

NUCLEAR MAGNETIC RESONANCE SPECTRA  
OF FERROCENYL CARBONIUM IONS

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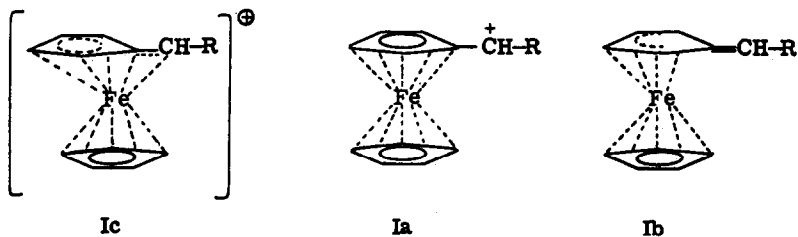
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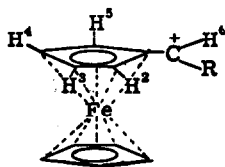
Recently it has been suggested (1) that the properties of  $\alpha$ -metallo-cenyl carbonium ions can be best explained in terms of mesomeric ring effects not involving metal participation (2). The Ware and Traylor interpretation (1) suggests Ib as the major mesomeric form contributing to the resonance stabilization of the ion I, whereas the metal participation concept (2) envisages the contribution from Ic as the major stabilizing factor.



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In order to obtain further information on this problem we have measured the n. m. r. spectra\* of a number of  $\alpha$ -metallocenyl carbonium ions, I.

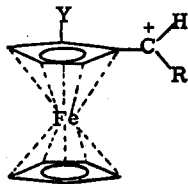


I

R = H, CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  
p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>, m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  
m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, o-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>.

The four protons, H-2-H-5, of the substituted cyclopentadienyl ring in I give two pairs of absorptions in the n. m. r. spectrum, one of which is located at about 70-100 c. p. s. higher field than the other.

Measurement of the n. m. r. spectra of the 2-deutero- and 2-methyl ferrocenyl carbonium ions, IIa - IIc,



II

- |    |                 |                               |
|----|-----------------|-------------------------------|
|    | $\frac{Y}{D}$   | $\frac{R}{H}$                 |
| a) | $\frac{D}{D}$   | $\frac{H}{H}$                 |
| b) | CH <sub>3</sub> | H                             |
| c) | CH <sub>3</sub> | C <sub>6</sub> H <sub>5</sub> |

\*The n. m. r. spectra of all the compounds were obtained by using solutions of the respective carbinols in concentrated sulfuric acid. All the carbinols have been fully characterized and have satisfactory elemental analyses. Solutions of the carbinols in trifluoroacetic acid and boron trifluoride-deuterium oxide gave n. m. r. spectra which, except for solvent effects, were similar to those in sulfuric acid. Measurements of the freezing-point depression of the carbinols in concentrated sulfuric acid confirmed the existence of four ions which correspond to the ferrocenyl carbonium ion, a hydronium ion, and two bisulfate ions.

has led to the assignment of the upfield absorption pair in the spectra of I to the H-2 and H-5 protons and the downfield pair to the H-3 and H-4 protons, a result not expected on the basis of simple models for the ferrocenyl carbonium ion.

In general, the nuclear magnetic resonances of the  $\alpha$ -protons (H-2 and H-5) of ferrocene rings monosubstituted with an electron withdrawing group occur at lower fields than do the corresponding resonances of the  $\beta$ -protons (H-3 and H-4) (3). Such deshielding of the  $\alpha$ -protons with respect to the  $\beta$ -protons is consonant with the concept that increased electron density should increase the shielding of the attached protons (4) and it is also predicted by simple molecular orbital calculations on a fulvene system with five  $\pi$ -electrons. Similar calculations predict that the ortho-protons of phenyl carbonium ions should be less shielded than the meta-protons and these predictions are borne out by experimental results (5).

