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Preliminary communication

Chirality in α-ferrocenylcarbonium ion as monitored using nuclei diastereotopism

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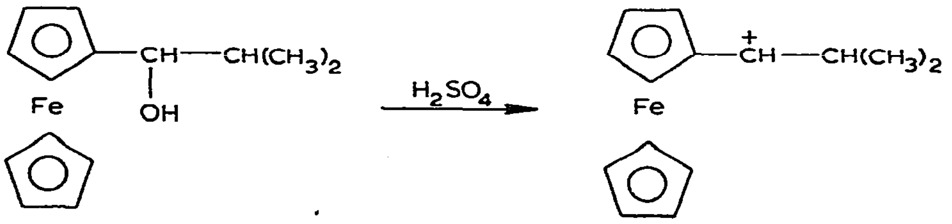
SUMMARY

Diastereotopism of ^{1}H and ^{13}C nuclei was observed in 1-ferrocenyl-2-methylpropyl cation due to its planar chirality.

The high stability of α-metallocenylcarbonium ions has been well-known for some years[1,2], and solvolysis of the related derivatives has been seen to proceed completely stereospecifically[3,4]. Although the extensive work was done in the last decade, the nature of the metal-stabilized carbocations is not yet clearly understood. In the stereochemical sense, one should make the choice between the possibilities; (a) the carbenium carbon[5] retains its nonplanar configuration and may further serve as a chiral centre; or (b) its configuration is planar and trigonal, and any chirality, if it resides in the cation, has a different source.

Now we wish to report that the nuclei diastereotopism appears to be a useful tool in the study of chirality in such species as long-lived carbocations. Diastereotopism[6] can be observed in NMR spectra of a molecule which contains at least one chiral and one prochiral moiety. In the metallocene derivatives both chiral centre and plane can be combined. Here we describe the observable diastereotopism of ^{1}H and ^{13}C nuclei in a parent molecule,



(I)

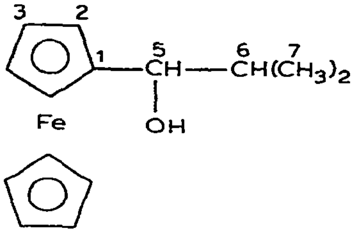
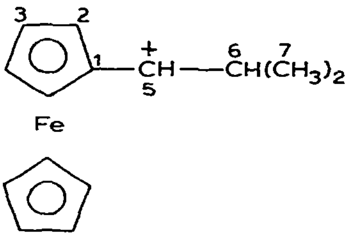
(II)

ferrocenylisopropylcarbinol(I)★ and the related 1-ferrocenyl-2-methylpropyl cation (II).

Protons and carbon atoms in methyl groups of I are anisochronous as expected, exhibiting $\Delta\nu^H$ 0.12 ppm in CCl_4 and 0.15 ppm in benzene, $\Delta\nu^C$ 0.13 ppm in $CHCl_3$★★. ^{13}C nuclei in the substituted cyclopentadienyl ring are also anisochronous, $\Delta\nu^C$ being equal to 0.3 ppm for both α- and β-atoms. ^{13}C chemical shifts and its changes are collected in Table 1 as well as $J(^{13}C\text{–}H)$.

TABLE 1

^{13}C NMR DATA FOR I AND II [a]

Carbon atom			$\Delta\delta$	$J(^{13}C\text{–}H)$
1	116.5	88.8	–27.7	
2	122.6	98.0	–24.5	181.2
	122.9	98.4	–24.6	
3	123.8	112.2	–11.6	183.1
	124.1	111.5	–12.6	
4	123.3	111.5	–11.8	183.1
5	98.5	59.9	–38.6	163.3
6	156.7	158.0	+1.3	118.4
7	172.8	165.0	–7.8	
	172.9	170.9	–2.0	

[a] Chemical shifts are in ppm from CS_2. Determined with Bruker-HFX-90 operating in Fourier-transform mode at 22.63 MHz related to chloroform taken as +114.0 ppm. One additional peak 126.7 ppm was found in the spectrum of I presumably corresponding to the unsubstituted ferrocene.

It should be noted that a sharp increase in the diastereotopic shift of methyl ^{13}C atoms in II with respect to I is observed up to $\Delta\nu^C$ 5.91 ppm while $\Delta\nu^H$ changes only slightly from 9.0 to 10.5 Hz. This difference is probably due to the dissimilar kinds of chirality in I and II. Of great significance are data concerning C-5. The chemical shift is beyond the region for the carbenium carbon and demonstrates the absence of an essential positive charge at this atom. The magnitude $J(^{13}C\text{–}H)$ 163.3 Hz is specific for sp^2-

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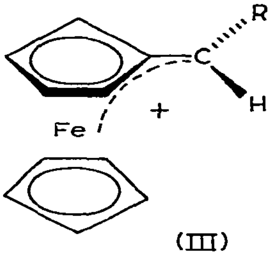
★Prepared by $LiAlH_4$ reducing of ferrocenylisopropylketone in ether.

★★The last value is less than similar one for any alkylisopropylcarbinol[7].

hybridized (olefinic) carbon[8,9]. Then the first conclusion may be drawn that II is not a "carbenium" ion with cationic centre at C-5. Previously, it was found from Mössbauer spectra[10] that the iron in α-ferrocenylcarbonium ions does not carry any extra positive charge compared to ferrocene itself. Putting these data together one can affirm that positive charge is spread over the cyclopentadienyl rings, especially the substituted one. Hence we prefer to depict these ions as III.



(III)

Such a formulation suggests the important role of a vertical stabilization in similar organometallic carbocations in the accordance with Traylor-Pettit concept[11—13]. We feel it is not necessary to suppose the bending of "fulvene" moiety speculated by Cais and coworkers[14,15] to interpret our NMR data.

Very recently Cais *et al.*[14,15] observed the diastereotopism of ring protons in the diferrocenylmethylcarbonium ion only at low temperatures. This is not surprisingly because the planar chirality develops due to the restricted rotation around the C—Cp bond. When two identical groups are present (ferrocenyl), the additional symmetry plane exists related to Fe-$\overset{+}{C}$H—R.

Diastereotopism in the related carbocations derived from other transition metal π-complexes is now under investigation. The importance of the data obtained for the elucidation of the cation structure will be discussed in a full paper.

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