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Preliminary communication

CHIRALITY, DIASTEREOTOPISM AND STRUCTURE OF α-METALLOCENYLCARBENIUM IONS INVESTIGATED BY NMR SPECTROSCOPY

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Summary

1-Metallocenyl-2-methylpropyl cations are found to be chiral using nuclei diastereotopism. The positive charge distribution over the cations and the effect of a central metal atom (iron, ruthenium, osmium) are discussed.

A body of information about the restricted rotation around the $Cp—\overset{+}{C}$ bond in α-ferrocenylcarbenium ions was collected during the last decade. Turbitt and Watts [1—3] have given the most clear-cut evidence for the chirality and optical activity in these cations. More recently we [4] and others [5] used ^{13}C NMR spectroscopy to get further data about the structure of these interesting species. The observable ^1H and ^{13}C diastereotopism in both the isopropyl group and in the substituted ring of the cation $C_5H_5FeC_5H_4\overset{+}{C}HCH(CH_3)_2$ proved its chirality immediately. Previously, some workers [6—8] have noticed the ring proton non-equivalence in several α-ferrocenylcarbenium ions without a clear indication of the underlying stereochemical reasoning*. To the best of our knowledge, no similar studies were reported with other metallocenes derivatives.

In this communication, we compare the isostructural derivatives of ferrocene, ruthenocene and osmocene with isopropyl groups as a probe. The compounds and sites therein will be depicted with a used for Fe, b for Ru, c for Os derivatives.

The experimental results are collected in the Tables 1—3. It can be seen, first of all, that the ruthenocene or osmocene moiety strongly stabilizes the carbocationic center at the adjacent carbon as does ferrocene. Ions IIIa—IIIc possess a planar chirality resulting in the observable diastereotopism of the isopropyl protons. The magnitude Δδ(H) is interestingly the same for alcohols

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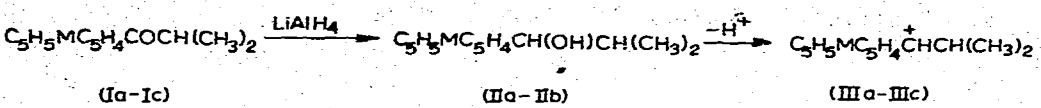
*Simply to suppose the restricted rotation or the unsymmetrical shift of a metal atom [8] is quite sufficient to explain the non-equivalence of the ring nuclei. However, when alkyl is isopropyl the two methyl groups are nonequivalent. This can and should be accounted for necessarily in terms of diastereotopism related to the planar chirality [4].



$$C_5H_5MC_5H_4COCH(CH_3)_2 \xrightarrow{LiAlH_4} C_5H_5MC_5H_4CH(OH)CH(CH_3)_2 \xrightarrow{-H^+} C_5H_5MC_5H_4\overset{+}{C}HCH(CH_3)_2$$

(Ia–Ic) (IIa–IIb) (IIIa–IIIc)

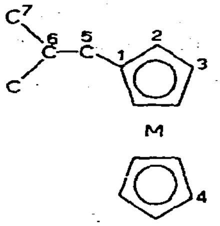


TABLE 1

^{1}H NMR SPECTRA OF KETONES Ia—Ic, ALCOHOLS IIa—IIc AND CATIONS IIIa—IIIc

Measured in CCl_4 at 60 MHz (Perkin—Elmer R-20) with Me_4Si as internal or (for cations) external standard.

	H(4)	H(2)	H(3)	H(5)	H(6)	H(7)		H(8)
Ia	4.15	4.75	4.40	—	3.05	1.15		—
Ib	4.54	5.03	4.69	—	2.85	1.12		—
Ic	4.74	5.14	4.85	—	2.84	1.10		—
IIa	4.15	4.05		4.0?	1.70	0.87	0.75	1.85
IIb	4.58	4.60 [a]	4.51 [a]	3.63	1.72	0.93	0.80	1.29
IIc	4.68	4.72 [a]	4.57 [a]	3.50	1.65	0.95	0.84	1.25
IIIa	5.24	6.45	5.18	7.20	2.67	1.62	1.42	—
		4.58						
IIIb	5.52	6.19	6.07	6.13	2.42	1.38	1.33	—
		5.11						
IIIc	5.67	6.26	5.23	6.14	2.35	1.42	1.30	—

[a] Shown are the centers of complicated multiplets.

TABLE 2

^{13}C NMR SPECTRA OF ALCOHOLS IIa—IIc AND CATIONS IIIa

Measured in CCl_4 (IIa—IIc) or H_2SO_4 (IIIa) at 22.63 MHz (Bruker-HFX-90). Chemical shifts are given relative to Me_4Si.

