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SYNTHETIC STUDIES WITH IRON CARBONYL COMPLEXES. FRAGMENTATION OF β-ALCOHOLIC TRICARBONYL(DIENE)IRON(0) COMPLEXES IN THE MASS SPECTROMETER; USE TO DISTINGUISH POSITIONAL ISOMERS

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Summary

Comparison is made between the mass spectra of two isomeric tricarbonyl-(cyclohexadiene)iron(0) complexes bearing 2-methyl-2-hydroxypropyl side-chains at either the 5-*exo*- or the 2-position. Both demonstrate a McLafferty rearrangement mechanism for an arene fragment bearing a coordinated atom of iron, but only the former shows a major competing pathway, since this involves a methylene group α to the point of attachment of the side-chain. The spectra of a variety of related complexes are discussed and a 1,3-shift of the residual C_6H_5Fe group is proposed.

Introduction

We report elsewhere the formation of tricarbonyl-2-(2-methyl-2-hydroxy-propyl)cyclohexa-1,3-dieneiron(0) (I) during the dehydration of tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (II) by *p*-toluenesulphonic acid in refluxing benzene [1]. These two isomeric complexes differ only in the point of attachment of the side-chain to the cyclohexadiene ring and yet show quite distinct fragmentation pathways in the mass spectrometer.

Results and discussion

The positions of the side-chains in the two isomeric complexes are established unambiguously by comparison of their ^{13}C NMR spectra. Peak assign-

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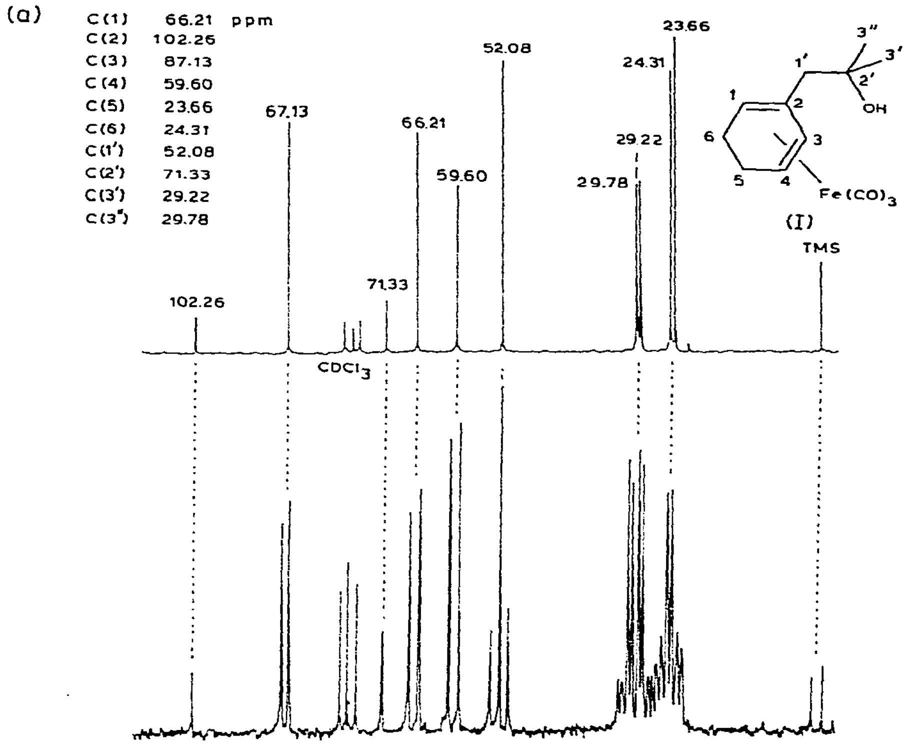


