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FLUXIONAL BEHAVIOUR OF PROTONATED SUBSTITUTED TROPONEIRON TRICARBONYLS

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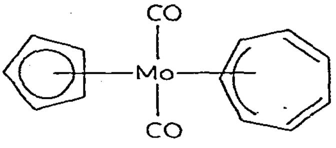
Summary

Iron carbonyl complexes of 2-mono-substituted tropones have been prepared and their fluxional behaviour in strongly acidic media studied.

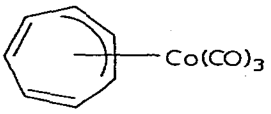
Introduction

In recent years there have been many investigations of compounds containing metal carbonyl moieties $M_n(CO)_m$, either mono- or poly-nuclear, bound to cyclic polyolefins, which show intramolecular mobility or generally display fluxionality*.

Most of the fluxional cyclic compounds containing π-bonded C(7) ligands have been shown to be neutral complexes such as I [3,4], II [4], III [2] and IV [5]. Compound V[6] is an exception, being a positively-charged mononuclear complex of a carbocyclic ligand in which the metal atom moves around the periphery of the ring by a series of 1,2 shifts.



(I)



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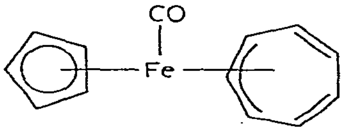

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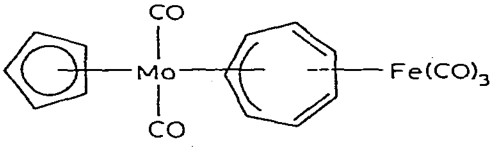

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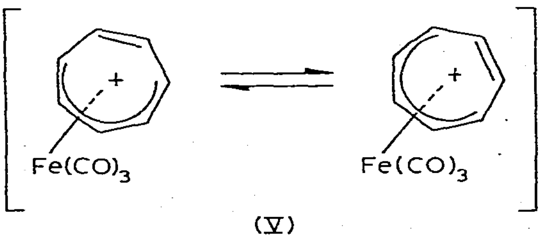

(V)

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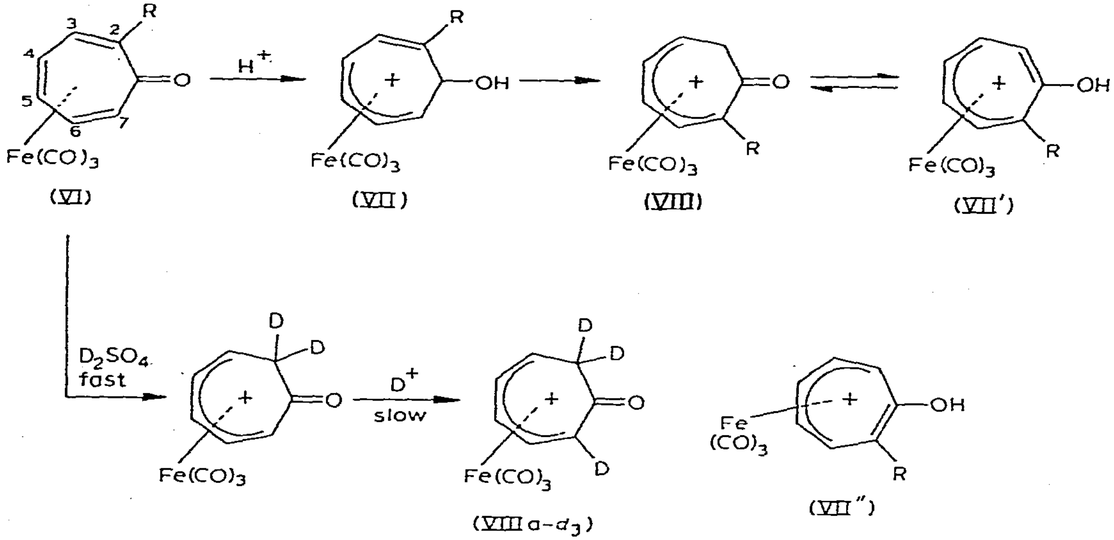
* For a review on fluxional organometallic molecules see ref. 1.

