REACTIONS OF THE ORGANIC LIGAND IN TRICARBONYLDIENEIRON COMPLEXES.

by

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The work described in this thesis is the candidate's own, except where otherwise stated. It was carried out in the Research School of Chemistry, The Australian National University from 1968 to 1971 during the tenure of a research scholarship from The Australian National University.

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SUMMARY.

The formation of tricarbonylcyclohexa-1,3-dieneiron complexes in the reaction of carbomethoxy substituted cyclohexa-1,4-dienes with iron pentacarbonyl, and abstraction of hydride ion from these complexes have been investigated with a view to discovering the effect of interaction of the strongly electron withdrawing group with the diene. The carbomethoxy group is not found to have significantly more directing effect than the previously studied alkyl and alkoxy substituents in these reactions.

Equilibration of isomeric mixtures in acid or base, however, leads to exclusive production of the isomer having the coordinated 1,3-diene fully-conjugated to the ester group. The cross-conjugated isomer has been obtained by direct reaction of the free cyclohexa-1,3-diene with iron pentacarbonyl. Carboxy substituted complexes have been synthesised via hydrolysis of the carbomethoxy compounds, and reduction with diborane leads, in turn, to the corresponding primary alcohols.

A bis(tricarbonyliron) complex has been isolated from the reaction of hexahydroanthracene with iron carbonyls; further reactions produce a series of related complexes.

Attempted isolation of two reported isomers from the reaction of tricarbonylthebaineiron with triphenylphosphine has led to the conclusion that only one isomer of the mono-phosphine complex is formed in the displacement reaction.

CONTENTS.

GENERAL INTRODUCTION

a. Historical.

Interest in transition metal complexes containing π-bonded ligands has increased rapidly over the last two decades. The discovery of ferrocene[1,2] and, more importantly, swift elucidation of its structure[3-8] in 1951-52 initiated many wide-ranging investigations and provided insight into the constitution of a number of previously reported but somewhat mystifying compounds.

The first of such compounds dated from the early 19th century; however lack of an adequate explanation of the new phenomena encountered led to the extremely slow development of organotransition metal chemistry. Only the comparatively recent advent of molecular orbital theory has brought forward a satisfactory description of the compounds.

In 1827 W.C. Zeise reported the preparation of a salt consisting of the elements $KCl.PtCl_2.C_2H_4.H_2O$.[9,10] The discoverer's claim that this stable, crystalline substance contained ethylene sparked a controversy[11] which was not finally resolved for many years.[12-14] In 1868 Birnbaum succeeded in isolating the propene- and pentene-containing analogues of this salt[15] which lent support to the essential validity of Zeise's views, but the exact nature of the compounds remained unknown.

Subsequently the first of the metal carbonyl compounds were discovered, $Ni(CO)_4$[16], $Fe(CO)_5$[17,18] and several chloroplatinum carbonyls[19] (1890-91) then the polynuclear iron carbonyls and $Co_2(CO)_8$ by 1910.[20] The uncertain stoichiometry and unknown structural details of these substances added further problems, apparently unrelated to Zeise's work, to the field of transition metal compounds.

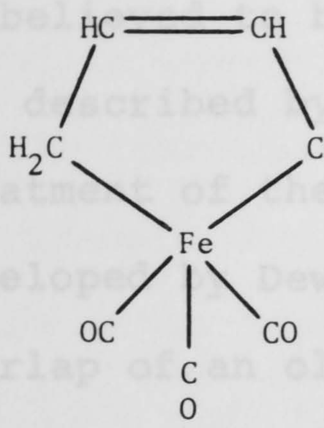
An investigation into the bonding of iron pentacarbonyl by Reihlen and coworkers in 1930 led to the first preparation of a metal complex containing a conjugated diolefin.[21] Heating the carbonyl with butadiene gave a yellow liquid, mildly unstable towards light and oxygen but distilling unchanged under vacuum, with an elemental analysis corresponding to $C_4H_6Fe(CO)_3$. The structure (1), involving carbon to iron σ-bonds, was postulated for their compound by these workers. Isoprene and 2,3-dimethylbutadiene appeared to give similar products but these were less well defined.

Later work, notably by Hel'man between 1936 and 1946, extended the range of known olefin complexes of platinum and also included carbonyl and nitrosyl ligands.[22-25] The beginnings of a successful molecular orbital description of the bonding in these compounds appeared in the early 1950's.[26,27]

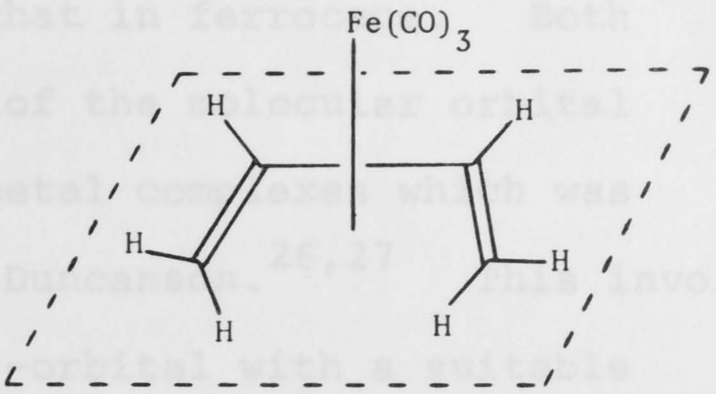
A reinvestigation of Reihlen's butadiene-iron tricarbonyl compound by Hallam and Pauson (1958) in the light of results stemming from studies of the ferrocene series suggested that the complex actually had the π-bonded structure (2).[28] The iron carbonyl unit here occupies a position above the planar cisoid diene. This structure has since been confirmed by X-ray diffraction.[29,30]

At the same time Hallam and Pauson prepared the analogous tricarbonylcyclohexa-1,3-dieneiron, a yellow liquid with physical properties similar to the butadiene complex. Both are diamagnetic and crystallise below room temperature.

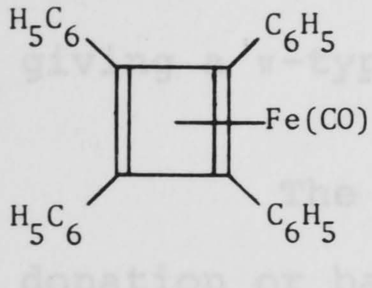
Many tricarbonyliron complexes containing a wide range of cyclic and acyclic dienes have since been synthesised. Apart from the biscyclopentadienyl metal series, these form one of the largest classes of transition metal organometallic compounds. Some examples are shown in structures (3) to (9).[31-38] The preferred formation of the diene-$Fe(CO)_3$ structural unit is seen in several of these compounds. A number of tetracarbonyliron complexes of mono-olefins are known[39-41], but no mononuclear complex containing a conjugated triene or an aromatic ligand combined with the dicarbonyliron group has yet been reported. Recently, however, Pettit and coworkers have prepared dicarbonyltrieneiron complexes containing a conjugated diene and one other isolated olefinic bond coordinated to a single iron atom which bears only two carbonyl groups.[42,43]


HC
CH
H_2C
CH_2
Fe
OC
CO
C
O

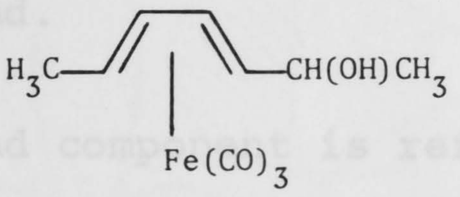
(1)


Fe(CO)$_3$
H
H
H
H
H
H

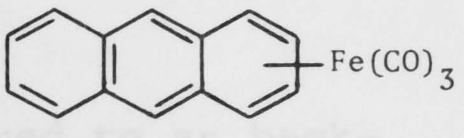
(2)


H_5C_6
C_6H_5
Fe(CO)$_3$
H_5C_6
C_6H_5

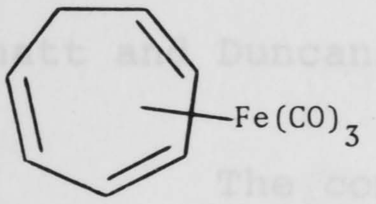
(3)


H_3C
CH(OH)CH$_3$
Fe(CO)$_3$

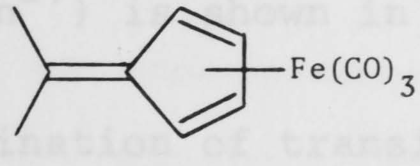
(4)


Fe(CO)$_3$

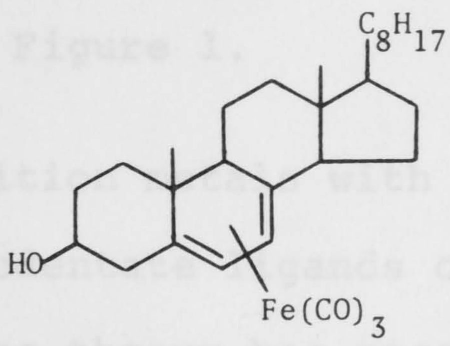
(5)


Fe(CO)$_3$

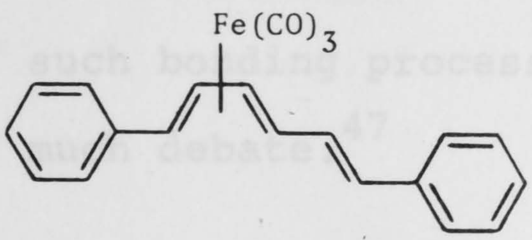
(6)


Fe(CO)$_3$

(7)


C_8H_{17}
HO
Fe(CO)$_3$

(8)


Fe(CO)$_3$

(9)

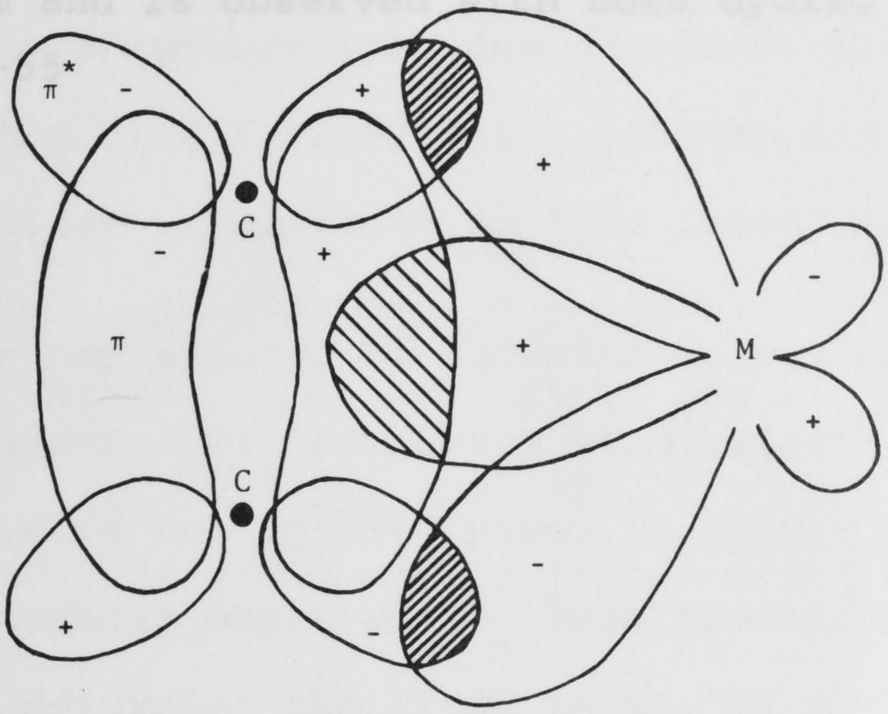
b. Bonding.

The organic ligand to iron bond in these compounds is believed to be similar to that in ferrocene. Both are described by an extension of the molecular orbital treatment of the mono-olefin metal complexes which was developed by Dewar, Chatt and Duncanson.[26,27] This involves overlap of an olefin bonding π-orbital with a suitable hybrid orbital on the metal atom to form a σ- (or μ-) type bond and simultaneous overlap of a different, filled metal hybrid orbital with the antibonding π-orbital of the olefin, giving a π-type bond.

The second component is referred to as back-donation or back-bonding from the metal to the ligand and plays an essential part in stabilising these complexes. A schematic representation of this bonding process (due to Chatt and Duncanson[27]) is shown in Figure 1.

The combination of transition metals with carbon monoxide and other unsaturated monodentate ligands can be described in the same terms, and the theory has recently been extended to acetylene-metal complexes.[44-46] The details of such bonding processes are, however, still the subject of much debate.[47]

In ferrocene and its analogues, and in the complexes of diene, triene and aromatic organic ligands, the orbitals involved in bonding are π- and π^*-molecular orbitals delocalised over all carbon atoms of the conjugated system, four in the diene case. This leads to the situation observed in the results of X-ray crystal structure



▨ σ - component overlap

▨ π - component overlap

Figure 1   Metal-olefin bond

determinations where the metal atom is approximately equidistant from (and therefore "equally bonded" to) all four carbon atoms of the planar diene. These carbons maintain essentially sp^2 hybridisation, although substituents on the terminal diene carbons are bent out of the plane of the diene, away from the metal. This twisting seems to allow better overlap of the diene orbitals with those of the iron atom and is observed with both cyclic and acyclic dienes.[30,48-55]

c. Spectral properties of tricarbonyldieneiron complexes.

The major practical problem faced in previous work on tricarbonylcyclohexa-1,3-dieneiron complexes, and in the studies described in the following pages, has been the detection of isomers produced by substitution at the different carbon atoms of the cyclohexadiene ring. Measurement of the H^1 nuclear magnetic resonance (nmr) spectra of the compounds provides the most effective physical method of differentiating between isomers, and has been utilised extensively in this research.

The nmr spectra of butadiene-, cyclohexadiene- and other diene-$Fe(CO)_3$ complexes were reported soon after the appearance of the initial paper of Hallam and Pauson.[34,56] From the resonances observed in these spectra attempts have been made to determine the exact nature of the bond to the metal atom, especially to distinguish between the fully delocalised π-bonding of (10) and the more localised electronic structure represented by (11).[56] The results, however, are not conclusive. More recent studies, including the calculation of theoretical spectra[57,58] and the measurement of C^{13} and F^{19} spectra [of the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ series][57,59,60] have yielded more definitive results.

Tricarbonylbutadieneiron shows three symmetrical bands of equal intensity at τ4.72, τ8.32 and τ9.78. The downfield signal is assigned to the hydrogens on the central carbon atoms of the butadiene molecule and the other two signals to one hydrogen on each of the two terminal carbons. The symmetrical peaks of the spectrum indicate a symmetrical environment for the butadiene molecule. The different chemical shifts of the exo and endo terminal hydrogens is ascribed to magnetic anisotropy associated with the tricarbonyliron group lying above the plane of the hydrocarbon.

The nmr spectrum of tricarbonylcyclohexa-1, 3-dieneiron is similar, showing complicated peaks at $\tau 4.78$, $\tau 6.86$ and $\tau 8.37$ with intensities in the ratio 1:1:2. These bands are assigned to the two "inner" diene hydrogens, the two "outer" diene hydrogens and the four methylene hydrogens respectively. Wilkinson et al. have measured the coupling constants between the two inner hydrogens (4.1 c/s), between inner and nearer outer hydrogen (6.6 c/s) and between inner and remote outer hydrogen (1.5 c/s).[34]

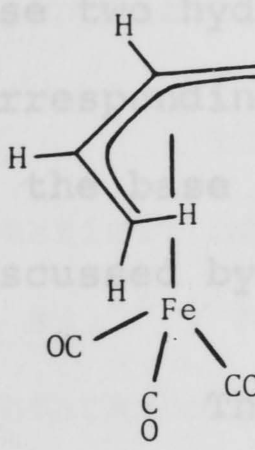
Complexes of substituted cyclohexa-1,3-dienes give analogous nmr spectra. The positions of substitution are readily determined by an examination of (i) the integrated ratios of peaks corresponding to the different positions on the ligand, (ii) the coupling constants observed in the spectrum, and (iii) the chemical shifts of any hydrogens on the substituents themselves. These last values are generally quite sensitive to the position of substitution. For example methyl and methoxy substituents on inner, outer and methylene carbons, respectively, of the cyclohexadiene ring have chemical shifts of $\tau 7.78$, 8.22, 9.10 (methyl) and $\tau 6.40$, 6.55, 6.85 (methoxy).[61] Similar effects are shown by other substituents described in later sections of this thesis.

The infrared (ir), ultraviolet (uv) and mass spectra of the complexes, although quite diagnostic of the presence of the tricarbonyldieneiron system, do not have the utility of nmr in the differentiation of isomeric compounds.

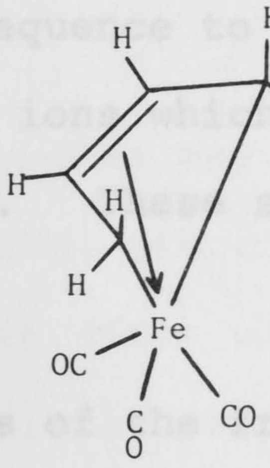
The carbonyl stretching bands are the major features of the ir spectra of the unsubstituted or substituted diene complexes. They occur as two very intense absorptions, one sharp and one broad, in the region of 2000 cm^{-1}. The broad, lower energy band in fact consists of two overlapping stretching frequencies, as required by the structural asymmetry observed in the tricarbonyldieneiron unit.[30] These two bands can be resolved in the ir spectra of some of the complexes.[60,62]

The unsubstituted butadiene and cyclohexadiene complexes show absorptions at 2053(sharp), 1980 (broad) cm^{-1} and 2045 (sharp), 1975 (broad) cm^{-1} respectively.[62]

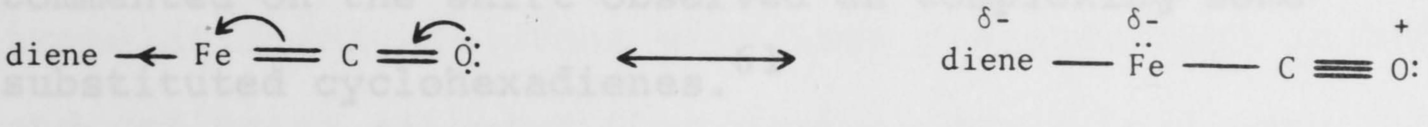
The values are sensitive to changes in the electronic properties of the dienes. Greater electron accepting capability of the diene induces greater back-donation of electrons from the iron atom and a consequent increase in the bond order of the carbonyl groups, as shown in Scheme 1. A larger contribution from mesomeric form (b) leads to a shift of the carbonyl frequencies to higher wavenumber in the ir spectrum. This effect is particularly apparent in the tricarbonyldienyliron cations where the two carbonyl bands occur at 2100-2120 cm^{-1} and 2040-2070 cm^{-1}.[32,61] Substitution of the diene by electron



(10)



(11)



(a)

(b)

Scheme 1

withdrawing groups produces a similar effect, the shifts to higher wavenumbers may be up to 70 cm^{-1}.[63]

Mass spectra of the complexes show a characteristic fragmentation process, with successive losses of three carbonyl groups then the iron atom from the parent molecular ion. The cyclohexadiene derivatives, in addition, lose two hydrogens during this sequence to form the corresponding aromatic molecular ions which usually appear as the base peaks of the spectra. These spectra have been discussed by Haas and Wilson.[64]

The uv absorption bands of the free dienes move to lower wavelengths on complex formation. Butadiene (λ_{max} 217mμ, log ε_{max} 4.3)[65] drops to λ_{max} 211mμ, log ε_{max} 4.36 in $C_4H_6Fe(CO)_3$[28] and cyclohexadiene (λ_{max} 256mμ, log ε_{max} 3.9)[66] to λ_{max} 207mμ, log ε_{max} 4.36 in $C_6H_8Fe(CO)_3$.[28] Uv spectra, however, have not been utilised to any great extent in studies of the complexes. Birch <u>et</u> <u>al</u>. have commented on the shift observed on complexing some substituted cyclohexadienes.[61]

d. Chemistry of the tricarbonylcyclohexadieneiron complexes.

As the substituted cyclohexa-1,3-diene complexes form the exclusive subject matter of following sections, only their chemical behaviour is reviewed here. Any details of the chemistry of related complexes which are pertinent to later discussions are introduced in the appropriate sections.

The preparation of a complex may be tackled by a variety of methods. The original procedure of Reihlen et al.[21], heating the appropriate diene with iron pentacarbonyl, remains a synthetically useful one. The introduction of a refluxing solvent rather than reaction of the neat diene with iron pentacarbonyl in an autoclave adds convenience to this method. The solvent of choice is di-n-butyl ether, which Cais and Moaz found to give higher yields than less polar hydrocarbon solvents.[63]

Other methods of preparation include ultraviolet irradiation of the diene with iron pentacarbonyl in benzene, and refluxing either diiron enneacarbonyl in diethyl ether or triiron dodecacarbonyl in benzene with the diene. The yield of complex is usually low in all of these reactions. Refluxing the diene and iron pentacarbonyl in dibutyl ether gives the most satisfactory result in many cases, with yields between 15% and 40%.

The most significant feature of the above procedures is the isomerisation of 1,4- to 1,3-dienes under the influence of the iron carbonyl, generally with simultaneous formation of the 1,3-diene complex. First observed by Arnet and Pettit[67], extensive use has since been made of this reaction, especially in the preparation of substituted tricarbonylcyclohexa-1,3-dieneiron complexes.

The ease of synthesis of certain substituted cyclohexa-1,4-dienes via the Birch reduction of the corresponding benzene derivatives[68] has led to the production of many complexes which otherwise would have been accessible only by more laborious pathways. The majority of such complexes bear methyl and methoxy substituents which, in some cases, bring about distinct modifications to the reactions of the unsubstituted complex.

Tricarbonylcyclohexa-1,3-dieneiron itself undergoes one notable reaction. Abstraction of a hydride ion from one methylene carbon gives rise to the stable tricarbonylcyclohexadienyliron cation.[69] Birch _et al_. have given a comprehensive report of this reaction, applied both to the unsubstituted complex and its methyl and methoxy substituted derivatives.[61]

The nmr spectrum of the cyclohexadienyl complex shows five lines with integrated ratios of 1:2:2:1:1.[70] Their chemical shifts and assignments are: τ2.66 (triplet, the hydrogen on the central carbon atom of the dienyl system), τ4.08 and τ5.66 (triplets, both actually overlapping double doublets, the two inner dienyl hydrogens and the two outer dienyl hydrogens respectively), τ6.86 and 7.09 (double triplet, one methylene hydrogen, probably in the _exo_ position) and τ7.85 and 8.11 (doublet, the second methylene hydrogen). Coupling constants observed between different pairs of hydrogens in the spectrum are: central hydrogen and inner, 5.5 c/s; inner and outer, 6.0 c/s; outer and the lowfield methylene, 6.5 c/s; and between the geminal methylene hydrogens, 15.0 c/s.

As in the case of the neutral cyclohexadiene complexes, the substituted cationic complexes have nmr spectra analogous to the unsubstituted one. The positions of substitution are determined by an examination of the three criteria listed previously.

The ir carbonyl absorptions of the cyclohexadienyl complexes were discussed above. Tricarbonylcyclohexadienyliron shows these bands at 2115 cm^{-1} (sharp, very strong) and 2053 cm^{-1} (broad, very strong). An additional feature of the spectra of this complex and its substituted derivatives is a sharp peak of low to medium intensity at 3010-3080 cm^{-1}, assigned to the C-H stretching frequency of the dienyl system.[70] Absorptions due to the anion associated with the complexed cation (e.g. BF_4^-, PF_6^-, ClO_4^-) are of course also observed.

Hydride abstraction is generally accomplished using triphenylmethyl fluoroborate in methylene chloride solution, the complexed carbonium ion being isolated as its yellow fluoroborate salt. The unsubstituted salt is soluble in water giving a stable solution of the cation, which can be precipitated by the addition of fluorophosphate anion. Precipitation in this way has been used to purify substituted cyclohexadienyl complexes.

In solution the cation is susceptible to attack by a variety of nucleophiles, including H^- (as $NaBH_4$), CN^-, OH^-, CH_3^- (as CH_3Li), OCH_3^-, secondary amines (pyrrolidine, piperidine, morpholene) and active methylene groups (malonic ester, acetylacetone, dimedone). Specific attack of the nucleophile on the terminal carbon atom of the dienyl system produces a 5-exo-substituted tricarbonylcyclohexa-1, 3-dieneiron complex. Further triphenylmethyl fluoroborate treatment of the OH, OCH_3, CN and $CH(COCH_3)_2$ substituted compounds so obtained serves to specifically re-abstract the nucleophile and regenerate the initial salt.

Methyl and methoxy substituted complexes give an analogous hydride abstraction reaction. Substitution of the cyclohexadiene ring creates the possibility of loss of hydride from one of two non-equivalent methylene carbons. This possibility is generally realised in practice and the reaction of a single substituted complex leads to the isolation of two substituted tricarbonylcyclohexadienyliron cations.

Similarly, attack of a nucleophile on a non-symmetrically substituted dienyl cation gives two products. Factors influencing preferential hydride abstraction from, and nucleophilic additions to, unsymmetrical complexes have been studied by Haas.[71]

The properties of the cyclohexadienyl complexes are not greatly affected by alkyl substituents. A methoxy group at one terminal carbon of the dienyl system, however, allows a facile hydrolysis in warm water with production of tricarbonylcyclohexa-2,4-dienoneiron. The organic ligand here is a tautomer of phenol, stabilised by complex formation.[61]

As with the cyclohexadienyl cations described above, methoxy substitution of the neutral cyclohexadiene complexes affects their reactions to a greater degree than does alkyl substitution. Hallam and Pauson found that tricarbonylcyclohexadieneiron could be recovered unchanged from its solution in cold concentrated sulphuric acid[28], and this acid has since been employed in the equilibration of isomers of alkyl substituted complexes.[72] Any of the methoxy substituted isomers, however, react under these conditions to produce cyclohexadienyl salts.[72] An initial equilibration followed by loss of methoxide ion from the terminal carbon atom of the developing dienyl group gives the cyclohexadienyl complex. Several substituted complexes not easily accessible by other routes have been prepared in this manner.

Displacement of the carbonyl groups in the cyclohexadiene complexes by triphenylphosphine and similar ligands has also received attention. Ultraviolet irradiation of tricarbonylcyclohexa-1,3-dieneiron with triphenylphosphine gives the products of replacement of one and two carbon monoxide groups.[73] The monophosphine derivative is stable and its chemical behaviour seems to be largely unchanged from the tricarbonyl compound. The diphosphine compound is rather less stable, while isolation of the product resulting from complete replacement of the carbonyl groups has yet to be reported. Similar reactions on the complexes of other dienes have led to displacement of the organic ligand from the metal in some cases, while replacement of the carbonyl groups occurs in others.[74,79,108] Section C discusses an extension of this reaction to the complex of a larger organic molecule.

One further property of the complexes which deserves mention is the ability of the tricarbonyliron moiety to prevent a coordinated diene entering into many of the usual reactions of this system. Thus the butadiene complex is found to be "unaffected by hydrogen in the presence of Adams catalyst and by boiling with maleic anhydride in benzene solution for 48 hours".[28] This property has been used to carry out selective reactions (*e.g.* hydrogenation) on one part of a molecule while protecting the complexed site.[61,75,76]

SECTION A. CARBOXY SUBSTITUTED COMPLEXES AND DERIVATIVES.

INTRODUCTION

The majority of previous work on tricarbonylcyclohexa-1,3-dieneiron complexes has been concerned with those containing simple alkyl and alkoxy substituents, notably methyl and methoxy (see General Introduction and references quoted therein).

These substituents do not exert a great influence, steric or electronic, on the course of the reactions investigated. The initial formation of complexes from a substituted cyclohexa-1,4-diene and an iron carbonyl gives a mixture of isomers usually inseparable by physical or chemical means. For example 1-methoxy-5-methylcyclohexa-1,4-diene (dihydro-*m*-cresol methyl ether) gives three tricarbonyliron complexes when reacted with triiron dodecacarbonyl.[61]

Further reactions lead to more complicated mixtures, again inseparable. *e.g.* Hydride abstraction from the mixture quoted above may be expected to give up to five differently substituted tricarbonylcyclohexadienyliron cations. Nucleophilic attack on these cations could, in turn, produce ten different isomers of the (methyl-methoxy-nucleophile) substituted complex.

In general the properties of the complexes referred to above have yielded little information about the extent to which the position of the diene in the ring may be influenced by electronic interactions with substituents.

In view of the complexity encountered in the reactions of complexes bearing alkyl and alkoxy groups, it was of interest to turn to other substituents with stronger electron donating or withdrawing properties. These would have potentially greater directing effects on the coordinated diene system. The inclusion of such substituents would allow comparison with previous results and would lead ideally to the production of single isomers, or at least simpler mixtures, both in the initial formation of complexes and in their subsequent reactions.

The choice of a substituent capable of strong electronic interaction with the complexed diene was limited to one which was available as a benzene derivative and which was not affected by the conditions of the Birch reduction. Most electron-rich groups conjugated to an aromatic ring are reduced then hydrogenolysed before the aromatic system is attacked by the metal-ammonia-alcohol medium.[68] A benzylic oxygen substituent (alcohol or ether) generally suffers hydrogenolysis, and a benzylic carbonyl group undergoes facile reduction and similar hydrogenolysis before reduction of the ring commences. Styrene, benzyl alcohol, benzylmethyl ether, benzaldehyde and acetophenone all give alkylbenzenes as initial products then alkyl-1,4-dihydrobenzenes on further reduction.

Benzoic acid, however, is reduced cleanly to its 1,4-dihydro derivative.[77,78] Reduction and hydrogenolysis of the carboxylic acid are prevented by formation of the benzoate anion in the alkali metal-liquid ammonia solution. The resulting negative charge on the carboxylate function forces electron addition, and therefore reduction, to occur in the aromatic system. Benzamide is similarly reduced to 1,4-dihydrobenzamide[77]; an analogous anion formation is presumed to operate in this case.

1,4-dihydrobenzoic acid therefore presented itself as the most convenient starting point for an investigation of the effects outlined above.

Tricarbonyldieneiron complexes bearing carboxy and derived substituents have been reported in the buta-1,3-diene series by King, Manuel and Stone[79] and later by Cais and Moaz.[63] Sorbic (12a) and muconic (12b) acids as well as their esters (12c, 12d) and sorbamide (12e) are converted to complexes in the reactions of the various ligands with triiron dodecacarbonyl in benzene[79] or iron pentacarbonyl in dibutyl ether.[63] The stability and other properties of the products do not show any unexpected deviations from those of the unsubstituted butadiene complex.

It was anticipated, therefore,that complexes derived from 1,4-dihydrobenzoic acid would exhibit properties closely related to those of the tricarbonylcyclohexa-1,3-dieneiron compounds hitherto reported and that similar experimental procedures and techniques should be applicable to their investigation.

RESULTS AND DISCUSSION.

a. Tricarbonyl-1-,-2-, and -5-carbomethoxycyclohexa-1,3-dieneiron.

The direct reaction of 3-carboxycyclohexa-1,4-diene (1,4-dihydrobenzoic acid) with iron pentacarbonyl in dibutyl ether leads only to copious decomposition of the iron carbonyl and no complex is isolable from the resulting mixture. This result must be contrasted with the formation of complexes from sorbic (12a) and muconic (12b) acids under similar conditions[63], but seems to be associated with the free hydroxy group on the organic ligand. The attempted reaction of 3-(hydroxymethyl)cyclohexa-1,4-diene (1,4-dihydrobenzyl alcohol) with iron pentacarbonyl produces similar decomposition and no complex (see Section A.d).

Methylation of the acid is accomplished smoothly with diazomethane[78], and the reaction of 3-carbomethoxycyclohexa-1,4-diene with iron pentacarbonyl gives a 34% yield of complex as an orange oil which the nmr spectrum shows to be a mixture of two isomers. The major component, tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) has characteristic peaks at $\tau 6.32$ (singlet, OCH_3) and $\tau 4.6$ (complicated multiplet, two inner diene hydrogens H_2 and H_3).

The second isomer shows a singlet at $\tau 6.21$ (OCH_3) and a signal due to an inner diene hydrogen at $\tau 3.93$ (doublet of doublets, J's 7c/s and 2 c/s) which could be assigned either to H_2 of the 1-carbomethoxy isomer (14) or H_3 of the 2-carbomethoxy isomer (15). Each of these hydrogens would be expected to be similarly deshielded by the adjacent carbomethoxy group and to show similar spin-spin splitting. The peak due to H_3 of isomer (14) would, if present, be anticipated to overlap with the inner hydrogen peaks of (13).

A positive assignment of the structure of the second product could be made only after synthesis and characterisation of samples of each isomer (14) and (15) (see following results). The 1-carbomethoxy substituent is found to have its methoxy signal at $\tau 6.30$ while the 2-carbomethoxy group occurs at $\tau 6.21$.

The mixture of complexes from 3-carbomethoxycyclohexa-1,4-diene thus consists of tricarbonyl-2- and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron, (15) and (13) respectively. The proportion of the 2-isomer, calculated from the relative intensities of the inner hydrogen peaks, varies between 22% and 50% of the total yield of complex in different runs. There is no apparent reason for this variation which affects only the two isomers initially observed: none of the 1-isomer is ever detected in the reaction product.

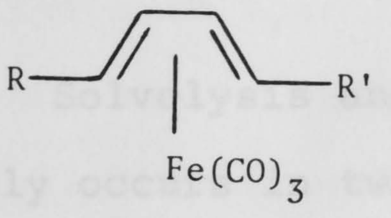
Synthesis of the pure 2-isomer (15) can be accomplished by the direct reaction of 2-carbomethoxycyclohexa-1,3-diene with iron pentacarbonyl in dibutyl ether.

Plieninger et al. have described the alkaline conjugation of 3-carboxycyclohexa-1,4-diene to 2-carboxycyclohexa-1,3-diene.[78] Methylation of the latter acid with diazomethane, followed by reaction with iron pentacarbonyl gives 38% yield of a low-melting yellow solid whose nmr spectrum shows it to be pure tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15): τ3.93 (1 hydrogen, H_3, doublet of doublets; $J_{3,4} = 7$ c/s, $J_{3,1} = 2$ c/s), τ6.21 (3 hydrogens, $COOCH_3$, singlet), τ6.30 (1 hydrogen, H_1, doublet with complicated fine splitting), τ6.64 (1 hydrogen, H_4, doublet with complicated fine splitting) and τ8.1-8.5 (4 hydrogens, H_5 and H_6). This spectrum confirms the presence of (15) in the product from 3-carbomethoxycyclohexa-1,4-diene and iron pentacarbonyl.

In an effort to prepare the pure 5-isomer (13), attempts were made to hydrolyse tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (16), which has been prepared by Pauson _et_ _al_.[80] and later by Birch _et_ _al_.[61] Since nitriles are generally hydrolysed more effectively with acid than with base, and the complexes are more stable under acidic conditions, solvolysis was first tried using a 10% solution of sulphuric acid in methanol.

Refluxing for 24 hours gives a yellow oil in high yield, whose ir spectrum shows the presence of the iron tricarbonyl moiety (2056, 1987 cm^{-1}) and of an ester group (1698, 1250 cm^{-1}). The carbonyl stretching frequency at 1698 cm^{-1}, however, appears at lower wavenumber than that of (13) (1718 cm^{-1}) and (15) (1717 cm^{-1}) which indicates that the product is actually the fully-conjugated isomer, tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14). The nmr spectrum confirms this structure: τ3.95 (1 hydrogen,

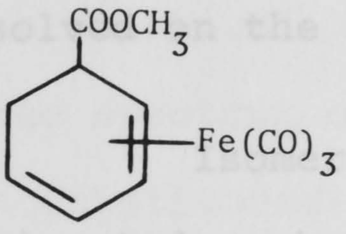
H_2, doublet; $J_{2,3}$ = 4 c/s, $J_{2,4}$ is not observed as a splitting), τ4.64 (1 hydrogen, H_3, doublet of doublets; $J_{3,2}$ = 4 c/s, $J_{3,4}$ = 6 c/s), τ6.30 (3 hydrogens, $COOCH_3$, singlet), τ6.64 (1 hydrogen, H_4, doublet with complicated fine splitting) and a complicated set of peaks τ7.6–8.7 (4 hydrogens, H_5 and H_6).



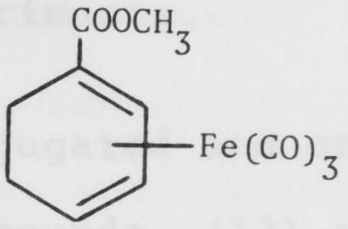
(12)

	R	R'
(12a)	CH_3	COOH
(12b)	COOH	COOH
(12c)	CH_3	$COOCH_3$
(12d)	$COOCH_3$	$COOCH_3$
(12e)	CH_3	$CONH_2$

Solvolysis and conjugation of the nitrile complex presumably occurs in two separate steps. The question of whether conjugation of the diene system to the nitrile takes place before solvolysis, or whether the carbomethoxy group is formed before conjugation occurs, can not be resolved on the basis of the above experiments.