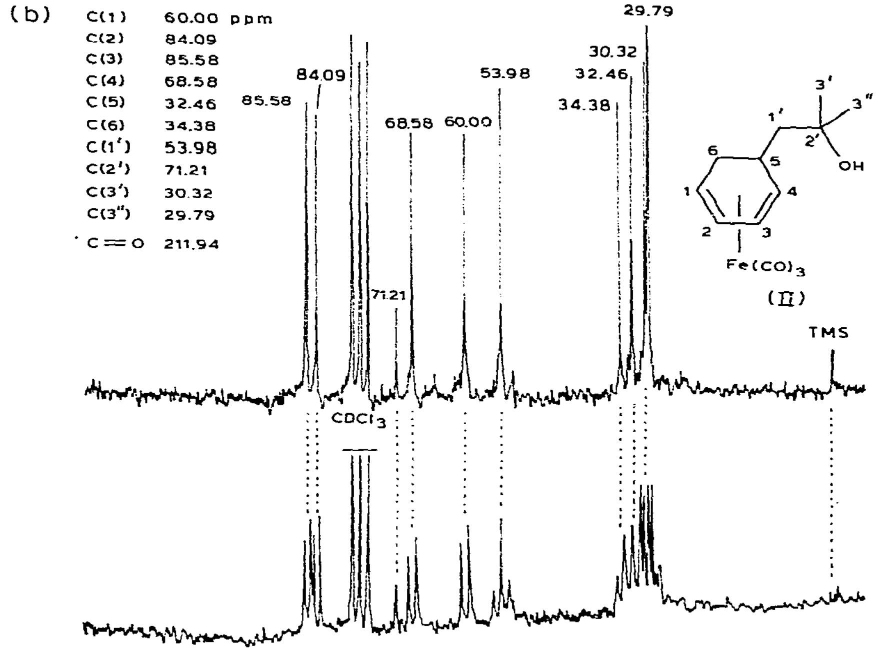


Fig. 1a. ^{13}C NMR spectrum of compound I.

Fig. 1b. ^{13}C NMR spectrum of compound II.

ments are assisted by off-resonance decoupled spectra showing residual C—H coupling. The peaks due to C(2) and C(3) of the coordinated cyclohexadiene ring occur typically about 85 ppm, and indeed two peaks are found in the spectrum of II at 85.6 and 84.1 ppm corresponding to C(3) and C(2), respectively. Both these signals appear as doublets in the off-resonance spectrum indicating one hydrogen atom attached to each.

The spectrum of I, however, has only a single peak in this region, a doublet at 87.1 ppm in the off-resonance spectrum, which corresponds to C(3). The other peak is considerably further downfield at 102.3 ppm, and is much reduced in intensity. This peak remains a singlet in the off-resonance spectrum and is clearly associated with the point of attachment of the alkyl side-chain. The remainder of the resonances occur in similar positions except that C(5) and C(6) of compound II both appear as clear triplets and are moved to higher field relative to those of compound I. This structural assignment is supported by the appearance of methylene protons in the side-chain as a simple AB spin system in the proton NMR, showing them to be isolated from significant coupling to other protons.

In the mass spectrometer, both complexes show the loss of H_2 and sequential loss of three molecules of CO which is well known for tricarbonyl(cyclohexadiene)iron(0) complexes possessing two hydrogens on the M-*endo* face of the ligand [2].

In competition with this, is loss of water from the alcohol which ultimately results in the formation of the fragment of mass 188, $C_{10}H_{12}Fe^+$. A major peak in both spectra, is the base peak of the spectrum of complex I, the 2-position

