

## Preliminary communication

Organometallic carbonium ions. NMR studies of *cis*- and *trans*-pentadienyliron tricarbonyl cations

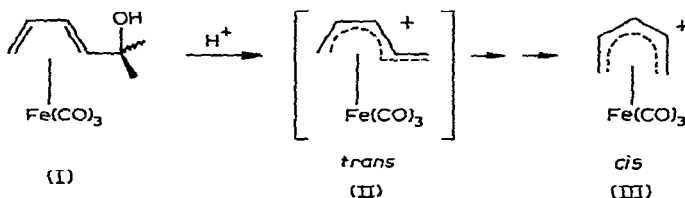
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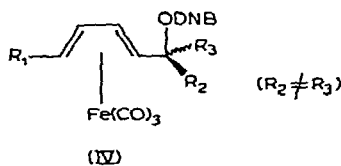
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*trans*-Pentadienyliron tricarbonyl cations (II) have been proposed by Mahler and Pettit<sup>1</sup> as intermediates in the formation of the geometrically inverted *cis*-pentadienyliron tricarbonyl cations (III) from the alcohol complexes (I).

Scheme 1



More recently, Clinton and Lillya<sup>2</sup> have offered more direct evidence for the elusive *trans* ions (II) by observing complete retention in all but one case for the solvolysis of several pentadienyl ester complexes (IV).

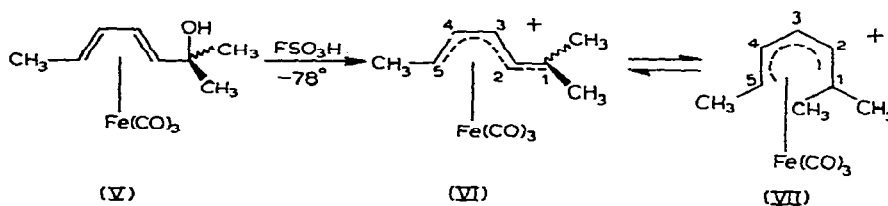


We wish to report the direct NMR observation of such a *trans* species (II) and some interconversions of the *cis* ions which are important in connection with the mechanism of the geometric inversion occurring in Scheme 1.

Direct low temperature addition of the alcohol complex (V)\* to fluorosulfuric acid under an inert atmosphere gave deep red solutions of the *trans*-pentadienyliron tri-

\*Satisfactory spectral and analytical data have confirmed the structure of (V).

carbonyl cation (VI) in equilibrium with the corresponding *cis* form (VII)\*\*. Attempted isolation of (VI) or (VII) as  $\text{BF}_4^-$  or  $\text{PF}_6^-$  salts was unsuccessful.



Compound (V) was chosen as a likely precursor to a *trans* cation for two reasons; (1) the resulting *trans* cation would show a simplified and characteristic NMR spectrum and (2) the *cis* form of the ion is forced to accept a large steric interaction between the *anti* methyl group and the hydrogen at C-5.

The NMR spectrum of a strong acid solution of (V) is shown in Fig. 1. Assignments were confirmed by direct and indirect<sup>3</sup> double resonance experiments. Chemical shifts, expressed in tau ( $\tau$ ) units, are based on internal tetramethyl ammonium standard<sup>4</sup>, taken as  $\tau$  6.9.

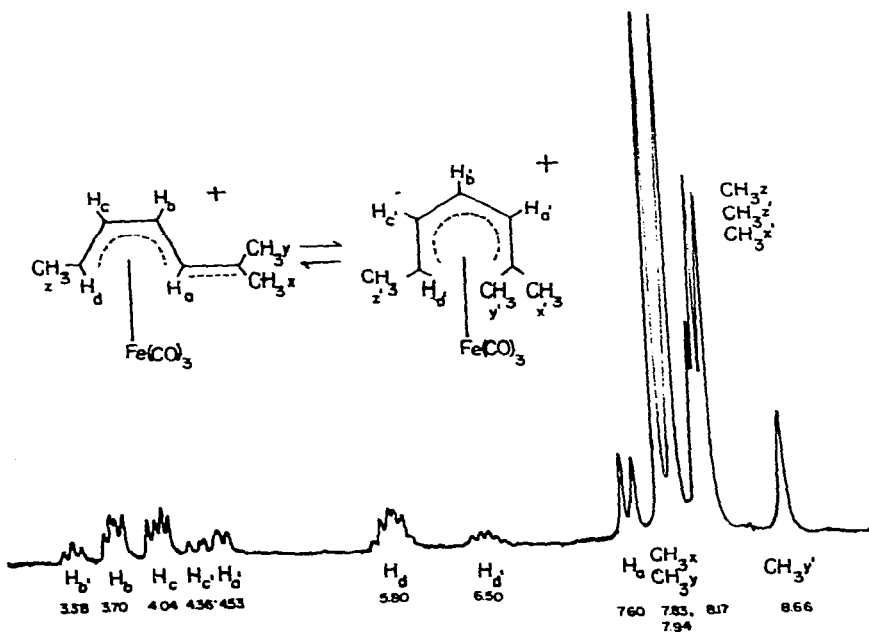


Fig. 1. 100 MHz NMR spectrum of fluorosulfuric acid solution of (V). Chemical shifts are given in tau ( $\tau$ ) units with respect to tetramethyl ammonium ion at  $\tau$  6.9 as an internal reference<sup>4</sup>.