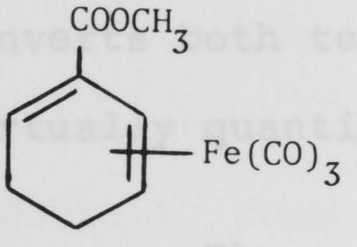


(13)

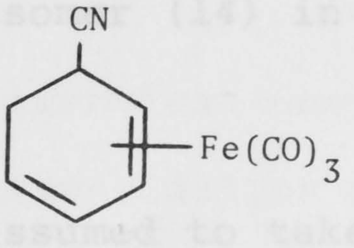


(14)

Isomerisations of the non-conjugated and cross-conjugated carbomethoxy substituted compounds, (13) and (15) respectively, are effected under the conditions employed for solvolysis of the nitrile substituted complex. Twenty-four hours' refluxing in sulphuric acid-methanol solution converts both to the fully-conjugated isomer (14) in virtually quantitative yield.



(15)



(16)

The conjugation reaction is assumed to take place via protonated species in the acidic reaction medium. That (14) is not formed during reactions at 140° with iron pentacarbonyl in refluxing dibutyl ether would seem to exclude the possibilities that the reaction (i) is a purely thermal one, and (ii) is dependent upon the ability of tricarbonyldieneiron complexes to isomerise unsaturated systems.[67,81-83]

H_2, doublet; $J_{2,3}$ = 4 c/s, $J_{2,4}$ is not observed as a splitting), τ4.64 (1 hydrogen, H_3, doublet of doublets; $J_{3,2}$ = 4 c/s, $J_{3,4}$ = 6 c/s), τ6.30 (3 hydrogens, $COOCH_3$, singlet), τ6.64 (1 hydrogen, H_4, doublet with complicated fine splitting) and a complicated set of peaks τ7.6-8.7 (4 hydrogens, H_5 and H_6).

Solvolysis and conjugation of the nitrile complex presumably occurs in two separate steps. The question of whether conjugation of the diene system to the nitrile takes place before solvolysis, or whether the carbomethoxy group is formed before conjugation occurs, can not be resolved on the basis of the above experiments.

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In order to further elucidate the mechanism of the conjugation, the conversions of (13) and (15) into (14) were conducted in deuterated methanol-deuterated sulphuric acid mixtures.

Each gives a monodeuterated isomer of (14), as shown by the mass spectrum with a molecular ion at m/e 279. Measurements of the relative intensities of peaks at m/e 278-281 indicate virtually exclusive monodeuteration, the maximum proportions of non-, di- and trideuterio isomers being 17%, 3% and 1% respectively. Surprisingly, however, the nmr spectrum of each product strongly suggests that it is an identical hydrogen, appearing as a multiplet τ7.6-8.0 in the spectrum of the nondeuterated compound, which has been substituted by deuterium. The methylene regions of the spectra now extend only over the range τ8.0-8.7 (cf. τ7.6-8.7 originally) and integration shows the presence of only three hydrogens (see Figure 2).

Refluxing an undeuterated sample of (14) under the same conditions once again gives an identical monodeuterio product. This result indicates that isomerisation of (13) and (15) occurs with no exchange of protons from the reaction medium and that stereospecific incorporation of the single deuterium takes place after the conjugation reaction.

An assignment of the methylene hydrogen at lowest field in the nmr spectrum can not be made with complete certainty. Endo and exo hydrogens in the majority of complexes of this class are not resolved by nmr and it is uncertain as to which should be expected at lower field.[84] The deshielding

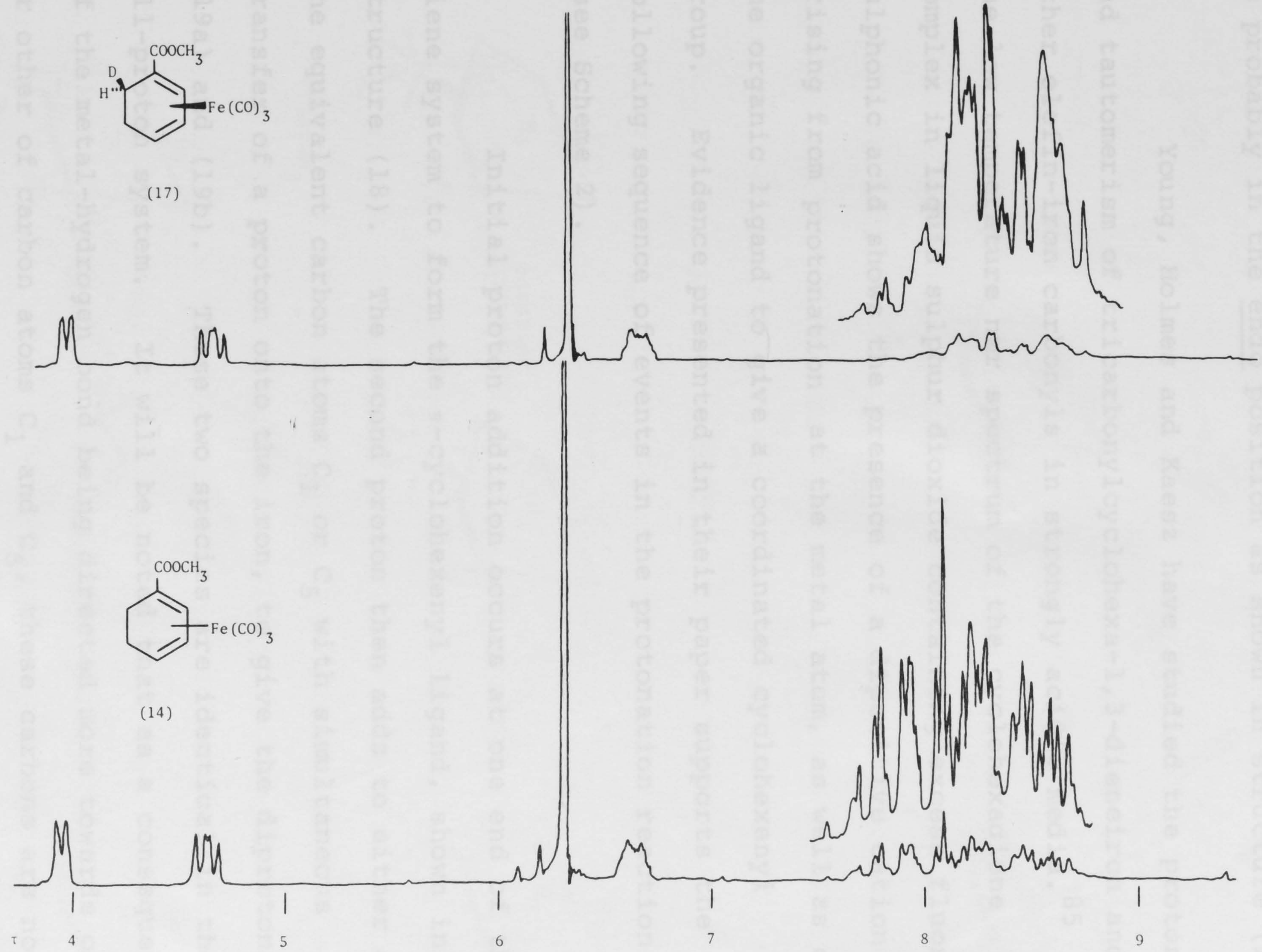


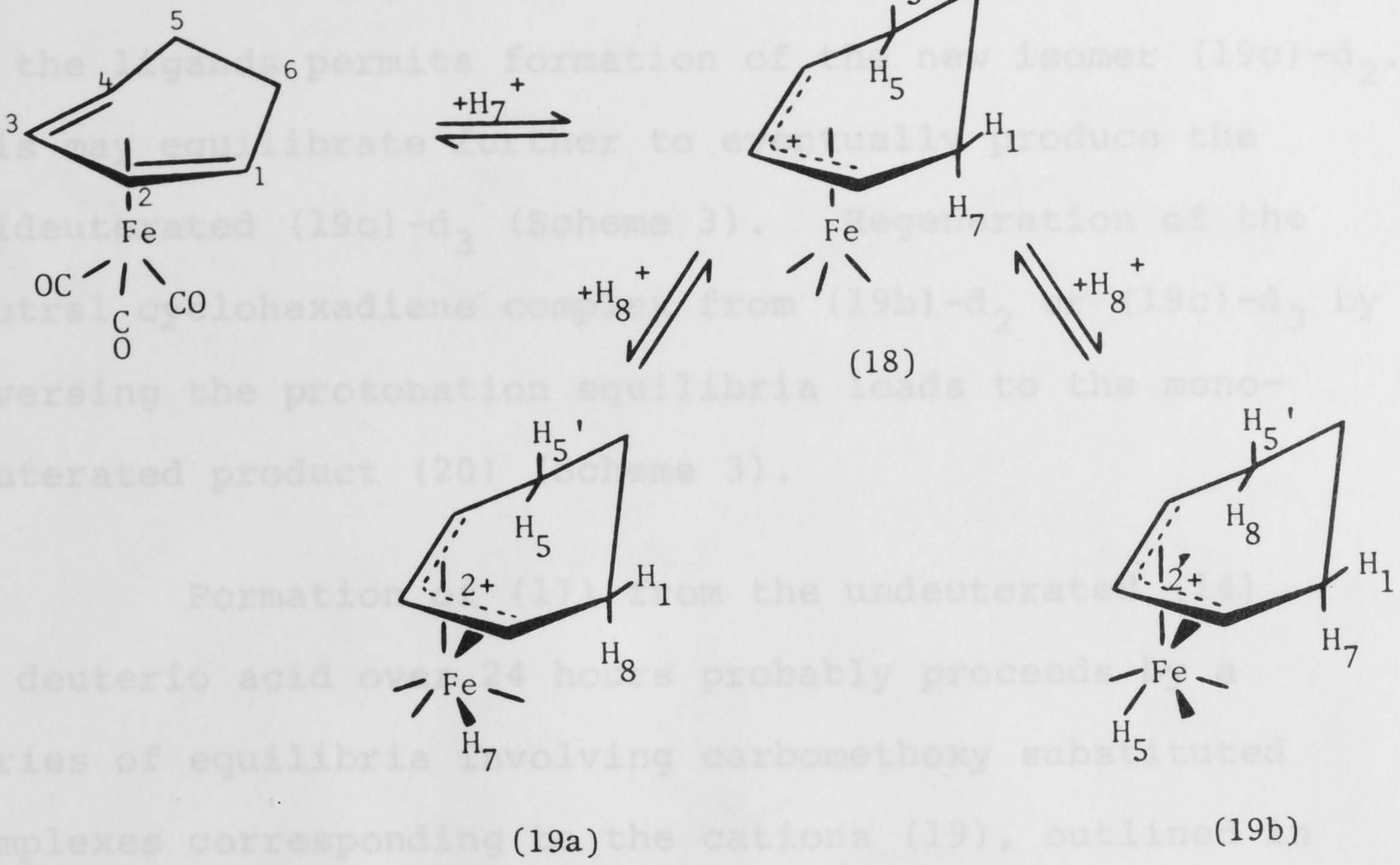
Figure 2. N.m.r. spectra of non-deuterated and deuterated tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron. Measured at 100 Mc in CDCl$_3$ solution with TMS as internal reference.

effect of the adjacent carbomethoxy function points to the hydrogen under consideration being on carbon atom 6, and the following discussion leads to the conclusion that it is probably in the endo position as shown in structure (17).

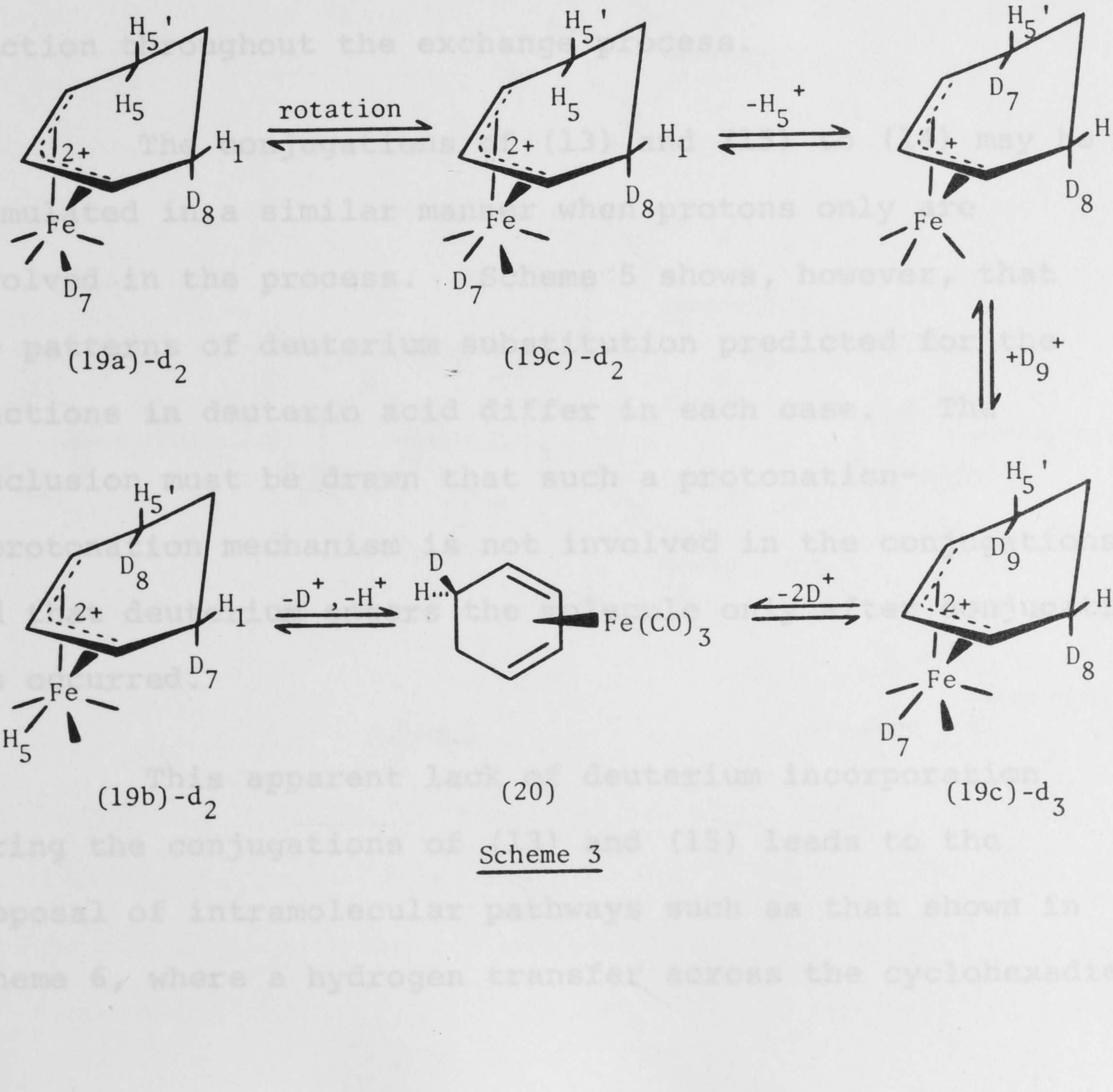
Young, Holmes and Kaesz have studied the protonation and tautomerism of tricarbonylcyclohexa-1,3-dieneiron and other olefin-iron carbonyls in strongly acidic media.[85] The low temperature nmr spectrum of the cyclohexadiene complex in liquid sulphur dioxide containing excess fluorosulphonic acid shows the presence of a dipositive cation arising from protonation at the metal atom, as well as on the organic ligand to give a coordinated cyclohexenyl group. Evidence presented in their paper supports the following sequence of events in the protonation reaction (see Scheme 2).

Initial proton addition occurs at one end of the diene system to form the π-cyclohexenyl ligand, shown in structure (18). The second proton then adds to either of the equivalent carbon atoms C_1 or C_5 with simultaneous transfer of a proton onto the iron, to give the diprotonated (19a) and (19b). These two species are identical in the all-proton system. It will be noted that as a consequence of the metal-hydrogen bond being directed more towards one or other of carbon atoms C_1 and C_5, these carbons are no longer equivalent.

In deuterio acid (19a)-d_2 and (19b)-d_2 are formed in an analogous manner. One more deuterium may then be incorporated into (19a)-d_2 over long periods of time. Slow



Scheme 2



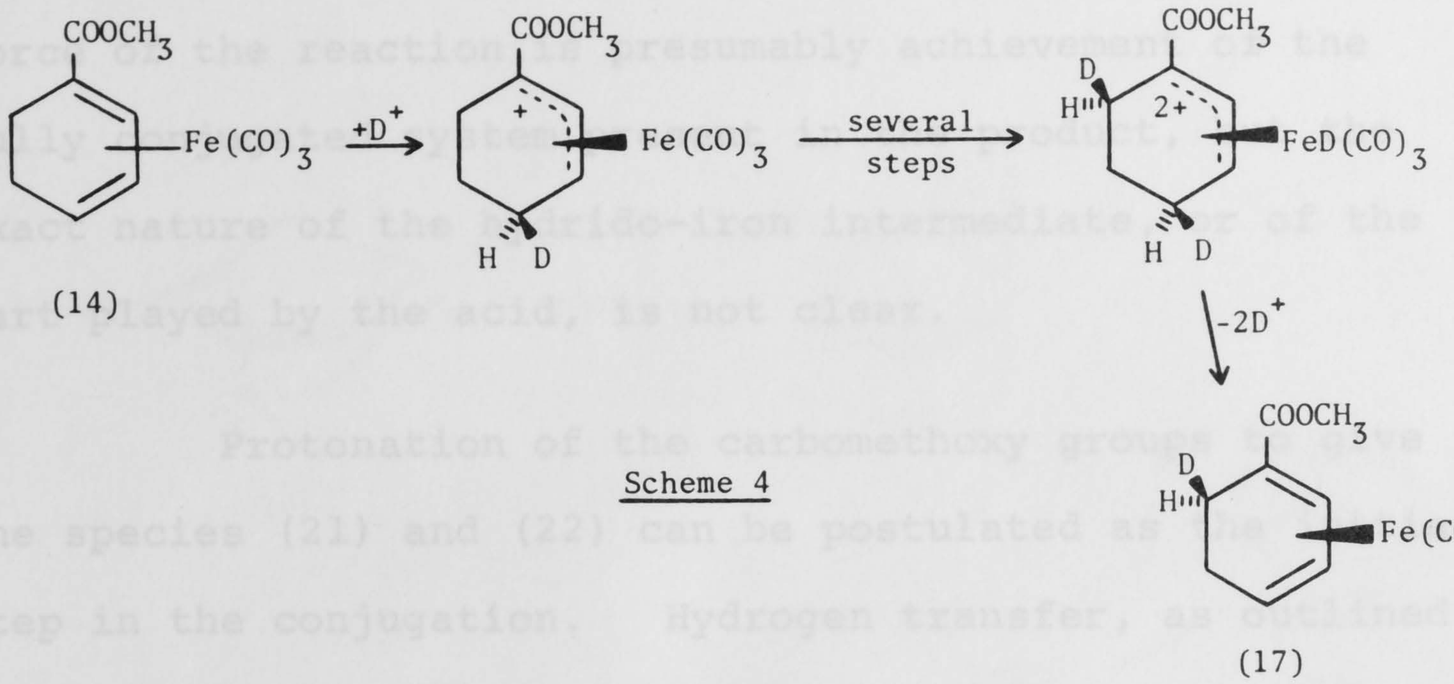
Scheme 3

rotation of the organic group with respect to the remainder of the ligands permits formation of the new isomer (19c)-d_2. This may equilibrate further to eventually produce the trideuterated (19c)-d_3 (Scheme 3). Regeneration of the neutral cyclohexadiene complex from (19b)-d_2 or (19c)-d_3 by reversing the protonation equilibria leads to the monodeuterated product (20) (Scheme 3).

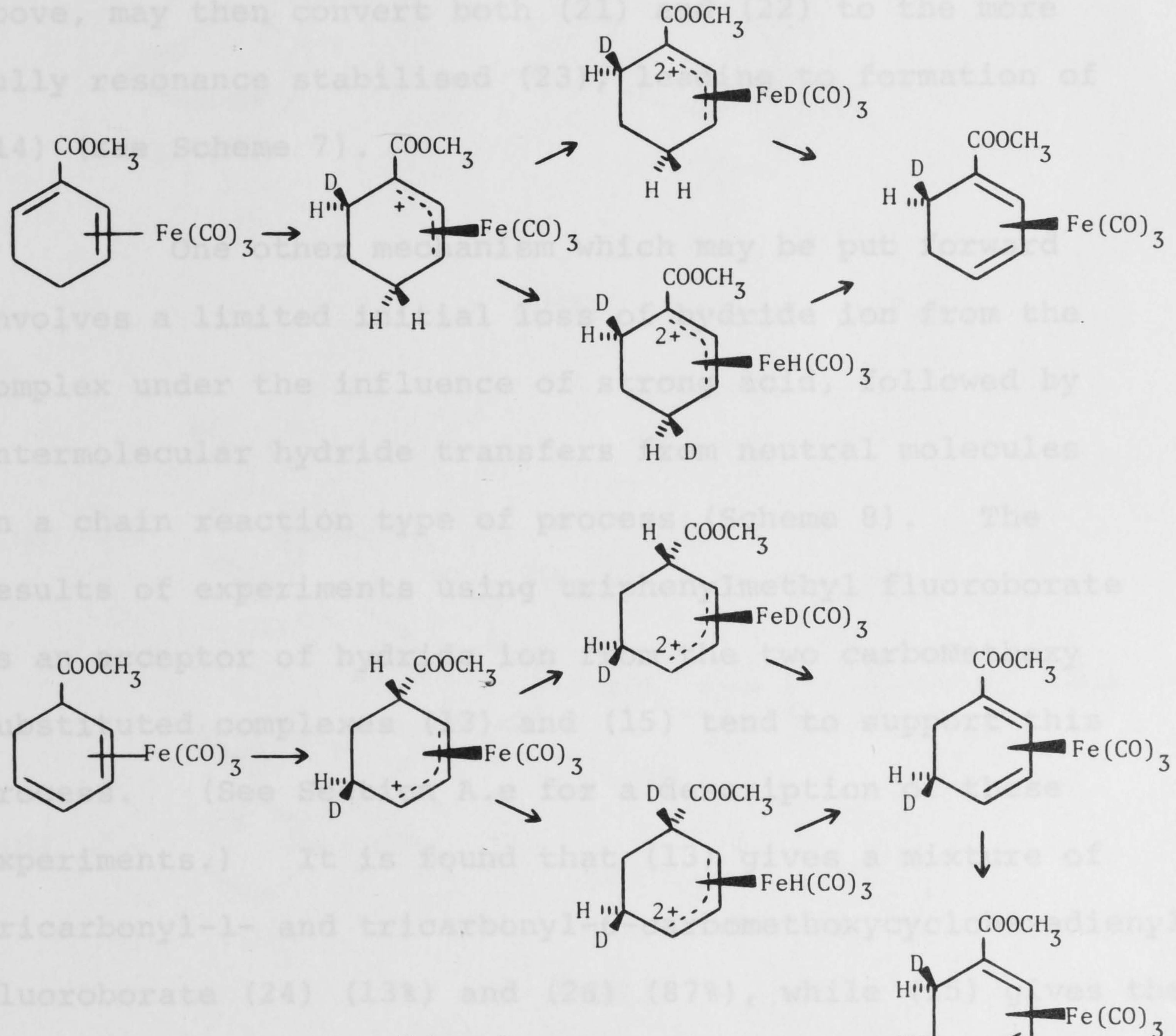
Formation of (17) from the undeuterated (14) in deuterio acid over 24 hours probably proceeds by a series of equilibria involving carbomethoxy substituted complexes corresponding to the cations (19), outlined in Scheme 4. This reaction mechanism places the deuterium in the 6-endo position of the complex. It will be noted that the π-allyl system remains in conjugation with the carbonyl function throughout the exchange process.

The conjugations of (13) and (15) to (14) may be formulated in a similar manner when protons only are involved in the process. Scheme 5 shows, however, that the patterns of deuterium substitution predicted for the reactions in deuterio acid differ in each case. The conclusion must be drawn that such a protonation-deprotonation mechanism is not involved in the conjugations and that deuterium enters the molecule only after conjugation has occurred.

This apparent lack of deuterium incorporation during the conjugations of (13) and (15) leads to the proposal of intramolecular pathways such as that shown in Scheme 6, where a hydrogen transfer across the cyclohexadiene



Scheme 4

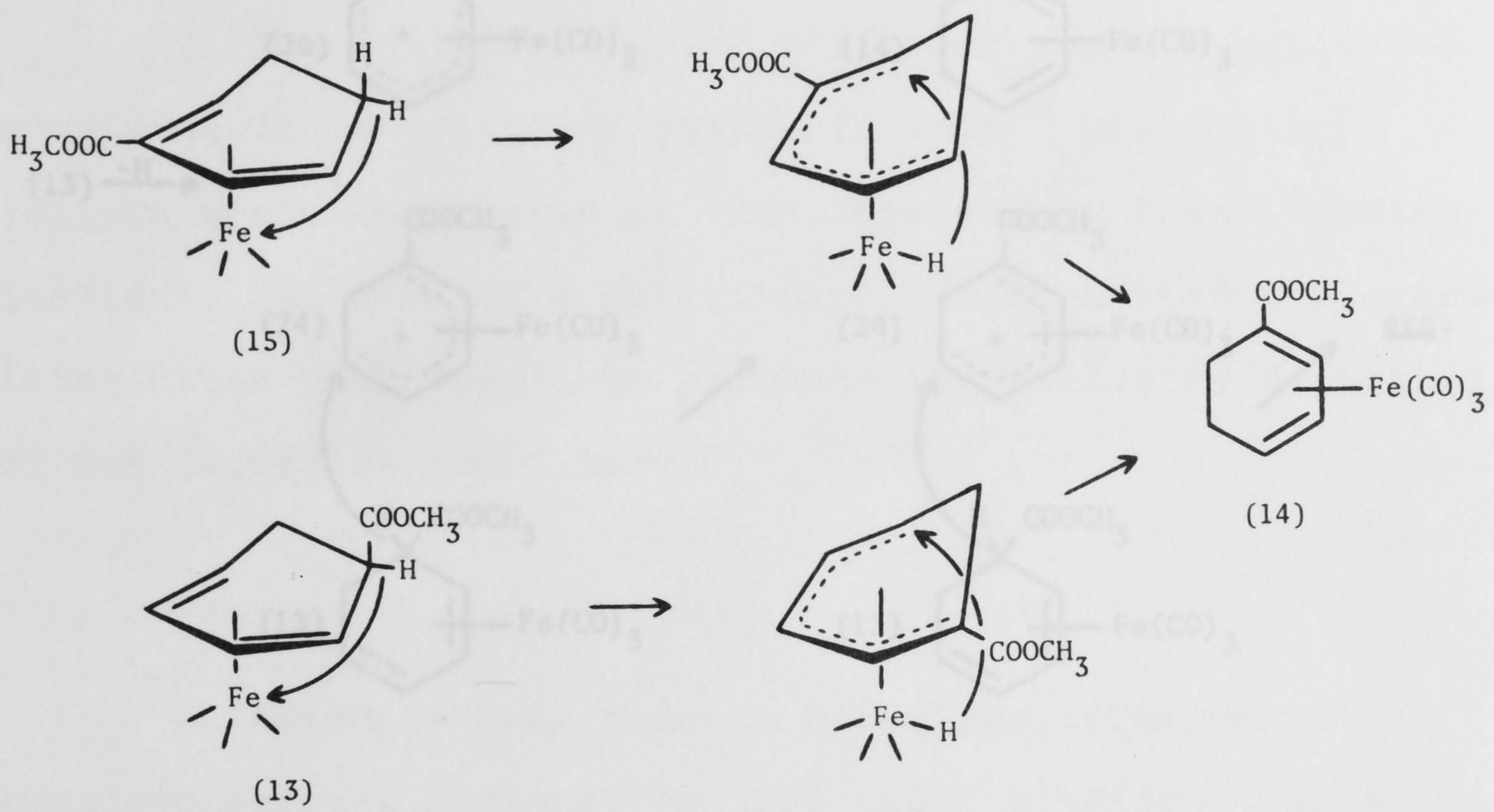


Scheme 5

ring via the iron atom eliminates the possibility of exchange with deuterium in the solvent system. The major driving force of the reaction is presumably achievement of the fully conjugated system present in the product, but the exact nature of the hydrido-iron intermediate, or of the part played by the acid, is not clear.

Protonation of the carbomethoxy groups to give the species (21) and (22) can be postulated as the initial step in the conjugation. Hydrogen transfer, as outlined above, may then convert both (21) and (22) to the more fully resonance stabilised (23), leading to formation of (14) (see Scheme 7).

One other mechanism which may be put forward involves a limited initial loss of hydride ion from the complex under the influence of strong acid, followed by intermolecular hydride transfers from neutral molecules in a chain reaction type of process (Scheme 8). The results of experiments using triphenylmethyl fluoroborate as an acceptor of hydride ion from the two carbomethoxy substituted complexes (13) and (15) tend to support this process. (See Section A.e for a description of these experiments.) It is found that (13) gives a mixture of tricarbonyl-1- and tricarbonyl-6-carbomethoxycyclohexadienyliron fluoroborate (24) (13%) and (26) (87%), while (15) gives the 2- and 3-carbomethoxy isomers (25) (20%) and (27) (80%). Readdition of hydride ion to cations (26) and (27) serves only to regenerate the original complexes (13) and (15). It is recognised (i) that the action of sulphuric acid as a hydride ion abstractor may differ from that of the triphenylmethyl

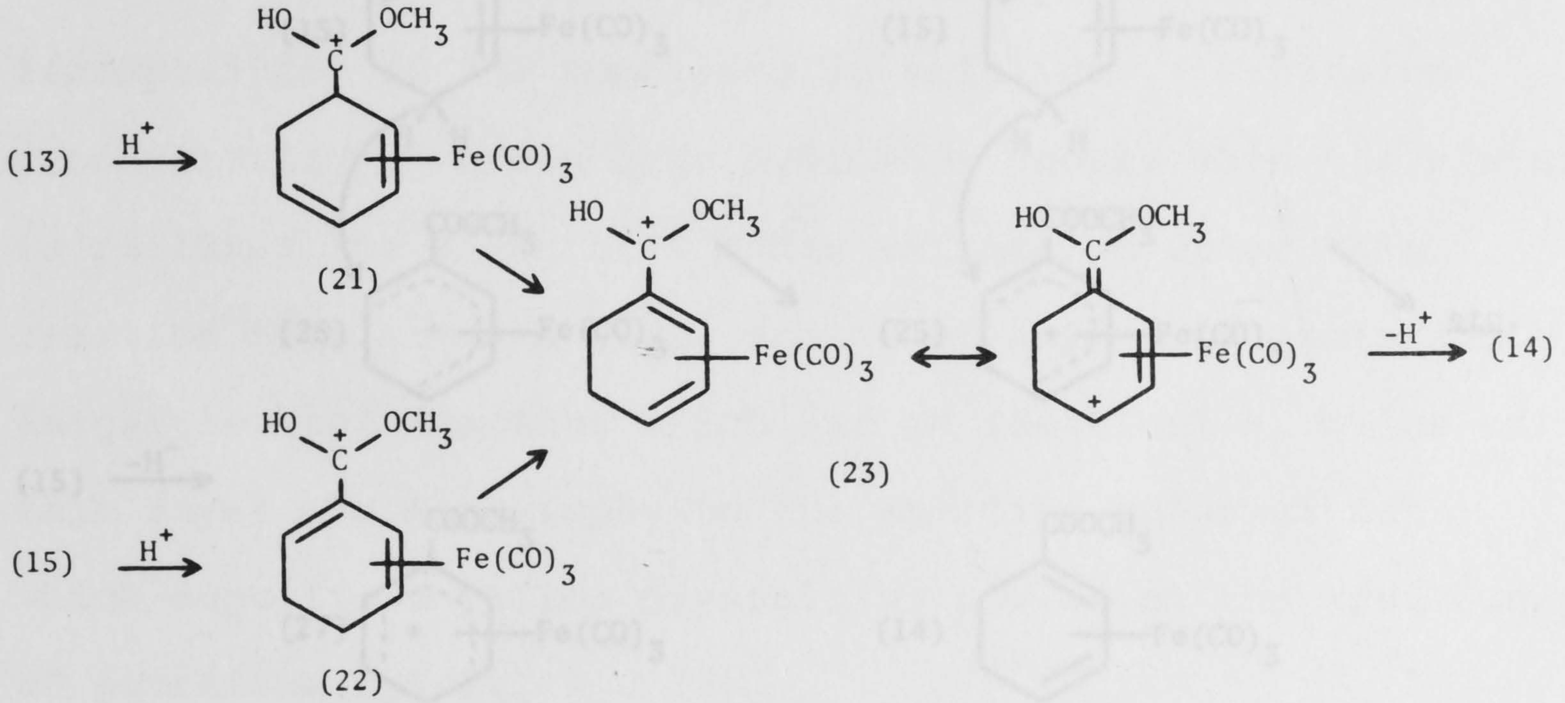


(15)

(14)

(13)

Scheme 6

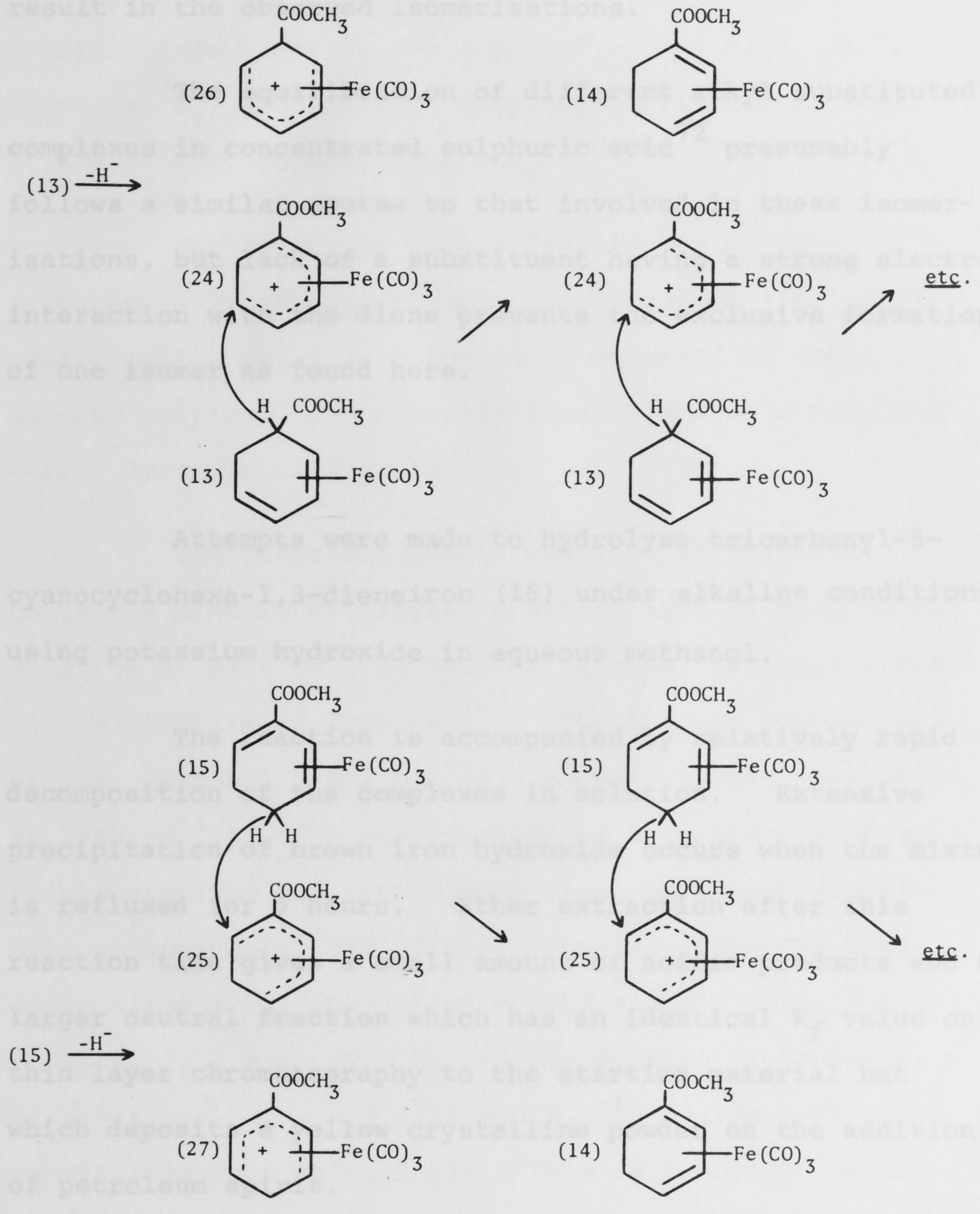


(21)

(23)

(22)

Scheme 7



Scheme 8

cation, and (ii) that hydride transfers subsequent to the initial step would have to proceed in a specific manner to result in the observed isomerisations.