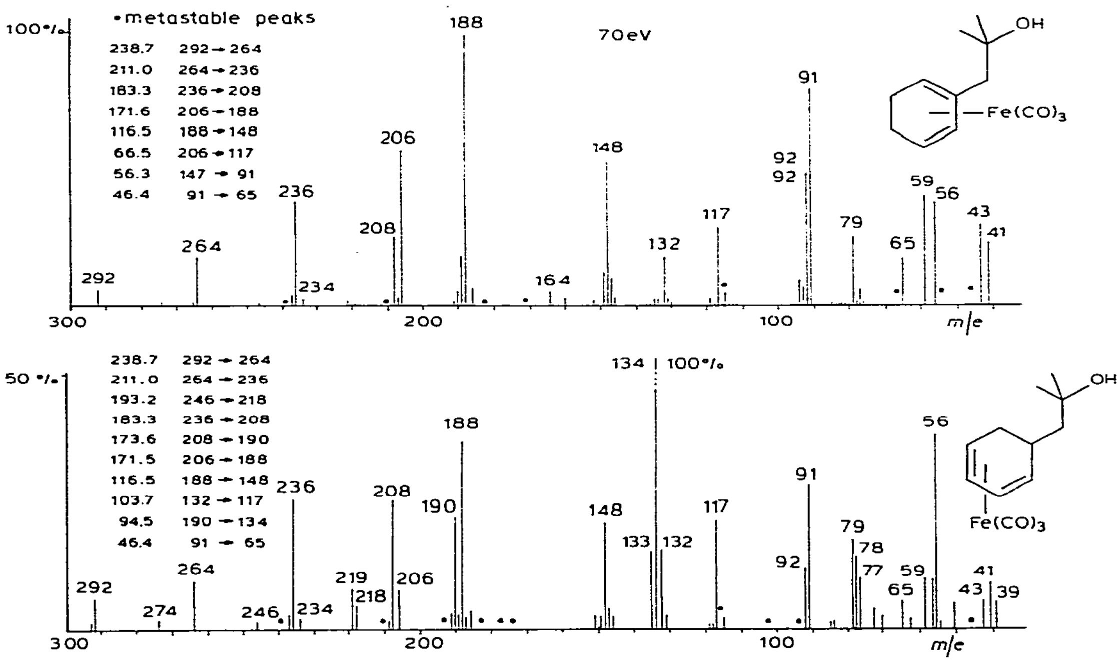
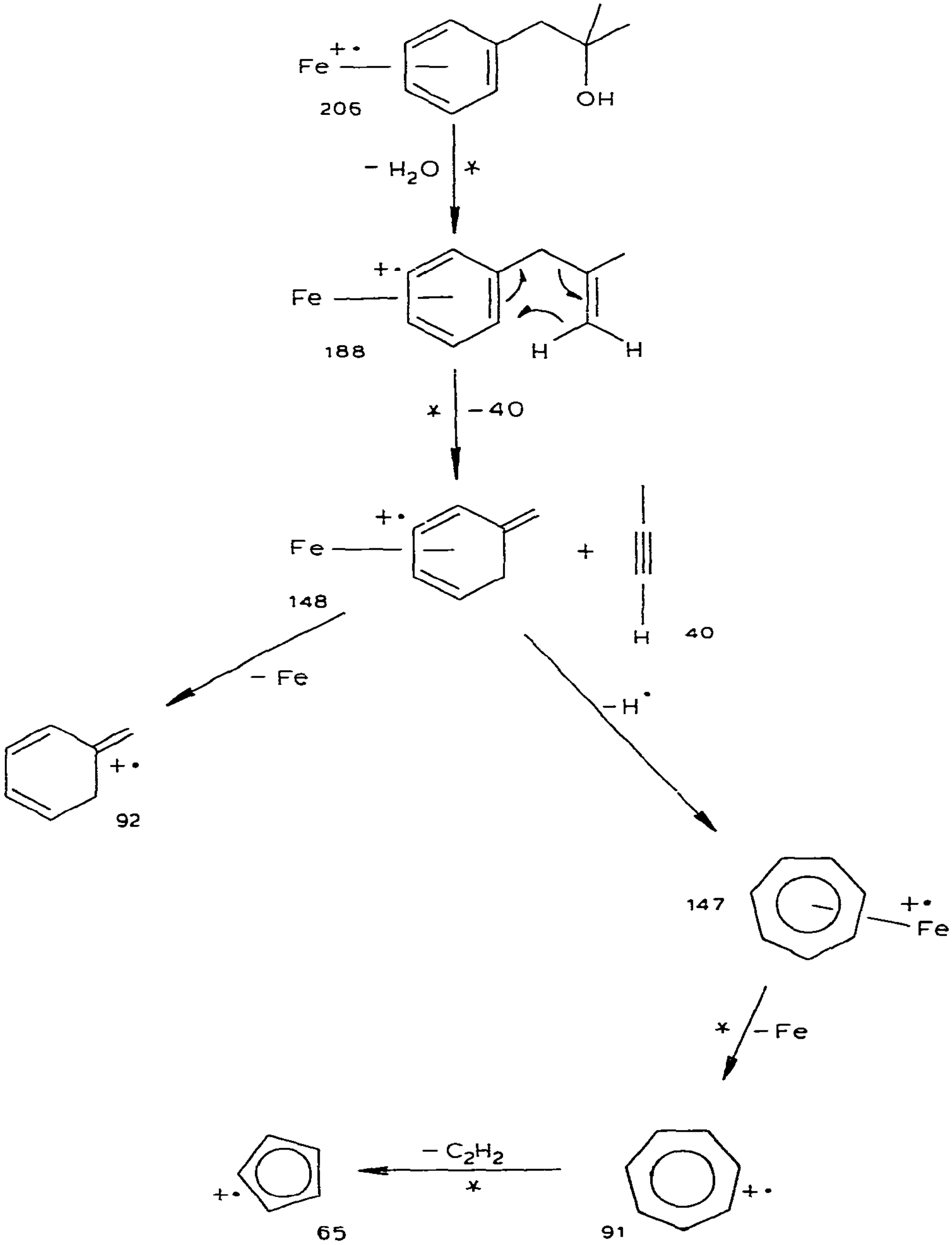