Results and discussion

We recently studied cation VII, [7], which is formed by protonation of troponeiron tricarbonyl (VIa) in H_2SO_4, probably via the hydroxytropyliumiron tricarbonyl (VIIa). On deuteration of VIa, we found three D atoms per cation VIII*. The incorporation of the third deuterium atom at C(7) was explained in terms of a 1,2-shift of the pentadienyliron tricarbonyl moiety around the ring (i.e. ring fluxional isomerism).



a, R = H; b, R = CH_3; c, R = Cl; d, R = Ph

We suggested that full conjugation in VIII in the protonated troponeiron tricarbonyl could be achieved by enol—ketone equilibria in which the positive enol form VII can either tautomerize to give VIII, or isomerize by a 1,2-shift to VII'' as in tropyliumiron tricarbonyl (V) [6]. The major difference between cation V and the hydroxytropylium intermediate VII in the context of their fluxional behaviour lies in the total number of instantaneous structures for each of them where, only 2 being possible in the later molecule (VII' and VII'').

We have now carried out a study of the influence of two factors on the above fluxional process: (1) changing the substituents at C(2) of the troponeiron tricarbonyl (VI) molecule; (2) replacement of one carbon monoxide attached to the metal by another good-acceptor ligand.

Treatment of 2-methyltropone [9], 2-chlorotropone [10] or 2-phenyltropone [11] with $Fe_2(CO)_9$ gave the corresponding 2-substituted troponeiron tricarbonyls in high yield, VIb-VId** (see Table 1 for NMR, mass spectral and m.p. data). The NMR spectra indicate that in all three substituted complexes, the metal is coordinated to the double bonds which do not carry the substituent.

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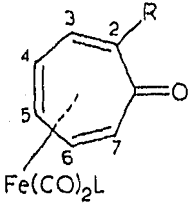
* A very similar report to our results has recently appeared [8].

** All new compounds gave satisfactory C, H analyses and/or mass spectra.

TABLE 1

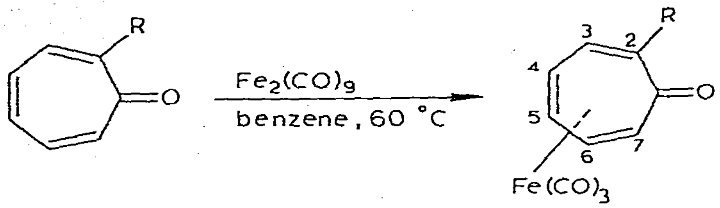
NMR (τ, ppm) AND MASS SPECTRAL DATA AND MELTING POINTS FOR COMPOUNDS VIb-VId



Compound	NMR					M.p. (°C)	Mass spectrum
	R	H_3	H_4	$H_{5,6}$	H_7		
VIb(L = CO)[a]	8.52 d $J(H_3{-}CH_3)$ 1.5 Hz	3.64 m	7.32 bt	3.64 m	6.85 m	71-72	M^+ m/e 260
VIc(L = CO)[a]	—	3.27 d $J_{3,4}$ 10 Hz	7.39 ddd	3.68 m	6.78 quintet	130-131	M^+ m/e 280
VId(L = CO)[a]	2.85 s (5H)	3.38 d	7.2 bt	3.7 m	6.7 m	146-148 decomp.	M^+ m/e 322
VIa(L = Ph$_3$P)[b]	5.05 dd $J_{2,3}$ 11.0 Hz $J_{2,7}$ 2.0 Hz	3.48 dq $J_{3,4}$ 8.0 Hz $J_{3,5}$ 1.5 Hz	7.92 dt	4.4 m (H_5) 3.97 bt (H_6)	7.26 bt	Ref. 13	—