	C(1)	C(2) and C(3)		C(4)	C(5)	C(6)	C(7)	
IIa	92.6 [a]	68.5	68.3	67.9	64.5 [a]	34.5	18.4	18.2
		67.4	67.1					
IIb	98.9	73.9	72.3	70.5	70.5?	34.4	19.3	19.8
		69.9	68.8					
IIc	77.7	65.5	63.4	64.4	64.1	?	19.5	
IIIa	102.4	93.2	92.9	79.7	131.3	33.1	26.2	20.3

[a] Previous assignment [4] for C(1) and C(5) in IIa should be reversed.

TABLE 3

^{1}H AND ^{13}C DIASTEREOTOPIC SHIFTS IN ALCOHOLS IIa—IIc (CCl_4) AND CATIONS IIIa—IIIc (H_2SO_4)

	IIa	IIb	IIc	IIIa	IIIb	IIIc
$\Delta\delta$(H)	0.12	0.13	0.11	0.18	0.05	0.12
$\Delta\delta$(C)	0.13	0.50	0.0	5.9	[a]	[a]

[a] Not measured.

IIa—IIc but the ions IIIa—IIIc display a big difference $\Delta\delta(H)$ being decreased in the sequence Fe > Os > Ru. The quantitative interpretation of diastereotopic shifts is generally a very complicated problem and the reason of the fact mentioned is not clear nor is the enormous $\Delta\delta(C)$ increase upon moving from IIa to IIIa. There is no doubt, at least, that solely the intrinsic diastereotopism [9] is being dealt with here. It is clear also that the diastereotopic shift magnitude is effected by different processes for ^1H and ^{13}C nuclei within the same molecule. In IIa—IIc $\Delta\delta(H)$ is constant and $\Delta\delta(C)$ changes dramatically to reach an observed zero for osmium.

The signal of unsubstituted ring protons H(4) is shifted downfield about 1 ppm for IIIa—IIIc in accordance with the charge delocalization into this ring. The chemical shift change of the isopropyl group methine proton H(6) suggests that the alkyl group is much more involved in the charge delocalization for an iron derivative IIIa. On the contrary, for Ru and Os the stabilization due to metallocene moiety plays a relatively greater role. This is in qualitative agreement with the kinetic data on the α-metallocenylcarbenium ion stability derived from early studies on solvolysis [10] and acid addition to vinylmetallocenes [11].

These results demonstrate again that the cations III conventionally considered as α-metallocenylcarbenium ions have, in fact, the positive charge extensively distributed over the whole metallocenyl moiety. At present it would be inconclusive to assign the C(2) and C(3) ring carbons separately as attempted recently [5] on the basis of $\delta(C)$ values because it has a minimum for the key C(1) atom which is, however, the nearest one to the ionic center. The detailed mechanism for the interaction between carbenium ion and metallocene nucleus is not yet known. Therefore this assignment cannot be made correctly until the selectively substituted models have been examined. The direct comparison is now meaningful only for "carbenium" C(5) and key C(1) atoms. The relative position of their resonances is shown in Fig. 1 for the differently substituted cations.

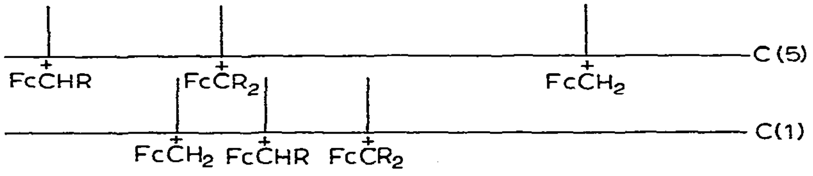


Fig. 1.

It is generally accepted that ^{13}C chemical shifts are linearly correlated with the magnitudes of the partial positive charge on the central carbon atom. As long as this idea can be taken as a reliable one the conclusion may be drawn that the charge delocalization into ferrocene moiety is mostly effective in the parent ion Fc—$\overset{+}{C}H_2$ and a successive alkyl substitution prevents this pathway of delocalization. So, C(5) chemical shift in Fc—$\overset{+}{C}(CH_3)_2$ is 125.3 ppm while only 87.7 ppm in Fc—$\overset{+}{C}H_2$. The stability of Fc—$\overset{+}{C}R_2$ is generally decreased owing to the possibility of a facile decomposition to give fulvenes [12]. It should be emphasized that both ^1H and ^{13}C NMR data show the occurrence of some antagonism between the metallocenyl and alkyl parts of a cation for the preferential stabilization of a positive charge.

The relative significance of alkyl substituents, cyclopentadienyl rings and a central metal atom for the stabilization of similar cations will be discussed in more detail later.

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