Fig. 2. Mass spectra of compounds I and II.

isomer. Subsequent loss of 40 mass units is accompanied by a metastable peak. This corresponds to a loss of methylacetylene in a McLafferty rearrangement process [3], reported in this case for a fragment with an iron atom coordinated to the arene unit. Next lost is H$^{\bullet}$, and this must be rapidly followed by loss of iron (147, 91) accompanied by a metastable peak at 56.3, resulting in the formation of $C_7H_7^+$, the tropylium cation. As expected, this loses acetylene to form $C_5H_5^+$ 65. This process is summarised in Scheme 1 and accounts for the

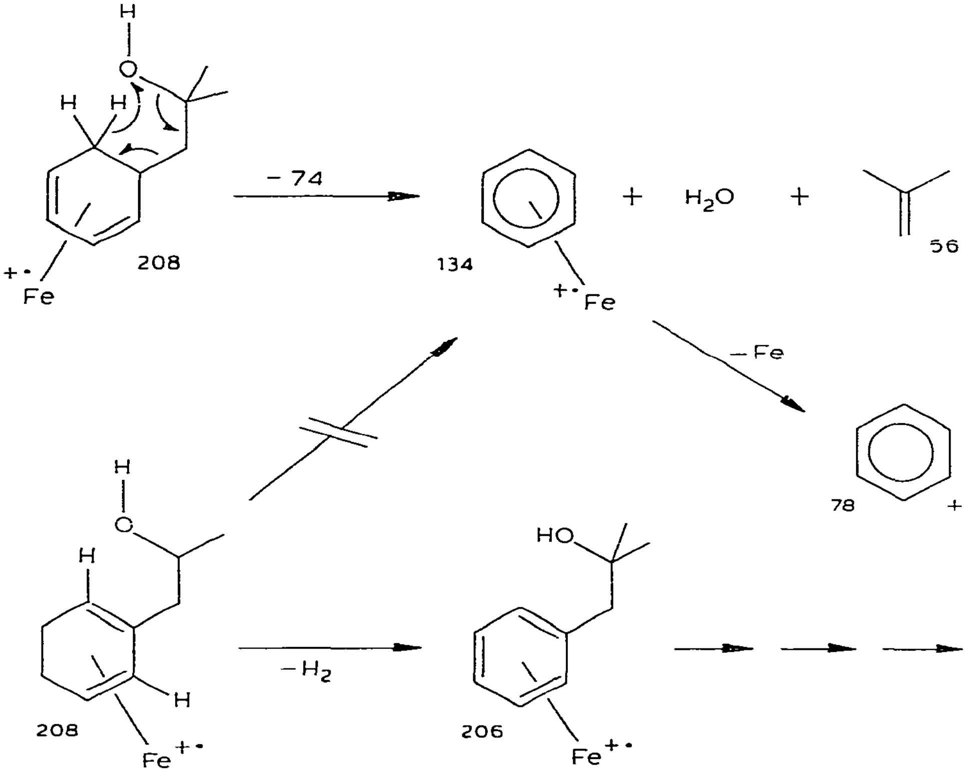
Scheme 1. Further fragmentation of $C_{10}H_{14}OFe^+$. * Process supported by metastable peak.



