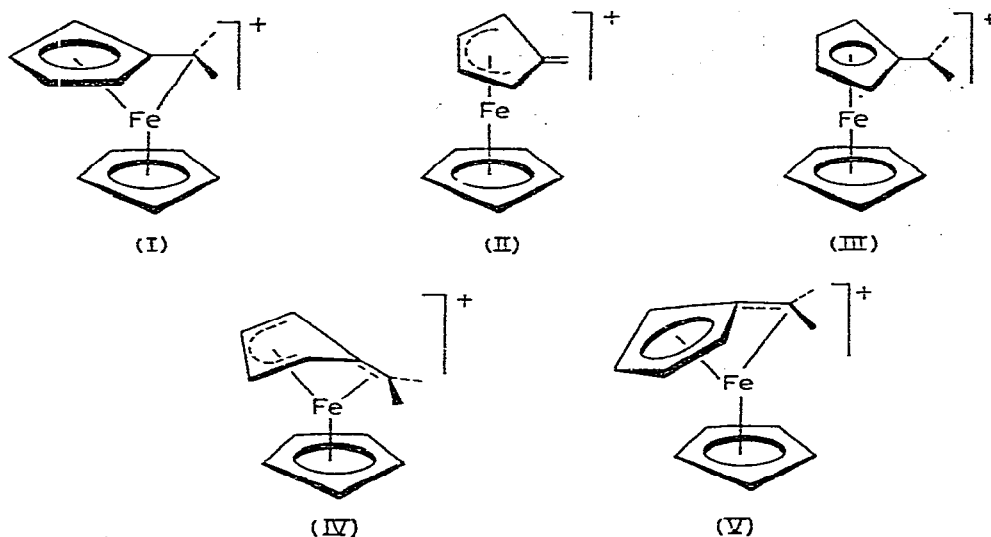
The high stability of ferrocenylcarbenium ions has generated considerable interest and much speculation as to the origin of their stability [1,2 and earlier references cited therein].

In attempts to account for this enhanced stability, several models have been proposed for these cations. Richards [3] suggested that metal—ligand bonding would be optimised if the $\pi\text{-C}_5\text{H}_5\text{Fe}$ group were displaced intact towards the exocyclic carbon atom (C_{exo}) of the planar substituted cyclopentadienyl ligand (I).

According to another viewpoint, bonding between C_{exo} and the iron atom is insignificant. Thus Pettit [4] proposed structure II (but later retracted [5]) in which only the α - and β -carbon atoms of the fulvene ligand are bonded to the metal. Traylor [6] depicted a carbenium ion as a resonance hybrid of canonical structures II and III, with the former regarded as the more important contributor.

At the same time Cais [7] suggested structure IV in which the fulvene ligand is non-planar, arguing that such deformation would permit better overlap between metal and ligand orbitals. Recently, from extended Hückel calculations, Glejter and Seeger [8] produced energy minimum structure V in which C_{exo} is displaced from the plane of the adjacent ring towards the iron atom and in which the rings are tilted.

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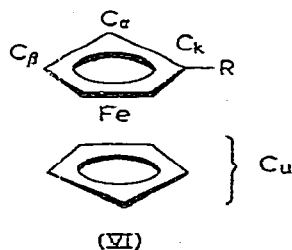


We ourselves [9–11] and other authors [12–15] have employed ^{13}C NMR spectroscopy for the study of ferrocenylcarbenium ions. This method has also been used for the study of stable cyclobutadienyl tricarbonyliron- [16], (nona-carbonyltricobalt)carbon- [17,18] and cyclopentadienyltricarbonylmanganese-substituted carbenium ions [19].

The present paper is concerned with ^{13}C NMR data on ferrocenylcarbenium ions and some uncharged ferrocene derivatives, using deuterium labelling.

Results and discussion

The ^{13}C - $\{^1\text{H}\}$ NMR spectra of the monosubstituted ferrocenes VI show four types of signals from cyclopentadienyl rings: an intensive signal due to the five carbons of the unsubstituted ring (C_u), two less intensive signals from the α - and β -carbons of the substituted ring, and a weak signal from the directly substituted C_k carbon atoms. When a ferrocene derivative contains a chiral centre in the substituent R, its α - and β -positions become diastereotopic: in this case the α, α' - and β, β' -carbons are pairwise magnetically nonequivalent. The anisochronic character of the α, α' - and β, β' -carbons is also observed in ferrocenylcarbenium ions containing different substituents at the C_{exo} atom.