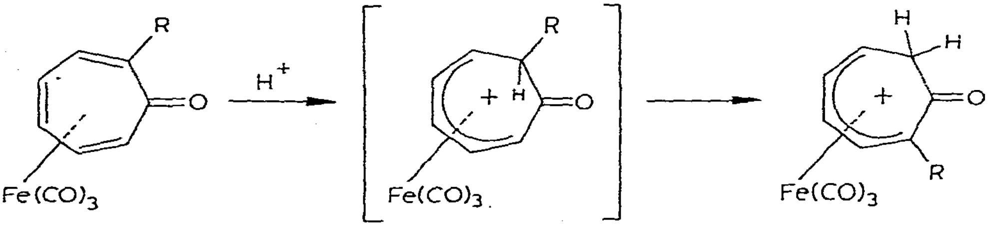
[a] Measured in CDCl$_3$ with TMS as internal standard at 60 MHz.

[b] Measured in CDCl$_3$ at 100 MHz with decoupling.



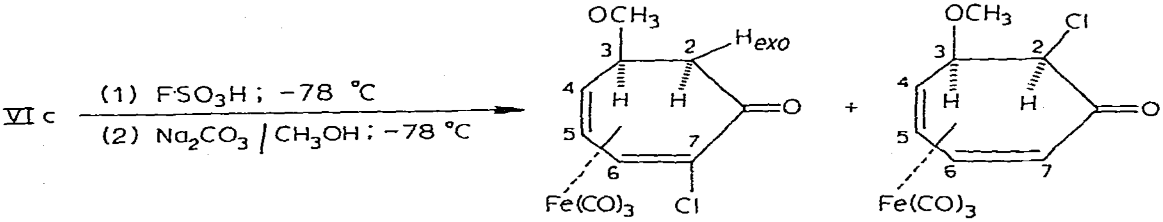
(VIa-VId)

When VIb-VId were extracted from CH_2Cl_2 solutions into concentrated H_2SO_4 (98%) at 0°C and the NMR spectra were measured at ambient temperature 15-20 minutes afterwards, only the completely isomerized ions VIIIb-VIIId were observed (see Table 2)*. These results suggest higher rates of isomerism for the $Fe(CO)_3$ moiety in all the protonated 2-substituted coordinated tropones then in the parent ion VIIIa [7], (which exhibits a half-life of ca. 30 min at room temperature).



(VIb-VId) (IXb-IXd) (VIIIb-VIIId)

Proof of the intermediacy of a cation of the type IX was obtained by quenching cation IXc (prepared with FSO_3H) with a CH_3OH/Na_2CO_3 suspension at −78°C. The two products were separated in 1/1 ratio on a Silica column; NMR analysis showed them to be the 7-chloro- and 2-chloro-3-methoxy-4,5,6,7-*tetrahapto*-cycloheptadienone, $Fe(CO)_3$ complexes, X and XI, respectively**.



(X) (XI)

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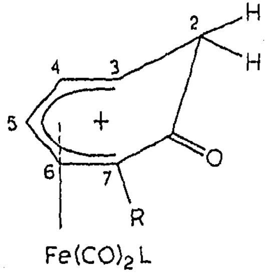
* The rate constants for the shift of the substituent R from C(2) to C(7) during the fluxional isomerism, would enable us to estimate their quantitative effects on the above isomerization. We are planning to measure the kinetic parameters in SO_2—FSO_3H and SO_2—FSO_3D at low temperatures.

** Quenching the fluorosulphonic acid solution of VIb in CH_3OH at −78°C gave a 1/1 mixture of the two isomers: they could not be separated by either chromatography or distillation, but the composition was determined from the NMR spectrum of the mixture.