The equilibration of different alkyl substituted complexes in concentrated sulphuric acid[72] presumably follows a similar course to that involved in these isomerisations, but lack of a substituent having a strong electronic interaction with the diene prevents the exclusive formation of one isomer as found here.

Attempts were made to hydrolyse tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (16) under alkaline conditions, using potassium hydroxide in aqueous methanol.

The reaction is accompanied by relatively rapid decomposition of the complexes in solution. Extensive precipitation of brown iron hydroxide occurs when the mixture is refluxed for 5 hours. Ether extraction after this reaction time gives a small amount of acidic products and a larger neutral fraction which has an identical R_f value on thin layer chromatography to the starting material but which deposits a yellow crystalline powder on the addition of petroleum spirit.

The ir spectrum of this material exhibits iron carbonyl bands at 2060 and 1970 cm^{-1}, and additional absorptions at 3480, 3150, 1650 and 1600 cm^{-1} indicate the presence of a primary amide group. The nmr spectrum shows the compound to be tricarbonyl-1-amidocyclohexa-1,3-dieneiron

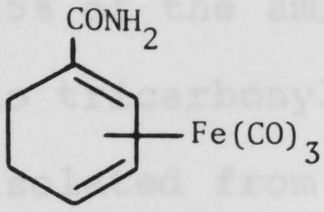
(28): τ3.90 (1 hydrogen, H_2, doublet of doublets; $J_{2,3}$= 4 c/s, $J_{2,4}$ = 1 c/s), τ4.10 (2 hydrogens, NH_2, broad and exchanging slowly with added D_2O), τ4.62 (1 hydrogen, H_3, doublet of doublets; $J_{3,2}$ = 4 c/s, $J_{3,4}$ = 6 c/s), τ6.71 (1 hydrogen, H_4, doublet with complicated fine splitting), τ7.9-8.6 (4 hydrogens, H_5 and H_6).

Nmr shows the acidic fraction to contain tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29) as the sole complex, but this compound is obtained in small amounts only and is not easily separable from uncomplexed acidic decomposition products.

The petroleum spirit washings of the amide contain a mixture displaying a strong nitrile band in the ir spectrum at 2210 cm^{-1} as well as terminal carbonyl stretches in the vicinity of 2000 cm^{-1}. (The 5-cyano complex has similar carbonyl bands but only a weak nitrile absorption at 2240 cm^{-1}.) The nmr spectrum of this mixture shows mainly aromatic and uncomplexed dihydroaromatic material with approximately 30% of tricarbonyl-1-cyanocyclohexa-1,3-dieneiron (30), identified by the signals of H_2 (τ5.79, doublet, $J_{2,3}$ = 6 c/s), H_3 (τ4.66, doublet of doublets; $J_{3,2}$ = 6 c/s, $J_{3,4}$ = 4 c/s) and H_4 (τ6.54, doublet with complicated fine splitting). This is the only complex present in the mixture.

Yields are low, those of the amide complex (28) varying between 3% and 30% in different runs and those of the acidic fraction between 10% and 17% (calculated as the pure 5-carboxy complex).

Refluxing a sample of (28) with potassium hydroxide under the above conditions results in a small acidic fraction whose nmr spectrum contains no peaks due to complexed material, 65% of the amide is recovered unchanged. Significantly, no tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29) is isolated from this reaction. It must therefore be formed independently of (13) in the hydrolysis of the nitrile (16).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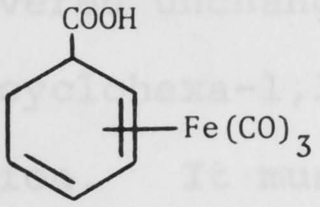
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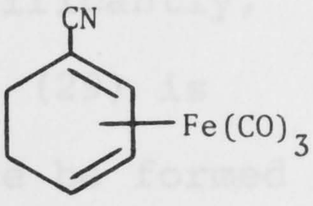
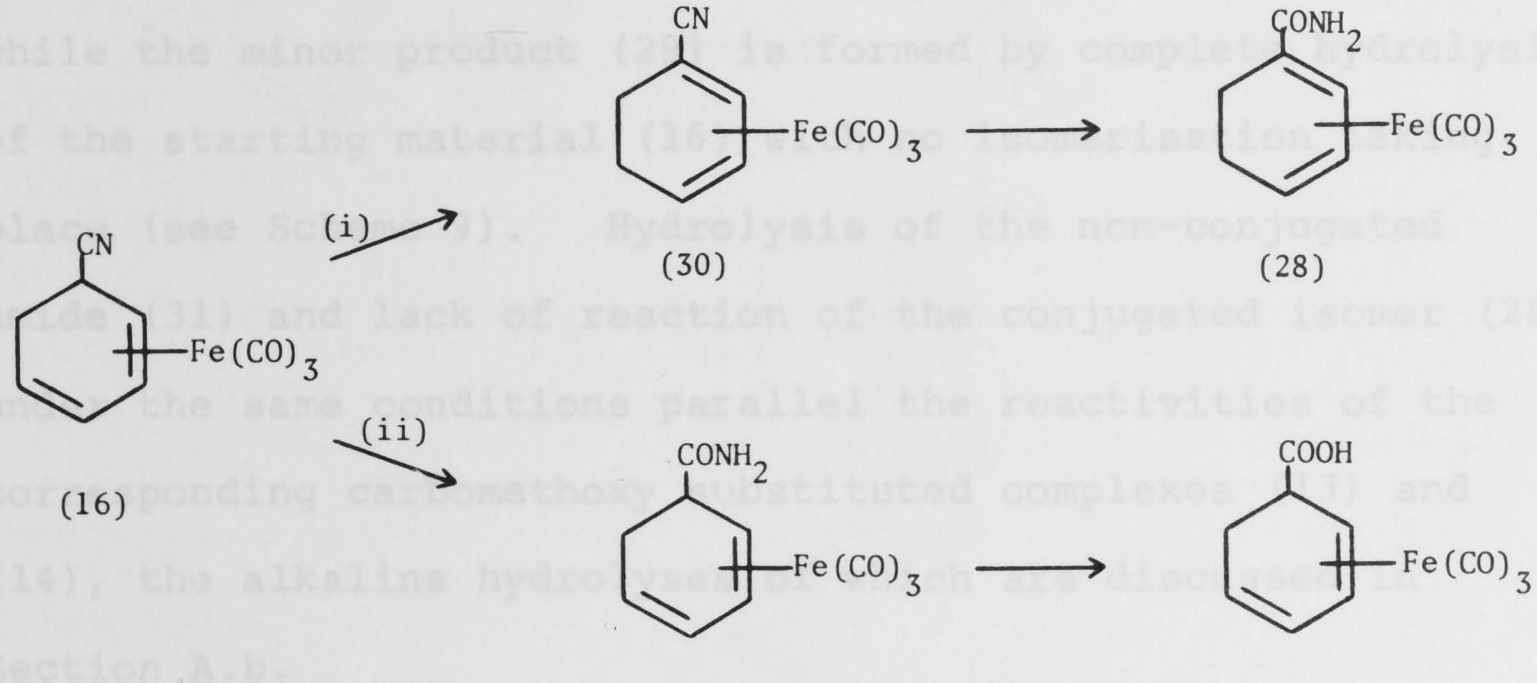

(30)

These results indicate that hydrolysis of the complex (16) occurs via two pathways. The major route involves initial conjugation to the 1-cyano isomer (30) followed by hydrolysis to the amide (28) but no further, while the minor product (29) is formed by complete hydrolysis of the starting material (16) with no isomerisation taking place (see Scheme 9). Hydrolysis of the non-conjugated amide (31) and lack of reaction of the conjugated isomer (28) under the same conditions parallel the reactivities of the corresponding carbomethoxy substituted complexes (13) and (14), the alkaline hydrolyses of which are discussed in Section A.b.



Scheme 9

The conjugation of the nitrile complex is assumed to operate by a deprotonation-protonation mechanism, shown in Scheme 10. This reaction appears to be the first example of isomerisation of a tricarbonyldieneiron complex under basic conditions.

Further basic isomerisations were attempted.

Refluxing a mixture of the 2- and 5-carbomethoxy

Refluxing a sample of (28) with potassium hydroxide under the above conditions results in a small acidic fraction whose nmr spectrum contains no peaks due to complexed material, 65% of the amide is recovered unchanged. Significantly, no tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29) is isolated from this reaction. It must therefore be formed independently of (13) in the hydrolysis of the nitrile (16).

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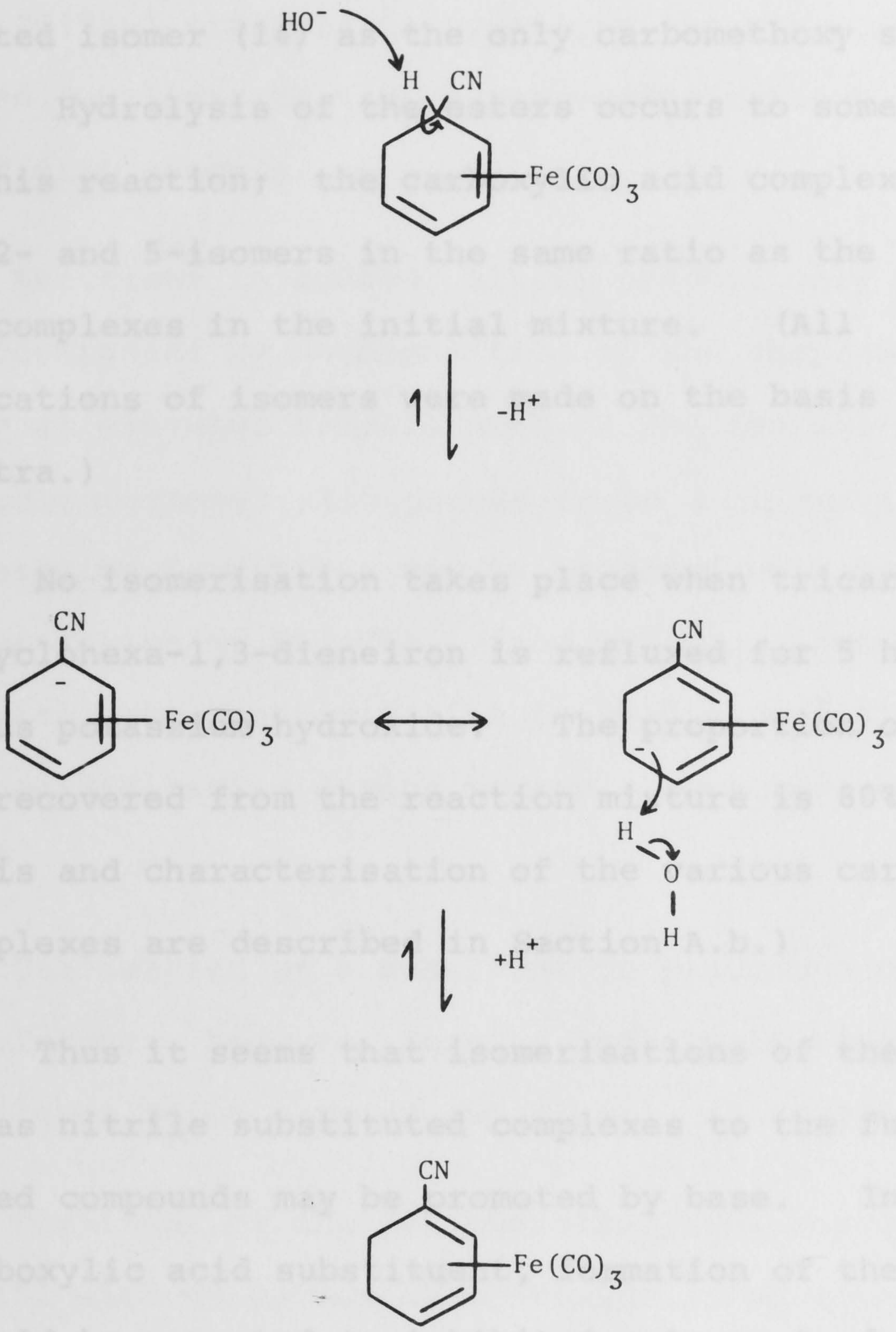


Scheme 10

substituted complexes (15) and (13) in an 8% solution of sodium methoxide in methanol for 5 hours gives the 1-substituted isomer (14) as the only carbomethoxy substituted product. Hydrolysis of the esters occurs to some extent during this reaction; the carboxylic acid complexes isolated are the 2- and 5-isomers in the same ratio as the 2- and 5-ester complexes in the initial mixture. (All identifications of isomers were made on the basis of their nmr spectra.)

No isomerisation takes place when tricarbonyl-1-carboxycyclohexa-1,3-dieneiron is refluxed for 5 hours in 3% aqueous potassium hydroxide. The proportion of starting complex recovered from the reaction mixture is 80%. (Synthesis and characterisation of the various carboxylic acid complexes are described in Section A.b.)

Thus it seems that isomerisations of the ester as well as nitrile substituted complexes to the fully conjugated compounds may be promoted by base. In the case of a carboxylic acid substituent, formation of the carboxylate anion would be expected to inhibit development of further negative charge on the molecule. Subsequent deprotonation of the ring is apparently prevented and no isomerisation (conjugation or deconjugation) occurs.

b. Hydrolysis of the carbomethoxy substituted complexes.

Initial attempts to hydrolyse the carbomethoxy substituted complexes to the corresponding carboxylic acids met with little success.

Reactions in aqueous alkali proceed only slowly and are accompanied by decomposition of the complexes, especially at elevated temperatures. The formation of triiron dodecacarbonyl also proves to be a nuisance. The present reaction conditions may be compared with those used in the preparation of $Fe_3(CO)_{12}$ from $Fe(CO)_5$, involving reaction with base then oxidation in acidic conditions. In this case acidification during workup allows the second step to proceed.

Utilisation of a cosolvent to produce homogeneous reaction mixtures, however, permits hydrolysis of two of the three complexes to be carried out cleanly at room temperature.

Treatment of the 2-carbomethoxycyclohexadiene complex (15) with 4% potassium hydroxide in aqueous methanol for 2 hours gives complete reaction of the ester, no decomposition products being observed. The product is pure tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32), a yellow crystalline solid, mp 157°. The structure is supported by the ir and nmr spectra, the signals of the diene hydrogens in the latter showing the expected resemblance to those of the carbomethoxy substituted precursor (15).

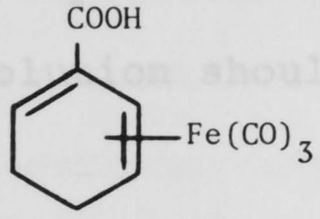
Similar treatment of the mixture of 2- and 5-carbomethoxy isomers (15) and (13), obtained from the reaction of 3-carbomethoxycyclohexa-1,4-diene with iron pentacarbonyl (Section A.a), gives a yellow solid which the nmr spectrum identifies as a mixture of the 2- and 5-carboxylic acids (32) and (29) in a ratio unchanged from that of the original methyl esters. This mixture of acids does not recrystallise satisfactorily and all efforts to separate the isomers by fractional crystallisation have failed.

Surprisingly, tricarbonyl-1-carbomethoxycyclohexa-1, 3-dieneiron (14) is not hydrolysed under the above conditions. After 3 hours at room temperature, when much decomposition of the complex is evident, extraction of the reaction mixture allows recovery of 55% of the ester complex and affords an acidic fraction which accounts for the remainder of the starting material but contains no iron carbonyl bands in the ir. The failure of this hydrolysis would appear to be due to the conjugation of the ester function with the diene system, resulting in an increased electron density at the acyl carbon atom (as in the third mesomeric form shown in Scheme 11). Attack by hydroxide ion at the acyl carbon atom is inhibited as a consequence. An analogous effect on the rates of hydrolysis of substituted benzoic acid esters is well documented.[86-88]

Hydrolysis of this third isomer is achieved, however, by acid catalysis. Refluxing for 24 hours in 15% aqueous sulphuric acid gives an 80% yield of a yellow solid, mp 175°, which nmr confirms as tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33).

The products of acid hydrolyses of the 2- and

5-carbomethoxy substituted complexes under these conditions were anticipated to involve conjugations similar to those observed in sulphuric acid - methanol solution (Section A.4). Indeed each gives the 1-carboxy complex in good yield. The previous discussion of the conjugations in methanol solution should apply equally to these reactions.



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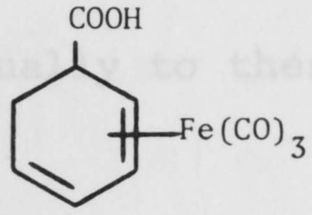

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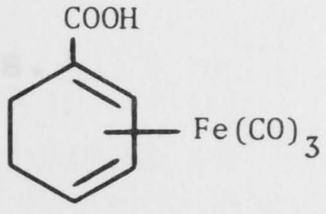
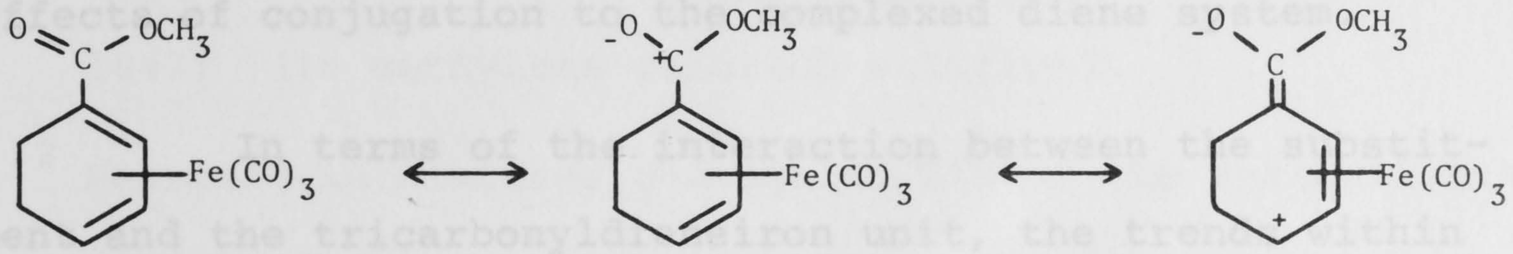


(33)

It is of interest to examine the infrared spectra of the carboxylic ester and acid substituted complexes described thus far. Their carbonyl stretching frequencies are listed in Table 1. It will be noted that the iron carbonyl frequencies show small but significant shifts between the differently substituted complexes and that the acyl carbonyl bands in both the ester and acid series exhibit the effects of conjugation to the complexed diene system.



Scheme 11

In terms of the interaction between the substituent and the tricarbonyldieneiron unit, the trends within the two groups indicate that the diene and its substituent have considerable mutual influence; that the diene electrons are not completely tied up in the bond to iron.

The effects of the diene-substituent interaction are transmitted through the diene-iron bond to affect the terminal carbonyl frequencies. Withdrawal of electrons by the acyl group from the diene increases with the degree of conjugation between the two and shows up as a shift to higher wavenumber in the iron carbonyl frequencies. (For a discussion of this effect, see the General Introduction.)

5-carbomethoxy substituted complexes under these conditions were anticipated to involve conjugations similar to those observed in sulphuric acid - methanol solution (Section A.a). Indeed each gives the 1-carboxy complex in good yield. The previous discussion of the conjugations in methanol solution should apply equally to these reactions.

It is of interest to examine the infrared spectra of the carboxylic ester and acid substituted complexes described thus far. Their carbonyl stretching frequencies are listed in Table 1. It will be noted that the iron carbonyl frequencies show small but significant shifts between the differently substituted complexes and that the acyl carbonyl bands in both the ester and acid series exhibit the effects of conjugation to the complexed diene system.

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Substituent	Iron carbonyl bands	Acyl carbonyl band
unsubstituted[1]	2045 cm^{-1}, 1975 cm^{-1} (broad)	-
5-carbomethoxy[2]	2050 cm^{-1}, 1977 cm^{-1} (broad)	1718 cm^{-1}
2-carbomethoxy	2053 cm^{-1}, 1983 cm^{-1} (broad)	1717 cm^{-1}
1-carbomethoxy	2056 cm^{-1}, 1987 cm^{-1} (broad)	1698 cm^{-1}
5-carboxy[2]	2051 cm^{-1}, 1976 cm^{-1} (broad)	1709 cm^{-1}
2-carboxy	2053 cm^{-1}, 1983 cm^{-1} (broad)	1706 cm^{-1}
1-carboxy	2057 cm^{-1}, 1988 cm^{-1} (broad)	1666 cm^{-1}

Table 1. Infrared carbonyl absorptions of the complexes.

In chloroform solution; Perkin-Elmer 225 spectrometer.

Estimated error ± 1 cm^{-1}.

[1] Values from K. Noack, Helv. Chim. Acta., 1962, 45, 1847; (in methylene chloride solution).

[2] Measured in mixtures containing 22% of the 2-substituted complexes.

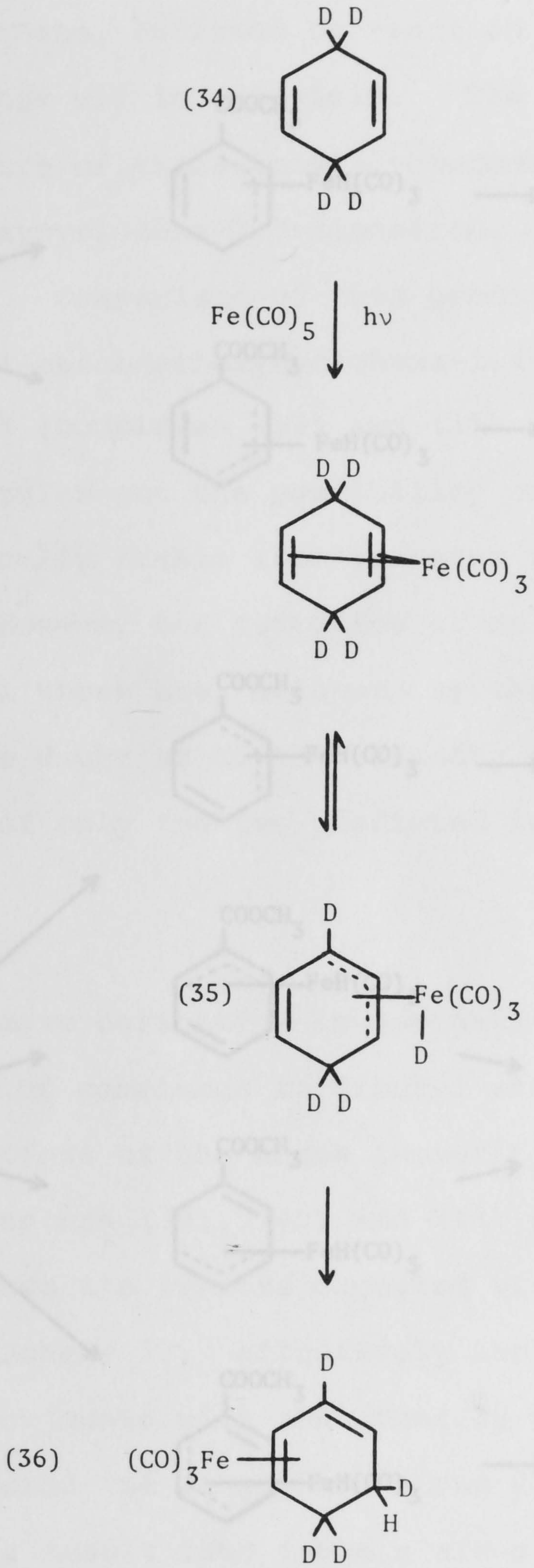
c. Mechanism of formation of complexes from 1,4-dienes.

The capacity of iron carbonyls to conjugate 1,4- to 1,3-dienes has been recognised for some time[61,67,79,81,89] (see General Introduction). Alper, LePorte and Wolfe have investigated the mechanism of formation of tricarbonylcyclohexa-1,3-dieneiron in the photolytic reaction of cyclohexa-1,4-diene with iron pentacarbonyl in benzene.[90] The pathway proposed by them to account for the conversion of 3,3,6,6-tetradeuteriocyclohexa-1,4-diene (34) to the specifically deuterated complex (36) is shown in Scheme 12.

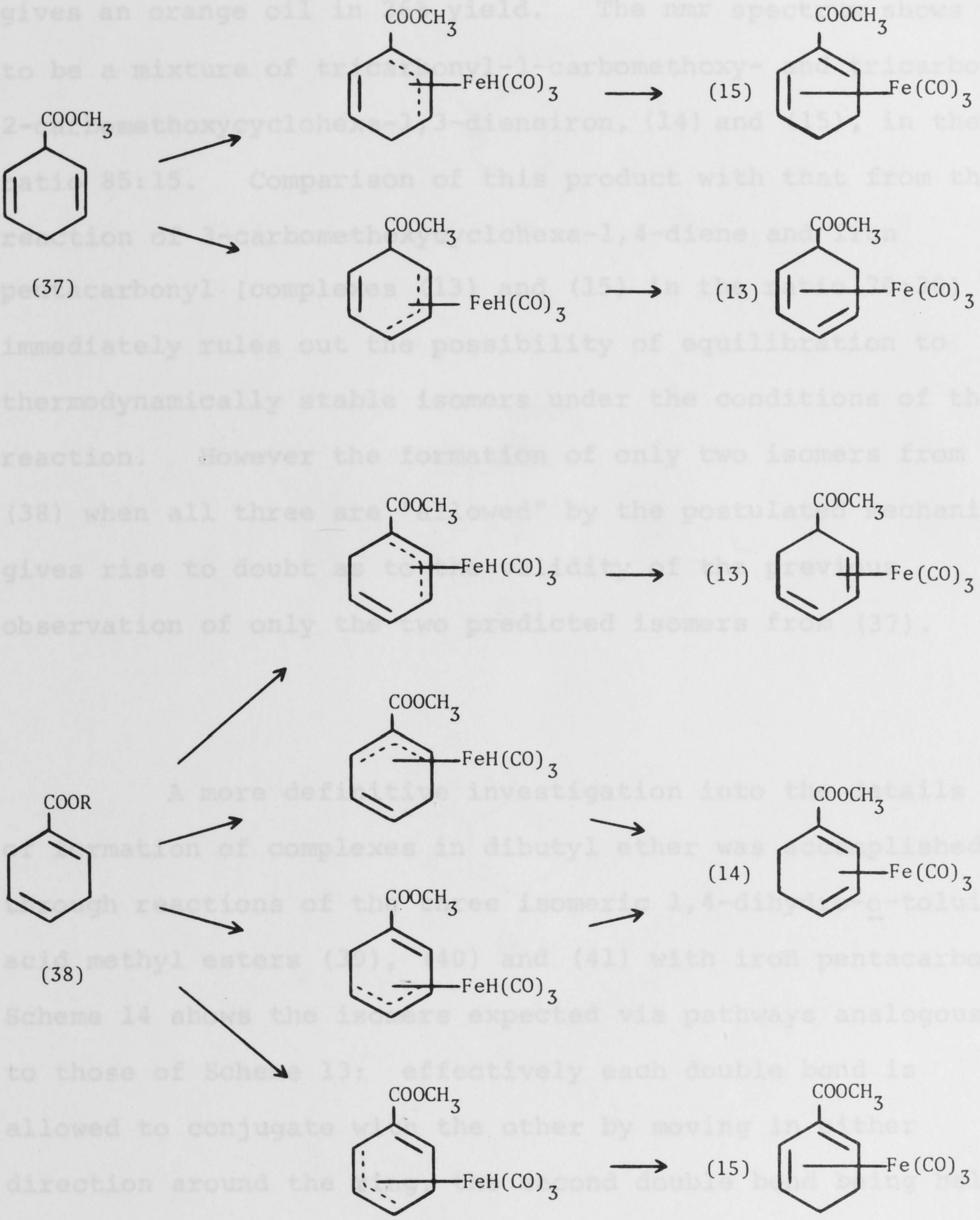
With reference to the formation of complexes from substituted dienes, the mechanism shown predicts that 1- and 3-substituted cyclohexa-1,4-dienes should proceed through different sets of π-allylic intermediates to give differing isomeric mixtures (Scheme 13). The observation of only two of the three possible isomers in the reaction between 3-carbomethoxycyclohexa-1,4-diene (37) and iron pentacarbonyl (see Section A.a) is explained on the basis of this mechanism and implies that thermal reactions in dibutyl ether may follow a similar course to the photochemical reaction studied by the above workers.

As an initial test of the applicability of their results to reactions in dibutyl ether, an examination was made of the mixture of isomers obtained on reaction of 1-carbomethoxycyclohexa-1,4-diene (38) ($R = CH_3$) with iron pentacarbonyl.

The 1,4-diene (38) (R = H) is synthesised in 95% yield by the Diels-Alder reaction between butadiene and



Scheme 12

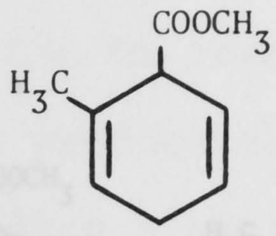

COOCH3
(37)
COOCH3
FeH(CO)3
(15)
COOCH3
Fe(CO)3
COOCH3
FeH(CO)3
(13)
COOCH3
Fe(CO)3
COOR
(38)
COOCH3
FeH(CO)3
(13)
COOCH3
Fe(CO)3
COOCH3
FeH(CO)3
(14)
COOCH3
Fe(CO)3
COOCH3
FeH(CO)3
COOCH3
FeH(CO)3
(15)
COOCH3
Fe(CO)3

Scheme 13

propiolic acid.[91-94] Methylation of the carboxylic acid with diazomethane, followed by reaction with iron pentacarbonyl gives an orange oil in 26% yield. The nmr spectrum shows this to be a mixture of tricarbonyl-1-carbomethoxy- and tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron, (14) and (15), in the ratio 85:15. Comparison of this product with that from the reaction of 3-carbomethoxycyclohexa-1,4-diene and iron pentacarbonyl [complexes (13) and (15) in the ratio 70:30] immediately rules out the possibility of equilibration to thermodynamically stable isomers under the conditions of the reaction. However the formation of only two isomers from (38) when all three are "allowed" by the postulated mechanism gives rise to doubt as to the validity of the previous observation of only the two predicted isomers from (37).

A more definitive investigation into the details of formation of complexes in dibutyl ether was accomplished through reactions of the three isomeric 1,4-dihydro-*o*-toluic acid methyl esters (39), (40) and (41) with iron pentacarbonyl. Scheme 14 shows the isomers expected via pathways analogous to those of Scheme 13; effectively each double bond is allowed to conjugate with the other by moving in either direction around the ring, the second double bond being held fixed. As a result four isomers are predicted in each case, the isomeric mixture differing in all three cases.

The Birch reduction of *o*-toluic acid[95] and the Diels-Alder reaction between tetrolic acid and butadiene[91] give pure samples of 3-carboxy-2-methyl- (48) and 1-carboxy-2-methylcyclohexa-1,4-diene (49) respectively. Reactions



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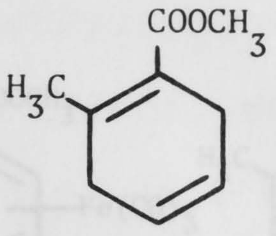

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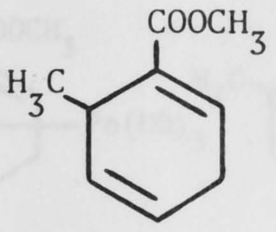
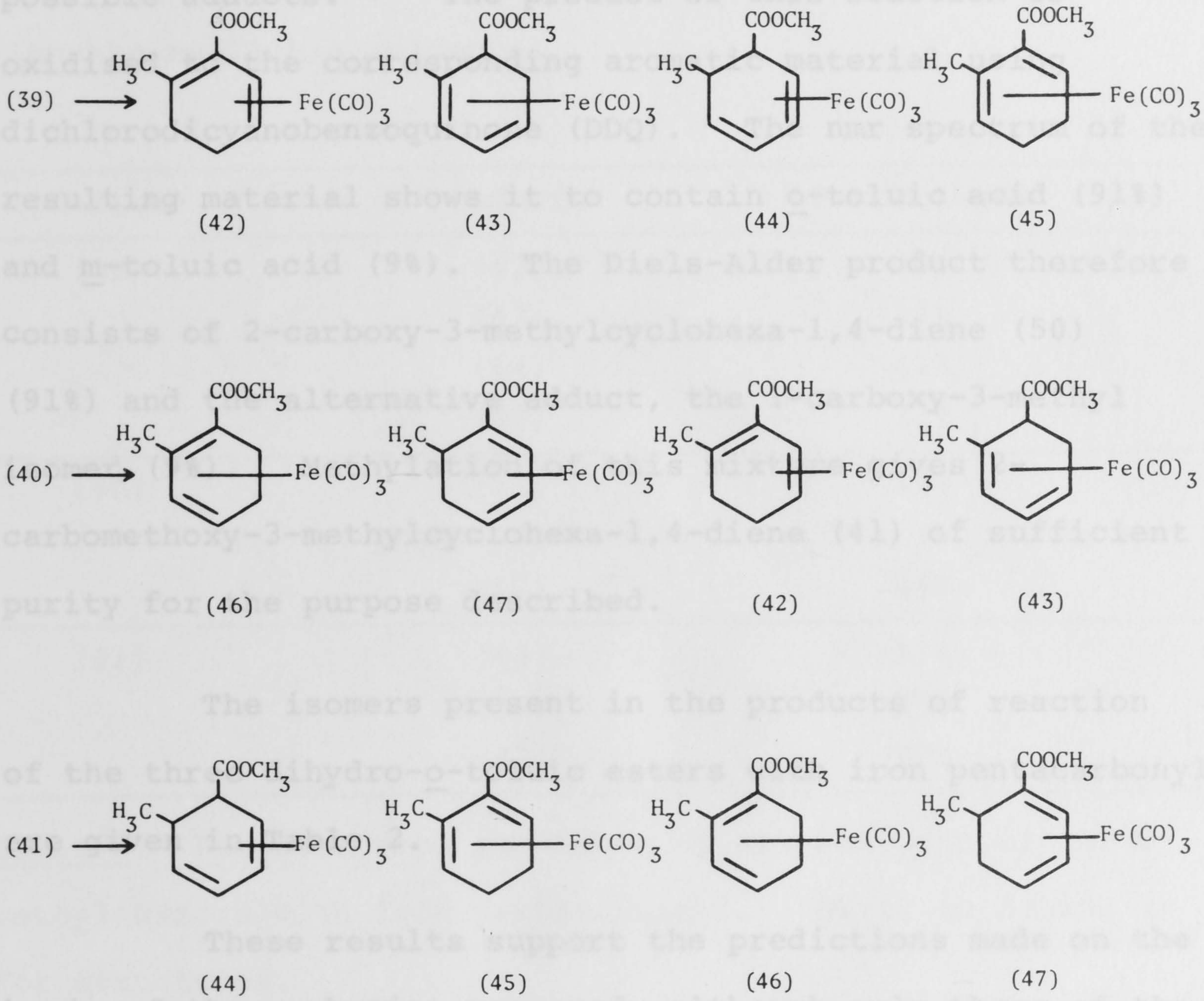


(41)



Scheme 14

with diazomethane give the corresponding methyl esters (39) and (40).

The Diels-Alder reaction of propiolic acid with piperylene has been reported to lead to only one of the two possible adducts.[93] The product of this reaction is oxidised to the corresponding aromatic material using dichlorodicyanobenzoquinone (DDQ). The nmr spectrum of the resulting material shows it to contain o-toluic acid (91%) and m-toluic acid (9%). The Diels-Alder product therefore consists of 2-carboxy-3-methylcyclohexa-1,4-diene (50) (91%) and the alternative adduct, the 1-carboxy-3-methyl isomer (9%). Methylation of this mixture gives 2-carbomethoxy-3-methylcyclohexa-1,4-diene (41) of sufficient purity for the purpose described.

The isomers present in the products of reaction of the three dihydro-o-toluic esters with iron pentacarbonyl are given in Table 2.

These results support the predictions made on the basis of the mechanism proposed, although only three of the four allowed isomers are detected in two cases. No strong directing effect of the carbomethoxy substituent is apparent in the formation of the complexes.

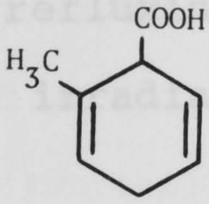
The details of the mechanism of Alper et al. (Scheme 12) deserve some comment.

It would seem reasonable to assume that initial displacement of carbon monoxide from iron pentacarbonyl by the 1,4-diene leads to the olefin-tetracarbonyliron complex (51). That such complexes can exist is shown by the formation of tetracarbonylbutadieneiron, although only mild reaction conditions allow its isolation.[39] The question of whether the tetracarbonyliron intermediate reacts further to produce a tricarbonyliron complex before, after or during the subsequent hydrogen transfer reaction cannot be resolved with the available evidence.

1,4-diene	Products	Percentages
(39)	(42)	10%
	(43)	37%
	(44)	42%
	(45)	11%
(40)	(46)	45%
	(47)	7%
	(42)	48%
(41)	(44)	< 10%
	(45)	< 10%
	(47)	90%

Table 2. Products from reactions of dihydro-o-toluic acid methyl esters with iron pentacarbonyl. Refer to Scheme 14 for structures.
Structures and percentages are derived from the nmr spectra of the mixtures; for descriptions and analyses of the spectra see Experimental section. It is noted that the percentages quoted could have an absolute error of up to 10% in either direction.

