Tetrahedron Letters No.12, pp. 1299-1303, 1966. Pergamon Press Ltd.
Printed in Great Britain.

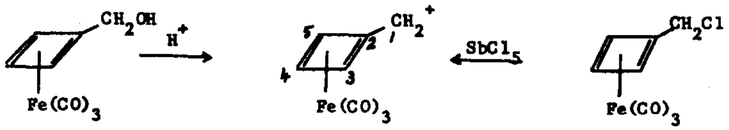
THE CYCLOBUTADIENYL-IRON TRICARBONYL CARBINYL CATION

J. D. Fitzpatrick, L. Watts and R. Pettit

Department of Chemistry, University of Texas, Austin, Texas

(Received 3 January 1966)

During studies pertaining to the chemistry of cyclobutadiene-iron tricarbonyl and its derivatives, it was observed that hydroxymethylcyclobutadiene-iron tricarbonyl (I) was quantitatively converted to the corresponding chloride II upon brief treatment with concentrated aqueous HCl[1]. The chloride II also was found to undergo rapid solvolysis in water or methanol to give the corresponding alcohol or the methyl ether. By analogy with other organic systems these reactions strongly suggest involvement of a stable cationic intermediate the structure of which is the subject of this communication.



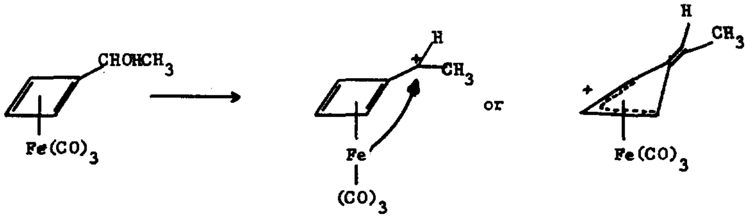
I III II

The existance of such a stable cation was confirmed through isolation of a hexachloroantimonate salt upon treatment of the chloride II with $SbCl_5$.

The salt crystalised in yellow needles from nitromethane; when kept cold it was stable, but on warming, particularly in solution, it decomposed readily with loss of carbon monoxide.

The same cation is obtained upon solution of the primary alcohol I in concentrated H_2SO_4. The n.m.r. spectrum of these stable solutions displayed three single (but broad) peaks at 3.12, 4.09 and 4.91 τ with areas 1:2:2 respectively. Although this data does not allow a complete assignment of the spectrum, it is sufficient however to eliminate structure III from consideration for it would surely be expected that the two equivalent protons on the primary cationic center would lie at lowest field if such a system were realised.

A more informative spectrum is afforded when the analogous secondary alcohol complex IV is dissolved in sulfuric acid. The spectrum is shown in Fig. 1. The methyl group on C_1 appears as a doublet at 8.22 τ and the proton on the exocyclic carbon displays the expected quartet at 3.81 τ .



IV V VI

The ring protons on the carbons 3 and 5 are now nonequivalent because of the restricted rotation about the 1,2 bond and these appear as doublets at 4.56 and 4.16 τ . The proton on C_4 appears at lowest field as a singlet at 3.48 τ . (It is interesting to note that the transannular coupling $J_{3,5}$

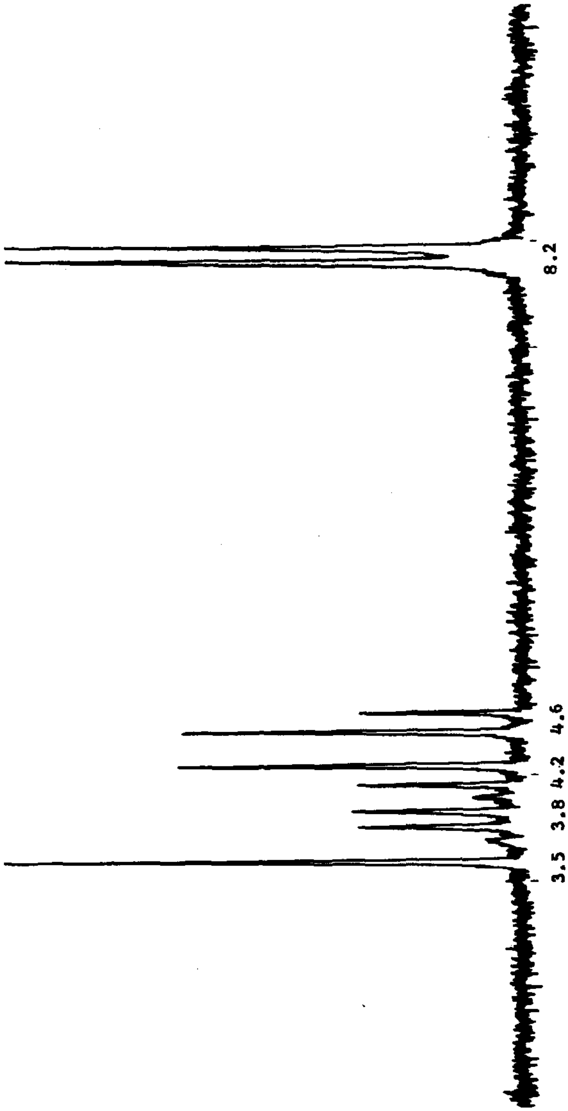


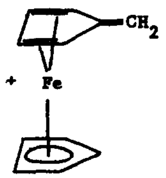
Fig. 1 NMR spectrum of IV in conc. H_2SO_4.

is large (9.0 c.p.s.) whereas the coupling between neighboring hydrogens is close to zero.)

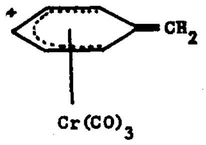
As with the case of the primary alcohol a structure involving a bare exocyclic carbonium ion type formulation seems untenable. Two further structures which could be considered are shown by formulas V and VI. In the first of these, the iron atom is displaced towards the exocyclic carbon and the charge on the cationic center is reduced by coordination of electrons on iron to this carbon atom in the same manner as has been proposed in the case of the α -metallocenyl cations[2]. In the π -allyl formulation, VI, the iron atom is displaced in the opposite direction and is attached to the organic ligand through three carbons; the bonding is then similar to that involved in other known π-allyl-iron tricarbonyl cations[3]. Although it is not possible to decide with certainty, the latter of these two formulations seems to be preferred.

The principal virtue of structure VI over structure V is that it readily explains the appearance of the proton on C_4 at lowest field in the n.m.r. spectrum, for the proton on the central carbon atom in other π-allyl-$Fe(CO)_3$ cations is known to occur at lowest fields. It seems difficult to reconcile this particular feature of the spectrum with a structure such as VI or other formulations.

If this formulation VI is correct then the question might be raised as to whether the α -ferrocenyl and the benzyl-chromium tricarbonyl cations[4], both of which are found to be relatively stable, could not also be formulated as the analogous exocyclic double bond structures VII[5] and VIII respectively.



VII



VIII

Acknowledgements

We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial assistance.

References

1. J. D. Fitzpatrick, L. Watts, G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.* **87**, 3254 (1965).
2. E.A. Hill and J. H. Richards, *J. Am. Chem. Soc.* **83**, 3840 (1961).
3. G. F. Emerson, J. E. Mahler and R. Pettit, *Chem. and Ind.* 836 (1964).
4. J. D. Holmes, D. A. K. Jones and R. Pettit, *J. Organometal. Chem.* In press.
5. On the basis of the rates of solvolysis of various substituted chloromethyl ferrocenes, J. C. Ware and T. G. Traylor have also proposed recently the structure VII to be the intermediate cationic species involved. *Tetrahedron Letters*, No. 18, 1295 (1965).