TABLE 2

NMR SPECTRAL DATA (τ, ppm) OF COMPOUNDS VIIIa-VIIId



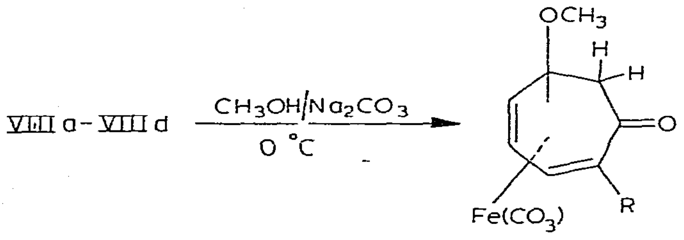
(VIIIa - VIIId)

Cation	H_{exo}	H_{endo}	H_3	H_4	H_5	H_6	R
VIIIa(L = CO)[a,c]	7.68	6.77	5.0	3.5	2.7	3.5	5.3
VIIIb(L = CO)[a,c]	7.78 dd $J_{exo,endo}$ 17 Hz	6.78 dd $J_{endo,3}$ 8 Hz	5.32 bt	3.6 t	2.98 dt	3.45 d $J_{6,5}$ 7.5 Hz	7.99 s
VIIIb(L = CO)[b,c]	8.0	7.15	5.43	3.8	3.02	3.71	Hidden under CD_3CN
VIIIb(L = CO)[d,c]	—	—	5.32 d $J_{3,4}$ 7.5 Hz	3.8	3.02	3.71	7.99
VIIIc(L = CO)[a,c]	7.68	6.73	5.07	3.6	2.81	3.71	—
VIIId(L = CO)[a,c]	7.37	6.43	5.03	3.6	2.45	2.95	2.42
VIIIa(L = Ph_3P)[a]	7.56	6.4	5.45 bt	3.0 t	3.35 t	3.8 m	5.15 d

[a] Measured in H_2SO_4 98% as a solvent. [b] Fluoroborate salt measured in CD_3CN. [c] CH_2Cl_2 as internal reference. [d] Measured in D_2SO_4.

The isolation of XI was taken to indicate that at —78° C a relatively high proportion of protonated VIc existed as the cationic species IX. It also supports our postulated mechanism, that the initial protonation takes place at the uncoordinated double bond at C(2) of VIc, and is followed by rapid 1,2 shifts of the $Fe(CO)_3$ moiety. This disproves the recent conclusion by Hunt [8] that formation of cation VIIIa occurs by preferential attack at the terminal carbon of the diene-$Fe(CO)_3$ moiety in VIa*. We assume that in the quenching step the methoxy group attacks from the *exo* side of the cation. In addition, the coupling constant $J_{2,3}$ 4.5 Hz in XI suggest a *cis* relationship between these two protons and an *endo* configuration in relation to the metal. Thus, an *endo*-geometry for the H_2 would indicate that in FSO_3H at —78° C, protonation of VIc occurs stereoselectively from the *endo* rather than *exo* side of the uncoordinated double bond. This is in accordance with the observation by Whitesides et al. [12] that cyclohexadiene · $Fe(CO)_3$ is protonated from the *endo* side of the organic ligand in CF_3COOH.

Quenching the acidic solutions of VIIIb-VIIId in rapidly stirred suspension of sodium bicarbonate in methanol at 0° C gave high yields in Xa-Xd (Table 3 lists the NMR data).



(X a - X d)

Troponeiron dicarbonyltriphenylphosphine [13], was likewise protonated in H_2SO_4 at the uncoordinated double bond carbon C(2). The main difference between the behaviour of this complex and VIa was that when XII was dissolved in sulfuric acid-d_2, it took 68 hours for the complete deuteration at C(2) to give 2,2'-XIII-d_2. Incorporation of a third deuterium into XIII did not occur under these conditions. (The NMR spectra of the cations XIII and of the quenched products XIV with the aid of repeated integrations indicated the extent of D-incorporation in each case.)

