

Cycloaddition Reactions of Metal-complexed Fulvenes

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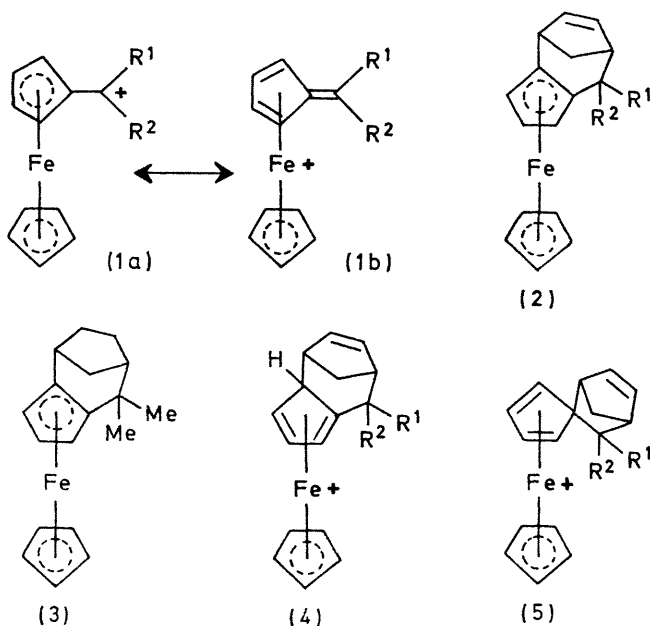
Summary The reaction of ferrocenylcarbonium ions with cyclopentadiene proceeds stereospecifically to give 1:1 cycloaddition products.

In recent years, evidence has accumulated to suggest that the reaction pathways followed by π -hydrocarbons in orbital-symmetry-controlled reactions may be diverted when the hydrocarbon functions as a ligand to a transition metal.¹ In such complexes, mixing of the ligand orbitals with those of the metal serves to modify the energy requirements for pericyclic processes such that reactions may be observed which are disfavoured in the metal-free system.

Accordingly, we have investigated the cycloaddition reactions of cationic hydrocarbon-metal complexes and report herein preliminary results obtained with ferrocenylcarbonium ions (1) as substrates. These cations, whose electronic structure is a subject of controversy,² may be formally represented as metal-complexed fulvenes [cf. (1a) \leftrightarrow (1b)]. Hydrocarbons of this class normally function as 2π or 4π addends in [4 + 2] cycloadditions (Diels-Alder reactions)³ although an example of a [6 + 4] process has recently been described⁴ in which 6,6-dimethylfulvene apparently acts as a 6π addend.

The tertiary carbonium ion (1; $R^1 = R^2 = \text{Me}$) was generated in dichloromethane by abstraction of the hydroxy-group from the corresponding alcohol (Fc-CMe₂-OH) with triphenylmethyl tetrafluoroborate and was treated *in situ* with a large excess of cyclopentadiene. Chromatography of the product on alumina afforded a compound (m.p. 100–101°; ca. 10%) of molecular formula C₁₈H₂₀Fe (mass spectrum) to which the structure (2; $R^1 = R^2 = \text{Me}$) is assigned on spectroscopic evidence.[†] The presence of one double bond was confirmed by catalytic hydrogenation which proceeded with uptake of an equimolar amount of hydrogen giving a quantitative yield of the saturated product (3) (m.p. 67–68°). Similarly the secondary cation (1; $R^1 = \text{Me}$, $R^2 = \text{H}$) reacted with cyclopentadiene to give a single 1:1 cycloaddition product (2; $R^1 = \text{Me}$, $R^2 = \text{H}$)[‡] (liquid), while the parent (2; $R^1 = R^2 = \text{H}$) (liquid), was obtained from the reaction of chloromethylferrocene (FcCH₂Cl) with cyclopentadiene in dichloromethane. The last reaction probably involves heterolysis of the weak C–Cl bond⁵ followed by capture of the diene by the intermediate primary cation (1; $R^1 = R^2 = \text{H}$).

The remaining products from these reactions have not yet been characterised but are clearly oligomeric. Although the overall stereochemistry of the cycloaddition products (2) is still under investigation,[§] the formation of a *single* 1:1



adduct in each case indicates the operation of a symmetry-controlled stereospecific process. These adducts may arise by [6 + 4] cycloaddition of the diene to the complexed fulvene followed by rapid proton elimination from an intermediate σ -complex (4). Alternatively, (4) may be produced by 1,5-sigmatropic rearrangement of a spiro-intermediate (5), the product of [4 + 2] cycloaddition of the diene to the exocyclic fulvene double bond. Further research is designed to differentiate between these pathways.

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[†] In particular, the vinylic resonances in the ¹H n.m.r. spectrum (CDCl₃) appear as two clean doublets of doublets centred at τ 3.8 and 4.3 while the methyl groups, which are *endo* and *exo* with respect to the iron atom, give rise to sharp singlets at τ 8.4 (*endo*) and 9.1 (*exo*).

[‡] The methyl group is assigned an *exo* configuration from the appearance of the methyl resonance as a doublet (J 8 Hz) centred at τ 9.1.

[§] The adducts (2) may exist in two stereoisomeric modifications [each a (\pm)-racemate] depending upon the location of the iron atom with respect to the double bond.

¹ R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, 1969, **47**, 71.

² M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435; E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 1969, **91**, 509; M. J. Nugent, R. E. Carter, and J. H. Richards, *J. Amer. Chem. Soc.*, 1969, **91**, 6145 and references cited therein.

³ E. D. Bergmann, *Progr. Org. Chem.*, 1955, **3**, 81; *Chem. Rev.*, 1968, **68**, 41.

⁴ K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Amer. Chem. Soc.*, 1970, **92**, 6392.

⁵ Cf. E. A. Hill, *J. Org. Chem.*, 1963, **28**, 3586.