In any event, the reaction must proceed through a tetracarbonyl- or tricarbonyl-hydrido-iron intermediate which



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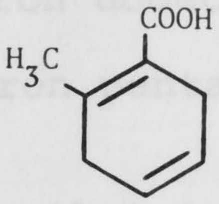

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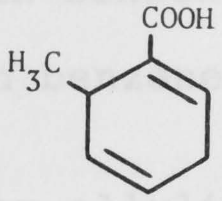
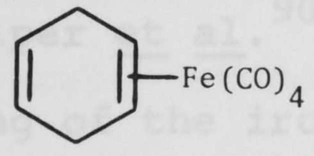


(50)



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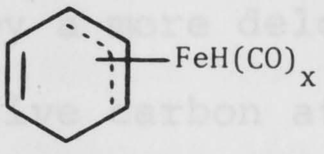
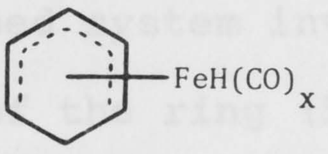


(35)



(52)

then irreversibly gives the final tricarbonyl-1,3-diene complex. The non-reversibility of this last step under the reaction conditions is shown by the isolation of differing isomer ratios from different isomers of the substituted 1,4-dienes. It has also been shown that isomers of the methoxy substituted complexes are not interconverted by (i) refluxing with triiron dodecacarbonyl in benzene, or (ii) irradiation with iron pentacarbonyl in benzene.[61]

If it is taken that transfer of an allylic hydrogen from the 1,4-diene to the iron atom is a reversible process, then the exact nature of the intermediate hydrido-iron complex becomes the major factor determining the structures and proportions of the final products. This intermediate may be represented by a π-allylic complex containing a free double bond (35), due to Pettit et al.[81] and Alper et al.[90], or by a more delocalised system involving bonding of the iron to five carbon atoms of the ring (52). This latter complex could be either a static structure or a fluxional version of (35), depending on the electron accepting capability of the iron atom. This capability depends in turn on the number of carbonyl groups coordinated to iron at this stage of the reaction.

The nature of the hydrogen transferred, whether anion, cation or neutral radical, is also of interest. The intermediates leading to the formation of the major products from the substituted cyclohexa-1,4-dienes may be drawn as substituted derivatives of (35) or (52). No clear preferential arrangement is seen of the delocalised π-systems with respect to the carbomethoxy substituent, which suggests that the π-system of the intermediate does not carry a high charge. Since the effect of the carbomethoxy group is to stabilise an adjacent negative charge and destabilise a positive one, the presence of a highly polarised intermediate would be expected to lead to the preferential production of conjugated or deconjugated products. From the absence of any strong directing effects it may be concluded that the allylic hydrogen transferred has essentially the character of a neutral radical. The precise factors affecting the ratios of isomers formed, whether electronic or steric, are not clear however.

Isomerisation of each of the three mixtures obtained above in concentrated sulphuric acid-methanol solution (refluxing for 24 hours) gives an identical product in each case. It consists of the two fully-conjugated isomers (46) and (47) comprising 82% and 16% respectively, as well as a trace (2%) of the cross-conjugated isomer (42).

d. Primary alcohols derived from the carboxy substituted complexes.

The reduction of simple esters to the corresponding primary alcohols by lithium aluminium hydride is a reaction widely employed in organic chemistry. It was of interest to apply this reaction to the carbomethoxy substituted complexes described in Section A.a, both as an investigation into the reactivities of the complexed organic molecules and as a route to a new series of complexes with potential for several further reactions.

Attempted lithium aluminium hydride reduction of the complexes, however, gives no reaction under a variety of conditions including refluxing in ether or tetrahydrofuran and only the original carbomethoxy substituted complexes are recovered. The percentage recovered drops with longer periods of reaction (several hours), indicating slow decomposition of the complexes under the conditions used. The production of a red oil, probably a hydrido-iron carbonyl anion, which turns to green triiron dodecacarbonyl during workup is also noted during these reactions (cf. Section A.b). This observation and the failure of lithium aluminium hydride to reduce the complexes are discussed later in this section.

Reductions of 3-carboxy- and 3-carbomethoxycyclohexa-1,4-diene with lithium aluminium hydride have been reported in the literature.[78,96,97] This reaction was used as a means to the direct preparation of hydroxymethyl substituted complexes.

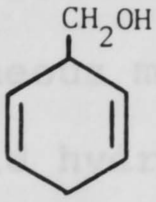
Refluxing 3-(hydroxymethyl)cyclohexa-1,4-diene (53) with iron pentacarbonyl in dibutyl ether gives only decomposition of the iron carbonyl and no isolable complex, as was mentioned in Section A.a. Protection of the free alcohol as its acetate or tetrahydropyranyl (THP) ether followed by reactions with iron pentacarbonyl prove to be more satisfactory procedures.

Iron pentacarbonyl and 3-(acetoxymethyl)cyclohexa-1,4-diene (54) give an orange oil in 28% yield. The nmr spectrum shows it to be pure tricarbonyl-5-(acetoxymethyl) cyclohexa-1,3-dieneiron (55): τ4.5-4.9 (2 hydrogens, H_2 and H_3, multiplet), τ6.2 (2 hydrogens, CH_2,triplet with complicated fine structure), τ6.7-7.1 (2 hydrogens, H_1 and H_4, complicated), τ7.5-9.2 (3 hydrogens, H_5 and H_6, complicated), τ7.96 (3 hydrogens, $COCH_3$, singlet).

Similarly the THP ether of 3-(hydroxymethyl) cyclohexa-1,4-diene (56) gives the pure 5-substituted complex (57) in 36% yield. The nmr spectrum is a series of complicated peaks: τ4.55-4.85 (2 hydrogens,H_2 and H_3), τ5.45 (1 hydrogen, H_8), τ6.0-7.1 (6 hydrogens; H_1, H_4, CH_2 and H_{12}), τ7.4-7.8 (1 hydrogen, H_5), τ7.8-8.9 (8 hydrogens; H_6, H_9, H_{10} and H_{11}).

The parent hydroxymethyl substituted complex of the above derivatives is obtained as a yellow oil on hydrolysis under basic and acidic conditions respectively. Both derivatives can be regenerated by suitable treatment of the alcohol complex.

The acetyl derivative (55) is hydrolysed by a solution of potassium hydroxide in aqueous methanol over 20 minutes at room temperature to give a high yield (90%) of tricarbonyl-5-(hydroxymethyl)cyclohexa-1,3-dieneiron (58). Aqueous methanol containing a few drops of hydrochloric acid hydrolyses the THP ether (57), in 1½ hours at room temperature, to an identical complex (90% yield). The nmr spectrum (all complicated peaks) is: τ4.5-4.9 (2 hydrogens, H_2 and H_3), τ6.3-7.1 (4 hydrogens: H_1, H_4 and CH_2), τ7.5-9.2 (4 hydrogens, 1 exchanging on addition of D_2O: H_5, H_6 and OH).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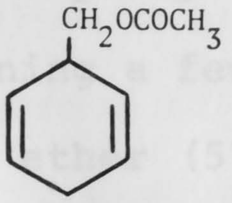
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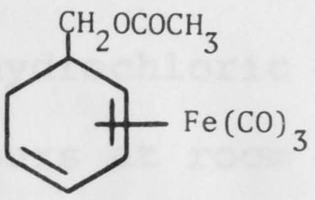
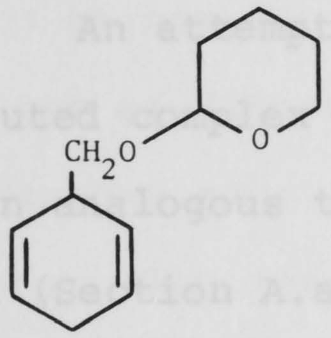

(55)

An attempt was made to obtain the 2-(hydroxymethyl) substituted complex directly from the 1,3-diene in a reaction analogous to the preparation of the 2-carbomethoxy complex (Section A.a).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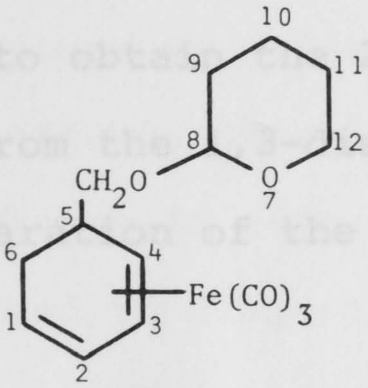
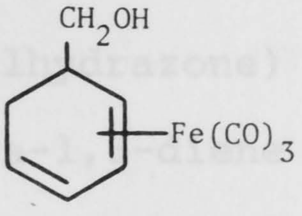


(57)

Lithium aluminium hydride reduction of 2-carbomethoxycyclohexa-1,3-diene, however, does not proceed in a straightforward manner. The product consists of cyclohexene-1-aldehyde (59) (55%, isolated and characterised as its 2,4-dinitrophenylhydrazone) and the desired 2-(hydroxymethyl)cyclohexa-1,3-diene (60) (45%). These two compounds are evidently the result of initial 1,4- and 1,2-additions, respectively, of the aluminohydride anion (AlH_4^-) to the starting material. Normal 1,2-addition across the carbonyl group of the ester produces the primary alcohol (60) while 1,4-addition, involving the 1,2-double bond, leads first to the dienolate anion (61) which is hydrolysed during workup to the α,β-unsaturated aldehyde (59) (see Scheme 15). Similar products of 1,4-addition have been


(58)

The acetyl derivative (55) is hydrolysed by a solution of potassium hydroxide in aqueous methanol over 20 minutes at room temperature to give a high yield (90%) of tricarbonyl-5-(hydroxymethyl)cyclohexa-1,3-dieneiron (58). Aqueous methanol containing a few drops of hydrochloric acid hydrolyses the THP ether (57), in 1½ hours at room temperature, to an identical complex (90% yield). The nmr spectrum (all complicated peaks) is: τ4.5-4.9(2 hydrogens, H_2 and H_3), τ6.3-7.1 (4 hydrogens; H_1, H_4 and CH_2), τ7.5-9.2 (4 hydrogens, 1 exchanging on addition of D_2O; H_5, H_6 and OH).

An attempt was made to obtain the 2-(hydroxymethyl) substituted complex directly from the 1,3-diene in a reaction analogous to the preparation of the 2-carbomethoxy complex (Section A.a).

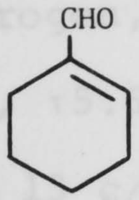
Lithium aluminium hydride reduction of 2-carbomethoxycyclohexa-1,3-diene, however, does not proceed in a straightforward manner. The product consists of cyclohexene-1-aldehyde (59) (55%, isolated and characterised as its 2,4-dinitrophenylhydrazone) and the desired 2-(hydroxymethyl)cyclohexa-1,3-diene (60) (45%). These two compounds are evidently the result of initial 1,4- and 1,2-additions, respectively, of the aluminohydride anion (AlH_4^-) to the starting material. Normal 1,2-addition across the carbonyl group of the ester produces the primary alcohol (60) while 1,4-addition, involving the 1,2-double bond, leads first to the dienolate anion (61) which is hydrolysed during workup to the α,β-unsaturated aldehyde (59) (see Scheme 15). Similar products of 1,4-addition have been isolated from the reduction of certain α,β-unsaturated ketones.[98-101]

The two products are not readily separable, and reactions of the alcohol with acetic anhydride or dihydropyran in the presence of the aldehyde lead to complicated mixtures. The subsequent synthesis of the 2-hydroxymethyl complex by a different route, described below, prompted abandonment of this procedure.

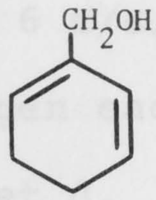
An investigation into alternative methods of reducing carboxylic acids or esters to primary alcohols led to the use of diborane, which effects smooth reduction of all three carboxy substituted complexes in tetrahydrofuran solution. The reactions proceed to completion in 2-3 hours at 25° with no evident decomposition taking place. Yields are about 80% after chromatography of the products.

Tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33) gives tricarbonyl-1-(hydroxymethyl)cyclohexa-1,3-dieneiron (62), a yellow solid, mp 63°. Nmr spectrum: τ4.61 (1 hydrogen, H_2, doublet; $J_{2,3}$ = 4 c/s, $J_{2,4}$ is not observed as a splitting), τ4.80 (1 hydrogen, H_3, doublet of doublets; $J_{3,4}$ = 6 c/s, $J_{3,2}$ = 4 c/s), τ6.18 (2 hydrogens, CH_2, doublet collapsing to a singlet on the addition of D_2O), τ6.81 (1 hydrogen, H_4, doublet with further fine splitting), τ8.0 - 8.6 (5 hydrogens, 1 exchanging with D_2O; H_5, H_6 and OH).

Tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32)



(59)



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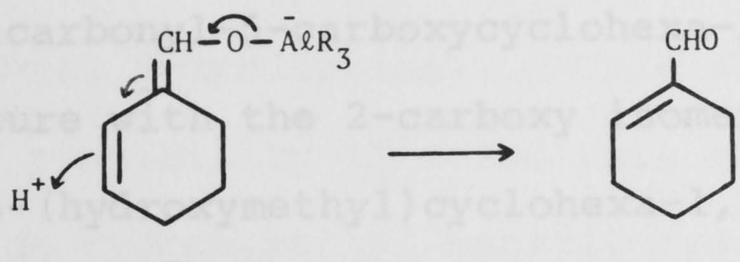
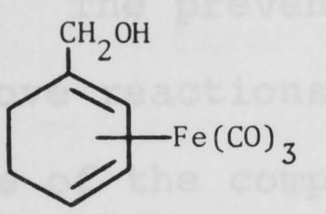
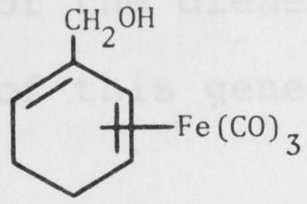


Scheme 15



(62)



(63)

gives tricarbonyl-2-(hydroxymethyl)cyclohexa-1,3-dieneiron (63), also a yellow solid, mp 42°. Nmr spectrum: $\tau 4.58$ (1 hydrogen, H_3, doublet of doublets; $J_{3,4} = 6$ c/s, $J_{3,1} = 2$ c/s), $\tau 5.60$ and $\tau 5.94$ (2 doublets, 1 hydrogen each, CH_2, $J_{gem} = 13$ c/s), $\tau 6.73$ (1 hydrogen, H_1, doublet, $J_{1,3} = 2$ c/s), $\tau 6.86$ (1 hydrogen, H_4, doublet, $J_{4,3} = 6$ c/s), $\tau 7.82$ (1 hydrogen, exchanging with D_2O, OH), $\tau 8.0$-8.7 (4 hydrogens, H_5 and H_6).

Tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29), in mixture with the 2-carboxy isomer (32), gives tricarbonyl-5-(hydroxymethyl)cyclohexa-1,3-dieneiron (58) with an nmr spectrum identical to that described previously in this section.

The protection of dienes from various reactions (Diels-Alder, hydrogenation *etc*., see General Introduction) by the formation of tricarbonyldieneiron complexes has been noted. The prevention of hydroboration of the dienes in the above reactions is a further example of this general feature of the complexes.

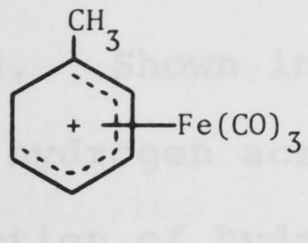
The ability of diborane to effect reduction where lithium aluminium hydride fails to react must be attributed to the different modes of action of the two reagents. The former is essentially electrophilic in nature, attacking the acyl oxygen[102-104], while reactions of the latter depend on an initial nucleophilic attack of hydride ion at the acyl carbon.[102,105] The formation of triiron dodecacarbonyl in the attempted lithium aluminium hydride reductions, probably via a hydrido-iron carbonyl anion, was described earlier.

This indicates some interaction between the iron carbonyl moiety and hydride ion which forestalls the expected reaction with the ester group. It has been demonstrated that nucleophilic attack by organolithium compounds occurs at the carbonyl carbon of some iron carbonyl species.[106]

The ability of the tricarbonyliron residue to stabilise carbonium ions as dienyl complexes has been mentioned (General Introduction). This stabilisation introduces the possibility of solvolysis and ring-expansion reactions of the hydroxymethyl substituted complexes to the tricarbonylcycloheptadienyliron cation[35,80] under the influence of strong acid. Mechanisms may be drawn whereby the primary carbonium ions generated by loss of hydroxide ion from each of the complexes (58),(62) and (63) rearrange to give this product.

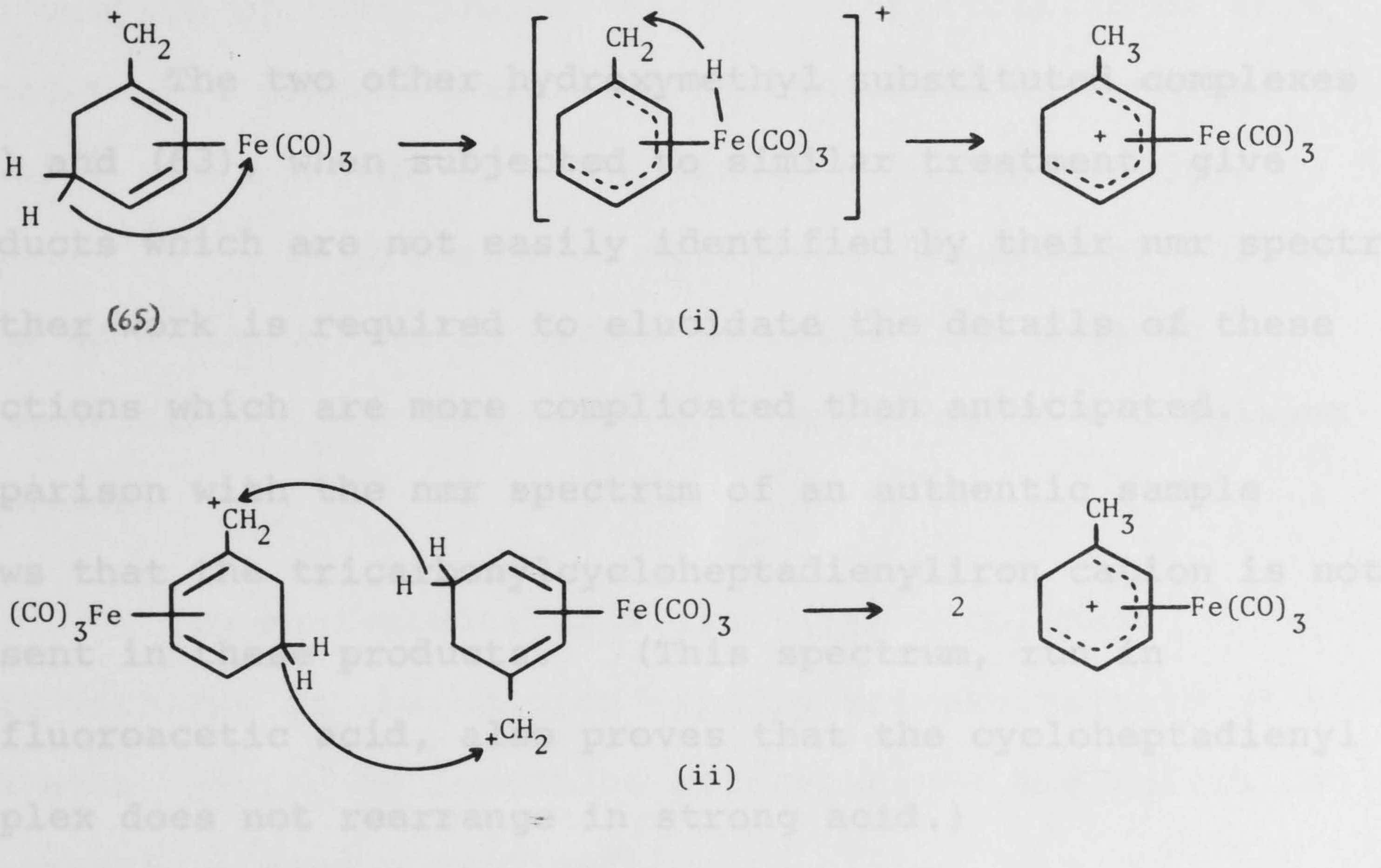
Treatment of the 1-(hydroxymethyl) complex (62) with fluoroboric acid in propionic anhydride gives an immediate reaction and precipitate of a yellow fluoroborate salt. The nmr spectrum in trifluoroacetic acid, however, shows the presence of the tricarbonyl-1-methylcyclohexadienyliron cation (64) only; none of the expected cycloheptadienyl salt is detected. Direct dissolution of (62) in trifluoroacetic acid gives an nmr spectrum identical to that obtained above. The same product is also isolated from the reaction of (62) with anhydrous hydrogen chloride in ether. This substituted cyclohexadienyl complex has previously been prepared only admixed with the 2- and 3-methyl substituted cations.[71]

Transformation of the carbonium ion (65) to (64) could proceed by intramolecular or intermolecular pathways similar to those proposed in Section A.a (Schemes 6 and 8) for isomerisations in acid. Shown in Scheme 16, these involve (i) transfer of a hydrogen across the ring via the iron atom, or (ii) abstraction of hydride ion from another molecule in solution by either bimolecular or chain reaction processes. The intermolecular bimolecular reaction (shown) may be favoured over the chain reaction which involves the formation of more highly charged intermediates.



(64)

The two other hydroxymethyl substituted complexes (58) and (63), when subjected to similar treatment, give products which are not easily identified by their nmr spectra. Further work is required to elucidate the details of these reactions which are more complicated than anticipated. Comparison with the nmr spectrum of an authentic sample shows that the tricarbonylcycloheptadienyliron cation is not present in these products. (This spectrum, run in trifluoroacetic acid, also proves that the cycloheptadienyl complex does not rearrange in strong acid.)



Scheme 16

As a logical extension to the series of complexes, attempts were made to oxidise the hydroxymethyl substituted complexes to the corresponding aldehydes.

Oxidation of the complexed organic molecules presents a difficulty, however, in that the complex itself is often sensitive to oxidising agents. Ferric and ceric salts have frequently been employed in the degradation of

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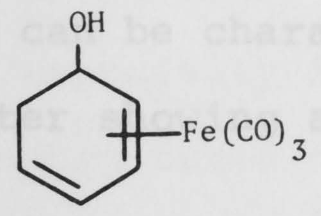
Oxidation of the complexed organic molecules presents a difficulty, however, in that the complex itself is often sensitive to oxidising agents. Ferric and ceric salts have frequently been employed in the degradation of tricarbonyldieneiron complexes[37,61,63,75,76,107-111] and other oxidising agents such as manganese dioxide[61], iodine[112], permanganate-periodate[108], hydrogen peroxide[74] and perbenzoic acid[74] have been shown to cause decomposition.

The successful oxidation of tricarbonyl-5-hydroxycyclohexa-1,3-dieneiron (66) to tricarbonylcyclohexa-2,4-dienoneiron (67) using chromium trioxide in pyridine has been briefly referred to in the literature[61], and a similar oxidation has been employed to obtain the tricarbonyliron complex of homotropone (68).[110] Application of this method to the present complexes is unsuccessful however. Use of a small excess of the chromium trioxide-pyridine complex[113,114] in pyridine or methylene chloride as solvent gives no reaction, while larger excesses lead only to decomposition of the complexes and isolation of uncomplexed aldehydes.

Two equivalents of silver (II) picolinate[115] react with one of the complex rapidly and exclusively at the iron atom, giving an immediate effervescence and releasing the organic ligand unoxidised.

The Moffatt oxidation, using N,N'-dicyclohexylcarbodiimide in dimethyl sulphoxide[116-120] is potentially a more suitable procedure in this situation. Reactions using pyridinium trifluoroacetate or phosphoric acid as catalyst do appear to be at least partially successful, as judged by an examination of the ir spectra of the products. However complete separation of the products from N,N'-dicyclohexylurea and residual dimethyl sulphoxide is extremely difficult. Partial purification



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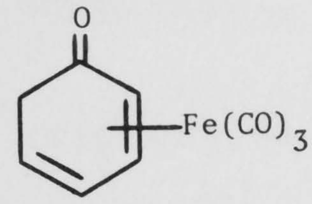

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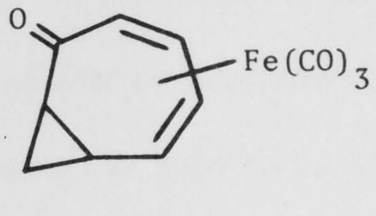


(68)

followed by addition of 2,4-dinitrophenylhydrazine reagent allows the isolation of low yields (less than 5%) of the 2,4-dinitrophenylhydrazones of the desired aldehydes. The small quantities obtained can be characterised by their ir and mass spectra, the latter showing a molecular ion at m/e 428.

e. Hydride abstraction reactions.

An investigation into the positions of hydride ion abstraction from the complexes described in the preceding sections was of interest, especially in the cases of the carboxy and carbomethoxy substituted compounds. The electron withdrawing character of the substituents in these molecules, combined with the positive charge formally located on the dienyl system of the products, would be expected to lead to marked, and hopefully predictable, specificity in the formation of cationic complexes.

The reaction of triphenylmethyl fluoroborate with each of the complexes in methylene chloride solution gives the products described below.

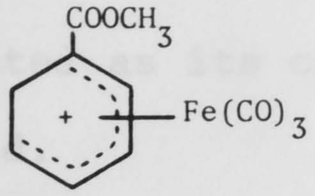
Tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14) gives the tricarbonyl-1-carbomethoxycyclohexadienyliron cation (24) in 46% yield. Addition of ether to the reaction mixture precipitates the fluoroborate salt as an orange gum which probably contains small amounts of the products of reaction of the cation with water. [Traces of water are necessary during the workup procedure to decompose excess triphenylmethyl fluoroborate. The facile reaction of water with (24) is described later in this section.] The cation is, however, regenerated from these products by strong acid (shown by experiment, described later in this section). The nmr spectrum in trifluoroacetic acid thus shows (24) as the only complex present: τ2.46 (1 hydrogen, triplet, H_3, $J_{3,2} = J_{3,4} = 6$ c/s), τ3.28 (1 hydrogen, doublet, H_2, $J_{2,3} = 6$ c/s), τ4.00 (1 hydrogen, triplet, H_4, $J_{4,3} = J_{4,5} = 6$ c/s), τ5.18 (1 hydrogen, triplet, H_5, $J_{5,4} = J_{5,6\underline{endo}} =$

6 c/s), τ6.02 (3 hydrogens, singlet, $COOCH_3$), τ6.55 (1 hydrogen, doublet of doublets, $H_{6\underline{endo}}$, $J_{6\underline{endo},6\underline{exo}}$ = 15 c/s, $J_{6\underline{endo},5}$ = 6 c/s), τ7.95 (1 hydrogen, doublet, $H_{6\underline{exo}}$, $J_{6\underline{exo},6\underline{endo}}$ = 15 c/s). The spectrum shows this complex to be contaminated by triphenylcarbinol and triphenylmethane as well as by ether and methylene chloride which are not eliminated even by prolonged evacuation of the sample.

Tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15) gives a mixture of the tricarbonyl-2- and tricarbonyl-3-carbomethoxycyclohexadienyliron cations (25) and (27) respectively. The mixture of fluoroborate salts is obtained as a yellow crystalline solid in 60% yield, complex (27) comprising 80% of the material isolated (as judged by intensities of peaks in the nmr spectrum). The two salts can not be separated but are identified in the mixture by their nmr spectra which overlap to a small extent only. (25): τ2.05 (1 hydrogen, doublet, H_3, $J_{3,4}$ = 6 c/s), τ3.97 (1 hydrogen, triplet, H_4, $J_{4,3} = J_{4,5}$ = 6 c/s), τ5.08 (1 hydrogen, doublet, H_1, $J_{1,6\underline{endo}}$ = 6 c/s), the H_5 signal is hidden by the H_1, H_5 peak of (27) at τ5.47, τ5.97 (3 hydrogens, singlet, $COOCH_3$), τ6.8 (1 hydrogen, multiplet, $H_{6\underline{endo}}$, overlapping with $H_{6\underline{endo}}$ of the 3-isomer), τ7.84 (1 hydrogen, doublet, $H_{6\underline{exo}}$, $J_{6\underline{exo},6\underline{endo}}$ = 16 c/s, coinciding with $H_{6\underline{exo}}$ of the 3-isomer). (27): τ3.50 (2 hydrogens, doublet, H_2 and H_4, $J_{2,1} = J_{4,5}$ = 7 c/s), τ5.37 (2 hydrogens, triplet, H_1 and H_5, $J_{1,2} = J_{5,4} = J_{1,6\underline{endo}} = J_{5,6\underline{endo}}$ = 7 c/s), τ5.76 (3 hydrogens, singlet, $COOCH_3$), τ6.8 (1 hydrogen, multiplet, $H_{6\underline{endo}}$), τ7.84 (1 hydrogen, doublet, $H_{6\underline{exo}}$, $J_{6\underline{exo},6\underline{endo}}$ = 16 c/s).

Tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) (reacted in mixture with the 2-carbomethoxy complex) gives a mixture of the tricarbonyl-1- and tricarbonyl-6-carbomethoxycyclohexadienyliron cations (24) and (26) in the ratio 21: 79. The yield of the reaction, including products from the admixed (15), is 66%. It is noted that (13) and (15) cannot give rise to common products in this reaction except by hydrogen migration, which has not been observed under these conditions. Elucidation of their individual reaction pathways is therefore facilitated. The 1-carbomethoxycyclohexadienyl complex (24), whose nmr spectrum is described above, is able to be identified in the mixture by the signal of H_2 (τ3.28) and by its $COOCH_3$ singlet (τ6.00). The 6-carbomethoxy substituted complex (26) (the major component) is identified by its nmr spectrum as follows: τ2.60 (1 hydrogen, triplet, H_3, $J_{3,2} = J_{3,4} = 6$ c/s), τ3.96 (2 hydrogens, triplet, H_2 and H_4, $J_{2,1} = J_{2,3} = J_{4,3} = J_{4,5} = 6$ c/s), τ5.48 (2 hydrogens, triplet, H_1 and H_5, $J_{1,2} = J_{1,6\underline{endo}} = J_{5,4} = J_{5,6\underline{endo}} = 6$ c/s), τ5.92 (3 hydrogens, singlet, $COOCH_3$), τ6.80 (1 hydrogen, distorted broad signal, $H_{6\underline{endo}}$).

The carboxy substituted complexes give hydride abstraction reactions virtually identical to those of the carbomethoxy complexes. The nmr spectra of the products from these reactions are almost superimposable on those of the analogous carbomethoxy substituted cations described above, with the $COOCH_3$ singlets omitted. The spectra are recorded in trifluoroacetic acid solution, so that COOH signals are not observed.



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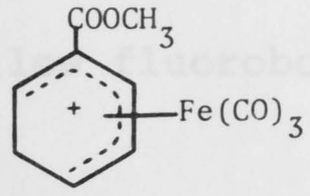

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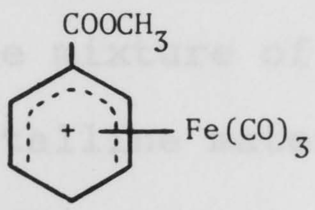

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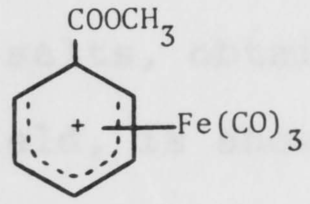

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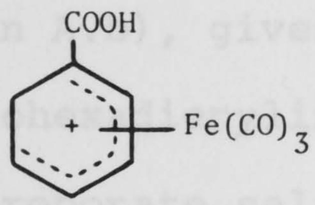

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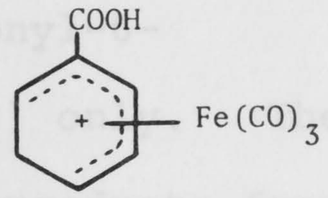

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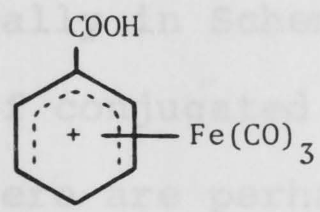

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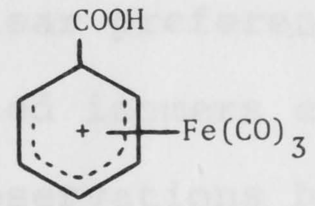


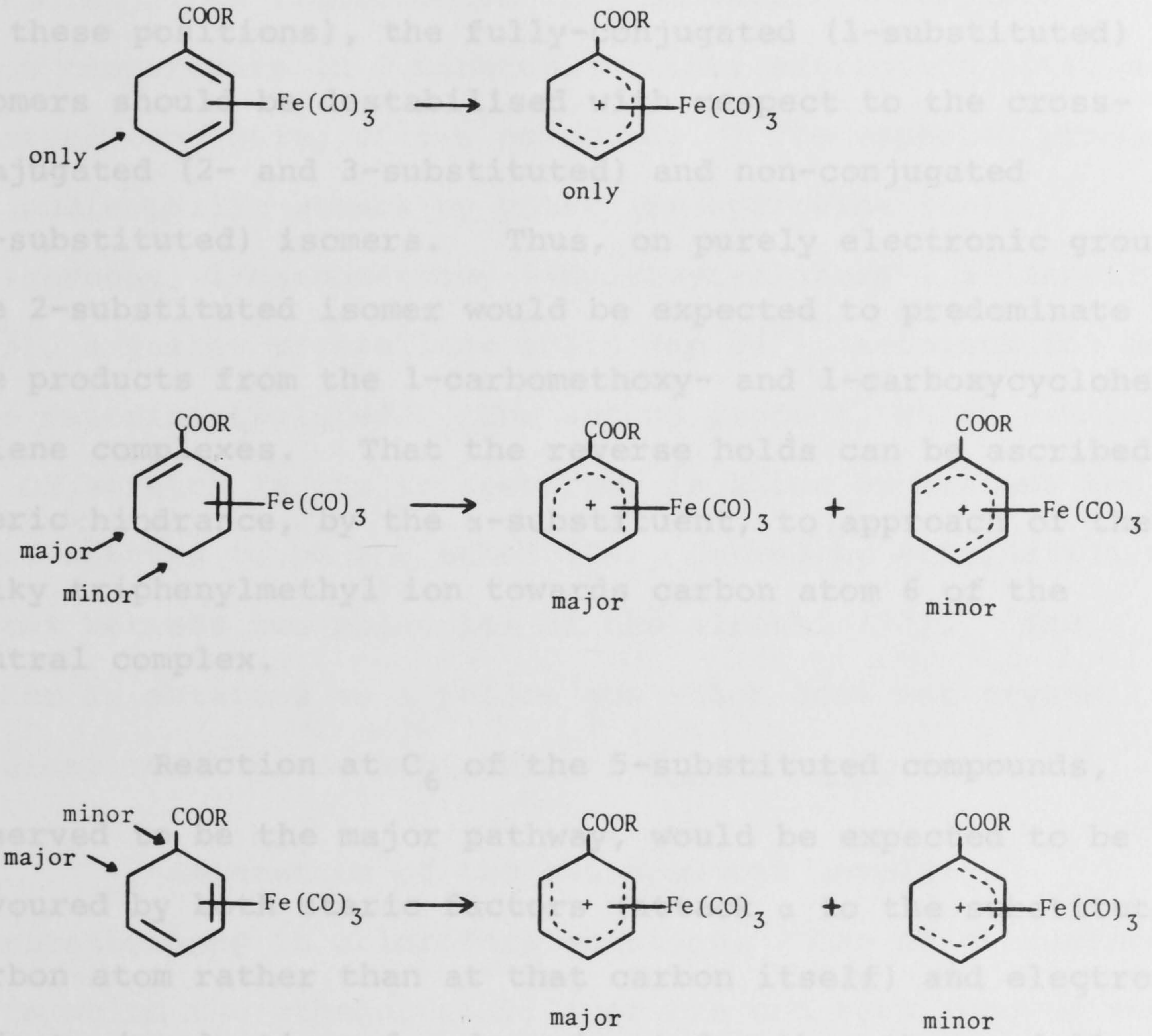
(72)

Tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33) gives the pure tricarbonyl-1-carboxycyclohexadienyliron cation (69), isolated as its crystalline yellow fluoroborate salt in 38% yield.

Tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32) gives a mixture of the tricarbonyl-2- and tricarbonyl-3-carboxycyclohexadienyliron cations (70) and (71) respectively. The mixture of fluoroborate salts, obtained as a yellow crystalline material in 64% yield, is shown by its nmr spectrum to contain (70) and (71) in the ratio 14:86.

Tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29), reacted in its mixture with the 2-carboxy isomer (32) (see Section A.b), gives the tricarbonyl-6-carboxycyclohexadienyliron cation (72) only. The yield of yellow fluoroborate salts, including products from the reaction of (29), is 43%.

