SOME REACTIONS OF TRICARBONYLCYCLOHEXA-1,3-DIENEIRON COMPLEXES

by

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As is well-known, the deep-rooted fear of ghosts is not vitiated by reason, and despite my past and present achievements, I do not flatter myself that I can disperse the fantasy of the supporters of the ethereal theory of the existence of an oil-forming gas in the ethereal compounds.

Liebig, 1837
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## Introduction

## Discussion

(a) Sodium borohydride reduction

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## Bibliography
The work described in this thesis is that of the candidate, except where otherwise stated, and has not been submitted for any other degree. It was carried out in the Department of Chemistry of the University of Manchester, England, and in the Research School of Chemistry of The Australian National University, Canberra, from 1966 to 1969 under a maintenance grant from The Australian National University.

I would also like to express my thanks to the staff and colleagues of this department, in particular Drs. E. B. Bradsher and A. C. Newnham.
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I wish to express my sincere gratitude to:
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SUMMARY

Tricarbonylcyclohexa-1,3-dieneiron complexes react with triphenylmethyl fluoroborate to yield tricarbonyl-\(\pi\)-cyclohexadienyliniron salts which react with sodium borohydride and other nucleophiles to give neutral compounds. An attempt, in Parts A and C, respectively, has been made to rationalise these two reactions by a consideration of the electronic and steric factors involved.

Part B describes the reactions of some neutral complexes with concentrated sulphuric acid, and includes a new method of preparing the \(\pi\)-dienyl cations, in high yield, by the abstraction of methoxyl from the 1- or 2- position of tricarbonylmethoxycyclohexa-1,3-dieneiron complexes.

Since no review of this general field existed at the time, one entitled "Reactivity of organo-transition metal complexes: proton addition and hydride abstraction reactions of the organic ligands" was undertaken during the course of this work.
GENERAL INTRODUCTION

The discovery of the metallocene and metallarene structures provided a new area of interest shared by both experimental and theoretical chemists. Traditionally the emphasis was laid on the effect of complex formation on the properties of the metal atom, and little consideration was given to the effect on the reactivity of the ligands.

However, modern industry is concerned with the activation of molecules by complex formation enabling them to undergo such reactions of commercial importance as oligomerisation, oxidation, and carbonylation.

The stage which has now been reached in this vigorously expanding field is the investigation of both the reactivity of attached ligands and the properties of the complexes themselves in a systematic way. To this end a number of reactions of tricarbonyliron compounds were studied in detail, and also a review was undertaken in which an attempt was made to bring together for the first time a large body of diverse reactions which, when considered together, lead to a greater insight into the properties of transition metal complexes.

The review also serves as a broad introduction to the work described in this thesis, and hence a copy of the proofs has been included. Each of the three parts will be prefaced by only a brief introduction confined to the group of compounds and actual reactions studied.
REACTIVITY OF ORGANO-TRANSITION METAL COMPLEXES: PROTON ADDITION AND HYDRIDE ABSTRACTION REACTIONS OF THE ORGANIC LIGANDS

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I. INTRODUCTION

Within each of the two major sections the transition metal complexes have been classified according to the type of ligand rather than by Periodic Group of the metal. This is the system adopted by Green [76], and is the most appropriate for the present review. The compounds are classified by the organic ligands attached to the metal according to the number of electrons which the ligand is considered to donate to the metal.

II. PROTON ADDITION

Protonation of organo-transition metal complexes normally occurs on the organic ligand, giving rise to a variety of both charged and uncharged species. However, in π-cyclopentadienyl complexes protonation of the metal seems to be the rule, and metal hydrides are obtained: ferrocene, ruthenocene and other mono- and binuclear π-cyclopentadienyl transition metal complexes give rise to cationic hydrides in strong acid media [30,38].
Another class of complexes which undergo metal protonation is that of the tricarbonylarenechromium series which yield hydrides in strong acids such as concentrated sulphuric acid and fluorosulphonic acid [38], while tricarbonylnorbornadieneiron also gives a metal hydride in fluorosulphonic acid/sulphur dioxide [52], presumably because no stable complex can result from C-protonation.

The chemistry of the metallocenes in general [13,144,153,164], and metallocenyl carbonium ions in particular [16,17], has already been well reviewed, as has that of metal hydride complexes [74,75,80], and hence these two areas will not be included in this review.

A. One-electron ligands

1. σ-Allyl complexes

A number of σ-organo-transition metal complexes in which the organic ligand has an unsaturated β-carbon atom are readily protonated by dry hydrogen chloride to yield cation complexes containing propene as a ligand: M-σ-CH₂CH=CH₂ gives [M-C₃H₆]⁺ which can be isolated as the hexafluorophosphate salt (M = π-C₅H₅Fe(CO)₂ [83,86], π-C₅H₅W(CO)₃ [91], π-C₅H₅Mo(CO)₃ [27]), e.g. scheme 1.

The mechanism proposed involves attack at C-3 of the σ-allyl ligand resulting in an intermediate carbonium ion which may transfer its positive charge to the metal atom, and finally
bond to it in a manner similar to other olefin complexes as shown in scheme 2.

The protonation occurs at $\alpha$-3 is shown by deuterium experiments.