The ^{13}C chemical shifts of the carbinols, precursors of ferrocenylcarbenium ions, and some other neutral ferrocene derivatives, are given in Table 1, and data for ferrocenylcarbenium ions are listed in Table 2. For almost all samples, the

TABLE 1

 ^{13}C CHEMICAL SHIFTS OF FERROCENYL CARBINOLS AND OTHER FERROCENE DERIVATIVES
FeR [20]

R	Chemical shifts ^a				
	C _k	C _α	C _β	C _u	Substituent R
H	67.7	67.7	67.7	67.7	
CH ₃	83.4	68.9	66.8	68.4	14.4
C(CH ₃) ₃	101.7	64.8	66.7	68.2	30.2 (C), 23.2 (CH ₃)
CHO	79.2	68.0	72.6	69.2	192.2
COCH ₃	79.3	69.2	71.8	69.5	200.1 (CO), 26.9 (CH ₃)
CH=CH ₂	83.2	66.4	68.4	68.9	134.4 (CH), 110.4 (CH ₂)
C≡N	51.8	70.1	71.4	70.2	119.3
CH ₂ OH	87.8	67.9	68.0	68.0	60.1
CH(OH)CH ₃	94.1	66.0	67.5	68.1	65.1 (CH—OH), 23.4 (CH ₃)
		65.4	67.4		
CH(OH)CH(CH ₃) ₂	92.6	68.5 ^b	67.4 ^b	67.9	74.6 (CH—OH), 34.5 (CH), 18.4 18.2 (CH ₃)
		64.5 ^b	67.1 ^b		
CH(OH)C(CH ₃) ₃	91.4	69.4	67.3	68.0	77.4 (CH—OH), 34.7 (C), 25.6 (CH ₃)
		65.2	67.2		
C(CH ₃) ₂ OH	99.8	65.2	67.3	68.0	68.3 (C—OH), 30.6 (CH ₃)

^a For solutions in dichloroethane with TMS as internal standard. ^b Tentative assignment.

signal assignment of the C_α and C_β atoms was performed using deuterium labeling [11,20,21]. In the synthesis of the α,α'-dideuterated ferrocene derivatives the key compound was *N,N*-dimethylaminomethylferrocene, whose selective deuteration was performed by the Hauser method [22]. For the ions and carbinols our signal assignment is in agreement with the data of Braun, Abram and Watts [13] obtained by the selective double resonance method. Unlike other investigators, we studied not only ferrocenylcarbenium ions and their precursors, carbinols, but also a wide number of the selectively deuterated ferrocene derivatives with different substituents [20,23]. A comparison of the features of the ^{13}C NMR spectra of the latter compounds and ferrocenylcarbenium ions was employed in discussing the structure of these ions.

TABLE 2

 ^{13}C CHEMICAL SHIFTS OF FERROCENYL CARBENIUM IONS

Cation	Chemical shift ^a					
	C _k	C _α	C _β	C _u	C _{exo}	Other signals
FeC ⁺ H ₂	110.6	84.6	94.4	82.3	87.7	
FeC ⁺ HCH ₃	104.7	80.9	93.3	81.5	117.3	19.0 (CH ₃)
		80.0	93.0			
FeC ⁺ HCH(CH ₃) ₂ ^b	102.4	79.7	93.2	79.7	131.3	33.1 (CH), 26.2 20.3 (CH ₃)
		78.9	92.9			
FeC ⁺ HC(CH ₃) ₃	100.1	81.4	93.8	80.2	142.0	39.8 (C), 30.5 (CH ₃)
		80.2	93.6			
FeC ⁺ (CH ₃) ₂	100.0	78.7	93.4	81.9	156.0	27.6 (CH ₃)

^a Measured in concentrated H₂SO₄ with TMS as external standard. ^b One line of chemical shifts was omitted in composing the preliminary communication [9], cf.: Erratum, *J. Organometal. Chem.*, 92 (1975) C39.

Analysis of the data of Table 1 reveals the following features.