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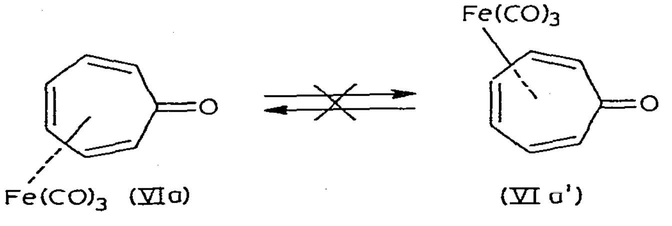
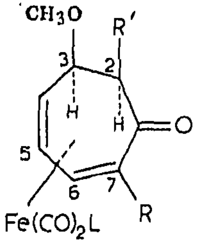
* Furthermore we have found that the NMR spectrum of tropone · $Fe(CO)_3$ in chlorobenzene is not temperature dependent (+40° C → 120° C), which rules out the following fluxional process:



(VIa) (VI a')

TABLE 3

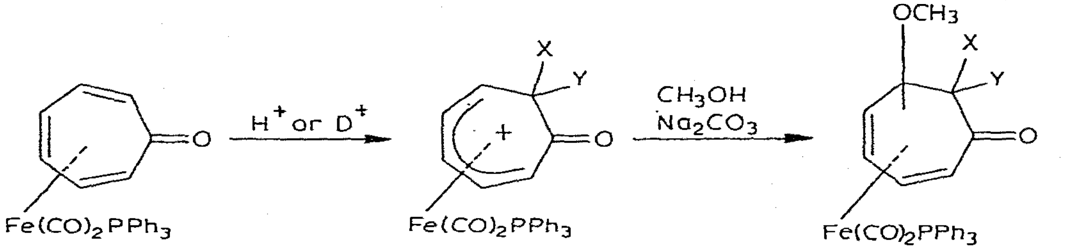
NMR SPECTRAL DATA (τ, ppm) AND MELTING POINTS OF COMPOUNDS IX AND Xa-Xd



(Xa-Xd)

Compound	R′	H_2	H_3	OCH_3	H_4	H_5	H_6	R	M.p. (°C)
Xa(R′ = R = H)	8.10	7.6	6.09	6.65	6.72	4.3	4.3	6.82	78-80
Xb(R′ = H; R = CH_3; L = CO)	8.17 t[a]	7.5 dddd	6.09 dddd	6.65 s	6.77 m $J_{4,5}$ 8.0 Hz	4.6 dd	4.18 d $J_{6,5}$ 5.5 Hz	8.34 s	oil
Xc(R′ = H; R = Cl; L = CO)	8.22	7.43	6.16	6.72	6.85	4.7	3.9	—	122-27
IX(R′ = Cl; R = H; L = CO)	—	5.87 dd $J_{2,3}$ 4.5 Hz	5.68 pentet	6.62	6.92 m	4.33	4.12 t	6.92 m	109-111
Xd(R′ = H; R = Ph; L = CO)	8.03	7.48	6.0	6.65	6.78	4.52	3.67	2.74	160-163
Xa(R = R′ = H; L = Ph_3P)	8.2	7.62	5.94	6.75	7.14	5.1	5.1	7.14	160 decomp.
Xa(R′ = D; H_2 = D R = H; L = Ph_3P)	—	—	5.97	6.77	7.14	5.1	5.1		100 decomp.

[a] $J_{exo,endo}$ 11 Hz.



(XII)

(XIII) X = Y = H

(XIII-d_2) X = Y = D

(XIV) X = Y = H

(XIV-d_2) X = Y = D

We suggest that inhibition of the ring fluxional isomerism in protonated XII may be due to: (1) Steric hindrance by the bulky ligand Ph$_3$P to the 1,2 shift of the pentadienyliron dicarbonyl; (2) the phosphine—iron diene bond has enhanced stability, which inhibits the fluxional process.