fragmentation of tricarbonyl-2-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0).

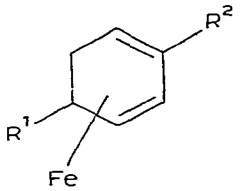
Tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) displays the same sequence of peaks, (188, 148, 91, 65) but the base peak occurs at 134, a peak not found at all in the spectrum of the 2-*exo* complex. This peak is over twice the height of any other peak in the spectrum and indicates the presence of a major fragmentation pathway in competition to the above. This can be accounted for by a concerted loss of water and isobutene from $C_{10}H_{10}OFe^{+\cdot}$ as shown in Scheme 2.

Scheme 2. Further fragmentation of two isomeric species $C_{10}H_{10}OFe^{+\cdot}$.



The process occurs prior to the metal-assisted loss of hydrogen and involves the transfer of a hydrogen atom from a position to the point of attachment of the side-chain, resulting in the formation of an arene fragment (iron coordinated to benzene). It is now clear why the process is not observed for tricarbonyl-2-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) since this does not possess the necessary methylene group. The resulting simplification of the fragmentation pathway accounts for the observed differences between the spectra of the two complexes. In support of this, the spectrum of tricarbonyl-(2-methylprop-1-enyl)cyclohexa-1,3-dieneiron(0), (III) was examined.

The spectrum is greatly simplified since the only possibility is the formation of $C_{10}H_{12}Fe^{+\cdot}$ 188. The only major peaks after the initial loss of 3 CO and H_2 were 188, 148, 91 and 56 (Fe). The proposed intermediate is produced while eliminating the complications due to the presence of the alcohol function in