Introduction of a substituent into ferrocene changes the shielding of the ^{13}C nucleus in both the substituted and unsubstituted cyclopentadienyl rings. In the latter case, however, only weak deshielding of the C_α signals with respect to the ferrocene signal (δ 67.7 ppm in dichloroethane) is observed. Depending on the substituent nature, the C_β signals undergo the most changes. Usually, the C_β signal shifts downfield, but if the C_β atom is combined with an *sp*-hybridized carbon then its signal shifts upfield (51.8 ppm for cyanoferrocene). As far as the C_α and C_β chemical shifts are concerned, depending on the nature of R, they are observed downfield or upfield of the ferrocene signal [20].

In ferrocenyl carbenium ions (Table 2) the ^{13}C resonances of all nuclei in the cyclopentadienyl rings are in a weaker field with respect to the starting carbinols [9,10,12]. The difference ($\Delta\delta$) in shielding of the individual carbons in carbenium ions and carbinols is greatest (26 ± 1 ppm) for the β -carbons with respect to those observed for C_α and C_α atoms. At the same time the $\Delta\delta$ values of C_β atoms vary widely, depending on the degree of C_{exo} substitution and the alkyl group nature.

The fact that on going from primary FcC^+H_2 to the tertiary ferrocenylcarbenium ion $\text{FcC}^+(\text{CH}_3)_2$ the C_β and C_α shielding varies negligibly suggests a decisive contribution of the ferrocenyl group to the stabilization of these systems.

Correlation of chemical shifts for carbon atoms has been made with electron densities obtained from molecular orbital calculations [24]. In the monosubstituted benzenes and phenylcarbenium ions a linear dependence is observed between the chemical shift of *para*-carbon and charge density [25]. One may assume that the degree of carbon shielding in ferrocene derivatives and ferrocenylcarbenium ions corresponds to an electron density distribution in these systems [20].

It was shown earlier by ^1H NMR study that for ferrocenylcarbenium ions the substituted ring β -protons are less shielded than the α -protons. This effect is opposite to that observed in ferrocene derivatives with electron-withdrawing substituents by resonance, e.g. acylferrocenes. In the Richards et al. paper [2] this fact served as evidence for structure I with the metal atom shifted from the C_β to the C_{exo} atom: if the iron is shifted as in I it should be nearer and therefore more strongly bonded to the α -carbons than to the β -carbons. This might decrease somewhat the positive charge on the α -carbons relative to the β -carbons. Moreover such a shift would result in the magnetically anisotropic shielding of the α -carbons nearest to the metal [2]. A similar explanation has been given by Seyferth et al. [12] for the greater shielding of ^{13}C nuclei in the α -position with respect to β -carbons. Watts [13] has pointed out that the relative shielding of α - and β -carbons observed could be due to rehybridization of the iron orbitals to facilitate interaction with C_{exo} atoms in structure V.

However, we found [11,20,21] that in ferrocene derivatives with electron-withdrawing substituents by resonance the β -carbons are more deshielded than the α -carbons. Table 1 shows that such a relative shielding of α - and β -carbons is observed for formyl-, acetyl-, vinyl-, and cyano-ferrocenes.

Inconsistency in the relative shielding of ^1H and ^{13}C nuclei in the α - and β -positions, e.g. in acylferrocenes, may be due to a magnetic anisotropy of the acyl group resulting in α -proton deshielding [26,27].

The relative shielding of carbons in ferrocenylcarbenium ions shows that β -

carbons possess higher positive charge with respect to α -carbons [20] and this contradicts the calculations [8], which thus seem to be not reliable for this reason. The relative shielding of α - and β -carbons has been explained by nonsymmetrical electron distribution around the iron atom in model V (such a model should lead to a differential magnetic anisotropic effect of the iron atom upon the C_α and C_β carbons) [13]. However, the X-ray data available are inconsistent with models of carbenium ions stabilized by the π -complexes with metal- C_{exo} bonding.

Thus in the bis(cyclobutadienyltricarbonyliron)phenylcarbenium ion the cyclopentadiene rings are coplanar with C_{exo} , and the Fe- C_{exo} distances are too large (2.85 and 2.94 Å) to support any significant direct metal-exocyclic carbon interaction [5].

In the diferrocenylcarbenium [28] and ferrocenyldiphenylcyclopropenium ions [29] the cyclopentadienyl ligands of the ferrocenyl groups are almost parallel. In the former, different bending modes were found for C_k-C_{exo} bonds from the planes of the two cyclopentadienyl rings to which they are attached (19.9° towards the iron atom, 17.7° away from the iron atom). Such deformation may be due to the crystal packing forces or to sterical reasons. Ferrocenyldiphenylcyclopropenium ion is not a convenient model for investigating the structure of ferrocenylcarbenium ions, because it contains the stable aromatic cyclopropenium ion.