The results of these experiments are shown diagramatically in Scheme 17. No clear preference for the formation of conjugated or deconjugated isomers can be seen, although there are perhaps too few observations here to show such trends. A combination of steric and electronic factors can explain the mode of attack of the triphenylmethyl cation in most of the individual cases (see below), but no overall rationale emerges. The results of hydride abstraction from a range of alkyl and alkoxy substituted complexes have been explained using similar arguments.[71]



COOR
Fe(CO)3
only
only
major
minor
major
minor
major
minor
major
minor

Scheme 17

If the positive charge on the complexed cation is largely localised at the terminal carbon atoms of the dienyl system (as predicted from a consideration of its mesomeric forms and as indicated by nucleophilic attack exclusively at these positions), the fully-conjugated (1-substituted) isomers should be destabilised with respect to the cross-conjugated (2- and 3-substituted) and non-conjugated (5-substituted) isomers. Thus, on purely electronic grounds, the 2-substituted isomer would be expected to predominate in the products from the 1-carbomethoxy- and 1-carboxycyclohexadiene complexes. That the reverse holds can be ascribed to steric hindrance, by the α-substituent, to approach of the bulky triphenylmethyl ion towards carbon atom 6 of the neutral complex.

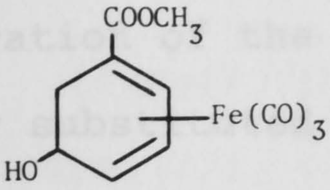
Reaction at C_6 of the 5-substituted compounds, observed to be the major pathway, would be expected to be favoured by both steric factors (attack α to the substituted carbon atom rather than at that carbon itself) and electronic effects (production of a deconjugated rather than a fully-conjugated system). The predominant attack at C_6 of the 2-substituted complexes, however, would appear to be governed by more subtle electronic considerations than those outlined above, no significant steric effects seeming likely in this case.

Attempted purification of the products obtained from each of the carbomethoxy substituted complexes, by dissolving the fluoroborate salts in water and reprecipitating as the fluorophosphate salts, leads to relatively rapid reactions of the cations with water.

The reaction of tricarbonyl-1-carbomethoxycyclohexadienyliron fluoroborate (24) in water is complete at room temperature in 3 minutes. Ether extraction gives a mixture consisting of two compounds. The expected product of nucleophilic attack by water (or hydroxide ion), tricarbonyl-1-carbomethoxy-5-hydroxycyclohexa-1,3-dieneiron (73), a yellow crystalline solid (mp 84°), accounts for half the material isolated. The second product, which exhibits no OH stretch in its ir spectrum, is shown by its nmr and mass spectra to be the ether (74), formed by elimination of water between two molecules of the alcohol (73). The ether is obtained as a yellow gum which does not crystallise, indicating it to be a mixture of d,l and meso forms.

Separation of the two products involves chromatography in chloroform solution. Use of chloroform from which the ethanol stabiliser has not been removed results in partial conversion of the alcohol (73) to its ethyl ether (75), presumably under the influence of traces of acid present in the chloroform. The formation of (74) from two molecules of (73) in water can be formulated in a similar way; in this instance fluoroboric acid, released by the initial attack of water on the complex fluoroborate salt, acts as catalyst (see Scheme 18).

The alcohol (73) can be converted to its methyl ether (76) by adding a trace of acid to a solution of the complex in methanol. Partial decomposition (to methyl m-methoxybenzoate) is also seen in this reaction. Regeneration of the cyclohexadienyl complex (24) from the hydroxy substituted complex is indicated as the initial step in this reaction (and in the ether formations described above) by the pale yellow aqueous solution obtained on addition of water and ether to the reaction mixture. The cation so formed then attacks methanol (or the alcohol complex or ethanol, respectively, in the previous cases) to give the complex isolated, tricarbonyl-1-carbomethoxy-5-methoxycyclohexa-1,3-dieneiron (76) (Scheme 18). Exclusive reaction at C_5 of (24) to give the observed product in each of the above reactions is not surprising, since it involves (i) the less sterically hindered end of the dienyl system, and (ii) formation of fully-conjugated neutral complexes.



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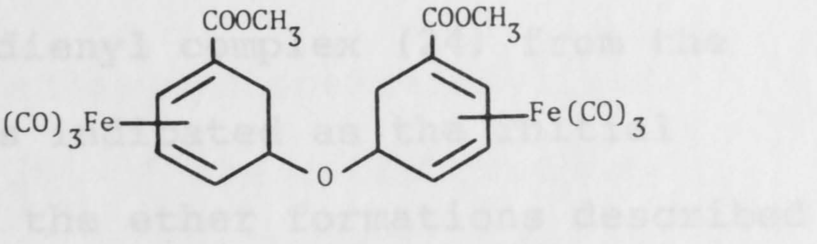

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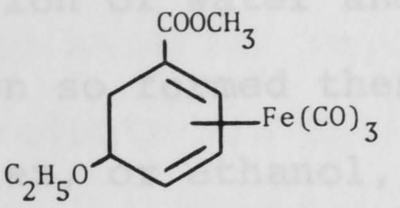

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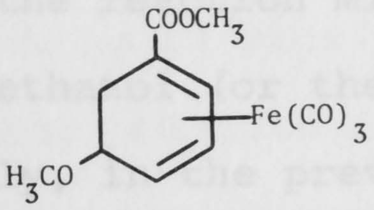

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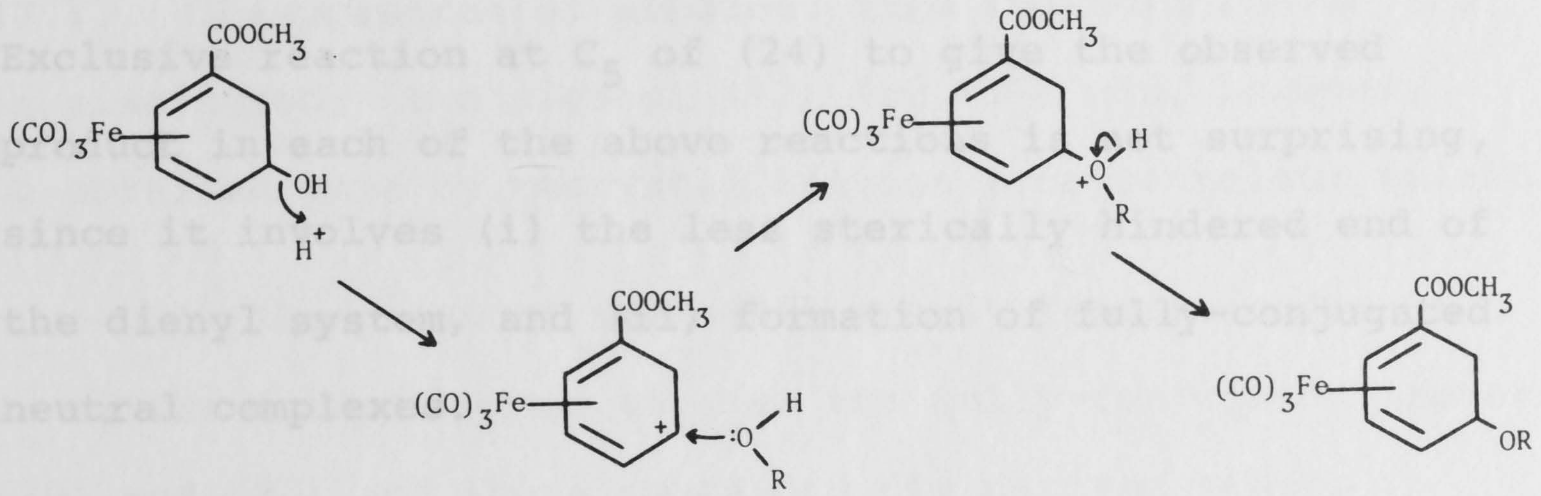
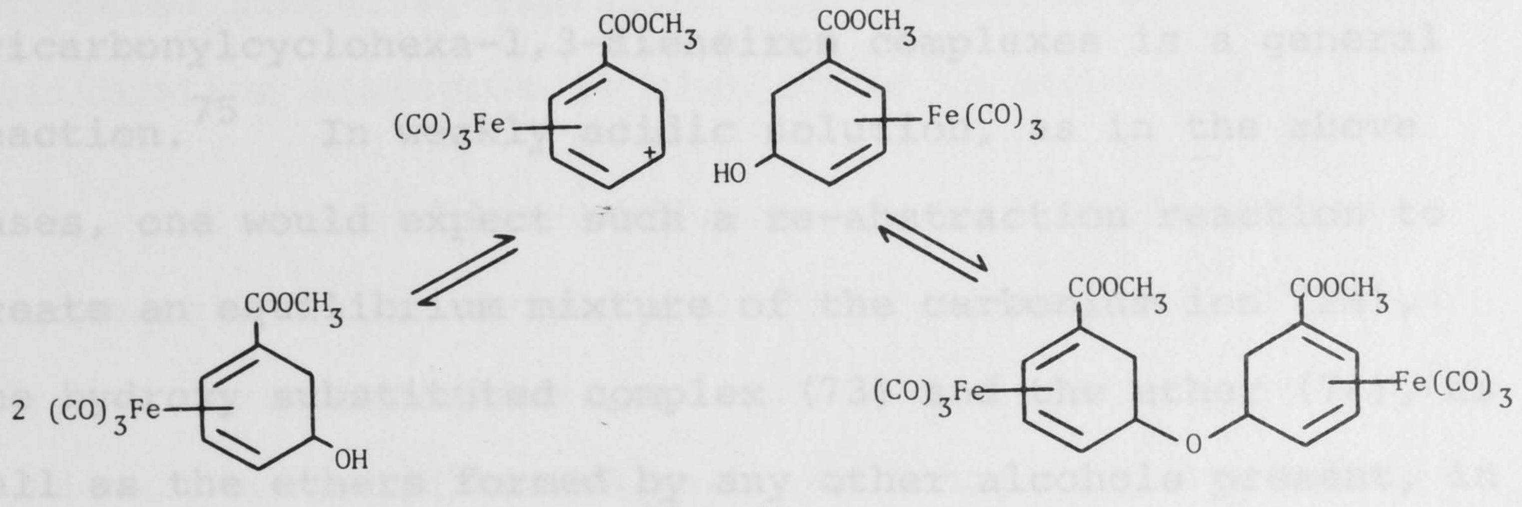


Scheme 18

Re-abstraction of certain nucleophiles, including hydroxide and methoxide ions, from the 5- or 6-position of tricarbonylcyclohexa-1,3-dieneiron complexes is a general reaction.[75] In weakly acidic solution, as in the above cases, one would expect such a re-abstraction reaction to create an equilibrium mixture of the carbonium ion (24), the hydroxy substituted complex (73) and the ether (74) as well as the ethers formed by any other alcohols present, in thermodynamically controlled proportions (Scheme 19). Such an equilibration accounts for the mixture of products isolated from the reaction of (24) in water.



Scheme 19

The action of strong acid on the ether (74) is demonstrated by recording its nmr spectrum in trifluoroacetic acid solution. Only resonances corresponding to m-methoxybenzoate) is also seen in this reaction.

Regeneration of the cyclohexadienyl complex (24) from the hydroxy substituted complex is indicated as the initial step in this reaction (and in the ether formations described above) by the pale yellow aqueous solution obtained on addition of water and ether to the reaction mixture. The cation so formed then attacks methanol (or the alcohol complex, or ethanol, respectively, in the previous cases) to give the complex isolated, tricarbonyl-1-carbomethoxy-5-methoxycyclohexa-1,3-dieneiron (76) (Scheme 18). Exclusive reaction at C_5 of (24) to give the observed product in each of the above reactions is not surprising, since it involves (i) the less sterically hindered end of the dienyl system, and (ii) formation of fully-conjugated neutral complexes.

Re-abstraction of certain nucleophiles, including hydroxide and methoxide ions, from the 5- or 6-position of tricarbonylcyclohexa-1,3-dieneiron complexes is a general reaction.[75] In weakly acidic solution, as in the above cases, one would expect such a re-abstraction reaction to create an equilibrium mixture of the carbonium ion (24), the hydroxy substituted complex (73) and the ether (74), as well as the ethers formed by any other alcohols present, in thermodynamically controlled proportions (Scheme 19). Such an equilibration accounts for the mixture of products isolated from the reaction of (24) in water.

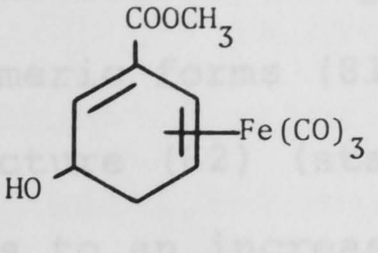
The action of strong acid on the ether (74) is demonstrated by recording its nmr spectrum in trifluoroacetic acid solution. Only resonances corresponding to the cation (24) are detected.

Tricarbonyl-3-carbomethoxycyclohexadienyliron fluoroborate (27), containing 20% of the 2-carbomethoxy substituted salt (25), reacts more slowly with water than the 1-carbomethoxy complex (24), complete conversion to ether soluble material requiring 30 minutes at room temperature. The products are analogous to those obtained from (24): tricarbonyl-2-carbomethoxy-6-hydroxycyclohexa-1,3-dieneiron (77) (70% of the product) and the ether (78) derived from (77). The presence of products from the reaction of (25) is also noted; the alcohol (77) (mp 83^{o}) can, however, be obtained pure by recrystallisation from petroleum spirit.

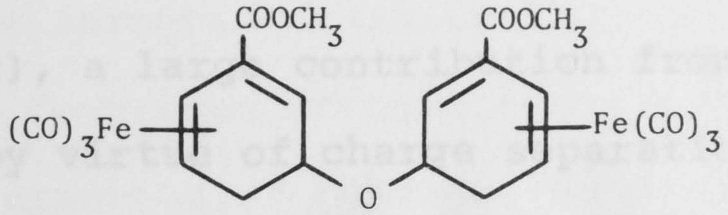
The products from (25) result from reaction at C_1 of the dienyl system to give the fully-conjugated isomers, (79) and (80), of the alcohol and its derived ether. These isomers must be favoured over the alternative cross-conjugated products, resulting from reaction at C_5, in an equilibration analogous to that shown in Scheme 19.

Tricarbonyl-6-carbomethoxycyclohexadienyliron fluoroborate (26), admixed with the cations (24), (25) and (27) (as described above), is attacked slightly more slowly by water than is (27), the reaction being complete after 1 hour at room temperature. The products appear to be analogous to those isolated from the other carbomethoxy substituted cations but identification of the components of the mixtures obtained is not easily accomplished.

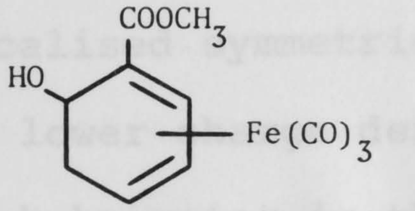
The observed trend in the reactivities of cations (24), (27) and (26) towards water follows that predicted by



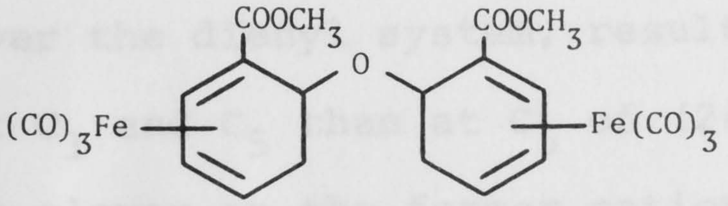
(77)



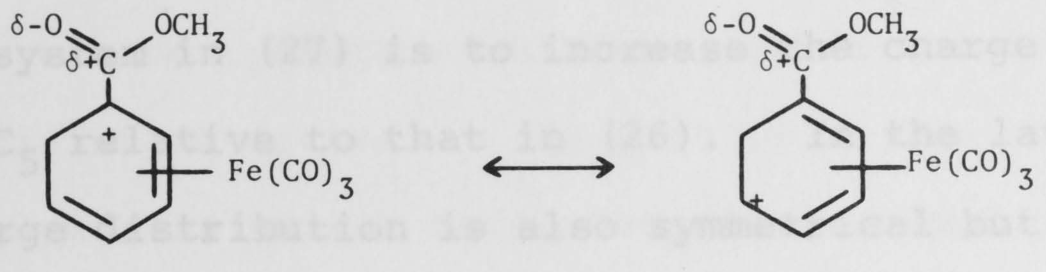
(78)



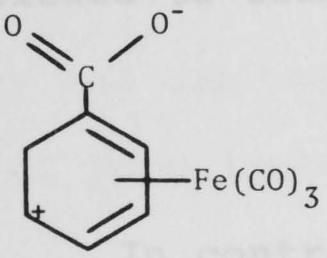
(79)

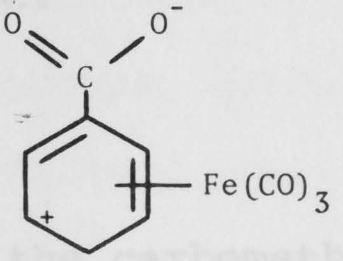


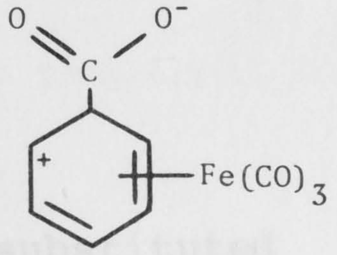
(80)



(81) (82)







(83) (84) (85)

a consideration of the consequences of electron withdrawal by the carbomethoxy substituent. In (24), represented by mesomeric forms (81) and (82), a large contribution from structure (82) (stabilised by virtue of charge separation) leads to an increased positive charge at C_5 which results in rapid and specific attack of water at this site.

In cation (27) the positive charge must be delocalised symmetrically over the dienyl system, resulting in a lower charge density at C_1 and C_5 than at C_5 of (24). Attack by water is therefore slower on the former cation than on the latter.

The effect of substitution at the centre of the dienyl system in (27) is to increase the charge density at C_1 and C_5 relative to that in (26). In the latter complex the charge distribution is also symmetrical but substitution at the methylene carbon atom could slightly reduce the positive charge at C_1 and C_5. Its reaction with water is thus slowed to some extent.

In contrast to the carbomethoxy substituted cyclohexadienyl complexes, the carboxy substituted compounds give stable solutions in water, although the cations are not reprecipitated on addition of ammonium fluorophosphate. (They are, however, precipitated as their reineckate salts.) This reversal of reactivity must be attributed to the presence of the acidic hydroxy group of the substituent. The cations perhaps exist in solution as zwitterionic species such as (83), (84) and (85), deriving stability from a delocalisation of charge over the organic ligand.

CONCLUSION

It is seen from the foregoing results that the reactions of major interest, formation of complexes from cyclohexa-1,4-dienes and abstraction of hydride ion from the cyclohexa-1,3-diene complexes, are not markedly affected by inclusion of the carbomethoxy group on the organic ligand. The course of each of these reactions appears to be governed by factors other than the simple electronic interaction of diene and substituent which was considered in the Introduction. As found by previous workers, mixtures of isomeric complexes are produced.

The effect of the electron withdrawing substituent is seen, however, where conditions permit interconversion of the different isomers. In particular, equilibration of the complexes in acidic media has allowed isolation of fully-conjugated isomers which are not obtained pure by other routes. Investigations of the reactions of individual isomers have thus been facilitated by the presence of the carboxy and carbomethoxy groups, as has the preparation and study of pure isomers of related complexes.

EXPERIMENTAL

General.

Melting points were determined on a Kofler hot-stage microscope and are uncorrected.

Routine infrared spectra were measured on Perkin-Elmer 257 and 457 spectrometers, solid samples as nujol mulls and liquids as thin films unless otherwise stated. More precise measurements of infrared absorption frequencies (quoted in Table 1) were carried out in chloroform solution using a Perkin-Elmer 225 spectrometer.

Ultraviolet and visible spectra were measured on a Unicam SP.800 spectrometer.

Nuclear magnetic resonance spectra were recorded at 60 and 100 Mc on JEOLCO C-60HL and Varian HR100 instruments respectively. The spectra were measured using tetramethylsilane as internal standard (60 Mc) or internal lock signal (100 Mc) and were recorded at 100 Mc in deuteriochloroform solution unless otherwise stated.

Mass spectra were recorded on an A.E.I. MS.902 mass spectrometer.

All reactions involving complexes were carried out in an atmosphere of nitrogen. All solvents were degassed by refluxing under nitrogen prior to commencing a reaction.

Reference to "extraction into ether" implies that the ether extract was washed with water (3x) followed by saturated sodium chloride solution (3x) then dried over magnesium sulphate and evaporated at room temperature under reduced pressure (rotary evaporator) to give the product.

Experimental procedures are given in the order they are mentioned in the previous discussion.

Reactions of cyclohexa-1,4-dienes with iron pentacarbonyl. - The diene and iron pentacarbonyl were refluxed in di-*n*-butyl ether under a slow stream of nitrogen for 16 hr. (See individual descriptions for quantities used.) The reaction mixture, which contained considerable amounts of solid material from decomposition of the iron pentacarbonyl, was allowed to cool then filtered through celite 535 by suction. The celite was washed with di-*n*-butyl ether until the washings were colourless. (Care was required here, as the finely divided material filtered off was often pyrophoric.) The combined filtrate and washings were evaporated as far as possible under reduced pressure on a rotary evaporator (water pump, bath temperature 80°). Di-*n*-butyl ether and unreacted iron pentacarbonyl distilled off.

The residual yellow liquid consisted of the desired tricarbonyldieneiron complex and unreacted diene, with some di-*n*-butyl ether. It was placed in a distillation flask, the di-*n*-butyl ether and diene were distilled off (under nitrogen) at 25-60°/0.05 mm, then one of two procedures was followed.

In method (A) the complex itself was distilled, generally around 90-100°/0.05 mm. In method (B) the complex remaining in the flask was taken up in petroleum spirit (bp 30-40° or 40-60°) and filtered through a short column of activity (III) acidic alumina. This removed fine particles of iron or iron oxides, products of decomposition during workup. Evaporation of the solvent (rotary evaporator, room temperature) left the complex.

Method (A) gave higher purity of products but involved greater loss of material than did method (B), which was especially useful for small scale preparations.

In general the liquid complexes were unstable when exposed to the atmosphere; they were stored at -20° under nitrogen. Solid complexes were generally more stable and were able to be stored at 4° in air without visible decomposition over periods of several months.

Section A.a.

Birch reduction of benzoic acid. - Benzoic acid was reduced to its 1,4-dihydro derivative essentially according to the method of Kuehne and Lambert.[121] It was found convenient, especially in large scale reductions (100g benzoic acid), to use lithium metal rather than sodium and to replace benzoic acid by an equimolar quantity of sodium benzoate. Use of a small excess (*ca.* 0.5 molar equivalent) of sodium or lithium over benzoic acid eliminated the aromatic compound from the product and did not result in significant contamination by tetrahydro or further reduced compounds.

Methylation of the acid to give 3-carbomethoxycyclohexa-1,4-diene was accomplished by reaction with diazomethane in ether at 0° in the normal manner.

Reaction of 3-carbomethoxycyclohexa-1,4-diene with iron pentacarbonyl. - The ester (14 g) and iron pentacarbonyl (25 ml, 36 g) were refluxed in di-*n*-butyl ether (75 ml), as described above, and worked up by method (A). The mixture of complexes distilled at 88°/0.01 mm to give 7.4 g (34%) of an orange oil consisting of tricarbonyl-2- (15) and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in the ratio 22:78. (The ratio varied between this value and 50:50 in different runs.) ν_{max} 2050, 1977, 1718, 1210 cm^{-1}. Nmr spectrum: τ3.93, doublet of doublets, H_3 of (15); τ4.6, complicated, H_2 and H_3 of (13); τ6.21, singlet, $COOCH_3$ of (15); τ6.32, singlet, $COOCH_3$ of (13); τ6.5-8.5, complicated, the remaining hydrogens of each complex. The integrated ratio of the peaks at τ3.93 and τ4.6 (35:123) allowed calculation of the ratio of the two isomers. Mass spectrum: molecular ion at m/e 278 ($C_{11}H_{10}FeO_5$ = 278) showing loss of 3 x CO, 1 x Fe (m/e 250, 222, 194, 138) to give the base peak m/e 138. (Found: C, 47.5; H, 3.8. $C_{11}H_{10}FeO_5$ requires C, 47.5; H, 3.6%.)

Conjugation of 3-carboxycyclohexa-1,4-diene. - The conjugation to 2-carboxycyclohexa-1,3-diene was carried out by refluxing the 1,4-diene in 10% aqueous potassium hydroxide for 4 hr under nitrogen, as described by Plieninger *et al*.[78] Reaction of the product with diazomethane as for the unconjugated acid gave 2-carbomethoxycyclohexa-1,3-diene.

Reaction of 2-carbomethoxycyclohexa-1,3-diene with iron pentacarbonyl. - The ester (10 g) was refluxed with iron pentacarbonyl (13 ml, 19 g) in di-*n*-butyl ether (40 ml). Method (A) gave pure tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15) (7.7 g, 38%) bp 78°/0.05 mm, an orange oil which solidified on standing. Recrystallisation from petroleum spirit (bp 40-60°) at -20° gave yellow needles, mp 40-41°. ν_{max} 2053, 1983, 1717, 1250 cm^{-1}. Nmr spectrum: τ3.93, doublet of doublets, H_3; τ6.21, singlet, $COOCH_3$; τ6.30, doublet with fine splitting, H_1; τ6.64, doublet with fine splitting, H_4; τ8.1-8.5, complicated, H_5 and H_6; $J_{1,3}$ = 2 c/s, $J_{3,4}$ = 7 c/s. The mass spectrum showed the same molecular ion and fragmentation pattern as those of the mixture with the 5-carbomethoxy isomer (13), described above. (Found: C, 47.6; H, 3.9. $C_{11}H_{10}FeO_5$ requires C, 47.5; H, 3.6%.)

Acidic methanolysis of tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (16). - The nitrile complex (380 mg) was refluxed in a mixture of methanol (50 ml) and concentrated sulphuric acid (5 ml) for 24 hr. Ether (20 ml) was added to the cooled reaction mixture, followed by ice water (80 ml). The yellow ether layer gave tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14) (360 mg, 80%), an orange oil which solidified at -20° but melted on warming to room temperature. ν_{max} 2056, 1987, 1698, 1250 cm^{-1}. Nmr spectrum: τ3.95, doublet, H_2; τ4.64, doublet of doublets, H_3; τ6.30, singlet, $COOCH_3$; τ6.64, doublet with fine splitting, H_4; τ7.6-8.7, complicated, H_5 and H_6; $J_{2,3}$ = 4 c/s, $J_{3,4}$ = 6 c/s. The mass spectrum showed a molecular ion m/e 278 ($C_{11}H_{10}FeO_5$ = 278) with a fragmentation pattern similar to that of (13) and (15), described above. (Found: C, 47.8; H, 3.6. $C_{11}H_{10}FeO_5$ requires C, 47.5; H, 3.6%.)

Conjugation of tricarbonyl-2- (15) and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in acid. - The mixture of (13) and (15), obtained from the reaction of 3-carbomethoxycyclohexa-1,4-diene with iron pentacarbonyl, (200 mg) was refluxed for 24 hr in methanol (25 ml) containing concentrated sulphuric acid (2.5 ml). There was no visible decomposition of the complexes under these conditions. Ether (20 ml) was added and the mixture worked up as described above for the nitrile complex to give a virtually quantitative yield of pure tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14) with properties identical to those described above.

Similar treatment of the pure 2-carbomethoxy isomer (15) gave the same product.

Deuteration of tricarbonyl-1- (14), tricarbonyl-2- (15) and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in acid. - Pure (14), or pure (15), or the mixture of (13) and (15), (200 mg) was refluxed in a solution of concentrated deuterio-sulphuric acid (0.3 ml) in deuterio-methanol (5 ml) for 24 hr. Workup as described above gave an identical product in each case, tricarbonyl-6-deuterio-1-carbomethoxycyclohexa-1,3-dieneiron (17) with physical properties as described above for the undeuterated complex (14). No difference was observed in the ir spectra of (14) and (17) (low resolution). The nmr spectrum of (17) was identical to that of (14) except that the methylene hydrogen peaks occupied the smaller range of τ8.0-8.7 and integration indicated the presence of only slightly more than 3 hydrogens. The mass spectrum had peaks at m/e 278, 279, 280, 281 with relative intensities 22:100:18.5:3.2 (the mean values of spectra run at 12, 15 and 70 eV. The variation between these spectra was not great). The percentages of non-, mono-, di- and trideuterated isomers were calculated to be 17, 79, 2.8 and 0.9% respectively. For this calculation, (i) it was noted that the (m-1) peak in the spectrum of the undeuterated compound was of negligible intensity, thus the peak at m/e 278 was taken to be due entirely to non-deuterated material, and (ii) allowances were made for isotopic contributions by the respective molecular ions (m) to (m + 1) and (m + 2) peaks of 14.9% and 1.4% (calculated from the natural isotopic abundances of C, H, Fe and O).

Hydrolysis of tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (16) in base. - The nitrile complex (1 g) was refluxed for 5 hr in a solution of potassium hydroxide (25 g) in methanol (225 ml) and water (25 ml). The reaction mixture was cooled and water (750 ml) was added. Ether extraction gave a neutral fraction which precipitated a crystalline material on addition of petroleum spirit (bp 30-40°). Recrystallisation of the precipitate from aqueous ethanol gave yellow needles of pure *tricarbonyl-1-amidocyclohexa-1,3-dieneiron* (28) (320 mg, 28%), mp 140° (sharp). ν_{max} 3480, 3150, 2060, 1970, 1650, 1600 cm^{-1}. Nmr spectrum: τ3.90, doublet of doublets, H_2; τ4.10, broad and exchanging slowly with D_2O, $CONH_2$; τ4.62, doublet of doublets, H_3; τ6.71, doublet with fine splitting, H_4; τ7.9-8.6, complicated, H_5 and H_6; $J_{2,3} = 4$ c/s, $J_{3,4} = 6$ c/s, $J_{2,4} = 1$ c/s. The mass spectrum showed a molecular ion m/e 263 ($C_{10}H_9FeNO_4 = 263$) with loss of 3 x CO, 1 x Fe, 2 x H (m/e 235, 207, 177, 121). It also showed a loss of H_2O to give the molecular ion of the corresponding nitrile complex m/e 245 which lost 3 x CO, 1 x Fe, 2 x H (m/e 217, 189, 161, 159, 103) to give the base peak of the spectrum at m/e 103. (Found: C, 45.8; H, 3.4. $C_{10}H_9FeNO_4$ requires C, 45.7; H, 3.4%.)

Evaporation of the petroleum spirit washings of the amide complex gave a yellow oil (150 mg) containing about 30% of *tricarbonyl-1-cyanocyclohexa-1,3-dieneiron* (30), the only complex present. It was identified in the mixture by the following spectral properties. ν_{max} 2210, 2060, 1980 cm^{-1}. Nmr spectrum: τ4.66, doublet of doublets, H_3; τ5.79, doublet, H_2; τ6.54, doublet with fine splitting, H_4; $J_{2,3} = 6$ c/s, $J_{3,4} = 4$ c/s. The nmr spectrum showed in addition a set of peaks τ2.2-2.5, corresponding to aromatic decomposition products, and two multiplets τ3.4 and τ4.3, the olefinic hydrogens of uncomplexed dihydroaromatic material. The ratio of aromatic (presumed to contain 5 hydrogens) to uncomplexed dihydroaromatic (1 and 2 hydrogens respectively for the two peaks observed) to complexed material was 1:3:2.

Acidification of the reaction mixture and re-extraction with ether gave an acidic fraction (180 mg) which contained tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29) as the sole complex. Identification was made on the basis of the nmr spectrum (in acetone-d_6): τ4.42, complicated, H_2 and H_3; τ6.72, complicated, H_1 and H_4; τ7.09, multiplet, H_5. The spectrum showed no peaks in the aromatic region, but a small multiplet at τ3.34 indicated the presence of some dihydroaromatic material (10% of the mixture).

Yields of the different fractions varied in successive runs of this reaction: those of the amide complex (28) between 3 and 28%; of the fraction containing the nitrile complex (30) between 15 and 18% of the mass of the starting material; and of the acidic fraction, calculated as pure (29), between 10 and 17%. Variations also occurred in the proportions of compounds present in each fraction.

Refluxing the amide complex (28) (200 mg) for 5 hr in the same potassium hydroxide-methanol-water mixture

(50 ml), followed by an extraction procedure similar to that described above, gave recovered amide (130 mg, 65%), identified by its ir spectrum. A small acidic fraction (23 mg) was also obtained. Its ir and nmr spectra showed it to consist entirely of uncomplexed material.

Conjugation of tricarbonyl-2- (15) and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in base. - The mixture of carbomethoxy substituted complexes, containing (13) and (15) in the ratio 3:1, was refluxed for 5 hr in dry methanol (7 ml) containing sodium methoxide (300 mg, prepared *in situ* by the addition of sodium metal to the methanol under nitrogen). The reaction mixture was cooled, poured into cold dilute sulphuric acid and extracted with ether. The ether solution was re-extracted with aqueous potassium bicarbonate to separate neutral and acidic fractions.

The nmr spectrum of the neutral fraction showed it to consist of tricarbonyl-1-carbomethoxycyclohexa-1,3-diene-iron (14) with 20% of aromatic material also present. The acidic fraction contained only tricarbonyl-2- (32) and tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29). Nmr spectrum (in acetone-d_6): τ3.84, doublet of doublets, H_3 of (32); τ4.5, complicated, H_2 and H_3 of (29); τ6.0, broad, exchanging with D_2O, COOH; τ6.24, doublet with fine splitting, H_1 of (32); τ6.49, doublet, H_4 of (32); τ6.8, complicated, H_1 and H_4 of (29); τ7.1, multiplet, H_5 of (29); τ7.7-8.5, complicated, methylene hydrogens. The integrated ratio of the peaks at τ3.84 and τ4.5 (7:22) gave the ratio of (32):(29) as 24:76, unchanged from (15):(13) in the starting material.

Treatment of tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33) with base. - The carboxylic acid complex (100 mg) was refluxed in 3% aqueous potassium hydroxide for 5 hr. Cooling, acidifying and extracting with ether gave solid material (80 mg) which the nmr spectrum (in acetone-d_6) showed to be mainly the starting material (about 70% of the mixture): τ3.90, doublet, H_2; τ4.43, doublet of doublets, H_3; τ6.52, doublet with fine splitting, H_4. The spectrum also contained peaks due to aromatic and uncomplexed dihydroaromatic compounds.

Section A.b.

Hydrolysis of tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15) in base. - A solution of (15) (2 g) in methanol (150 ml) was added to a solution of potassium hydroxide (8 g) in water (50 ml). The mixture was allowed to stand at room temperature for 2 hr, after which time there was no visible decomposition. Water (250 ml) was added, followed by extraction with ether to remove any unhydrolysed ester complex. Acidification with 5M sulphuric acid and ether extraction of the precipitated carboxylic acid gave tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32), a yellow solid (1.8 g, 94%). Recrystallisation from aqueous ethanol gave yellow needles, mp 157-158°. The sample for analysis was sublimed at 120°/0.5 mm and had the same melting point. ν_{max} 2053, 1983, 1706 cm^{-1}. Nmr spectrum (in acetone-d_6): τ3.5, broad and exchanging with D_2O, COOH; τ3.84, doublet of doublets, H_3; τ6.24, doublet with fine splitting, H_1; τ6.49, doublet with fine splitting, H_4; τ8.35, complicated, H_5 and H_6; $J_{3,4}$ = 7 c/s, $J_{1,3}$ = 2 c/s. The mass spectrum showed a molecular ion m/e 264 ($C_{10}H_8FeO_5$ = 264) with loss of 3 x CO, 1 x Fe, 2 x H (m/e 236, 208, 180, 122). A further loss of OH gave the base peak of the spectrum at m/e 105. (Found: C, 45.4; H, 3.2. $C_{10}H_8FeO_5$ requires C, 45.5; H, 3.1%.)

Hydrolysis of tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in base. - A mixture of the carbomethoxy substituted complexes (13) and (15) in the ratio 77:23

(from the reaction of 3-carbomethoxycyclohexa-1,4-diene with iron pentacarbonyl) (500 mg) was treated with potassium hydroxide in aqueous methanol (50 ml) as described for pure (15), above. The same procedure gave an orange oil, solidifying on cooling to 0^{o}, containing tricarbonyl-2- (32) and tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29) in the ratio 23:77 (calculated from the nmr spectrum). The mixture did not recrystallise satisfactorily, precipitating as an oil from all solvent systems tried. ν_{max} 2051, 1976, 1709 cm^{-1}. The nmr spectrum (in acetone-d_6) showed the spectrum of (32) (described above) as a series of minor peaks; signals which could be assigned to (29) were: τ4.5, complicated, H_2 and H_3; τ6.8, complicated, H_1 and H_4; τ7.10, multiplet, H_5. The ratio of the two isomers was calculated from the intensities of the H_3 peak of (32) (τ3.84) and the H_2, H_3 peak of (29) (τ4.5) which were in the ratio 9:62. The mass spectrum showed a molecular ion at m/e 264 ($C_{10}H_8FeO_5$ = 264) and a fragmentation pattern similar to pure (15) (see above).