Experimental

NMR data were obtained on Varian Associate HA-100 and Jeol-60 Hz instruments using TMS as the internal standard. CH$_2$Cl$_2$ was used as internal reference for the acid solutions. IR spectra were measured on Perkin—Elmer 337 and 257 grating spectrophotometers. Melting points were determined on Thomas—Hoover capillary-Melting Point apparatus, and are uncorrected. Mass spectra were determined with an Atlas CH4 Mass Spectrometer fitted with TO-4 ion source with direct inlet system, courtesy of Prof. A. Mandelbaum, Israel Institute of Technology, Haifa.

(4,5,6,7-tetrahapto-3-Substituted-tropone)iron tricarbonyl(VIb-VId)

Synthesis. A mixture of the corresponding keto ligand (1.0 g) in 30 ml dry benzene and diiron enneacarbonyl (4.0 g) was heated at 55° C under nitrogen for 1.5 h. Filtration of the reaction mixture, and evaporation of the solvent afforded an oily residue which on crystallization from hexane gave a red-orange solid. An alternative purification involved chromatography on neutral alumina activity III. The yields were in the range between 60-80% for the three ketones. Physical data, together with mass spectra, are listed in Table 1.

NMR of VIb-VId in sulfuric acid. VIb-VId (50 mg) was dissolved in 1 ml CD$_2$Cl$_2$ at 0° C and extracted into 0.4 ml sulfuric acid (98%). The lower-acidic layer was monitored by NMR (cations VIIIa-VIIId Table 2).

(4,5,6,7-tetrahapto-3-Methoxy-7-substituted cycloheptatrienone)iron tricarbonyl (Xb-Xd)

A general method. VIb-VId (286 mg) were dissolved in 5 ml of CH$_2$Cl$_2$ at 0° C and extracted into 1.6 ml of conc. sulfuric acid. After 30 min the bottom layer of the sulfuric acid solution was poured into a cold rapidly stirred excess suspension of sodium carbonate in methanol at 0° C. The resulting mixture was diluted with water and after the evolution of carbon dioxide had ceased, it was extracted with 2 × 25 ml CH$_2$Cl$_2$. The combined CH$_2$Cl$_2$ extracts were washed with water followed by saturated aqueous NaCl, dried (MgSO$_4$) and evaporated.

The resulting yellow residue was purified by crystallization from hexane or by chromatography on Silicar or neutral alumina, to give 211 mg Xb-Xd see Table 3 for NMR data).

Reaction of VIc with fluorosulfonic acid at —78° C. A precooled solution of VIc (140 mg) in 2 ml CH_2Cl_2 at —78° C was added to a rapidly stirred solution of 0.3 ml FSO_3H in 2 ml CH_2Cl_2 at —78° C. After 15 min the mixture was poured quickly into a stirred methanol/sodium carbonate suspension at the same temperature. After 10 min the mixture was allowed to warm to room temperature, and the procedure used for Vb-Vd was followed. TLC showed the presence of the two isomers Xc and XI, which were separated on silica column, with XI was the first to be eluted, 50 mg. m.p. 109-111° C (Found: C, 41.62; H, 3.16 $C_{11}H_9O_5FeCl$ calcd.: C, 42.27; H, 2.89%), Xc was then eluted, 40 mg. m.p. 123-125° C (Found C, 42.53; H, 2.96. Calcd.: C, 42.27; H, 2.89%).

Preparation of the tetrafluoroborate salts VIIIb-VIIId

A general method is described for the preparation of VIIIc. 151 mg Xc in 1 ml Ac_2O (prepared from 1.5 ml 40% aq. HBF_4 in 4 ml acetic anhydride) was cooled in an ice bath to give a yellow precipitate. Precipitation was completed by stirring in 25 ml ether for a few min. Filtration followed by washing with ether, gave 105 mg of a fine yellow salt (Found: C, 31.02; H, 1.47. $C_{10}H_6O_4FeBF_4$ calcd.: C, 32.7; H, 1.63%).

Acknowledgements

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