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Preliminary communication

Evidence of distortion of the fulvene ligand in ferrocenylcarbonium ions

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SUMMARY

^{1}H NMR spectroscopic evidence has been obtained in support of the suggestion (Cais, Gleiter) that the fulvene ligands of ferrocenylcarbonium ions are distorted from planarity.

A number of structural models have been proposed for ferrocenylcarbonium ions (alternatively, π-cyclopentadienyl-π-fulveneiron cations). Richards[1], Pettit[2], Traylor[3], and Yamakawa[4] concurred in assigning a planar geometry to the fulvene ligand but disagreed on the relative location of the five-membered rings and on the question of the importance of a bonding interaction between the metal atom and the exocyclic carbon atom of the fulvene ligand. The Richards and Pettit models were later rendered untenable as further experimental information was obtained[5-7]. Cais[8] and more recently Gleiter[9], on the other hand, have suggested structures in which the fulvene ligand is distorted from planarity although rather different modes of deformation were envisaged (Fig.1). In this communication, we present evidence to show that such distortion must, in fact, occur.

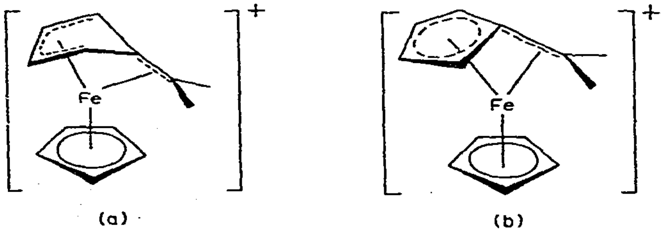
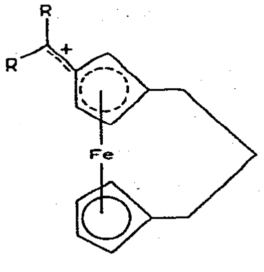
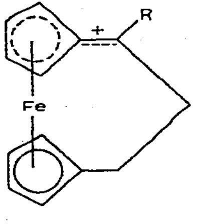


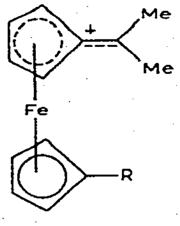
Fig.1. Structural models proposed by (a) Cais and (b) Gleiter for ferrocenylcarbonium ions.



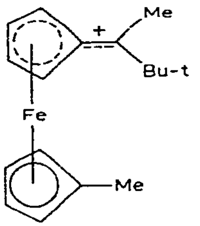
(I)



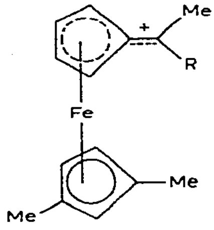
(II)



(III)



(IV)



(V)

In the ^1H NMR spectra (CF_3CO_2H solvent) of ferrocenylcarbonium ions★ in which the rotation of the rings is restricted [*e.g.* (I)], the protons of the alkyl-substituted ring are held in different steric environments with respect to the fulvene ligand and show appreciable chemical-shift distinction★★. A similar effect is apparent[10] in the spectra of bridged cations of the type (II), the protons of the alkyl-substituted ring appearing as well-resolved multiplets. In the spectra of non-bridged systems of the type (III; R = Me, Et, i-Pr, t-Bu), on the other hand, the protons of the C_5H_4R ring show very little difference in their chemical-shift values and appear as a broadened singlet resonance. It follows, therefore, that the alkyl substituents, R, exert a minimal differential effect upon the shielding of the α- and β-cyclopentadienyl protons and that the C_5H_4R ring must be able to rotate freely about the metal-ring axis.

The ring protons α- and β- to the methyl substituent in the C_5H_4Me ligand of the cation (IV), however, occupy different time-averaged magnetic environments. In the ^1H NMR spectrum, they appear as two well separated, equally intense multiplets (approximately two triplets; A_2B_2 pattern) centred at τ 4.85 and 5.22 (*vs.* Me_4Si). From the foregoing, it is clear that the rotational freedom of this ring must be restricted, presumably as a result of steric repulsion between its methyl substituent and the bulky t-butyl group attached to the fulvene ligand. As indicated previously, there is no such evidence of restricted rotation of the ligands in the isomeric cation (III; R = t-Bu).

★ These cations are generated quantitatively when the corresponding alcohols are dissolved in trifluoracetic acid. A detailed account will be given later.

★★ These resonances are readily distinguishable from the absorptions due to the ring protons of the fulvene ligand whose chemical-shift values conform to a well established pattern (see refs. 6, 8 and 10).

If the fulvene ligands of ferrocenylcarbonium ions were planar, a steric hindrance of the same severity would necessarily be associated with the relative torsion of the ligands in these isomeric cations (III; R = t-Bu, and IV). The spectroscopic results show that this cannot be the case. However, if the fulvene ligands were distorted in the manner suggested by Cais or Gleiter (Fig. 1), it is apparent from inspection of Dreiding stereomodels that the rotation of the C_5H_4R ring would be more impeded in the cation (IV) than in its isomer (III; R = t-Bu), in accordance with the spectroscopic findings.

Evidence of restricted ligand rotation in other cations of the type (IV) has also been obtained. For example, the ring protons of the 1,3-dimethylcyclopentadienyl ligand of the cation (V; R = t-Bu) appear as two multiplets centred at τ 4.96 (2H) and 5.52 (1H) in the ^{1}H NMR spectrum. The corresponding protons of the cation (V; R = Me), in which the ligands are free to rotate, on the other hand, give rise to a three-proton singlet resonance at τ 5.38.

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