Hydrolysis of tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14) in acid. - The ester complex (14) (700 mg) was refluxed in 15% sulphuric acid for 24 hr to give an almost insoluble orange solid suspended in the hot reaction mixture. No visible decomposition occurred. The mixture was cooled and extracted with ether to give tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33) (520 mg, 78%). Recrystallisation from aqueous ethanol gave yellow plates, mp 175^{o} (sublimes). ν_{max} 2057, 1988, 1666 cm^{-1}. Nmr spectrum (in acetone - d_6): τ3.90, doublet, H_2; τ4.43, doublet of doublets, H_3; τ4.5, broad and exchanging with D_2O, COOH; τ5.63, doublet with fine splitting, H_4; τ7.6-8.7, complicated, H_5 and H_6; $J_{2,3}$ = 4 c/s, $J_{3,4}$ = 6 c/s. The mass spectrum showed a molecular ion m/e 264 ($C_{10}H_8FeO_5$ = 264) and a fragmentation pattern similar to that of the carboxy substituted complexes described above. (Found: C, 45.6; H, 3.1. $C_{10}H_8FeO_5$ requires C, 45.5; H, 3.1%).

Conjugation and hydrolysis of tricarbonyl-2- (15) and tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13) in acid. - Treatment of pure (15), or a mixture of (13) and (15), with sulphuric acid in the manner described above for hydrolysis of (14) gave pure tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33) in 70-80% yield and with properties identical to those listed above.

Section A.c.

Diels-Alder reaction between 1,3-butadiene and propiolic acid. - In a procedure similar to that reported in the literature[91-94], butadiene (23 ml, 15.4 g) and propiolic acid (10 g, containing 4% water) were reacted in toluene (40 ml) in the presence of hydroquinone (500 mg) (sealed tube, 140° for 24 hr). The product, 1-carboxycyclohexa-1, 4-diene, a white crystalline solid (17.2 g, 97%), was methylated with diazomethane to give 1-carbomethoxycyclohexa-1,4-diene (38) (R = CH_3).

Reaction of 1-carbomethoxycyclohexa-1,4-diene (38) (R = CH_3) with iron pentacarbonyl. - The ester (5 g) and iron pentacarbonyl (8 ml, 12 g) were refluxed in di-*n*-butyl ether (50 ml). Method (A) gave an orange oil bp 92°/0.1 mm (2.6 g, 26%) which was shown to be a mixture of tricarbonyl-1- (14) and tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15) in the ratio 85:15. ν_{max} 2060, 1980, 1710, 1250 cm^{-1}. The nmr spectrum of the mixture allowed identification of the components and calculation of their proportions: τ3.88, downfield half of doublet of doublets, H_3 of (15); τ3.96, doublet, H_2 of (14), obscuring the upfield half of the previous signal; τ4.64, doublet of doublets, H_3 of (14); τ6.20, singlet, $COOCH_3$ of (15); τ6.30, singlet, $COOCH_3$ of (14); H_1 of (15) was obscured by the $COOCH_3$ peaks; τ6.64, doublet with fine splitting, H_4 of (14) and H_4 of (15); τ7.6-8.8, complicated, the methylene hydrogens of both complexes. The integrated ratio of the peak corresponding to H_3 of (15) plus H_2 of (14) (τ3.8-4.0) to that corresponding to H_3 of (14) (τ4.64) was 13:11, indicating the ratio of isomers quoted above.

Diels-Alder reaction between 1,3-butadiene and tetrolic acid. - This reaction was performed following the procedure used for the reaction between butadiene and propiolic acid (described above). Tetrolic acid was prepared by the method of Carpino.[122]

A mixture of butadiene (9 ml, 6.5 g), tetrolic acid (5 g) and hydroquinone (250 mg) in toluene (20 ml) was reacted in a sealed tube at 150° for 24 hr. The resulting mixture was extracted into ether then the ether solution was extracted with saturated sodium bicarbonate. Acidification of the bicarbonate and extraction of the precipitate into ether gave a white crystalline product. The yield of 1-carboxy-2-methylcyclohexa-1,4-diene (49) from this reaction was low (0.16 g, 2%), as reported in the literature.[91] Repetition of the reaction with addition of water (0.2 ml) to the mixture (*cf*. the presence of water in the Diels-Alder reaction described above) increased the yield to 2.13 g (26%).

Methylation of the product with diazomethane gave 1-carbomethoxy-2-methylcyclohexa-1,4-diene (40).

Diels-Alder reaction between piperylene and propiolic acid. - This reaction was carried out in the manner described above.

A mixture of piperylene (25 ml, 35 g, a mixture of *cis* and *trans* isomers), propiolic acid (12 g, containing 4% water), hydroquinone (800 mg) and toluene (15 ml) was heated in a sealed tube for 24 hr at 160°. A white crystalline product (18.9 g, 80%) was obtained.

A sample of the product (300 mg) was refluxed for 4 hr in dry benzene (30 ml) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (600 mg). Extraction of the aromatised material into saturated sodium bicarbonate solution then precipitation by acidification of the bicarbonate gave a mixture of *o*-toluic acid (92%) and m-toluic acid (8%). The nmr spectrum showed methyl resonances at τ7.33 and τ7.59 in the ratio 57:5.

The product of the Diels-Alder reaction therefore contained 2-carboxy-3-methyl- (50) and 1-carboxy-3-methylcyclohexa-1,4-diene, with the major isomer (50) comprising 92% of the mixture. Methylation of the mixture with diazomethane gave the corresponding methyl esters.

Birch reduction of o-toluic acid. - The reduction was carried out as described in the literature.[95] Methylation of the resulting 3-carboxy-2-methylcyclohexa-1,4-diene (48) with diazomethane gave 3-carbomethoxy-2-methylcyclohexa-1,4-diene (39).

Reaction of 1-carbomethoxy-2-methylcyclohexa-1,4-diene (40) with iron pentacarbonyl. - The diene (40) (2.4 g) and iron pentacarbonyl (5 ml, 7.3 g) were refluxed in di-*n*-butyl ether (50 ml) in the usual manner. Method (B) gave an orange oil (2.2 g, 48%). The product was a mixture of tricarbonyl-2-carbomethoxy-1-methyl- (42) (48% of the mixture), tricarbonyl-1-carbomethoxy-2-methyl- (46) (45%) and tricarbonyl-1-carbomethoxy-6-methylcyclohexa-1,3-dieneiron (47) (7%). ν_{max} 2060, 1980, 1730, 1710 cm^{-1}. Nmr spectrum: τ3.95, doublet, H_2 of (47); τ4.15, doublet, H_3 of (42); τ4.58, triplet, H_3 of (47); τ4.82, doublet, H_3 of (46); τ6.17, singlet, $COOCH_3$ of (42); τ6.92, singlet, $COOCH_3$ of (46) and (47); τ6.78, multiplet, H_4 of (42), (46) and (47); τ7.53, singlet, CH_3 of (46); τ8.12, singlet, CH_3 of (42); τ9.14, doublet, CH_3 of (47); τ7.6-8.8, complicated, the methylene hydrogens of all three complexes. Coupling constants observed were: (42) $J_{3,4}$ = 7 c/s; (46) $J_{3,4}$ = 6 c/s; (47) $J_{2,3}$ = $J_{3,4}$ = 6 c/s. The integrated ratio of the peaks at τ3.95, τ4.15, τ4.58 and τ4.82 was 2:14:2:13, giving the ratio (42):(46):(47) as 14:13:2.

Reaction of 2-carbomethoxy-3-methylcyclohexa-1,4-diene (41) with iron pentacarbonyl. - The diene (41), containing 8% of 1-carbomethoxy-3-methylcyclohexa-1,4-diene (see above), (5.5 g) and iron pentacarbonyl (7.5 ml, 11.0 g) were refluxed in di-n-butyl ether (70 ml). Method (B) gave 1.13 g (11%) of an orange oil, a mixture of tricarbonyl-5-carbomethoxy-6-methyl- (44) (less than 10% of the mixture), tricarbonyl-2-carbomethoxy-3-methyl- (45) (less than 10%) and tricarbonyl-1-carbomethoxy-6-methylcyclohexa-1,3-dieneiron (47) (90%). ν_{max} 2060, 1980, 1710 cm^{-1}. Nmr spectrum: τ3.92, doublet, H_2 of (47); τ4.58, triplet, H_3 of (47), with minor peaks τ4.4-4.8, complicated, H_2 and H_3 of (44); τ6.21, singlet, $COOCH_3$ of (45); τ6.30, singlet, $COOCH_3$ of (47); τ6.38, singlet, $COOCH_3$ of (44); τ7.64, singlet, CH_3 of (45); τ8.87, doublet, CH_3 of (44); τ9.13, doublet, CH_3 of (47); τ6.3-8.7, complicated, $H_{1'}$, H_4 and methylene hydrogens of all three complexes. Coupling constants observed were: (44) $J_{6,methyl}$ = 7 c/s; (47) $J_{2,3}$ = $J_{3,4}$ = 5 c/s, $J_{6,methyl}$ = 6 c/s. A small amount of tricarbonyl-1-carbomethoxy-3-methylcyclohexa-1,3-dieneiron was also detected (the major product formed in the reaction of 1-carbomethoxy-3-methylcyclohexa-1,4-diene with iron pentacarbonyl). The proportions of isomers present could not be determined with great accuracy from the integration of the spectrum. The signals of hydrogens belonging to (47), however, were of far greater intensity than any others present.

<u>Reaction of 3-carbomethoxy-2-methylcyclohexa-1,4-diene (39) with iron pentacarbonyl</u>. - The diene (39) (21 g) and iron pentacarbonyl (24 ml, 35 g) were refluxed in di-*n*-butyl ether (75 ml). Method (A) gave an orange oil (4.95 g, 12%), bp 100-104°/0.3 mm. ν_{max} 2060, 1980, 1730 cm^{-1}. The nmr spectrum showed a series of complicated peaks for inner, outer and methylene hydrogens. The only complex whose identity was immediately obvious from the spectrum was (42), showing a doublet at τ4.14 (H_3, see above). The absence of a doublet at τ3.95, H_2 of (47), and a singlet at τ7.53, CH_3 of (46), eliminated these two isomers as possible components of the mixture, leaving only the four isomers predicted (see discussion). The ratio of isomers present with (42) was

determined from the integrated ratio of inner diene hydrogen peaks (τ4.5-5.0): $COOCH_3$ peaks (τ6.17, 6.20, 6.30, 6.36): outer diene hydrogen peaks (τ6.6-7.1) which was 47:90:46. The H_3 doublet of (42) had an intensity of 3 units on this scale. Subtracting the contributions of (42) to the above three sets of peaks (0, 9 and 3 units respectively), the ratio of the remaining three isomers was calculated by solving three equations in the three unknown concentrations:

$$2a + 2b = 47 \text{ (inner hydrogens)}$$

$$3a + 3b + 3c = 81 \text{ (COOCH}_3\text{)}$$

$$a + 2b + 2c = 43 \text{ (outer hydrogens)}$$

where a, b and c represent the contributions of one hydrogen of (43), (44) and (45), respectively, to the measured intensities. This calculation gave the ratio (42):(43):(44):(45) as 6:22:25:7. The product thus consisted of tricarbonyl-2-carbomethoxy-3-methyl- (42) (10%), tricarbonyl-6-carbomethoxy-1-methyl- (43) (37%), tricarbonyl-5-carbomethoxy-6-methyl- (44) (42%) and tricarbonyl-2-carbomethoxy-3-methylcyclohexa-1,3-dieneiron (45) (11%). This result is supported by the observed chemical shifts and intensities of the $COOCH_3$ resonances: τ6.17 and τ6.20 (low intensity), τ6.30 and τ6.36 (strong).

Conjugation of the carbomethoxy-methyl substituted complexes (42)-(47) in acid. - The mixtures of isomers obtained from the above three reactions were refluxed for 24 hr in concentrated sulphuric acid - methanol solution, as described for conjugations of the carbomethoxy substituted complexes (13) and (15). An identical mixture was isolated in each case, consisting of tricarbonyl-1-carbomethoxy-2-methyl- (46) (82%), tricarbonyl-1-carbomethoxy-6-methyl- (47) (16%) and tricarbonyl-2-carbomethoxy-1-methylcyclohexa-1,3-dieneiron (42) (2%). ν_{max} 2060, 1980, 1705 cm^{-1}. Nmr spectrum: τ3.96, doublet, H_2 of (47); τ4.16, doublet, H_3 of (42); τ4.60, triplet, H_3 of (47); τ4.84, doublet, H_3 of (46); τ6.21, singlet, $COOCH_3$ of (42); τ6.32, singlet, $COOCH_3$ of (46) and (47); τ6.82, multiplet, H_4 of all three complexes; τ7.55, singlet, CH_3 of (46); τ9.14, doublet, CH_3 of (47); τ7.6-8.7, complicated, methylene hydrogens. The ratio of isomers was calculated from the relative intensities of the peaks at τ3.96, τ4.16, τ4.60 and τ4.84 (18:2:18:93).

Section A.d.

Acetate and THP ether of 3-(hydroxymethyl)cyclohexa-1,4-diene (53). - Reduction of 3-carbomethoxycyclohexa-1,4-diene to the primary alcohol (53) was carried out as described in the literature.[78]

A solution of (53) (7 g) in acetic anhydride (20 ml) and pyridine (0.3 ml) was allowed to stand overnight at room temperature. Water (50 ml) was added and excess acetic anhydride was allowed to hydrolyse before the mixture was extracted with ether. The ether solution was washed in turn with 2M hydrochloric acid and saturated sodium bicarbonate solution then dried in the usual manner and evaporated down to give 3-(acetoxymethyl)cyclohexa-1,4-diene (54) (8.6 g, 88%) as a colourless oil.

A mixture of (53) (5 g) and freshly distilled dihydropyran (3.8 g) was cooled to 0° and 1 drop of concentrated hydrochloric acid was added with shaking. An immediate exothermic reaction occurred. After standing for 5 hr at room temperature, the mixture was taken up in chloroform and chromatographed on a column of silica gel. The first compound eluted by chloroform was the THP ether of 3-(hydroxymethyl)cyclohexa-1,4-diene (58), a colourless oil (7.5 g, 85%).

Reaction of 3-(acetoxymethyl)cyclohexa-1,4-diene (54) with iron pentacarbonyl. - The acetate (54) (14 g) and iron pentacarbonyl (21 ml, 31 g) were refluxed in di-*n*-butyl ether (100 ml). Method (A) gave tricarbonyl-5-(acetoxymethyl)cyclohexa-1,3-dieneiron (55) (8 g, 30%), an orange oil, bp $94^{o}/0.02$ mm. ν_{max} 2060, 1950, 1735, 1235 cm^{-1}. Nmr spectrum: $\tau 4.5-4.9$, complicated, H_2 and H_3; $\tau 6.20$, triplet with fine splitting, CH_2; $\tau 6.7-7.1$, complicated, H_1 and H_4; $\tau 7.60$, multiplet, H_5; $\tau 7.96$, singlet, $COCH_3$; $\tau 7.8-8.8$, complicated, H_6. The mass spectrum showed a molecular ion m/e 292 ($C_{12}H_{12}FeO_5$ = 292), losing 3 x CO (m/e 264, 236, 208) then successively CH_3, CO, OH, CH_2 (m/e 193, 165, 148, 134) to give the base peak of the spectrum m/e 134 (C_6H_6Fe = 134). That these fragments contained Fe was shown by the peaks at m/e 191, 163, 146, 132 of approximately 7% of the intensity of the peaks two mass units above. (Natural abundance of Fe^{54} = 6.4% of Fe^{56}).

Reaction of THP ether of 5-(hydroxymethyl)cyclohexa-1,4-diene (56) with iron pentacarbonyl.-The THP ether (56) (7.5 g) and iron pentacarbonyl (10 ml, 15 g) were reacted in di-*n*-butyl ether (100 ml) in the usual manner. Method (B) gave the THP ether of tricarbonyl-5-(hydroxymethyl)-cyclohexa-1,3-dieneiron (57) (3.3 g, 36%), an orange oil. ν_{max} 2060, 1950, 1130, 1040 cm^{-1}. Nmr spectrum: (all complicated peaks) $\tau 4.5-4.9$, H_2 and H_3; $\tau 5.45$, H_8; $\tau 6.0-7.1$, H_1, H_4, CH_2 and H_{12}; $\tau 7.4-7.8$, multiplet, H_5; $\tau 7.8-8.9$, H_6, H_9, H_{10} and H_{11}. The mass spectrum showed a molecular ion m/e 334 ($C_{15}H_{18}FeO_5$ = 334) with loss of 3 x CO (m/e 306, 278, 250) to give the base peak of the spectrum m/e 250. Successive loss of C_5H_9O (the tetrahydropyranyl moiety, with H transfer to the remaining ion), H_2O and CH_2 (m/e 166, 148, 134) led to a strong peak at m/e 134 (cf. the mass spectra of the acetate, above, and the alcohol, below).

Hydrolysis of tricarbonyl-5-(acetoxymethyl)cyclohexa-1,3-dieneiron (55). - The acetate complex (55) (3 g) was dissolved in a solution of potassium hydroxide (2 g) in water (25 ml) and methanol (75 ml) at room temperature. The reaction was complete after 30 min (monitored by tlc). Addition of water (100 ml) followed by ether extraction gave an almost quantitative yield of tricarbonyl-5-(hydroxymethyl) cyclohexa-1,3-dieneiron (58), a yellow oil. ν_{max} 3320 (broad), 2060, 1970, 1040 cm^{-1}. Nmr spectrum: (all complicated peaks) τ4.5-4.9, H_2 and H_3; τ6.3-7.1, H_1, H_4 and CH_2; τ7.5-9.2, H_5, H_6 and OH (exchanged with D_2O). The mass spectrum showed a molecular ion m/e 250 ($C_{10}H_{10}FeO_4$ = 250) and a fragmentation pattern analogous to those of the acetyl and THP ether derivatives, with loss of 3 x CO, H_2O and CH_2 (m/e 222, 194, 166, 148, 134).

Hydrolysis of THP ether of tricarbonyl-5-(hydroxymethyl) cyclohexa-1,3-dieneiron (57). - The THP ether (57) (1 g) was dissolved in a mixture of methanol (60 ml) and water (8 ml) then concentrated hydrochloric acid (1 ml) was added. Tlc showed the reaction to be complete after 80 min at room temperature. Water (50 ml) was added and the complex extracted into ether to give a yellow oil, in high yield, whose properties and spectral data were identical to those of (58) obtained from the acetate (see above).

The acetate and THP ether complexes (55) and (57) were reformed by treatment of (58) as described for the formation of the corresponding derivatives of 3-(hydroxymethyl)cyclohexa-1,4-diene.

Lithium aluminium hydride reduction of 2-carbomethoxycyclohexa-1,3-diene. - The ester (8.5 g) in dry ether (30 ml) was added slowly and with vigorous stirring to a slurry of lithium aluminium hydride (2.5 g) in ether (100 ml) at room temperature. The mixture was refluxed for a further 2 hr then cooled to 0^o and saturated ammonium chloride solution added cautiously. Filtering to remove the precipitated hydroxides and drying the ether solution in the usual manner gave a colourless oil (4.88 g) consisting of cyclohexene-1-carboxaldehyde (59) (55%) and 2-(hydroxymethyl)cyclohexa-1,3-diene (60) (45%). ν_{max} 3400 (broad), 3020, 1675, 1640 cm^{-1}. The nmr spectrum was a superimposition of the individual spectra described below. The integrated ratio of the peaks H_2 of (59): H_1, H_3 and H_4 of (60) (τ3.18, τ4.3) was 8:20, indicating a ratio (59):(60) of 6:5.

Addition of 2,4-dinitrophenylhydrazine reagent to the mixture gave a red precipitate of the dinitrophenylhydrazone of (59), mp 213-215^o (from acetic acid) (lit.[123-129] mp ranges from 205-206^o to 223-224^o). ν_{max} 3280 (sharp), 1617, 1590 cm^{-1}. Nmr spectrum: τ-1.06, broad singlet, NH; τ0.88, doublet; τ1.69, doublet of doublets; τ2.08, doublet;

H_3, H_5 and H_6 of the aromatic ring; τ2.27, singlet, -CH=N-; τ3.74, complicated, H_2 of cyclohexene ring; τ7.6, complicated, H_3 and H_6 of cyclohexene ring; τ8.25, complicated, H_4 and H_5 of cyclohexene ring. Mass spectrum: molecular ion m/e 290 ($C_{13}H_{14}N_4O_4$ = 290).

A small sample of the mixture was separated into its components by chromatography in chloroform on silica gel (100 g to 1 g of mixture). The compounds were identified by their ir and nmr spectra. (59): ν_{max} 3020, 1675, 1640 cm^{-1}; τ0.56, singlet, CHO; τ3.18, multiplet, H_2; τ7.7, complicated, H_3 and H_6; τ8.3, complicated, H_4 and H_5. (60): ν_{max} 3400 (broad), 3020 cm^{-1}; τ4.3, complicated, H_1, H_3 and H_4; τ6.50, doublet, CH_2; τ7.6, broad and exchanging with D_2O, OH; τ7.8-8.9, complicated, H_5 and H_6. The latter nmr spectrum also showed the presence of benzyl alcohol.

<u>Diborane reduction of tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33)</u>. - The carboxylic acid complex (33) (500 mg) was dissolved in dry THF (20 ml) at room temperature. A solution of diborane in THF (IM in BH_3) (5 ml) was added under nitrogen, and a further 5 ml portion after 1 hr. Tlc indicated the reaction to be almost complete at the end of a second hour. Ethanol (2 ml) was added slowly, followed by saturated sodium chloride solution (500 ml). (Addition of water alone led to emulsification of the mixture on attempted ether extraction.) Extraction into ether gave a yellow oil (700 mg, containing THF) which was

chromatographed on silica gel (20 g) in chloroform. The product was an orange oil, solidifying on standing (450 mg, 95%). Recrystallisation from petroleum spirit (bp 40-60^o) at -20^o gave yellow needles of tricarbonyl-1-(hydroxymethyl)cyclohexa-1,3-dieneiron (62), mp 63-64^o. ν_{max} 3220 (broad), 2050, 1970, 1950 cm^{-1}. Nmr spectrum: τ4.61, doublet, H_2; τ4.80, doublet of doublets, H_3; τ6.18, doublet collapsing to singlet on addition of D_2O, CH_2; τ6.81, doublet with fine splitting, H_4; τ8.0-8.6, complicated, H_5, H_6 and OH (the last exchanging with D_2O); $J_{2,3}$ = 4 c/s, $J_{3,4}$ = 6 c/s, $J_{CH_2, OH}$ = 3 c/s. Mass spectrum: molecular ion m/e 250 ($C_{10}H_{10}FeO_4$ = 250). (Found: C, 48.1; H, 4.2. $C_{10}H_{10}FeO_4$ requires C, 48.0; H, 4.0%)

Diborane reduction of tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32). - Reduction of (32) (500 mg) was accomplished in the manner described above for the reaction of (33) with diborane. The product was an orange oil (380 mg after chromatography, 80%) which solidified on standing. Recrystallisation from petroleum spirit (bp 40-60^o) at -20^o gave yellow needles of tricarbonyl-2-(hydroxymethyl)cyclohexa-1,3-dieneiron (63), mp 42-43^o. ν_{max} 3220 (broad), 2050, 1960 cm^{-1}. Nmr spectrum: τ4.58, doublet of doublets, H_3; τ5.60 and τ5.94, each a doublet, forming an AB quartet, CH_2; τ6.73, doublet, H_1; τ6.86, doublet H_4; τ7.82, broad singlet exchanging with D_2O, OH; τ8.0-8.7, H_5 and H_6; $J_{1,3}$ = 2 c/s, $J_{3,4}$ = 6 c/s, J_{gem} (CH_2) = 13 c/s. Mass spectrum:molecular ion m/e 250 ($C_{10}H_{10}FeO_4$ = 250).

Diborane reduction of tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29). - Reduction of the mixture of (29) and (32), obtained on hydrolysis of the product from 3-carbomethoxycyclohexa-1,4-diene and iron pentacarbonyl, gave an orange oil by the procedure described above. The nmr spectrum was a superimposition of the individual spectra of the alcohols (58) and (63), described above, in a ratio unchanged from that of (29) and (32) in the starting material.

Reaction of tricarbonyl-1-(hydroxymethyl)cyclohexa-1,3-dieneiron (62) in strong acid. - An anhydrous solution of fluoroboric acid was prepared by slowly adding 43% aqueous fluoroboric acid (1.5 ml, 2 g) to ice-cold propionic anhydride (5 ml). The alcohol (62) (100 mg) was dissolved in propionic anhydride (0.12 ml), cooled in ice, and the fluoroboric acid-propionic anhydride solution (0.20 ml) was added. An immediate reaction occurred, giving a yellow precipitate. After 15 min ice-water (1 ml) was added then the precipitate was filtered off and washed with dry ether. The product was tricarbonyl-1-methylcyclohexadieneyliron fluoroborate (64) (70 mg, 55%). ν_{max} 3100, 3070, 2120, 2080, 1065 cm^{-1}. Nmr spectrum (in trifluoroacetic acid): τ2.89, triplet, H_3; τ4.15, triplet, H_4; τ4.54, doublet, H_2; τ5.80, triplet, H_5; τ6.98, doublet of doublets, $H_{6\underline{endo}}$; τ7.70, doublet, $H_{6\underline{exo}}$; τ8.12, singlet, CH_3; $J_{2,3} = J_{3,4} = 5$ c/s, $J_{4,5} = J_{5,6\underline{endo}} = 6$ c/s, $J_{6\underline{endo},\,6\underline{exo}} = 17$ c/s.

Dissolving (32) directly in trifluoroacetic acid gave an identical nmr spectrum, indicating 100% conversion to the cation (64). Bubbling dry hydrogen chloride gas through a solution of (32) in dry ether for several hr gave a precipitate of the chloride of (64). The yield, however, was only 20%.

Attempted N,N'-dicyclohexylcarbodiimide-dimethyl sulphoxide (DCC-DMSO) oxidation of the hydroxymethyl substituted complexes. - In a typical experiment, tricarbonyl-5-(hydroxymethyl)cyclohexa-1,3-dieneiron (58) (100 mg) and phosphoric acid (8 mg) were dissolved in dry DMSO (10 ml) then DCC (250 mg) was added at room temperature. After stirring for 24 hr, tlc showed the majority of (58) to have been consumed. Oxalic acid (150 mg) in methanol (3 ml) was added to convert excess DCC to N,N'-dicyclohexylurea. Water and ether were added to give two phases and the insoluble dicyclohexylurea was filtered off leaving a colourless water layer beneath a yellow ether solution. The ether solution gave a yellow oil which was chromatographed on silica gel in chloroform to give a fraction showing ν_{max} 2060, 1970, 1720 cm^{-1} as well as a strong band at 1680 cm^{-1} belonging to dicyclohexylurea.

Addition of 2,4-dinitrophenylhydrazine reagent gave a few milligrams of a red dinitrophenylhydrazone, mp 175-177^{o} (from ethanol). ν_{max} 3295 (sharp), 2060, 1970, 1620, 1595 cm^{-1}. The mass spectrum showed a molecular ion m/e 428 ($C_{16}H_{12}FeN_4O_7$ = 428) with loss of 3 x CO, 1 x Fe, 2 x H (m/e 400, 372, 344, 286).

Section A.e.

Hydride abstraction reactions: general. - Triphenylmethyl fluoroborate was prepared by the method of Dauben, Honnen and Harmon[130] and stored in a tightly stoppered bottle at -20°. Prior to reaction the cyclohexadiene complexes were dissolved in methylene chloride; the carbomethoxy substituted complexes in approximately their own volume of solvent and the less soluble carboxy substituted compounds in the minimum volume possible at room temperature, gentle heat being used to ensure saturated solutions.

A solution of triphenylmethyl fluoroborate (1.1 equivalents) in the minimum volume of methylene chloride (solubility approximately 200 mg/ml at room temperature) was added with shaking to the solution of complex in methylene chloride and the mixture allowed to stand for 1 hr at room temperature. Ether (not dried, traces of water serving to convert excess of the triphenylmethyl cation to triphenylcarbinol) was added to precipitate the tricarbonylcyclohexadienyliron fluoroborate salt which was filtered off and washed with sodium dried ether.

Hydride abstraction from tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14). - The neutral complex (14) (1 g) gave an orange gum (940 mg) on addition of ether to the reaction mixture. The gum was washed with dry ether and as much solvent as possible removed by evacuation at 0.05 mm for several hours (room temperature). ν_{max} (nujol) 3070, 2130, 2090, 2070, 1715, 1275, 1050 cm^{-1}. The nmr spectrum in trifluoroacetic acid showed the only complex present to be <u>tricarbonyl-1-carbomethoxycyclohexadienyliron fluoroborate</u> (24): τ2.46, triplet, H_3; τ3.28, doublet, H_2; τ4.00, triplet, H_4; τ5.18, triplet, H_5; τ6.02, singlet, $COOCH_3$; τ6.55, doublet of doublets, $H_{6\underline{endo}}$; τ7.95, doublet, $H_{6\underline{exo}}$; $J_{2,3} = J_{3,4} = J_{4,5} = J_{5,6\underline{endo}} = 6$ c/s, $J_{6\underline{endo}, 6\underline{exo}} = 15$ c/s. The ir and nmr spectra also indicated the presence of triphenylcarbinol, converted to the triphenylmethyl cation in trifluoroacetic acid (ν_{max} 3460, 770, 705 cm^{-1}. τ1.6-2.4, multiplet), triphenylmethane (τ2.80, broad singlet; τ5.79, singlet), methylene chloride (τ4.78, singlet) and ether (τ6.20,quartet; τ8.68, triplet). These impurities comprised approximately 25% of the total mixture (by integrated intensities of peaks in the nmr spectrum). The yield of (24) from the reaction was therefore 610 mg (46%).

<u>Hydride abstraction from tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron (15).</u> - The neutral complex (15) (1 g) gave a yellow crystalline fluoroborate salt (780 mg, 60%) which began to crystallise from the reaction mixture after 20 min. Precipitation was completed after 1 hr by addition of ether as described above. The ir and nmr spectra showed the product to be a mixture of <u>tricarbonyl-2-</u> (25) (20%) and <u>tricarbonyl-3-carbomethoxycyclohexadienyliron fluoroborate</u> (27) (80%). ν_{max} 3080, 2130, 2105, 2090, 2065, 1725, 1310, 1070 cm^{-1}. Nmr spectrum (in trifluoroacetic acid): τ2.05, doublet, H_3 of (25); τ3.50, doublet, H_2 and H_4 of (27); τ3.97, triplet, H_4 of (25); τ5.08, doublet, H_1 of (25); τ5.37, triplet, H_1 and H_5 of (27), H_5 of (25) is

obscured by this peak; τ5.76, singlet, $COOCH_3$ of (27); τ5.97, singlet, $COOCH_3$ of (25); τ6.6-7.0, multiplet, $H_{6\underline{endo}}$ of both complexes; τ7.84, doublet, $H_{6\underline{exo}}$ of both complexes. Coupling constants observed were: (25) $J_{3,4} = J_{4,5} = J_{1,6\underline{endo}} = 6$ c/s, $J_{6\underline{endo},\ 6\underline{exo}} = 16$ c/s; (27) $J_{1,2} = J_{4,5} = J_{1,6\underline{endo}} = J_{5,6\underline{endo}} = 7$ c/s, $J_{6\underline{endo},\ 6\underline{exo}} = 16$ c/s. The ratio of intensities of the peaks at τ2.05 and τ3.50 was 7:58, indicating the proportion of isomers given above.

Hydride abstraction from tricarbonyl-5-carbomethoxycyclohexa-1,3-dieneiron (13). - The neutral complex (13) was reacted in mixture with (15) (1 g total). The product began to crystallise from the methylene chloride solution after 40 min. Complete precipitation by addition of ether after 1 hr gave a yellow crystalline solid (860 mg, 66%) which the ir and nmr spectra showed to be a mixture of the fluoroborate salts (25) and (27) from reaction of (15) (see preceding experiment) as well as tricarbonyl-1- (24) (described above) and tricarbonyl-6-carbomethoxycyclohexadienyliron fluoroborate (26) ν_{max} 3080, 2125, 2105, 2080, 1725, 1305, 1070 cm^{-1}. Nmr spectrum (in trifluoroacetic acid): showed the resonances given in the preceding experiment for (25) and (27), and τ2.60, triplet, H_3 of (26); τ3.28, doublet, H_2 of (24); τ3.96, triplet, H_2 and H_4 of (26), this signal obscures H_4 of (24); τ5.48, triplet, H_1 and H_5 of (26); τ5.92, singlet, $COOCH_3$ of (26); τ6.00, singlet, $COOCH_3$ of (24). Coupling constants observed in the spectrum of (26) were: $J_{1,2} = J_{4,5} = J_{2,3} = J_{3,4} = J_{1,6endo} = J_{5,6endo} =$ 6 c/s. The ratio (24):(26) was 21:79 (given by the ratio of integrated intensities of the peaks at τ3.28 and τ2.60, which was 4:15).

Hydride abstraction from tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (33). - The carboxylic acid complex (33) (400 mg) gave a yellow crystalline precipitate of tricarbonyl-1-carboxycyclohexadienyliron fluoroborate (69) (200 mg, 38%) ν_{max} 3240 (broad), 3070, 2130, 2080, 1723, 1230, 1090 cm^{-1}. Nmr spectrum (in trifluoroacetic acid): τ2.41, triplet, H_3; τ3.22, doublet, H_2; τ3.95, triplet, H_4; τ5.12, triplet, H_5; τ6.52, doublet of doublets, $H_{6\underline{endo}}$; τ7.92, doublet, $H_{6\underline{exo}}$; $J_{2,3} = J_{3,4} = J_{4,5} = J_{5,6\underline{endo}} = 6$ c/s, $J_{6\underline{endo},\ 6\underline{exo}} = 15$ c/s.

The fluoroborate salt was soluble in water giving a stable yellow solution. The cation was not precipitated from solution on addition of aqueous ammonium fluorophosphate. Ammonium reineckate solution, however, gave a pink precipitate of the reineckate salt, $[C_6H_6COOH.\ Fe(CO)_3][Cr(SCN)_4(NH_3)_2]$. ν_{max} 3300, 3250, 3150, 2120, 2080, 1687, 1605, 1245 cm^{-1}. (Found: C, 28.3; H, 2.3; N, 14.3. $C_{14}H_{13}CrFeN_6O_5S_4$ requires C, 28.4; H, 2.2; N, 14.2%.)

Hydride abstraction from tricarbonyl-2-carboxycyclohexa-1,3-dieneiron (32). - The carboxylic acid complex (32) (200 mg) gave a yellow crystalline precipitate, a mixture of tricarbonyl-2- (70) (14%) and tricarbonyl-3-carboxycyclohexadienyliron fluoroborate (71) (86%) (total yield 170 mg, 64%). ν_{max} 3080, 2670 (broad), 2570 (broad), 2140, 2100, 1705, 1317, 1065 cm^{-1}. Nmr spectrum (in trifluoroacetic acid): τ2.01, doublet, H_3 of (70); τ3.50, doublet, H_2 and H_4 of (71); τ3.96, triplet, H_4 of (70); τ5.05, complicated, H_1 and H_5 of (70); τ5.33, triplet, H_1 and H_5 of (71); τ6.6-7.0, multiplet, $H_{6\underline{endo}}$ of both complexes; τ7.80, doublet, $H_{6\underline{exo}}$ of both complexes. Coupling constants observed were: (70) $J_{3,4}$ = 6 c/s; (71) $J_{1,2} = J_{4,5} = J_{1,6\underline{endo}} = J_{5,6\underline{endo}}$ = 6 c/s, $J_{6\underline{endo},\ 6\underline{exo}}$ = 17 c/s. The ratio (70):(71) was calculated from the integrated intensities of the peaks at τ2.01 and τ3.50, which were in a ratio 4:50.

The fluoroborate salts behaved similarly to (69) in water (see above), giving a precipitate of pink reineckate salts. ν_{max} 3300 (broad), 3220, 3160, 3060, 2117, 2080, 2060, 1705, 1675, 1267 cm^{-1}.

Hydride abstraction from tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (29). - The mixture of carboxylic acid complexes (29) and (32) (400 mg) gave a yellow crystalline precipitate (230 mg, 43%). ν_{max} 3600-2500 (broad), 3080, 2140, 2120, 2105, 2080, 1755, 1710, 1323, 1070 cm^{-1}. The nmr spectrum of this material showed it to consist of (70) and (71) from reaction of (32) (see preceding experiment) as well as tricarbonyl-6-carboxycyclohexadienyliron fluoroborate (72): (in trifluoroacetic acid) τ2.58, H_3 of (72); τ3.91, H_2 and H_4 of (72); τ5.50, H_1 and H_5 of (72); τ6.4-7.0, $H_{6\underline{endo}}$ of all three complexes. The spectrum was broad, many of the expected splittings were not well resolved.

