Tricarbonyl(*trans*-π-pentadienyl)iron Cations†

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MAHLER and Pettit[1] have shown that tricarbonyl(*cis*-π-pentadienyl)iron cations (I) are unusually stable. Reactions designed to produce *trans*-cations (II) give the presumably more stable *cis*-cations (I) instead, and no direct evidence for the existence of *trans*-cations has previously been obtained. We report here on evidence for such ions and on some of their properties.

Relative solvolysis rates in 80% *aqueous acetone at* 30·0°

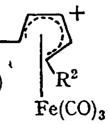
Compound		Configuration	k_{rel}
(IIIb)	R^2 = DNB	*ψ-endo*	1^a
(IIIa)	R^2 = DNB	*ψ-endo*	2·2
(Va)	R^2 = DNB		4·2
(Vb)	R^2 = DNB		8·5
(IVb)	R^2 = DNB	*ψ-exo*	100^b
(IVa)	R^2 = DNB	*ψ-exo*	290^b

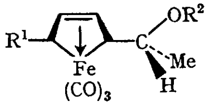
[a] $k_1 = (2{\cdot}48 \pm 0{\cdot}05) \times 10^{-4}\,\text{sec}^{-1}$; [b] Extrapolated from measurements at 7°, 14°, and 20°.

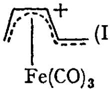
Solvolysis rates for compounds (IIIa)—(Va), (IIIb)—(Vb) (R^2 = 3,5-dinitrobenzoyl, DNB)‡ in 80% aqueous acetone are listed in the Table. Salt effects and production of methyl ethers in methanolysis show that these are S_N1 reactions involving alkyl–oxygen fission. The iron compounds, with the exception of (IVb) which gives 3% *ψ-exo*-alcohol, give the corresponding alcohols of retained configuration, exclusively.

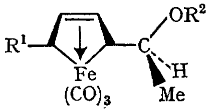
The large *ψ-exo*-: *ψ-endo*-rate ratios demonstrate the existence of a preferred stereochemistry for departure of 3,5-dinitrobenzoate ion and suggest strongly that bonding changes involving iron occur during ionization.[2] Examination of scale models shows that in the most stable conformation of the *ψ-exo*-compounds the 3,5-dinitrobenzoate group is *exo* with respect to iron. In the case of the *ψ-endo*-compounds placing 3,5-dinitrobenzoylate *exo*- to iron requires severe steric interactions between methyl and one of the terminal carbonyl ligands as well as the diene residue. Thus, we suggest that the leaving group departs *exo*- to iron.§ Though they are less reactive than their uncomplexed analogues the *ψ-endo* esters still undergo stereospecific solvolysis. This suggests that the "unassisted" reaction is slow in these complexes, perhaps due to reduction of conjugation in the complexed diene.

These reactions bear all the usual kinetic and stereochemical characteristics required by direct participation of iron to give cations of structure (VI). An alternative structure (VII)[1], which is similar to Traylor's structure for the ferrocenyl carbinyl cation,[3] is equally consistent with our data, however. It is highly unlikely that *cis*-π-pentadienyl cations (I) intervene in these reactions, since solvolysis of (IIIe) and (IVb) (R^2 = DNB) give no rearranged alcohol (VIII). This conclusion is unequivocal for solvolysis of IX, which gives no rearranged product. Hydrolysis of the possible *cis*-intermediate (I; R^1 = Me, R^2 = H) has been shown to lead exclusively to an alcohol with the carbon skeleton of (IV; R^1=R^2=H).[4]

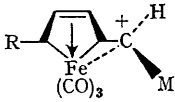

(I)

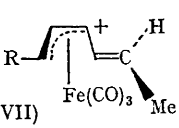

(III) a, R^1=Me
b, R^1=Ph

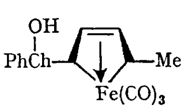

(II)

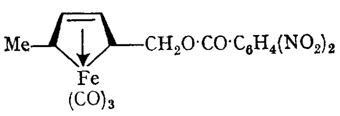

(IV) a, R^1=Me
b, R^1=Ph


(V)a, R^1=Me;b, R^1=Ph


(VI)


(VII)


(VIII)


(IX)

[†] Presented in part at the Southeastern Regional A.C.S. Meeting, Atlanta, Georgia, November 1st—3rd, 1967.

[‡] Satisfactory analytical and spectral data has been obtained for all new compounds. Stereochemistry was assigned on the basis of relative R_F values for diasteriomeric alcohols on alumina and silica gel thin layers and relative steric encumbrance of hydroxyl groups as estimated using scale models.

[§] Experiments with cyclic compounds of unambiguous stereochemistry confirm this (unpublished work of D. E. Kuhn).

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