\*\*A pentadienyliron tricarbonyl cation constrained in a *trans* form has been observed in  $\text{FSO}_3\text{H}/\text{SO}_2$  at  $-80^\circ$ .<sup>7</sup>

Comparison of the differences in chemical shifts of the *cis* and *trans* ions is complicated by possible changes in the shielding effects of iron, but the fact that the geminal methyl groups lie at lower field in the *trans* ion is consistent with greater charge density at  $C_1$ .

The equilibrium constant for the *cis*  $\rightleftharpoons$  *trans* interconversion (presumably involving rotation about the  $C_2-C_3$  bond) is  $3.0 \pm 0.3$  at  $-50^\circ$  favoring the *trans* form.

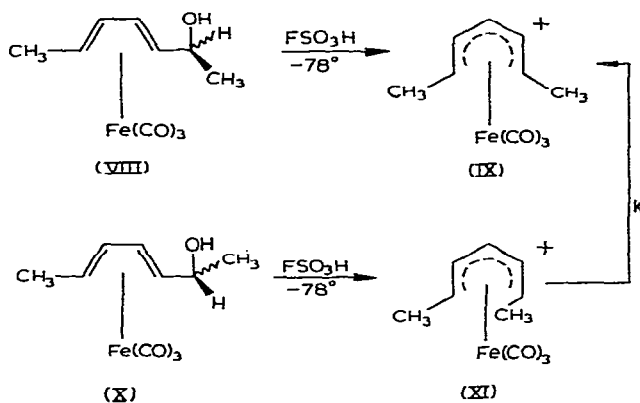
It thus appears that a cisoid arrangement of five  $\pi$  centers is not a prerequisite for stable pentadienyl iron cation complexes and that with suitable substitution, the *trans* form can be made more stable\*.

A study of the rate of interconversion (VI)  $\rightleftharpoons$  (VII) by a modification of the nuclear magnetic double resonance method of Forsén and Hoffman<sup>5</sup> has verified that an equilibrium situation exists and leads to a rate constant of  $0.75 \text{ sec}^{-1}$  at  $-32.5^\circ$  and an energy barrier ( $E_a$ ) for *trans*  $\rightarrow$  *cis* in the order of 13 kcal.\*\*

The  $C_1$  geminal methyl groups in (VI) (see Fig. 1) appear as sharp singlets separated by 11 cps at 100 MHz (7 cps at 60 MHz) and do not show any signs of coalescence below temperatures where line broadening, characteristic of the *cis*  $\rightleftharpoons$  *trans* process commences (approximately  $-10^\circ$ ). Any rotation about the  $C_1-C_2$  bond in (VI) leading to equivalence of the geminal methyl groups is then slower than rotation about the  $C_2-C_3$  bond leading to the *cis* ion.

In contrast to Mahler and Pettit<sup>1</sup> who isolated only the *cis*, *syn*, *syn* ion (IX) from either of the diastereomeric alcohol complexes (VIII) or (X)<sup>6</sup>, we find that (VIII) and (X) show clean, stereospecific conversion to the *cis* ions (IX) and (XI) in strong acid solutions at low temperature\*\*\* (Scheme 2).

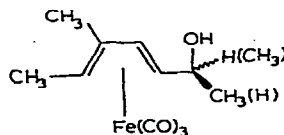
Scheme 2.



\*The stability of the *trans* ion (VI) cannot be interpreted solely on the basis of steric factors alone, cf. discussion below.

\*\*Further refinements in the rate data for the interconversion (VI)  $\rightleftharpoons$  (VII) are in progress and will be reported in a future paper.

\*\*\*Similar stereospecific conversions have also been observed<sup>7</sup> for



The NMR spectra of fluorosulfuric acid solutions of (VIII) and (X) are given in Fig.2.