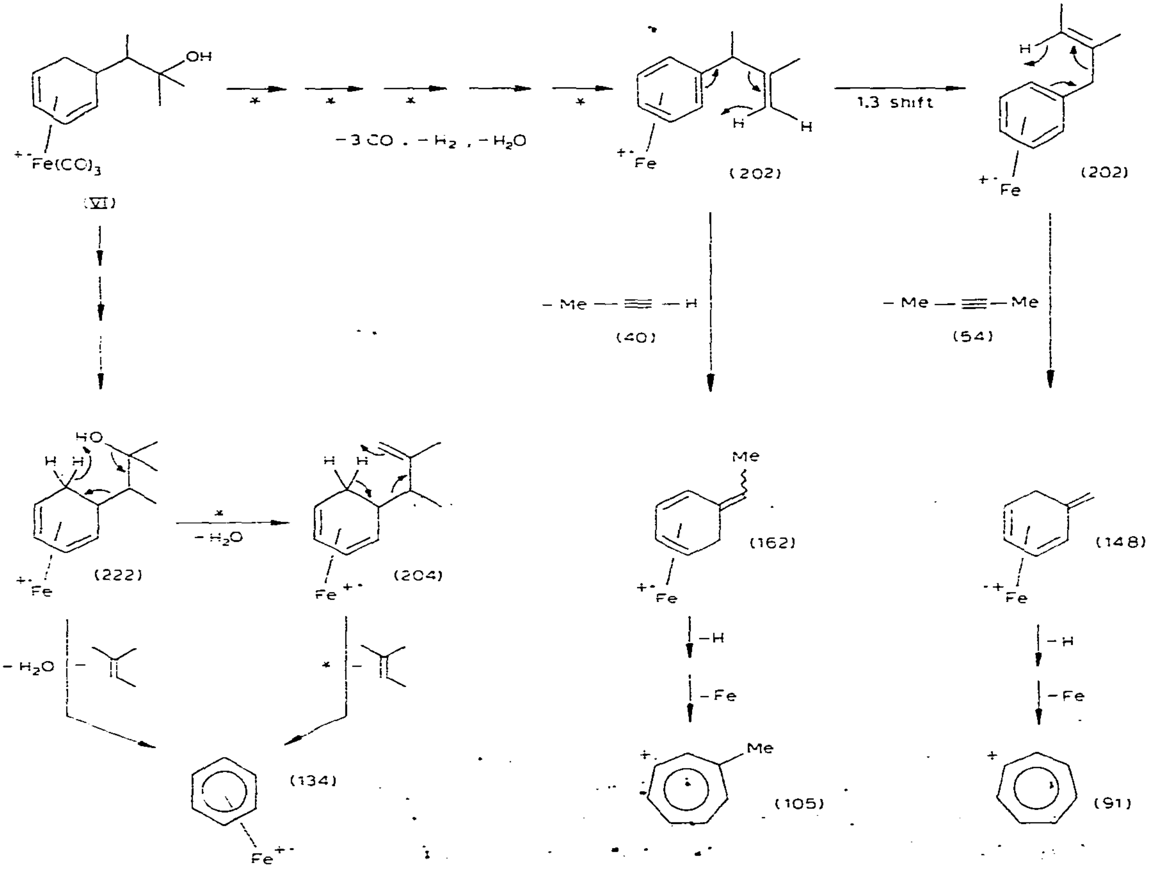


(III, R^1 = H, R^2 = $CH{=}CH(CH_3)_2$;
IV, R^1 = $CH_2CH(OH)(CH_3)$, R^2 = H;
V, R^1 = $CH_2C(OH)(CH_3)_2$, R^2 = OMe;
VI, R^1 = $CH(CH_3)\,C(OH)(CH_3)_2$, R^2 = H)

the molecule, and only the fragmentation pathway shown in Scheme 1 is observed. The position of the double bond in the side-chain is readily rearranged under the conditions in the mass spectrometer.

These processes appear to be of some generality. Tricarbonyl-5-*exo*-(2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (IV) differs from II only in having one less methyl group shows analogous behaviour in the mass spectrometer. Loss of acetylene (—26) rather than methylacetylene (—40) and of water and propene (—60) rather than isobutene (—74), a process supported in this case by a metastable peak at 92.6 (194, 134, $C_9H_{13}OFe^{+\cdot}$, $C_6H_6Fe^{+\cdot}$ + H_2O + C_3H_6), is observed, and the base peak at 134 is unchanged. Similarly for tricarbonyl-2-methoxy-5-*exo*-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0)

Scheme 3. * indicates presence of associated metastable peak.