The mixture of salts was soluble in water with properties similar to those described for (69), (70) and (71). The mixture of pink reineckate salts had ν_{max} 3460 (broad), 3300, 3160, 2120, 2080, 1720, 1603, 1250 cm^{-1}.

Reaction of tricarbonyl-1-carbomethoxycyclohexadienyliron fluoroborate (24) with water and alcohols. - Addition of water to the gum obtained on reaction of tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron (14) with triphenylmethyl fluoroborate (see above), (1 g) gave an immediate reaction with production of yellow, water-insoluble material. Extraction into ether gave an orange oil which was chromatographed on activity (III) neutral alumina (20 g) in ethanol-free chloroform to give two fractions.

The first yellow band eluted yielded a viscous orange oil turning to a gum on evacuation of traces of solvent. It did not recrystallise successfully from any solvent system tried at room temperature or -20°. It was identified as *the ether* (74) (200 mg, 20%) by its spectral properties. ν_{max} 2060, 1980, 1700, 1250 cm^{-1}. Nmr spectrum (broad, possibly due to the presence of *d,l* and *meso* forms): τ3.84, doublet, H_2 and H_2'; τ4.56, doublet of doublets, H_3 and H_3'; τ6.00, doublet with fine splitting, H_5 and H_5'; τ6.33, singlet, $COOCH_3$ and $COOCH_3'$; τ6.90, complicated, H_4 and H_4'; τ7.33, multiplet, H_6 and H_6', probably *endo*; τ8.71, distorted triplet with fine splitting, H_6 and H_6', probably *exo*; $J_{2,3}$ = 4 c/s, $J_{3,4}$ = 8 c/s. The mass spectrum did not show a molecular ion but had peaks at m/e

294 and m/e 278 corresponding to fragment ions resulting from fission of the ether linkage (with hydrogen transfers). The peak at m/e 294 displayed a fragmentation pattern identical to that of the alcohol (73), described below. The fragment m/e 278 showed loss of 3 x CO, 2 x H, 1 x Fe (m/e 250, 222, 194, 192, 136). This latter series of peaks was not present in the mass spectrum of the alcohol (73).

The second yellow band eluted gave an orange oil, solidifying on standing. Recrystallisation from petroleum spirit (bp 30-40°) at -20° gave yellow needles of *tricarbonyl-1-carbomethoxy-5-hydroxycyclohexa-1,3-dieneiron* (73) (215 mg, 20%), mp 84-85°. ν_{max} 3400 (broad), 2060, 1980, 1705, 1250 cm^{-1}. Nmr spectrum: τ3.74, doublet, H_2; τ4.51, triplet, H_3; τ5.57, broad, sharpening to doublet of triplets on addition of D_2O, H_5, probably *endo*; τ6.30, singlet, $COOCH_3$; τ6.82, triplet with fine splitting, H_4; τ7.21, doublet of doublets, H_6, probably *endo*; τ7.93, broad doublet exchanging with D_2O, OH; τ8.86, doublet of doublets, H_6, probably *exo*; $J_{2,3} = J_{3,4}$ = 5 c/s, $J_{4,5\text{endo}}$ = 3 c/s, $J_{5\text{endo},OH}$ = 4 c/s, $J_{5\text{endo}, 6\text{exo}}$ = 4 c/s, $J_{5\text{endo}, 6\text{endo}}$ = 10 c/s, $J_{6\text{endo}, 6\text{exo}}$ = 15 c/s. The mass spectrum showed a molecular ion m/e 294 ($C_{11}H_{10}FeO_6$ = 294) with loss of 3 x CO, 1 x H_2O, 1 x Fe (m/e 266, 238, 210, 192, 136) to give the base peak at m/e 136. The sample for analysis was sublimed at 65°/0.05 mm and had mp 84-85°. (Found: C, 45.2; H, 3.5. $C_{11}H_{10}FeO_6$ requires C, 44.9; H, 3.4%.)

Use of chloroform containing traces of ethanol in the above chromatographic separation resulted in isolation of a first fraction containing (75), the *ethyl ether of (73)*, in mixture with (74). The two ethers (74) and (75) were separated by chromatography on activity (III) neutral alumina in benzene. The first yellow band eluted was the ethyl ether (75). ν_{max} 2060, 1980, 1705, 1250 cm^{-1}. Nmr spectrum [sharp, *cf*. the broad spectrum of (74)]: τ3.81, doublet, H_2; τ4.52, triplet, H_3; τ6.00, doublet of triplets, H_5, probably *endo*; τ6.33, singlet, $COOCH_3$; τ6.58, quartet, OCH_2; τ6.76, complicated, H_4; τ7.32, doublet of doublets, H_6, probably *endo*; τ8.63, doublet of doublets, H_6, probably *exo*; τ8.88, triplet, CH_3; $J_{2,3}$ = 4 c/s, $J_{3,4}$ = 5 c/s, $J_{4,5\mathit{endo}}$ = 3 c/s, $J_{5\mathit{endo},\ 6\mathit{endo}}$ = 10 c/s, $J_{5\mathit{endo},\ 6\mathit{exo}}$ = 3 c/s, $J_{6\mathit{endo},\ 6\mathit{exo}}$ = 15 c/s.

Addition of concentrated hydrochloric acid (1 drop) to a solution of the alcohol (73) (50 mg) in methanol (10 ml) and extraction of the complex into ether after 1 hr gave *tricarbonyl-1-carbomethoxy-5-methoxycyclohexa-1,3-dieneiron* (76). ν_{max} 2060, 1975, 1700, 1250 cm^{-1}. The nmr spectrum was identical to that of the ethyl ether (75), described above, with the OCH_2CH_3 triplet-quartet replaced by an OCH_3 singlet at τ6.74, overlapping with the H_4 signal.

Reaction of tricarbonyl-2- (25) and tricarbonyl-3-carbomethoxycyclohexadienyliron fluoroborate (27) with water.

- The mixture of (25) (20%) and (27) (80%), obtained from the reaction of tricarbonyl-2-carbomethoxycyclohexa-1,3-dieneiron with triphenylmethyl fluoroborate, (1 g) was added to water (30 ml) and ether (30 ml) and stirred at room temperature until the aqueous layer was colourless (about 30 min). The resulting yellow ether solution gave an orange oil which was separated into two fractions as described in the previous experiment.

The first fraction, an orange gum similar to the one obtained previously (100 mg, 10%), contained mainly *the ether* (78) formed from (27). *The ether* (80), arising from (25) via formation of the fully-conjugated alcohol complex (79), was also present (23% of the total). ν_{max} 2060, 1980, 1720, 1250 cm^{-1}. In the nmr spectrum the major product showed peaks as follows: (broad spectrum, as above) τ3.67, doublet, H_3 and H_3'; τ5.97, doublet of triplets, H_6 and H_6', probably *endo*; τ6.15, singlet, $COOCH_3$ and $COOCH_3'$; τ6.30, complicated, H_1 and H_1'; τ6.90, complicated, H_4 and H_4'; τ7.67, multiplet, H_5 and H_5', probably *endo*; τ8.58, triplet with fine splitting, H_5 and H_5', probably *exo*; $J_{3,4}$ = 6 c/s, $J_{1,6\underline{endo}}$ = 3 c/s, $J_{6\underline{endo},\,5\underline{endo}}$ = 10 c/s, $J_{6\underline{endo},\,5\underline{exo}}$ = 3 c/s. The minor product was identified by its peaks at τ3.90, doublet, H_2 and H_2'; τ4.50, triplet, H_3 and H_3'; τ6.36, singlet, $COOCH_3$ and $COOCH_3'$. The ratio (78):(80) was obtained from the integrated ratio of the peaks at τ3.67 [including H_2 of (80), τ3.90] and τ4.50 which was 13:3.

The second fraction (240 mg, 23%) contained the alcohols *tricarbonyl-2-carbomethoxy-6-hydroxy-* (77) (85% of the total) and *tricarbonyl-1-carbomethoxy-6-hydroxycyclohexa-1,3-dieneiron* (79) (15%). ν_{max} 3400, 2060, 1980, 1720, 1250 cm^{-1}. Nmr spectrum: τ3.65, doublet,

H_3 of (77); τ3.86, doublet, H_2 of (79); τ4.36, triplet, H_3 of (79); τ5.60, complicated, collapsing to doublet of triplets on addition of D_2O, H_6, probably endo, of (77); τ6.15, singlet, $COOCH_3$ of (77); τ6.28, singlet, $COOCH_3$ of (79); τ6.46, doublet of doublets, H_1 of (77); τ6.92, multiplet, H_4 of (77); τ7.63, multiplet, H_5, probably endo, of (77); τ7.70, doublet exchanging with D_2O, OH of (77); τ8.50, doublet with fine splitting, H_5, probably exo, of (77). Coupling constants observed were: (77) $J_{3,4}$ = 7 c/s, $J_{1,3}$ = 1.5 c/s, $J_{1,6\underline{endo}}$ = 4 c/s, $J_{5\underline{endo},\ 6\underline{endo}}$ = 10 c/s, $J_{5\underline{exo},\ 6\underline{endo}}$ = 3 c/s, $J_{5\underline{endo},\ 5\underline{exo}}$ = 15 c/s; (79) $J_{2,3}$ = $J_{3,4}$ = 5 c/s. The ratio (77):(79) was given by the integrated ratio of peaks τ3.65:τ3.86 which was 17:3.

Recrystallisation of this fraction several times from petroleum spirit (bp 30-40°) at -20° gave pure (77), mp 83-84°.

SECTION B. A SERIES OF BINUCLEAR COMPLEXES DERIVED FROM HEXAHYDROANTHRACENE.

INTRODUCTION.

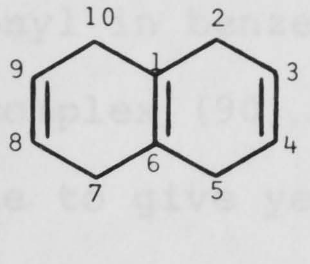
The formation of tricarbonyldieneiron complexes from the products of metal-ammonia reduction of naphthalene and anthracene has been reported by Birch *et al.*[61] Ultraviolet irradiation of bicyclo[4.4.0]deca-1(6),3,8-triene (86) (1,4,5,8-tetrahydronaphthalene) and iron pentacarbonyl in benzene gives tricarbonyl(1,2,3,6-*h*^{4}-bicyclo[4.4.0]deca-1(6),2,8-triene)iron (87), while refluxing triiron dodecacarbonyl in benzene with tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),5,12-tetraene (88) (1,4,5,8,9,10-hexahydroanthracene) gives tricarbonyl(3,4,5,8-*h*^{4}-tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),4,12-tetraene) iron (89). (The nomenclature used here follows that proposed by Cotton.[131] The prefix *hapto*, abbreviated to *h*, is used to designate carbons involved in bonding to the metal, these being cited before the name of the organic ligand. A superscript appended to the symbol *h* specifies the number of such carbon atoms involved in individual organo-metal fragments.) Both complexes are obtained as viscous orange oils.

In an investigation of the tricyclic complex (89) by the present author, difficulty was experienced in the separation of a mixture of the complex and unreacted hexahydroanthracene, obtained from the reaction outlined above. In an effort to reduce the proportion of uncomplexed material, the mixture was treated with further triiron dodecacarbonyl in refluxing benzene for 24 hours. Addition of petroleum spirit to the product prior to chromatography gave a yellow crystalline precipitate which was shown to be (3,4,5,8-h^{4}:1,10,11,12-h^{4}-tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),4,11-tetraene)*trans*-bis(tricarbonyliron) (90).

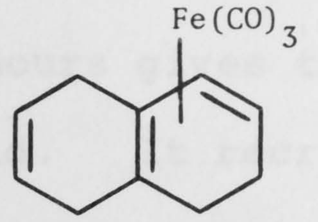
A study of this compound and several of its derivatives showed some interesting features not encountered in the chemistry of the monocyclic diene complexes.

RESULTS AND DISCUSSION.

Refluxing hexahydroanthracene (88) with triiron dodecacarbonyl in benzene for 40-80 hours gives the binuclear complex (90) in 10-30% yield. It recrystallises from benzene to give yellow plates which are only slightly soluble in cold organic solvents and which decompose, without melting, above 200^o. The same product is obtained by reacting iron pentacarbonyl with hexahydroanthracene in dibutyl ether for 16 hours (10-20% yield).

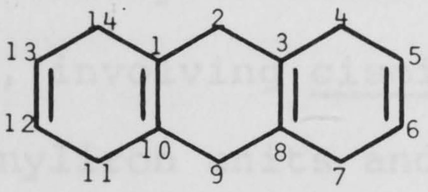


(86)



(87)

The products of the two reactions could be isomeric, involving cisoid and transoid arrangements of the tricarbonyliron units and of the butadiene systems. Four such isomers are possible, structures (90) and (91) show the transoid-transoid and cisoid-cisoid configurations respectively. The two products have been shown to be identical, however, since their X-ray powder patterns are found to be superimposable.



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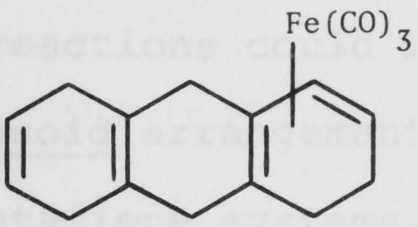
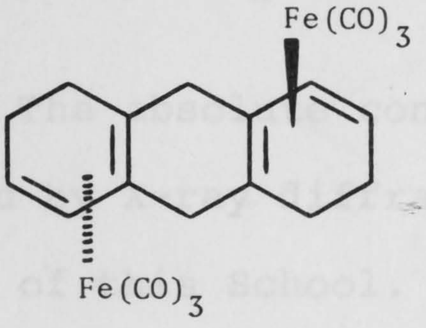


(89)

The absolute configuration of the complex has been determined by X-ray diffraction, carried out by Dr. G.B. Robertson of this School. The molecule is centrosymmetric in the crystal, this symmetry requiring the transoid-transoid configuration of structure (90). Structural details revealed by the X-ray analysis are shown in Figure 3.



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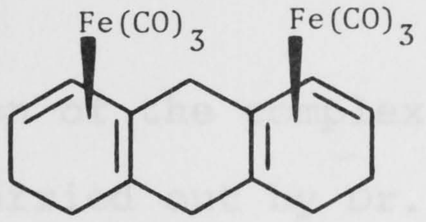

(91)

Elemental analysis and the ir, nmr and mass spectra are in accord with the structure shown. Low solubility of the complex necessitated the use of a computer of average transients (C.A.T.) to obtain the nmr spectrum.

RESULTS AND DISCUSSION.

Refluxing hexahydroanthracene (88) with triiron dodecacarbonyl in benzene for 40-80 hours gives the binuclear complex (90) in 10-30% yield. It recrystallises from benzene to give yellow plates which are only slightly soluble in cold organic solvents and which decompose, without melting, above 200°. The same product is obtained by reacting iron pentacarbonyl with hexahydroanthracene in dibutyl ether for 16 hours (10-20% yield).

The products of the two reactions could be isomeric, involving cisoid and transoid arrangements of the tricarbonyliron units and of the butadiene systems. Four such isomers are possible, structures (90) and (91) show the transoid-transoid and cisoid-cisoid configurations respectively. The two products have been shown to be identical, however, since their X-ray powder patterns are found to be superimposable.

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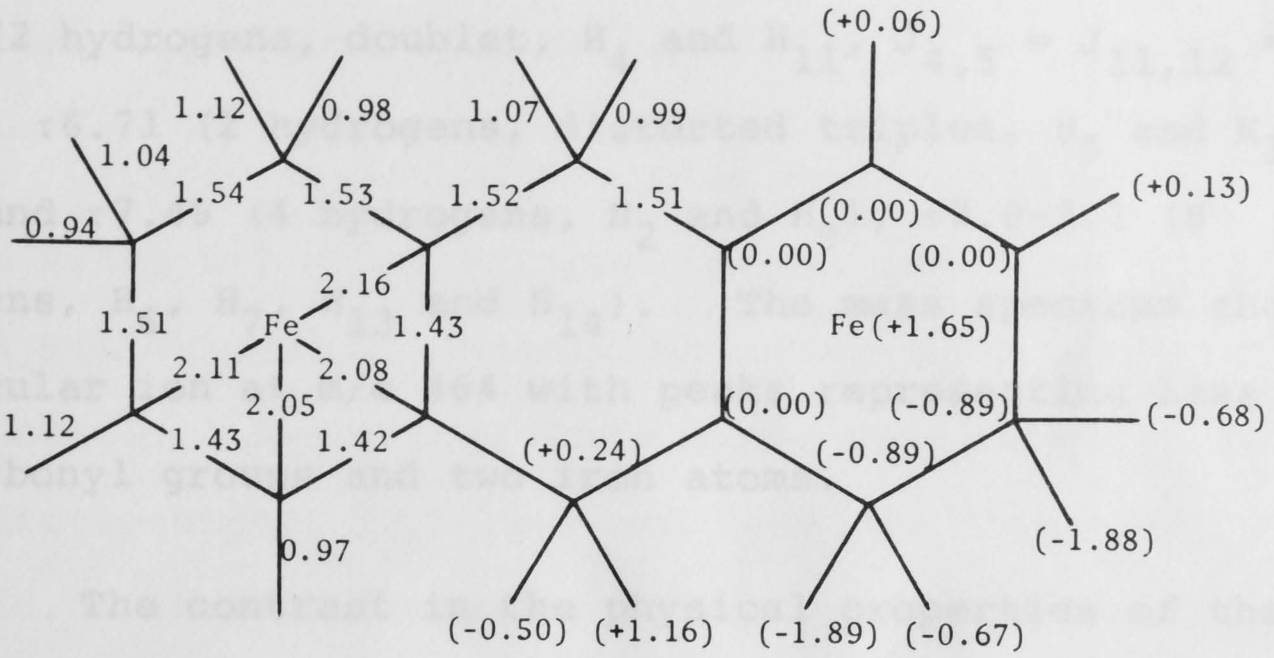


Bond lengths in A° (σ Fe-C = σ C-C = 0.006, σ C-H = 0.05A°).
Figures in parenthesis indicate distances of atoms above and below the plane of the butadiene fragments.

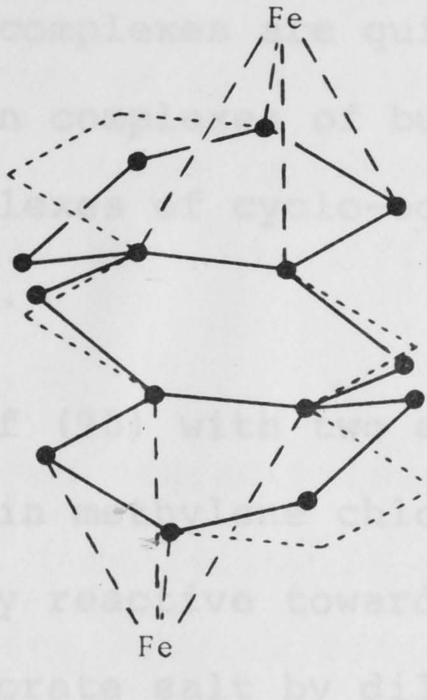


Figure 3. Crystal structure of $C_{14}H_{16}[Fe(CO)_3]_2$
(not to scale)

The average of 460 scans (in benzene-d_6 solution) shows: τ5.28 (2 hydrogens, doublet, H_4 and H_{11}, $J_{4,5} = J_{11,12} =$ 6 c/s), τ6.71 (2 hydrogens, distorted triplet, H_5 and H_{12}), τ7.31 and τ7.48 (4 hydrogens, H_2 and H_9), τ8.0-9.2 (8 hydrogens, H_6, H_7, H_{13} and H_{14}). The mass spectrum shows a molecular ion at m/e 464 with peaks representing loss of six carbonyl groups and two iron atoms.

The contrast in the physical properties of the tricarbonyliron and bis(tricarbonyliron) complexes formed from hexahydroanthracene, (89) (liquid, readily soluble in organic solvents) and (90) (solid, only slightly soluble in organic solvents and not melting on heating), is surprising at first sight. However similar differences between mono- and binuclear complexes are quite common; for example the tetracarbonyliron complexes of butadiene[39] and the tricarbonyliron complexes of cyclo-octatetraene[74,132-134] exhibit such effects.

Reaction of (90) with two equivalents of triphenylmethyl fluoroborate in methylene chloride gives a product which is particularly reactive towards water. Precipitation of the fluoroborate salt by dilution of the methylene chloride solution with moist ether (a standard procedure, traces of water serving to decompose excess triphenylmethyl fluoroborate) initially produces the expected yellow material. Continued addition of ether, however,or filtering the precipitate in the atmosphere gives a deep red colour to the product. The ir spectrum of the resulting mixture of red and yellow compounds shows bands of comparable intensities at 2110, 2070, 2050, 1990 and 1975 cm^{-1}, indicating the presence of both neutral tricarbonyldieneiron and cationic tricarbonyldienyliron systems.

Precipitation of the salt from the reaction mixture using dry ether or (preferably) petroleum spirit gives a yellow product containing unreacted triphenylmethyl fluoroborate. Analytical figures for this material are consistently higher in carbon and hydrogen than those expected. Attempted washing of the yellow product (e.g. with methylene chloride) gives the red coloration with increasing intensity as the proportion of triphenylmethyl fluoroborate is reduced in successive stages.

The nmr spectrum of the material in trifluoroacetic acid (which may be expected to regenerate a cyclohexadienyl cation from the product of its reaction with water, see Section A.e) shows a mixture of compounds, mostly uncomplexed, and does not allow positive identification of any complexed species present.

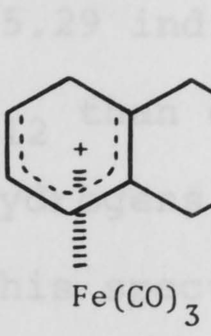
Isolation and characterisation of the red compound noted above (see following results) allow inference of the structure of the complex formed in the hydride abstraction reaction. A bis(tricarbonylcyclohexadienyliron) dication (92), derived from 1,5,9,10-tetrahydroanthracene is indicated as the most likely product. Formation of the dications (93) and (94) could also be expected in this reaction.

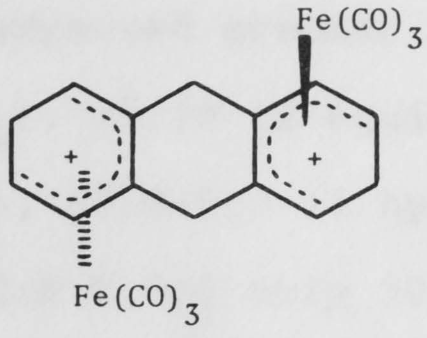
Addition of water to the impure fluoroborate salt gives an immediate reaction with production of a deep red ether-soluble compound. Allowing the reaction to proceed at 4° for 12 hours results in a colourless aqueous phase beneath a deep red ether layer. The ether solution gives a viscous oil which deposits a dark red, almost black crystalline substance on the addition of a small volume of dry ether. Due to its low solubility and instability when warmed in organic solvents, the solid material can not be recrystallised satisfactorily. However it is obtained almost pure from the crude oily product by the procedure described above.

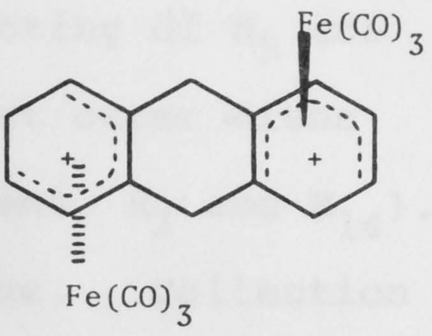
This substance does not display the expected hydroxy absorption in its ir spectrum, but has terminal carbonyl stretching frequencies at 2030, 1970 and 1955 cm^{-1}. Its mass spectrum shows a molecular ion at m/e 460, indicating an overall loss of two molecules of hydrogen from (90) by way of the hydride abstraction and subsequent hydrolysis reactions. The fragmentation pattern exhibited in the mass spectrum indicates the presence of two tricarbonyliron groups.

Avoiding the postulation of tricarbonyldieneiron units derived from fully aromatic rings leaves only one reasonable structure: (3,4,5,6-$\underline{h}^4$: 10,11,12,13-$\underline{h}^4$-tricyclo[8.4.0.$0^{3,8}$]tetradeca-1,3,5,8,10,12-hexaene)*trans*-bis(tricarbonyliron) (95), a complex derived from 1,5-dihydroanthracene with the ligand stabilised by complex formation.

The nmr spectrum supports this structure: τ4.87 (2 equivalent hydrogens, singlet, H_2 and H_9), τ5.29 (2 equivalent inner diene hydrogens, H_4 and H_{11}), τ5.32


(92)


(93)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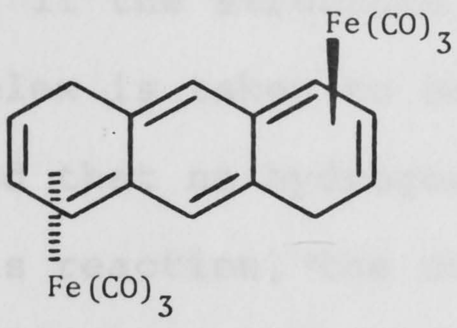
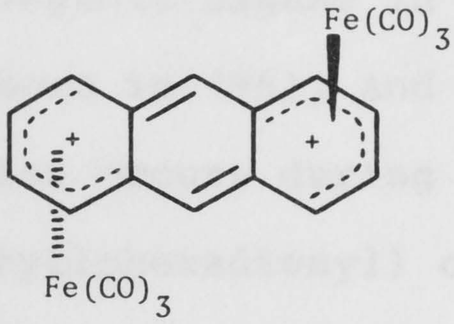

(95)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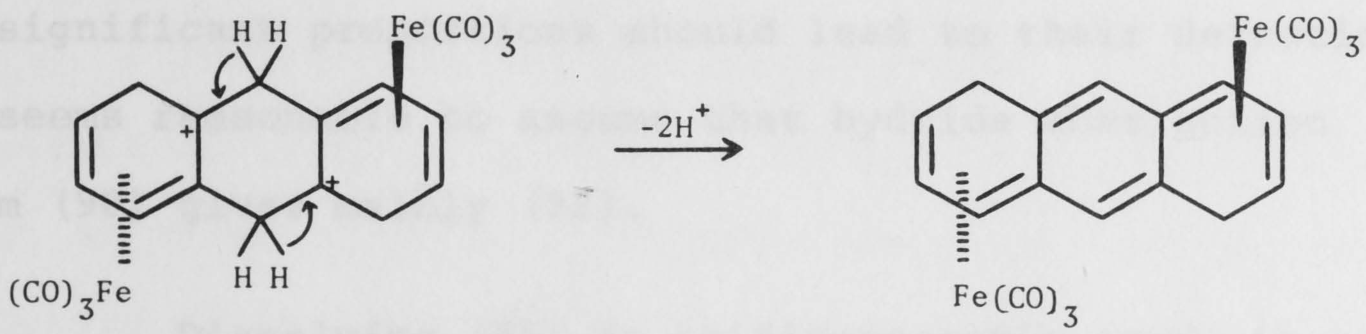


(92)

(95)

Scheme 20

(overlapping with the previous signal, 2 equivalent inner diene hydrogens, H_5 and H_{12}, this peak broader than that at τ5.29 indicating the expected greater splitting of H_5 and H_{12} than of H_4 and H_{11}), τ7.18 (2 equivalent outer diene hydrogens, H_6 and H_{13}), τ7.8-8.7 (4 hydrogens, H_7 and H_{14}). This spectrum is the C.A.T. of only 30 scans. Collection of more data and resolution of fine structure were precluded by slow decomposition of the complex in solution.

If the structure of the organic ligand in this last complex is taken to be that shown in (95), and if it is assumed that no hydrogen migration occurs during the hydrolysis reaction, the only bis(cyclohexadienyl) cation which can give rise to (95) by deprotonation is (92), as shown in Scheme 20. The low overall yield of (95) from (90) (34%) leaves the possibility that other binuclear complexes, formed from the dications (93) and/or (94) by hydrolysis, are not isolated. However the presence of such species in significant proportions should lead to their detection. It seems reasonable to assume that hydride abstraction from (90) gives mainly (92).

Dissolving (95) in trifluoroacetic acid, in an attempt to observe the nmr spectrum of (92), results only in decomposition of the complex. Similarly, attempts to hydrogenate the uncomplexed double bonds of (95) fail because of decomposition in solution.

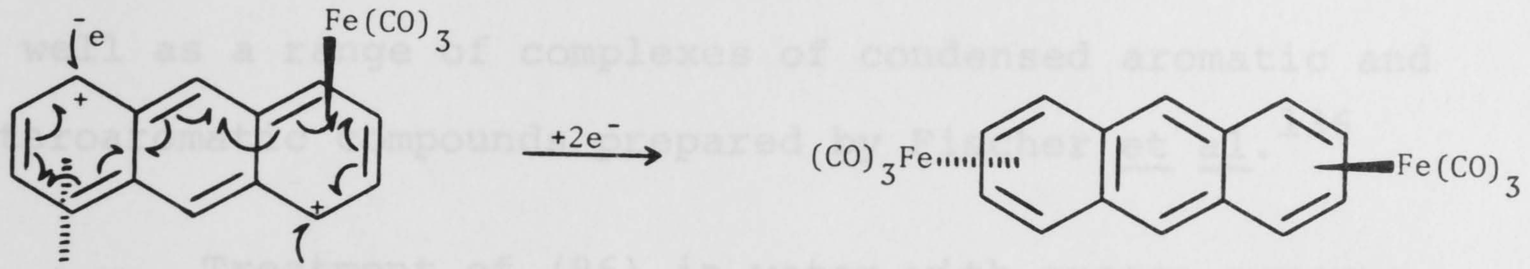
Treatment of (95) with triphenylmethyl fluoroborate gives a purple fluoroborate salt (87% yield) which is presumed to be (96), resulting from abstraction of hydride ion from each of the two methylene carbons of (95). This substance is unstable in solution (and to a lesser degree in the solid state) and has not been purified sufficiently to give a satisfactory elemental analysis. Its low solubility and instability have prevented the recording of its nmr spectrum.

The intense red and purple colours of complexes (95) and (96), respectively, are seen to be due to absorption bands centred in the visible region: (95) has λ_{max} 484 mμ (ε_{max} 1.1 x 10^4) with a shoulder at 400 mμ (ε 5.5 x 10^3); (96) shows λ_{max} 516 mμ (ε_{max} greater than 1.6 x 10^3). (The latter band decreases rapidly in intensity, with a half-life of 2-3 minutes in water. The extinction coefficient given here was measured as quickly as possible after dissolving the complex.) Considerable interaction between the complexed and uncomplexed double bonds is indicated by these values.

Addition of two electrons to (96), formally a complexed dication of anthracene, might be expected, at least in part, to produce a rearrangement of the electronic structure of the ligand and give the hitherto unknown hexacarbonylanthracenediiron (97) as shown in Scheme 21.

Direct reaction of anthracene with triiron dodecacarbonyl gives tricarbonylanthraceneiron (98), but the binuclear complex of anthracene is not formed under these conditions, nor is the analogous tricarbonyliron complex of naphthalene.[33] Trials carried out by the present author show that refluxing anthracene with iron pentacarbonyl in dibutyl ether gives no isolable complex.

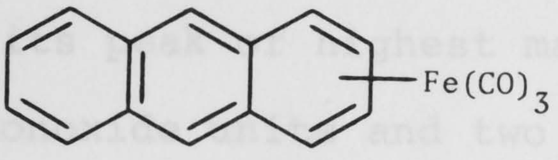
Other reported tricarbonyldieneiron complexes utilising double bonds of aromatic systems include the hexacarbonyldiiron complexes of _m_- and _p_-divinylbenzene[135] and the tricarbonyliron complex of 1-vinylnaphthalene[33], as well as a range of complexes of condensed aromatic and heteroaromatic compounds prepared by Fischer _et al._[illegible]



(96) (97)

Scheme 21

Treatment of (96) in water with excess aqueous chromous chloride gives a rapid reaction with the blue chromium (II) solution turning to green chromium (III). Decomposition of the complex is evident. Extraction of the mixture with ether yields a dark red oil. Chromatography on silica gel in petroleum spirit results in elution of a yellow solution which gives very small quantities of a yellow gum. The mass spectrum of this material shows its peak of highest mass at m/e 458; loss of six carbon monoxide units and two iron atoms gives m/e 178 (anthracene = 178).



(98)

The yellow gum shows ultraviolet absorption which increases in intensity from 450 mμ to 210 mμ, with a sharp increase over the range 270 mμ to 210 mμ. The only features of the spectrum are two small shoulders at λ303 and 290 mμ (both ε 1.1 x 10^4). This spectrum is suggestive of the central benzenoid ring of structure (97). Tricarbonylanthraceneiron (98), by way of analogy, shows λ_{max} 304 mμ (ε 2.5 x 10^4), 251 mμ (ε 2.5x 10^4) and 230 mμ (ε 2.7 x 10^4), a spectrum reminiscent of that of naphthalene.

Due to the small quantities isolated, no further proof of the structure of this compound has been obtained.

Other reported tricarbonyldieneiron complexes utilising double bonds of aromatic systems include the hexacarbonyldiiron complexes of m- and p-divinylbenzene[135] and the tricarbonyliron complex of 1-vinylnaphthalene[33], as well as a range of complexes of condensed aromatic and heteroaromatic compounds prepared by Fischer et al.[136]

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Due to the small quantities isolated, no further proof of the structure of this compound has been obtained.

Its identity as (98) thus can not be considered certain. In any case the yield from this reaction is so low as to render it of little preparative importance.

EXPERIMENTAL.

(For general experimental details, see Section A, Experimental.)

Anthracene was reduced to its hexahydro derivative (88) using lithium and ethanol in liquid ammonia, as described in the literature.[137]

Reaction of tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),5,12-tetraene (88) with triiron dodecacarbonyl. - Triiron dodecacarbonyl (5 g) was added to (88) (5 g) in dry benzene (100 ml) and the mixture refluxed under nitrogen. Two further portions of triiron dodecacarbonyl (5 g each) were added at intervals of 10 to 20 hr so as to preserve the green colour of the solution. Refluxing was then continued until all green colour had disappeared, which was generally 24 to 48 hr after the last addition. The mixture was filtered through celite 535 while still warm and the celite washed with boiling benzene until the washings were colourless. The resulting solution was evaporated down to give a yellow residue, partly an oil and partly solid. Trituration with petroleum spirit (bp 40-60^{o}) and washing the solid several times with this solvent left pure (3,4,5,8-h^4:1,10,11,12-h^4-tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),4,11-tetraene)trans-bis(tricarbonyliron) (90), a yellow crystalline solid. The yield of complex varied between 1.0 and 4.3 g (8-34%); it was normally about 2 g (16%). Recrystallisation from benzene under nitrogen gave yellow plates which decomposed without melting above 200^{o}.

ν_{max} (nujol) 3050 (weak), 2050, 2033, 1970, 1950, 1936 (all very strong), 1432, 1312, 1180, 955, 945, 916, 890 (all weak) cm^{-1}; (KBr) identical bands and in addition revealed 2942, 2915, 2840 cm^{-1}. Nmr spectrum (C.A.T. of 460 scans in benzene-d_6 solution, lock signal benzene): τ5.28, doublet, H_4 and H_{11}; τ6.71, distorted triplet, H_5 and H_{12}; τ7.31 and τ7.48, H_2 and H_9; τ8.0-9.2, H_6, H_7, H_{13} and H_{14}; $J_{4,5} = J_{11,12}$ = 6 c/s. (Chemical shifts relative to TMS were calculated from benzene in benzene-d_6 at τ2.85; this value was found by experiment.) Mass spectrum: molecular ion m/e 464 ($C_{20}H_{16}Fe_2O_6$ = 464), showing loss of 6 x CO, 2 x Fe, 6 x H (m/e 436, 408, 406, 378, 350, 348, 322, 320, 296, 294, 292, 290, 266, 264, 238, 236, 234, 178) to give the base peak at m/e 178 (anthracene, $C_{14}H_{10}$ = 178). (Found: C, 51.9; H, 3.4. $C_{20}H_{16}Fe_2O_6$ requires C, 51.8; H, 3.5%.)

The crystal for X-ray diffraction study was grown from benzene solution, by slow evaporation of the solvent (several weeks) under a stream of nitrogen at room temperature.

The petroleum spirit washings of the bis(tricarbonyliron) complex contained a mixture of the mononuclear complex described by Birch *et al.*[61] with hexahydroanthracene (88) and some anthracene (by nmr).

Reaction of tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),5,12-tetraene (88) with iron pentacarbonyl. - Iron pentacarbonyl (11 ml, 16 g) and (88) (5 g) were refluxed in di-*n*-butyl ether

(100 ml) for 16 hr. The reaction mixture was filtered through celite 535 while still warm and the celite washed with boiling benzene until the washings were colourless. The yellow solution was evaporated down under reduced pressure (rotary evaporator) to give a similar residue to that obtained from the above reaction with triiron dodecacarbonyl. The solid complex was recovered in the manner described above, giving the same bis(tricarbonyliron) complex (90) (2.74 g, 22%).