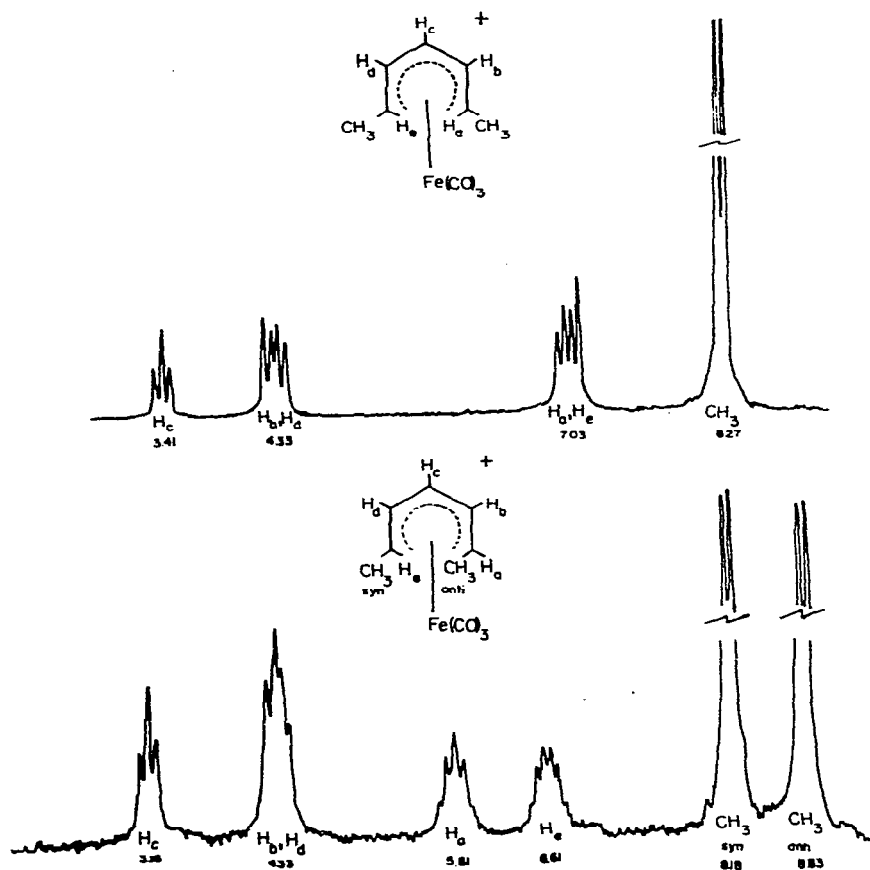


Fig.2. Top - 100 MHz NMR spectrum of fluorosulfuric acid solution of (VIII). Bottom - 100 MHz NMR spectrum of fluorosulfuric acid solution of (X). Chemical shifts given in tau ( $\tau$ ) units with respect to internal tetramethyl ammonium ion reference at  $\tau$  6.9<sup>4</sup>.

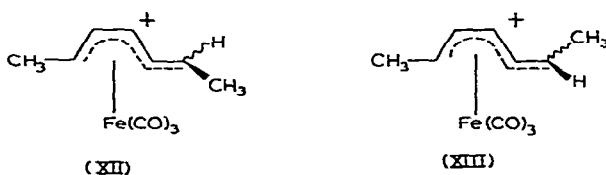
Assignments were confirmed by double resonance experiments and comparison with an authentic sample in the case of (IX)\*. No trace of a *trans* ion is seen in either case even though the steric situation in (XI) is similar to that in (VII). Steric effects alone do not give the complete answer but must be considered in conjunction with possible electronic effects. If charge density at C<sub>1</sub> is larger in the *trans* ion than in the *cis* ion, as NMR evidence tends to indicate, greater stabilization results in (VI) with a 3° center at C<sub>1</sub> than in a *trans* ion from (X) with a 2° center at C<sub>1</sub>.

NMR studies indicate that the conversion of *cis*, *syn*, *anti* ion (XI) to *cis*, *syn*, *syn*

\*Compound (IX) was prepared by the method of Mahler and Pettit, ref. 1.

ion (IX) becomes facile at temperatures  $> 0^\circ$ . Rate studies are currently in progress in order to verify that the *anti*  $\rightarrow$  *syn* conversion occurs in a *cis* ion and not through a small equilibrium concentration of a *trans* species.

A reasonable assumption in light of the above direct observation of a *trans*-penta-dienyl cation complex (VI) and the solvolytic results of Clinton and Lillya<sup>2</sup> is that both (VIII) and (X) initially convert to the corresponding *trans* cations (XII) and (XIII) respectively.



In strong acid media at low temperature where carbonium ion lifetimes are extended, rearrangement to the *cis* ion occurs<sup>\*</sup>; however under solvolytic conditions the *trans* ions are captured before rearrangement to give the products with retention.

Isolation of salts from acid solutions of (VIII) and (X) give the product of thermodynamic control, (IX).

#### ACKNOWLEDGEMENT

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<sup>\*</sup>In the case of (XII) and (XIII) the rearrangement is sufficiently rapid to preclude NMR detection at temperatures as low as  $-78^\circ$ .