(V) mass losses of 74 and 40 are observed but all the relevant peaks are shifted by 30 mass numbers due to the methoxy group on the cyclohexadiene ring. The base peak now occurs at 164 and a peak due to the methoxytropylium cation 121 is found. Finally, the spectrum of tricarbonyl-5-*exo*-(1,2-dimethyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (VI) was examined. This complex was obtained by the reaction of ethyl methyl ketone with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate in ethanol followed by the treatment of the resulting 1-methylacetonyl derivative (VII) with methyl magnesium iodide in ether to form VI in good yield. As expected the base peak of the mass spectrum occurs at 134 mass units, produced by loss of water and 2-methylbut-2-ene. A sequential pathway is also involved, revealed by metastable peaks at 187.5 (222, 204), and 88.0 (204, 134). Besides the expected loss of methylacetylene (—40) and the ultimate formation of the methyltropylium cation (105), there is also a competing fragmentation pathway from $C_{11}H_{14}Fe^{+\cdot}$ (202) to the familiar $C_7H_8Fe^{+\cdot}$ (148), a mass loss of 54. An associated metastable peak is found at 108.4. This may be due to a loss of dimethylacetylene or methylallene, but in either case a linear arrangement of four carbon atoms is required. This is best accounted for by a 1,3-shift of the C_6H_5Fe group followed by a loss of dimethylacetylene from the rearranged fragment.

It seems probable that such 1,3-shifts occur undetected in the fragmentation of all the complexes considered in this paper, but only in complex VI does this result in an alteration of the observed pattern of peaks.

Experimental

The mass spectra were recorded on an AEI MS12 spectrometer operating at 70 eV, with an accelerating voltage of 8 kV. Samples were introduced by means of a direct insertion probe at temperatures varying between 30 and 100°C. In many cases the spectra were repeated several times on different occasions, but showed no significant differences in the pattern of peaks observed.

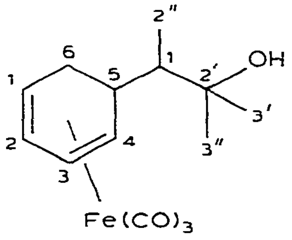
Tricarbonyl-5-exo-(2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (IV) and tricarbonyl-5-exo-(1-methylacetonyl)cyclohexa-1,3-dieneiron(0) (VII)

These compounds were prepared by the method of Birch et al. [4].

Tricarbonyl-5-exo-(1,2-dimethyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (VI)

Magnesium turnings (0.11 g, 4.6 mmol) were stirred with a slight excess of methyl iodide (0.67 g, 4.7 mmol) in dry diethyl ether (40 ml) for $1\frac{1}{2}$ h to form a cloudy suspension. Tricarbonyl-5-*exo*-(1-methylacetonyl)cyclohexa-1,3-dieneiron(0) (1.07 g, 3.7 mmol) was added in ether solution (20 ml). The mixture was stirred for 10 minutes, poured into distilled water, and extracted with ether (3 × 40 ml). The combined extracts were dried over magnesium sulphate. The solvent was removed in vacuo and the yellow gum chromatographed on silica with 50/50 petroleum (30—40)/diethyl ether to give VI as a golden oil (0.918 g, 3.0 mmol, 81%). Analysis. Found: C, 55.3; H, 6.10. $C_{14}H_{10}FeO_4$ calcd.: C, 54.9; H, 5.93%. Mass spectrum *m/e*: 306 — 3 CO, —H_2, —H_2O, —54;

306 — 3 CO, —H_2O, —70. Infrared (cyclohexane): 2045, 5976-1970 cm^{-1}; (liquid film): 3620w, 3430(br) cm^{-1}.

PMR data	Proton	Chemical shift τ(ppm)	Intensity	Multiplicity
	H(2), H(3)	4.50	2	m
	H(1), H(4)	6.79	2	m
	HO	7.25	1	(br)
	H(6'), H(5), H(1')	8.32 8.50	3	m m
	H(3'), H(3'')	8.62 8.70	6	d d
	H(6)	8.65	?	?
	H(2'')	9.18 930	3	d[a] d[a]

[a] Two isomers.

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