The apparently anomalous results obtained with the  $\alpha$ -ferrocenyl carbonium ions, namely, the deshielding of the  $\beta$ -protons (H-3 and H-4) with respect to the  $\alpha$ -protons (H-2 and H-5), can be explained on the basis of structure Ic, involving the concept of metal participation. Movement of the iron atom closer to the carbonyl carbon atom results in greater overlap of the appropriate orbitals of the iron, C-2 and C-5 atoms and consequently an increase in electron density in the regions of the H-2 and H-5 protons as compared to a slight decrease in electron density in the vicinity of the H-3 and H-4 protons. Additionally, and in our opinion more importantly, the effect of the induced field caused by the anisotropy of the iron atom, which has been estimated to be about 2 ppm in unsubstituted ferrocene (6), should also shield the H-2 and H-5 protons relative to the H-3 and H-4 protons.

On the basis of such an interpretation, one would expect that the shift of the iron atom with respect to the carbonyl carbon should be affected

by the nature of additional substituents on the latter. Electron-releasing groups, by supplying a flow of electrons towards the positively charged carbonyl carbon, should minimize the shift of the metal atom towards the charged center. Such a reduction in the shift of the iron atom should be reflected in a smaller degree of shielding of the H-2 and H-5 protons with respect to the H-3 and H-4 protons. In other words, the separation between the upfield and downfield peaks,  $\Delta\nu (= \nu_{\text{H}^{4,5}} - \nu_{\text{H}^{3,4}})$ , should be smaller, when an electron-releasing substituent is attached to the carbonyl carbon. The data in Table I agree with this prediction; the aryl substituents produce a smaller separation ( $\Delta\nu \approx 66\text{--}79$  cps) between the upfield and downfield absorptions than do the alkyl substituents ( $\Delta\nu \approx 90\text{--}94$  cps).

The positions of the n. m. r. absorption peaks assigned to the proton on the carbonyl carbon can also be reasonably interpreted on the assumption of metal participation. Thus, substitution of electron-releasing substituents onto the carbonyl carbon should cause the n. m. r. absorption peak of the attached proton to shift to higher fields (compare, e. g., the two diphenyl-carbonyl cations in Table I). Actually exactly the opposite is observed experimentally in  $\alpha$ -ferrocenyl carbonium ion derivatives. The resonances of the carbonyl hydrogen of  $\alpha$ -ferrocenyl carbonium ions occur at lower fields when R in structure I is aryl rather than when R is alkyl. This result can be interpreted on the basis of a model for the carbonium ion which includes metal participation. As the positive charge is more extensively delocalized into the aryl substituent, movement of the iron atom is reduced. The carbonyl hydrogen, therefore experiences less shielding from the magnetic anisotropy of the iron and, as a result, its resonance occurs at lower fields.

TABLE I

N. M. R. Data for  $\alpha$ -Metallocenylcarbinyl Cations, I.

<u>Substituent R</u> <u>in I</u>	$\Delta\nu^a$ <u>cps</u>	$\nu_{CH}^+$ <u><math>\delta</math> ppm</u>
H	118	5.75
CH <sub>3</sub>	94	7.03
CH(CH <sub>3</sub> ) <sub>2</sub>	93	6.98
C(CH <sub>3</sub> ) <sub>3</sub>	90	7.07
C <sub>6</sub> H <sub>5</sub>	66	7.92
<u>p</u> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	71	7.94
<u>p</u> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	76	7.96
<u>p</u> -CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	79	7.67
C <sub>6</sub> H <sub>5</sub> <sup>+</sup> CHC <sub>6</sub> H <sub>5</sub>	-	9.80
C <sub>6</sub> H <sub>5</sub> <sup>+</sup> CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	-	9.06

<sup>a</sup>The separation  $\nu_{H^2, H^5} - \nu_{H^3, H^4}$  between the centers of each pair of bands.

<sup>b</sup>Reference 7

Some of the n. m. r. data could be explained on the basis of formulation Ib in which the metal is regarded as complexed to a conjugated diene system and the  $\alpha$ -*exo*-cyclic double bond is effectively isolated from the rest of the  $\pi$ -electron system of the complex.\* However, the tendency of the iron atom in such carbonium ions to retain the ferrocene-type structure of eighteen electrons in its outer valence shell, as in I, in preference to sixteen electrons, as in Ib, has been recently demonstrated in the attempted synthesis of a benzopentalene iron complex (8). A full paper will expand on the above arguments.

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\* Such an explanation was suggested by Professor R. Pettit during a discussion at the 2nd International Symposium on Organometallic Chemistry, Madison, Wisconsin, September, 1965.

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