It may be pointed out that the slight deviations from planarity which could be observed from X-ray analysis of the carbenium ions should be interpreted with care. A widely adopted opinion on the necessary planar structure of the carbenium ion has been recently criticized. It was shown that as the electron-withdrawing power of the substituent X in XC^+H_2 increases, the out-of-plane bending becomes more difficult, and vice versa the greater electron transfer from X to CH_2 in XC^+H_2 will facilitate the bending of the carbenium ion centre [30]. Thus it is reasonable to expect that because of the known remarkable electron-donating capacity of the ferrocenyl group, in ferrocenylcarbenium ions such bending from planarity would be more likely than with other carbenium ions.

Table 2 shows that in ferrocenylcarbenium ions with different C_{exo} substituents a diastereotopism is observed for the α - and β -carbon pairs. Simply to suppose restricted rotation is quite sufficient to explain the non-equivalence of the ring nuclei. However, the two methyl groups in the cation $FcC^+CHCH(CH_3)_2$ are non-equivalent, and this should be accounted for necessarily in terms of diastereotopism related to the planar chirality [9]. Analogously to ferrocenylcarbinols with a chiral centre in the substituent the largest differences in chemical shifts were revealed for the α -carbons. Obviously, the degree of anisochronic character of these nuclei, $\Delta\delta C_\alpha = \delta C_\alpha - \delta C_{\alpha'}$, should be affected by two factors: electronic and steric. Earlier a competition between the stabilizing action of the alkyl groups and metallocenyl ring in metallocenylcarbenium ions was observed [9,1]. The greater the stabilizing effect of the alkyl part, the lower should be the metallocenyl participation, and thus the lower the barrier to rotation about the C_k-C_{exo} bonding [1]. (This barrier is considerably lower in phenylcarbenium ions where anisochrony of *ortho*-carbons in $C_6H_5C^+RR'$ ions is observed only at -60 to $-80^\circ C$ [25]).

On the other hand, the $\Delta\delta C_\alpha$ value should increase with the bulk of the alkyl

group at C_{exo} . This does actually happen in the series FeC^+HCH_3 , $FeC^+HCH(CH_3)_2$, $FeC^+HC(CH_3)_3$, where $\Delta\delta C_\alpha$ is equal to 0.9, 0.8 and 1.2 ppm respectively. The changes in the value on going from $FeC^+CHCH(CH_3)_2$ to $FeC^+HC(CH_3)_3$ is probably due to a steric factor.

The spin-spin coupling constant $^1J(^{13}C_{exo}-^1H)$ of $FeC^+HCH(CH_3)_2$ ion is equal to 163 Hz, i.e. the C_{exo} atom has sp^2 hybridization [10] and thus does not produce strong bonding with the iron. This is in agreement with ^{13}C NMR data on ferrocenylcarbenium ions enriched with ^{57}Fe isotope (nuclear spin 1/2) [11]; (in this work no constant $^1J(^{57}Fe-^{13}C_{exo})$ was observed).

Thus although the data available at the present time do not permit a final choice of the stabilization mechanism of metallocenylcarbenium ions, they are contradictory to structures I, II, IV and V. The results obtained are completely in accord with the structural model III for metallocenylcarbenium ions, without significant change in the metallocene geometry.

It could be suggested that an enhanced stability of the ferrocenylcarbenium ions is due to an interaction between occupied metal orbitals and an electron deficient center via the cyclopentadienyl ring system. Thus positive charge is delocalized efficiently over the ferrocenyl nucleus which is evident from the deshielding of all carbons in the ^{13}C NMR spectra. In other words an enhanced stability of metallocenylcarbenium and related ions may be explained by polarizability of the electron-rich organometallic substituent.

Experimental

All ferrocene derivatives were prepared by the literature methods. α,α' -Di-deuterioferrocenylcarbonyldimethylamine, the key compound for the synthesis of deuterated ferrocene derivatives, was prepared by four-fold metallation of the amine followed by treatment of its lithium derivative with deuterium oxide [22]. Ferrocenylcarbenium ions were generated by dissolving the respective carbinols in concentrated sulfuric acid.

The ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer under Fourier transform and $^{13}C-^1H$ noise decoupling.

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