X-ray powder patterns of the recrystallised products from the reactions of (88) with iron pentacarbonyl and with triiron dodecacarbonyl were obtained using Cu radiation with Ni filter. They showed identical diffraction patterns, 17 lines being observed and compared.

Reaction of the bis(tricarbonyliron) complex (90) with triphenylmethyl fluoroborate. - Triphenylmethyl fluoroborate (8.7 g) was dissolved in the minimum volume of methylene chloride (about 40 ml) at room temperature, the solution was cooled to 4° and the solid complex (90) (5.6 g) was added with stirring. The mixture was protected from entry of moisture and stirred at 4° for 5 hr then petroleum spirit (bp 40-60°) (200 ml) was added, giving a yellow precipitate. The precipitate was filtered off and washed with further petroleum spirit. The yellow solid began to turn red at once, and was generally reacted with water immediately. The mass of the material isolated was 8 g [115% calculated for pure (<u>3,4,5,6,8-$\underline{h}^5$: 1,10,11,12,13-$\underline{h}^5$-tricyclo[8.4.0.0^{3,8}]tetradeca-1(10),3(8),4,11-tetraen-6,13-diyl)</u><u>trans</u>-<u>bis(tricarbonyliron) fluoroborate</u> (92)]. A nujol mull (prepared in a dry nitrogen atmosphere but turning pink before the spectrum had been recorded) showed ν_{max} 3075, 2110, 2070, 2050, 1060 cm^{-1} with a weak band at 1975 cm^{-1}. The nmr spectrum in trifluoroacetic acid showed resonances at τ2.7, 4.0 and 5.5-7.8, but no fine structure was resolved. In some spectra run, however, the resonances at τ2.7 and τ4.0 had the appearance of the doublet and triplet expected for (92). Peaks of the triphenylmethyl cation (formed from triphenylcarbinol in trifluoroacetic acid) and other (unidentified) impurities were also present.

<u>Hydrolysis of the fluoroborate salt (92)</u>. - The yellow to red solid obtained above (8 g) was added to water (500 ml) and ether (500 ml) and the mixture stirred at 4° for 12 hr. A deep red colour developed immediately on addition to water; at the end of the 12 hr period there was a dark red solid suspended in the mixture, which separated into a colourless to light orange aqueous layer and a dark red ethereal solution. The solid was collected by filtration. The ether solution was dried then evaporated down to give a viscous oil. Addition of dry ether (10 ml) caused partial crystallisation of the oil; the crystals were washed by decantation several times with dry ether. They were identical to the solid first filtered off. Purification of the product was effected by dissolving in benzene at room

temperature, filtering the solution and evaporating to dryness under reduced pressure. Washing the residue with dry ether gave dark red crystals of <u>(3,4,5,6-h^4:10,11,12,13-h^4-tricyclo[8.4.0.0^{3,8}]tetradeca-1,3,5,8,10,12-hexaene)trans-bis(tricarbonyliron)</u> (95) (1.9 g), 34% yield from (90). The crystals decomposed without melting above 150°. ν_{max} (nujol) 2030, 1970, 1955 (all strong), 980, 885, 870, 830 (all weak) cm^{-1}. The ir spectrum in chloroform solution showed a weak band at 1605 cm^{-1}. Nmr spectrum (C.A.T. of 30 scans in benzene-d_6 solution, lock signal benzene): τ4.87, H_2 and H_9; τ5.29, H_4 and H_{11}; τ5.32, H_5 and H_{12}; τ7.18, H_6 and H_{13}; τ7.8-8.7, H_7 and H_{14}. The chemical shifts relative to TMS were calculated as explained above. Mass spectrum: molecular ion m/e 460 ($C_{20}H_{12}Fe_2O_6$ = 460) showing loss of 6 x CO, 2 x Fe, 2 x H (m/e 432, 404, 376, 348, 320, 318, 292, 264, 262, 236, 234, 178) to give the base peak at m/e 178 (anthracene, $C_{14}H_{10}$ = 178). λ_{max} (methanol) 484, 400 (shoulder) mμ; ε_{max} 1.1 x 10^4, 5.5 x 10^3. (Found: C, 52.6; H, 2.6. $C_{20}H_{12}Fe_2O_6$ requires C, 52.2; H, 2.6%.)

<u>Reaction of the red bis(tricarbonyliron) complex (95) with triphenylmethyl fluoroborate</u>. - Triphenylmethyl fluoroborate (1.6 g) was dissolved in the minimum volume of methylene chloride at room temperature then cooled to 4°. The bis(tricarbonyliron) complex (95) (1.0 g) was added, the mixture stirred for 5 hr at 4° and ether added to give a dark purple precipitate which was filtered off and washed with dry ether. The yield was 1.2 g (87%) of

(3,4,5,6,7-h^5:10,11,12,13,14-h^5-tricyclo[8.4.0.$0^{3,8}$]tetradeca-1,3,5,8,10,12-hexaen-7,14-diyl)trans-bis(tricarbonyliron) fluoroborate (96). ν_{max} 2105, 2063, 2000, 1988, 1070 cm^{-1}. λ_{max} (water) 516 mμ, ε_{max} 1.6 x 10^3. The complex was unstable in solution, shown by the decreasing intensity of the visible absorption band (see Discussion). No nmr spectrum was obtained because of its insolubility and instability.

Reaction of the purple fluoroborate salt (96) with chromium (II) chloride. - Chromous chloride solution was prepared by treating acidic chromic chloride solution with sodium amalgam (a standard procedure). The purple fluoroborate salt (96) (100 mg) was treated with excess chromous chloride solution, an immediate reaction turning the blue chromium (II) solution to green chromium (III) and precipitating a dark solid. The mixture was extracted with ether; the resulting orange-red ether solution gave a dark red solid. Chromatography of the product in petroleum spirit (bp 40-60^o) on a column of activity (III) acidic alumina gave a yellow band which yielded a yellow gum (2.7 mg) on evaporation of the solvent. ν_{max} 3050, 2050, 1970, 1940 cm^{-1}. Mass spectrum: m/e 458, 430, 402, 374, 346, 318, 290, 262, 234, 178 ($C_{20}H_{10}Fe_2O_6$ = 458). See Discussion for a description of the uv spectrum. Anthracene was also isolated from the reaction (identified by its ir and nmr spectra).

SECTION C. DICARBONYL(TRIPHENYLPHOSPHINE)THEBAINEIRON - A REINVESTIGATION.

INTRODUCTION.

Birch and Fitton have synthesised the tricarbonyldieneiron complex at the substituted cyclohexadiene ring of the opium alkaloid thebaine, and subsequently carried out a number of reactions in which the presence of the tricarbonyliron group was found to distinctly alter the reactivity of the thebaine molecule.[76]

It has also been reported that "The replacement of carbon monoxide in thebaine iron tricarbonyl by phosphine was readily accomplished by refluxing thebaine $Fe(CO)_3$ with triphenylphosphine in di-n-butyl ether. The nmr spectrum of the crude product indicated that two isomeric triphenylphosphine adducts were produced. One of these adducts was obtained pure by recrystallisation from acetone. The existence of two triphenylphosphine adducts can be explained by examining a model of thebaine $Fe(CO)_3$, which shows that the carbon monoxide groups are non-equivalent (there is no free rotation because of steric hindrance)."[138]

This reaction was repeated in the hope of purifying and characterising a sample of each isomer.

RESULTS AND DISCUSSION.

The nmr spectrum of the crude product from reaction of tricarbonylthebaineiron (99) (R = CO) with triphenylphosphine is, as quoted in the Introduction, indicative of the presence of two isomers of the monophosphine derivative. The region $\tau 4$-6 contains three peaks belonging to unreacted tricarbonyl material: $\tau 4.68$ (doublet of doublets, H_7; $J_{7,5} = 2$ c/s, $J_{7,8} = 5$ c/s), $\tau 5.07$ (doublet, H_5, $J_{5,7} = 2$ c/s) and $\tau 5.45$ (doublet, H_8, $J_{8,7} = 5$ c/s). In addition two other, more intense peaks are present: $\tau 5.00$ (doublet with a coupling of 1.5 c/s and showing further fine splitting) and $\tau 5.21$ (triplet of doublets, or two overlapping double doublets, with coupling constants of 4.5 and 1.5 c/s).

These latter two signals can be assigned to H_5 and H_7, respectively, of the triphenylphosphine substituted compound but they show twice the number of lines of the corresponding peaks in the spectrum of the tricarbonyl complex. The peak corresponding to H_8 of the phosphine derivative is shifted upfield relative to that of the tricarbonyl compound so as to be obscured by the aromatic methoxy singlet at $\tau 6.23$ (*cf.* the corresponding upfield shift, of 0.53 ppm, of H_7). A change of solvent, from deuteriochloroform to dimethyl sulphoxide-d_6, separates the H_8 and methoxy peaks. The former is revealed as a triplet (or two overlapping doublets) with a splitting of 4.5 c/s, instead of the expected doublet.

The duplication of signals of hydrogens intimately concerned with the site of complexing is a strong indication that two isomers could indeed be present. The intensities of the relevant peaks indicate roughly equal quantities of each isomer. It is noted, however, that none of the three methyl resonances present show any splitting; all remain sharp singlets.

Purification of the crude product by chromatography and recrystallisation from acetone, followed by attempted fractional crystallisation, gives material which shows only one spot on thin layer chromatography but has multiple peaks in its nmr spectrum identical to those observed in the crude mixture. No tricarbonyl compound remains after this treatment. The mother liquors of both recrystallisations have nmr spectra similar to that of the crude mixture but with an increase in the proportion of the tricarbonyl complex.

The observed multiplicities of H_7 and H_8 have, in fact, the appearance of genuine spin-spin splittings rather than of the fortuitous overlapping of individual signals. The occurrence of the three methyl peaks without this splitting (and the fact that tlc shows only one component, although the expected isomers may not have been resolved by this technique) lend support to an alternative explanation of the observations.

Heteronuclear decoupling shows that P^{31}-H coupling is responsible for the extra peaks present in the spectrum and that only one isomer of the phosphine complex is formed in the displacement reaction.

Irradiation at the phosphorus frequency (40,984, 120± 5) Hz sharpens H_5 to a simple doublet ($J_{5,7}$ = 1.5 c/s) and collapses H_7 to a broad doublet ($J_{7,8}$ = 4.5 c/s, $J_{7,5}$ is observed only as a broadening). In addition the lower and upper wings of the H_8 triplet which are originally visible on either side of the methoxy singlet, τ6.23, are observed to collapse into the singlet. The downfield peak of the presumed resulting doublet remains partially resolved (see Figure 4).

The decoupled spectrum corresponds to that of tricarbonylthebaineiron and indicates the presence of a single isomer only of the triphenylphosphine derivative. The value of the P^{31}-H coupling constant to H_7 and H_8 is 4.5 c/s (by chance identical to $J_{7,8}$), while to H_5 it is less than 1 c/s, as expected for an allylic hydrogen which lies outside the main influence of the metal-diene bonding system.

A retrospective examination of the nmr spectrum of the crude product from the substitution reaction shows it to be a superimposition of the spectra of the tricarbonyl and dicarbonyl(triphenylphosphine) thebaine complexes, in the ratio 13:87.

The structure of a derivative of tricarbonylthebaineiron has been determined by X-ray crystallography.[139] It confirms that the tricarbonyliron unit and the piperidine ring lie on the same side of the thebaine cyclohexadiene ring in the complex under consideration. Examination of a molecular model indicates that significant

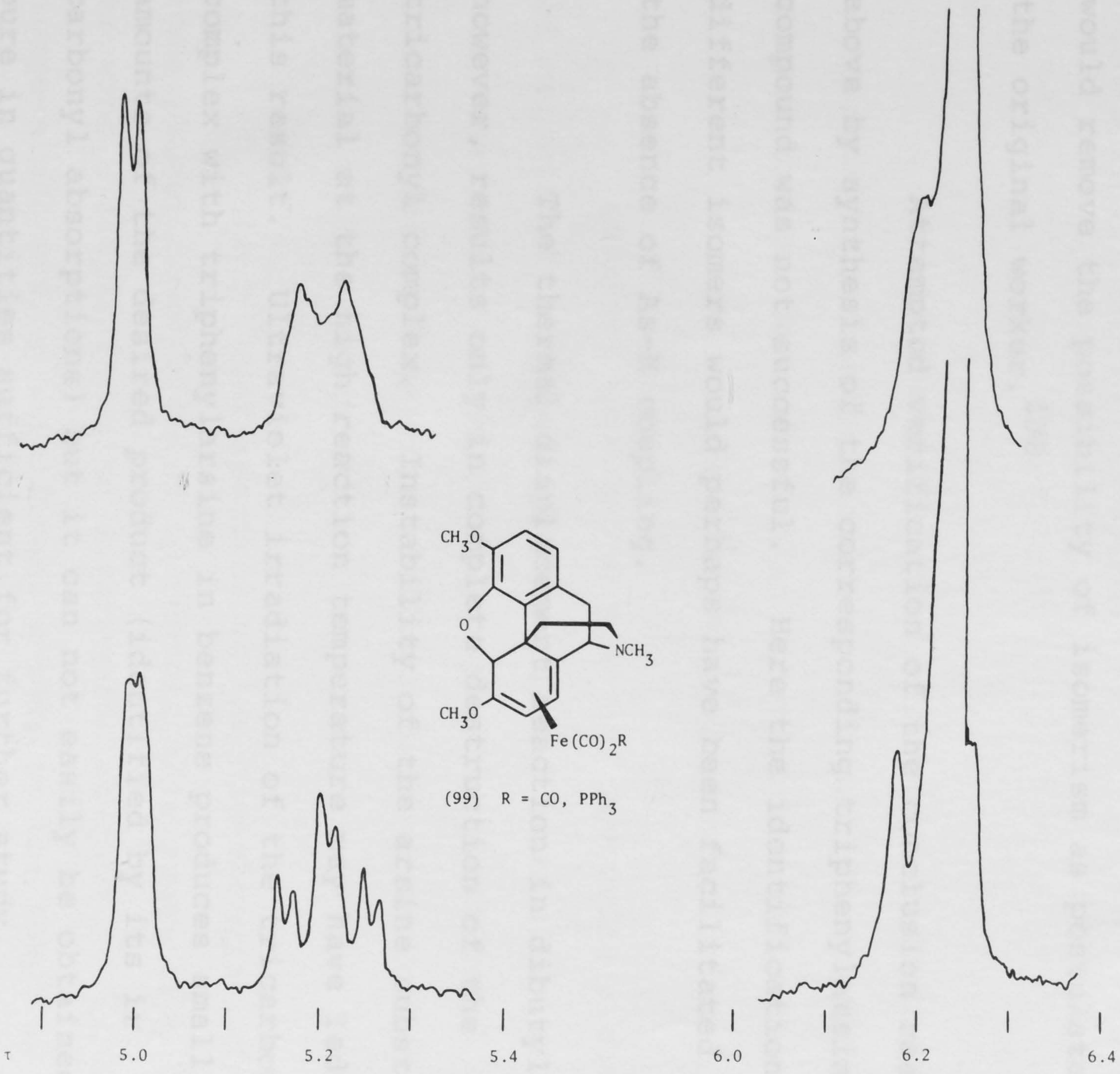

Figure 4. N.m.r. signals of H_5, H_7 and H_8 of dicarbonyl(triphenylphosphine)thebaineiron (99) (R = PPh_3). Lower trace: normal spectrum. Upper trace: phosphorus decoupled spectrum. Measured at 100 Mc in $CDCl_3$ solution with TMS as internal reference.

interaction between the bulky triphenylphosphine group and the thebaine molecule is inevitable. Without an X-ray diffraction study of tricarbonylthebaineiron itself, however, one can not be certain if sufficient interaction to restrict free rotation occurs between the smaller carbonyl groups and the organic ligand. Lack of the latter interaction would remove the possibility of isomerism as postulated by the original worker.[138]

Attempted verification of the conclusion reached above by synthesis of the corresponding triphenylarsine compound was not successful. Here the identification of different isomers would perhaps have been facilitated by the absence of As-H coupling.

The thermal displacement reaction in dibutyl ether, however, results only in complete destruction of the tricarbonyl complex. Instability of the arsine substituted material at the high reaction temperature may have led to this result. Ultraviolet irradiation of the tricarbonyl complex with triphenylarsine in benzene produces small amounts of the desired product (identified by its ir carbonyl absorptions) but it can not easily be obtained pure in quantities sufficient for further study.

The nmr spectrum of dicarbonyl(triphenylphosphine) cyclohexa-1,3-dieneiron (prepared by the photolytic reaction of tricarbonylcyclohexadieneiron and triphenylphosphine in benzene[73]) shows the presence of phosphorus to diene hydrogen coupling by its very complicated peaks which revert to the pattern of the spectrum of the tricarbonyl complex on phosphorus decoupling. Determination of the P^{31}-H coupling constants directly from the spectrum of this compound is precluded by the complexity of the peaks.

Analogous coupling to phosphorus has been noted in the nmr spectra of the butadiene-$Fe(CO)_x(PF_3)_{3-x}$ series ($x = 0,1,2$), referred to below.

Warren and Clark, in a recent investigation of tricarbonylbutadieneiron and its $C^{13}O$ and PF_3 substitution products, have demonstrated an inherent non-equivalence of one of the three carbonyl groups in this complex.[60]

Infrared absorption studies, involving a comparison of calculated and observed stretching frequencies, suggest that the unique carbonyl is specifically substituted by the first entering phosphorus trifluoride group in both thermal and photochemical exchange reactions.

The F^{19} nmr spectrum of the dicarbonyl(trifluorophosphine) complex tends to support this suggestion by showing a single fluorine environment at room temperature and no significant change in the spectrum on cooling to -100°. Any fluxional process operating in this molecule must therefore be of relatively low activation energy.

This evidence for the lack of ligand exchange between non-equivalent positions is, however, not conclusive, especially on consideration of the situation found in the carbonylbis(trifluorophosphine) and tris(trifluorophosphine) complexes. In both cases fluxional processes involving exchange between non-equivalent phosphines are observed. In the former complex the equilibrium is "frozen out" at -107°, but in the latter the time-averaged spectrum recorded at room temperature does not collapse completely, even at -100°.

An extension of these results to dicarbonyl(triphenylphosphine)thebaineiron suggests that the phosphine ligand of this complex may be situated in a unique environment. (It is noted that trifluorophosphine as a ligand bears a far closer resemblance in its electronic and steric properties to carbon monoxide than to triphenylphosphine.[60,140,141] This fact should not greatly affect the validity of the comparison made here.)

If this postulate is accepted,the existence of a second isomer of dicarbonyl(triphenylphosphine)thebaineiron is possible, at least in theory, even without the steric restriction to rotation about the iron-diene bond which was invoked earlier.

EXPERIMENTAL.

(For general experimental details, see Section A, Experimental.)

Dicarbonyl(triphenylphosphine)thebaineiron. - Tricarbonylthebaineiron was prepared by ultraviolet irradiation of thebaine with iron pentacarbonyl in benzene, as described in the literature.[76] ν_{max} 2030, 1970, 1943 cm^{-1}. Nmr spectrum: τ3.34, AB quartet, H_1 and H_2; τ4.68, doublet of doublets, H_7; τ5.07, doublet, H_5; τ5.45, doublet, H_8; τ6.16, singlet, aromatic OCH_3; τ6.40, singlet, diene OCH_3; τ7.54, singlet, NCH_3; $J_{5,7} = 2$ c/s, $J_{7,8} = 5$ c/s.

Triphenylphosphine (460 mg) was added over 2 hr to a refluxing solution of tricarbonylthebaineiron (800 mg) in di-*n*-butyl ether (70 ml). The mixture was refluxed for a further hour, the solvent distilled off under reduced pressure and the residue taken up in ether and filtered through a short column of activity (III) basic alumina. The resulting solution yielded a yellow solid (740 mg) which showed three spots on tlc, two of which had identical R_f values to thebaine and tricarbonylthebaineiron respectively. The third spot, the lowest R_f value, was the triphenylphosphine adduct. The nmr spectrum of this mixture showed tricarbonylthebaineiron and dicarbonyl(triphenylphosphine)thebaineiron (see Discussion).

Chromatography of the solid on a column of activity (III) basic alumina in ether gave two yellow bands. The first contained the tricarbonyl complex only (identified by ir and nmr spectra). The second fraction consisted of the triphenylphosphine adduct with some of the tricarbonyl compound. Recrystallisation twice from acetone gave pure dicarbonyl(triphenylphosphine)thebaineiron. (The nmr spectrum of the mother liquor from each recrystallisation showed no evidence of a second isomer of the triphenylphosphine compound.) ν_{max} 1970, 1910 cm^{-1}. Nmr spectrum: τ2.3-2.8, complicated, PPh_3; τ3.46, AB quartet, H_1 and H_2; τ5.00, broadened doublet, H_5; τ5.21, triplet of doublets, H_7; τ6.23, singlet, aromatic OCH_3, partially obscuring triplet, τ6.23, H_8; τ6.80, singlet, diene OCH_3; τ7.83, singlet, NCH_3; $J_{7,8} = J_{7,P} = J_{8,P} = 4.5$ c/s, $J_{5,7} = 1.5$ c/s. The spectrum in dimethyl sulphoxide-d_6 produced no change in the splittings but gave H_5, τ5.08; H_7, τ5.13; H_8, τ6.13; aromatic OCH_3, τ6.32. The decoupling of phosphorus in this spectrum is described in the Discussion.

Reaction of tricarbonylthebaineiron with triphenylarsine. - Refluxing triphenylarsine with the tricarbonyl complex in di-*n*-butyl ether (2½ hr) or in benzene (overnight) and working up in the manner described for the triphenylphosphine compound gave no detectable triphenylarsine adduct.

Irradiation of the substrates for 24 hr in benzene solution, at 3100 or 2500 A° in glass or quartz vessels gave, at best, only small amounts of the desired product. It was identified by diluting a small sample of the reaction mixture with chloroform and examining the ir absorption in the 2000 cm^{-1} region. Strong bands due to tricarbonylthebaineiron (see above) were always present, the arsine complex gave a band at 1910 cm^{-1}, always weak. Chromatography of the mixture containing this band (basic alumina in benzene) gave traces of <u>dicarbonyl(triphenylarsine)thebaineiron</u> free from the tricarbonyl complex. ν_{max} 1970, 1910 cm^{-1}. Insufficient amounts of the complex were isolated to permit further characterisation.

REFERENCES

1. T.J. Kealy and P.L. Pauson, Nature, 1951, 168, 1039.
2. S.A. Miller, J.A. Tebboth and J.F. Tremaine, J. Chem. Soc., 1952, 632.
3. G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, J. Amer. Chem. Soc., 1952, 74, 2125.
4. E.O. Fischer and W. Pfab, Z. Naturforsch., 1952, 7b, 377.
5. P.F. Eiland and R. Pepinsky, J. Amer. Chem. Soc., 1952, 74, 4971.
6. J.D. Dunitz and L.E. Orgel, Nature, 1953, 171, 121.
7. H.H. Jaffe, J. Chem. Phys., 1953, 21, 156.
8. W. Moffitt, J. Amer. Chem. Soc., 1954, 76, 3386.
9. W.C. Zeise, Pogg. Ann., 1827, 9, 632.
10. W.C. Zeise, Pogg. Ann., 1831, 21, 497.
11. J. Liebig, Annalen, 1837, 23, 12.
12. J. Chatt, J. Chem. Soc., 1949, 3340.
13. J.A. Wunderlich and D.P. Mellor, Acta Cryst., 1954, 7, 130.
14. J.A. Wunderlich and D.P. Mellor, Acta Cryst., 1955, 8, 57.
15. K. Birnbaum, Annalen, 1868, 145, 67.
16. L. Mond, C. Langer and F. Quincke, J. Chem. Soc., 1890, 57, 749.
17. L. Mond and F. Quincke, J. Chem. Soc., 1891, 59, 604.
18. L. Mond and C. Langer, J. Chem. Soc., 1891, 59, 1090.
19. W. Pullinger, Chem. Ber., 1891, 24, 2291.
20. L. Mond, H. Hirtz and M.D. Cowap, J. Chem. Soc., 1910, 97, 798.
21. H. Reihlen, A. Gruhl, G. v. Hessling and O. Pfrengle, Annalen, 1930, 482, 161.
22. A.D. Hel'man, Compt. rend. Acad. Sci. U.R.S.S., 1937, 16, 351. (Chem. Abs., 1938, 32, 2081.)

23. A.D. Hel'man, Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 532. (Chem. Abs., 1939, 33, 9281.)

24. A.D. Hel'man, Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 549. (Chem. Abs., 1940, 34, 1579.)

25. A.D. Hel'man and E.A. Meilakh, Compt. rend. Acad. Sci. U.S.S.R., 1946, 51, 207. (Chem. Abs., 1946, 40, 7042.)

26. J.S. Dewar, Bull. Soc. chim. France, 1951, 18C, 79.

27. J. Chatt and L.A. Duncanson, J. Chem. Soc., 1953, 2939.

28. B.F. Hallam and P.L. Pauson, J. Chem. Soc., 1958, 642.

29. O.S. Mills and G. Robinson, Proc. Chem. Soc., 1960, 421.

30. O.S. Mills and G. Robinson, Acta Cryst., 1963, 16, 758.

31. P.M. Maitlis and M.L. Games, J. Amer. Chem. Soc., 1963, 85, 1887.

32. J.E. Mahler and R. Pettit, J. Amer. Chem. Soc., 1963, 85, 3955.

33. T.A. Manuel, Inorg. Chem., 1964, 3, 1794.

34. R. Burton, L. Pratt and G. Wilkinson, J. Chem. Soc., 1961, 594.

35. H.J. Dauben and D.J. Bertelli, J. Amer. Chem. Soc., 1961, 83, 497.

36. E. Weiss and W. Hubel, Chem. Ber., 1962, 95, 1186.

37. H. Alper and J.T. Edward, J. Organometallic Chem., 1968, 14, 411.

38. H.W. Whitlock and Y.N. Chuah, Inorg. Chem., 1965, 4, 424.

39. H.D. Murdoch and E. Weiss, Helv. Chim. Acta, 1962, 45, 1156.

40. E. Weiss, K. Stark, J.E. Lancaster and H.D. Murdoch, Helv. Chim. Acta, 1963, 46, 288.

41. H.D. Murdoch and E. Weiss, Helv. Chim. Acta, 1963, 46, 1588.

42. P. Reeves, J. Henery and R. Pettit, J. Amer. Chem. Soc., 1969, 91, 5888.

43. J.S. Ward and R. Pettit, J. Amer. Chem. Soc., 1971, 93, 262.

44. E.O. Greaves, C.J.L. Lock and P.M. Maitlis, Canad. J. Chem., 1968, 46, 3879.

45. J.H. Nelson, K.S. Wheelock, L.C. Cusachs and H.B. Jonassen, *Chem. Comm.*, 1969, 1019.

46. J.H. Nelson, K.S. Wheelock, L.C. Cusachs and H.B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005.

47. "Bonding in Metallo-organic Compounds", *Discuss. Faraday Soc.*, No. 47, 1969.

48. A.A. Hock and O.S. Mills, *Acta Cryst.*, 1961, **14**, 139.

49. R.P. Dodge, *J. Amer. Chem. Soc.*, 1964, **86**, 5429.

50. B. Dickens and W.N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.

51. A. Robson and M.R. Truter, *Tetrahedron Letters*, 1964, 3079.

52. Y. Degreve, J. Meunier-Piret, M. Van Meerssche and P. Piret, *Acta Cryst.*, 1967, **23**, 119.

53. R. Eiss, *Inorg. Chem.*, 1970, **9**, 1650.

54. M.R. Churchill and R. Mason, *Proc. Roy. Soc. (A)*, 1967, **301**, 433.

55. M.R. Churchill, *Trans. N.Y. Acad. Sci., Ser. 2*, 1969, **31**, 280.

56. M.L.H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753.

57. H.G. Preston and J.C. Davis, *J. Amer. Chem. Soc.*, 1966, **88**, 1585.

58. H.S. Gutowsky and J. Jonas, *Inorg. Chem.*, 1965, **4**, 430.

59. H.L. Retcofsky, E.N. Frankel and H.S. Gutowsky, *J. Amer. Chem. Soc.*, 1966, **88**, 2710.

60. J.D. Warren and R.J. Clark, *Inorg. Chem.*, 1970, **9**, 373.

61. A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

62. K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.

63. M. Cais and N. Moaz, *J. Organometallic Chem.*, 1966, **5**, 370.

64. M.A. Haas and J.M. Wilson, *J. Chem. Soc. (B)*, 1968, 104.

65. K. Bowden, E.A. Braude and E.R.H. Jones, *J. Chem. Soc.*, 1946, 948.

66. V. Henri and L.W. Pickett, *J. Chem. Phys.*, 1939, **7**, 439.

67. J.E. Arnet and R. Pettit, J. Amer.Chem. Soc., 1961, 83, 2954.

68. A.J. Birch and G. Subba Rao, "The Birch Reduction" Adv. Org. Chem., ed. E.C. Taylor, John Wiley & Sons, New York, N.Y., in press.

69. E.O. Fischer and R.D. Fischer, Angew. Chem., 1960, 72, 919.

70. D. Jones, L. Pratt and G. Wilkinson, J. Chem. Soc., 1962, 4458.

71. M.A. Haas, Ph.D. thesis, Australian National University, 1969.

72. A.J. Birch and M.A. Haas, Tetrahedron Letters, 1968, 3705.

73. F.M. Chaudhari and P.L. Pauson, J. Organometallic Chem., 1966, 5, 73.

74. T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 1960, 82, 366.

75. P.E. Cross, Ph.D. thesis, Manchester University, 1966.

76. A.J. Birch and H. Fitton, Austral. J. Chem., 1969, 22, 971.

77. M.E. Kuehne and B.F. Lambert, J. Amer. Chem. Soc., 1959, 81, 4278.

78. H. Plieninger, G. Ege, F. Jung and W. Maier-Borst, Chem. Ber., 1961, 94, 2088.

79. R.B. King, T.A. Manuel and F.G.A. Stone, J. Inorg. Nuclear Chem., 1961, 16, 233.

80. M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, J. Chem. Soc. (A), 1967, 240.

81. R. Pettit, G. Emerson and J. Mahler, J. Chem. Educ., 1963, 40, 175.

82. I. Ogata and A. Misono, J. Chem. Soc. Japan, 1964, 85, 748. (Chem. Abs., 1965, 62, 12031.)

83. I. Ogata and A. Misono, J. Chem. Soc. Japan, 1964, 85, 753. (Chem. Abs., 1965, 62, 12031.)

84. M.L. Maddox, S.L. Stafford and H.D. Kaesz, Adv. Organometallic Chem., 1965, 3, 1.

85. D.A.T. Young, J.R. Holmes and H.D. Kaesz, J. Amer. Chem. Soc., 1969, 91, 6968.

86. E.S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, Chicago, San Francisco, Toronto, London, 1966, pp. 317-8.

87. J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, San Francisco, Toronto, London, 2nd. edn., 1962, p. 285.

88. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1953, pp. 757-8.

89. R. Pettit and G.F. Emerson, *Adv. Organometallic Chem.*, 1964, *1*, 1.

90. H. Alper, P.C. LePorte and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, *91*, 7553.

91. E.R.H. Jones, G.H. Mansfield and M.C. Whiting, *J. Chem. Soc.*, 1956, 4073.

92. S.L. Emerman and J. Meinwald, *J. Org. Chem.*, 1956, *21*, 375.

93. A.A. Petrov and K.B. Rall, *J. Gen. Chem. (U.S.S.R.) (Engl. transl.)*, 1956, *26*, 1779.

94. R. Grewe and I. Hinrichs, *Chem. Ber.*, 1964, *97*, 443.

95. A.J. Birch, *J. Chem. Soc.*, 1950, 1551.

96. N.A. Nelson, J.H. Fassnacht and J.U. Piper, *J. Amer. Chem. Soc.*, 1959, *81*, 5009.

97. N.A. Nelson, J.H. Fassnacht and J.U. Piper, *J. Amer. Chem. Soc.*, 1961, *83*, 206.

98. R.E. Lutz and J.S. Gillespie, *J. Amer. Chem. Soc.*, 1950, *72*, 2002.

99. R.E. Lutz and D.F. Hinkley, *J. Amer. Chem. Soc.*, 1950, *72*, 4091.

100. J.W. Cook, R.A. Raphael and A.I. Scott, *J. Chem. Soc.*, 1952, 4416.

101. C. Mantescu and A. Genunche, *Tetrahedron Letters*, 1966, 5675.

102. H.C. Brown and B.C. Subba Rao, *J. Org. Chem.*, 1957, *22*, 1135.

103. H.C. Brown, H.I. Schlesinger and A.B. Burg, *J. Amer. Chem. Soc.*, 1939, *61*, 673.

104. H.C. Brown and B.C. Subba Rao, *J. Amer. Chem. Soc.*, 1960, *82*, 681.

105. N.G. Gaylord, "Reduction with Complex Metal Hydrides", Interscience, New York, London, 1956, and references quoted therein.

106. D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, 1970, *9*, 1691.

107. J.E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1962, 84, 1511.

108. E.N. Frankel, E.A. Emken, H.M. Peters, V.L. Davison and R.O. Butterfield, *J. Org. Chem.*, 1964, 29, 3292.

109. J.E. Mahler, D.H. Gibson and R. Pettit, *J. Amer. Chem. Soc.*, 1963, 85, 3959.

110. J.D. Holmes and R. Pettit, *J. Amer. Chem. Soc.*, 1963, 85, 2531.

111. G.F. Emerson, J.E. Mahler, R. Kochhar and R. Pettit, *J. Org. Chem.*, 1964, 29, 3620.

112. I. Ogata and A. Misono, *J. Chem. Soc. Japan*, 1964, 85, 808. (*Chem. Abs.*, 1965, 63, 1682.)

113. W.G. Dauben, M. Lorber and D.S. Fullerton, *J. Org. Chem.*, 1969, 34, 3587.

114. J.C. Collins, W.W. Hess and F.J. Frank, *Tetrahedron Letters*, 1968, 3363.

115. T.G. Clarke, N.A. Hampson, J.B. Lee, J.R. Morley and B. Scanlon, *Canad. J. Chem.*, 1969, 47, 1649.

116. K.E. Pfitzner and J.G. Moffatt, *J. Amer. Chem. Soc.*, 1963, 85, 3027.

117. K.E. Pfitzner and J.G. Moffatt, *J. Amer. Chem. Soc.*, 1965, 87, 5670.

118. J.B. Jones and D.C. Wigfield, *Canad. J. Chem.*, 1966, 44, 2517.

119. A.H. Fenselau and J.G. Moffatt, *J. Amer. Chem. Soc.*, 1966, 88, 1762.

120. F.W. Sweat and W.W. Epstein, *J. Org. Chem.*, 1967, 32, 835.

121. M.E. Kuehne and B.F. Lambert, *Org. Synth.*, 1963, 43, 22.

122. L.A. Carpino, *J. Amer. Chem. Soc.*, 1958, 80, 599.

123. P. Seifert and H. Schinz, *Helv. Chim. Acta*, 1951, 34, 728.

124. W. Surber, V. Theus, L. Colombi and H. Schinz, *Helv. Chim. Acta*, 1956, 39, 1299.

125. M. Mousseron, R. Jacquier and R. Fraisse, *Compt. rend.*, 1956, 243, 1880.

126. E.A. Braude and E.A. Evans, *J. Chem. Soc.*, 1955, 3334.

127. I.N. Nazarov, L.A. Kazitsyna and I.I. Zaretskaya, *J. Gen. Chem. (U.S.S.R.) (Engl. transl.)*, 1957, 27, 693.

128. E.D. Bergman and A. Becker, J. Org. Chem., 1968, 23, 1553.

129. W. Treibs and R. Helbig, Chem. Ber., 1959, 92, 1559.

130. H.J. Dauben, L.R. Honnen and K.M. Harmon, J. Org. Chem., 1960, 25, 1442.

131. F.A. Cotton, J. Amer. Chem. Soc., 1968, 90, 6230.

132. T.A. Manuel and F.G.A. Stone, Proc. Chem. Soc., 1959, 90.

133. M.D. Rausch and G.N. Schrauzer, Chem. Ind., 1959, 957.

134. A. Nakamura and N. Hagihara, Bull. Chem. Soc. Japan, 1959, 32, 880.

135. T.A. Manuel, S.L. Stafford and F.G.A. Stone, J. Amer. Chem. Soc., 1961, 83, 3597.

136. R.A. Bauer, E.O. Fischer and C.G. Kreiter, J. Organometallic Chem., 1970, 24, 737.

137. R.G. Harvey and K. Urberg, J. Org. Chem., 1968, 33, 2570.

138. H. Fitton, Ph.D. thesis, Manchester University, 1967.

139. A.J. Birch, H. Fitton, M. McPartlin and R. Mason, Chem. Comm., 1968, 531.

140. Th. Kruck, Angew. Chem. Internat. Edn., 1967, 6, 53.

141. C.A. Udovich and R.J. Clark, Inorg. Chem., 1969, 8, 938.