The protonation of $\text{Mn(CO)}_5\sigma$-$\text{CH}_2$-$\text{CH}=$-$\text{CH}_2$ with hydrogen chloride gas or with sodium deuteride, $\text{NaD}_2$, proceeds a step further, and the olefin is displaced leading to $\text{Mn(CO)}_5\text{C}_2\text{H}_7$ perchloric acid is used, however, the intermediate $[\text{Mn(CO)}_5\text{C}_3\text{H}_7]^+$ species can be isolated [81,82].

These olefinic cations can also be prepared by hydride abstraction from $\sigma$-alkyl complexes using triphenylmethyl perchlorate [26,83,87], and this reaction will be discussed in section III, A.

Other systems containing unsaturated $\beta$-carbon atoms that can be protonated are $\sigma$-cyanocarbonyl complexes (X) to give coordinated betaines (XI) [31], or (contradionally) complexes (XII) to give coordinated allenes (XI) [81,82], and $\sigma$-oxoalkyl complexes (V) to give coordinated enols (VI) [47].

The protonation of the propargyl complex $\text{H}_2\text{C}=\text{C}=$-$\text{CH}_2$-$\text{Fe(CO)}_2$ with hydrogen chloride is reported to give the allenic cation $[\text{H}_2\text{C}=\text{C}=$-$\text{CH}_2$-$\text{Fe(CO)}_2]^+$ [3], though Pettit [104] in his work on the acid-catalysed isomerisation of $\text{H}_2\text{C}=\text{C}=$-$\text{CH}_2$-$\text{Fe(CO)}_2$ to $\text{H}_2\text{C}=\text{C}=$-$\text{CH}_2$-$\text{Fe(CO)}_2$, using anhydrous acids or chromatography through silica gel or acid-washed alumina, found the latter complex
bond to it in a manner similar to other olefin complexes; as shown in scheme 2.

That protonation occurs at C-3 is shown by deuteration experiments [86].

The reaction of Mn(CO)$_5$-$\sigma$-CH$_2$CH=CH$_2$ with hydrogen chloride gas or other acids, HA (A = NO$_3$, CF$_3$CO$_2$, HSO$_4$), proceeds a step further, and the olefin is displaced leading to Mn(CO)$_5$A. If perchloric acid is used, however, the intermediate [Mn(CO)$_5$C$_3$H$_6$]$^+$ species can be isolated [81,82].

These olefinic cations can also be prepared by hydride abstraction from $\sigma$-alkyl complexes using triphenylmethyl perchlorate [26,85,87], and this reaction will be discussed in section III, A.

Other systems containing unsaturated $\beta$-carbon atoms that can be protonated are $\sigma$-cyanoalkyl complexes (I) to give coordinated ketenimines (II) [2], $\sigma$-cyclopentadienyl complexes (III) to give coordinated olefins (IV) [81,88], and $\sigma$-oxoalkyl complexes (V) to give coordinated enols (VI) [4].

The protonation of the propargyl complex $\pi$-C$_5$H$_5$Fe(CO)$_2$-$\sigma$-CH$_2$C≡CH with hydrogen chloride is reported to give the allene cation [$\pi$-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CH]$^+$[3], though Pettit [104] in his work on the acid-catalysed isomerisation of $\pi$-C$_5$H$_5$Fe(CO)$_2$-$\sigma$-CH$_2$C≡CH to $\pi$-C$_5$H$_5$Fe(CO)$_2$-$\sigma$-C≡C-CH$_3$, using anhydrous acids or chromatography through silica gel or acid-washed alumina, found the latter complex
The reaction of the 6-nitro-3-cyclopentadiene-iron complex (I) with hydrochloric acid yields the 6-nitro-3-cyclopentadiene-iron chloride complex (II) which in turn can be rapidly hydrolyzed to the chloride complex (IV) to form the hydrochloric acid solution. The corresponding 6-alkyl complexes (V) and (VI) are also formed upon cleavage reactions and formation of (XIII) to the [Fe(CO)₅] (XIV; N = Na; K) complexes from the corresponding allyl substituent compounds (XIV; N = Na, K).
identical to that formulated by Green [3] as $\pi$-C$_5$H$_5$Fe(CO)$_2$-σ-CH$_2$-C≡CH.

The reaction of (VII) with ethanolic hydrochloric acid yields $\pi$-C$_5$H$_5$Fe(CO)$_2$-σ-COC$_2$H$_5$(X); the mechanism ($R = H$) postulated involving the intermediates (VIII) and (IX; $R = H$). Evidence for the carbene type intermediate (VIII) is found in the reaction of complex (VII) with anhydrous acetic acid which yields the σ-bonded complex (IX; $R = COCH_3$) which in turn can be rapidly hydrolysed to the σ-acyl compound (X) [104].

2. σ-Alkyl complexes

The reactions of the σ-alkylether complexes $\pi$-C$_5$H$_5$Fe(CO)$_2$-σ-CH$_2$OCH$_3$ and $\pi$-C$_5$H$_5$M(CO)$_3$-σ-CH$_2$OCH$_3$ ($M = Mo, W$) with acids is of interest in that short-lived metal-carbene complexes are postulated as intermediates. Hydrochloric acid cleaves the ether group in (XI) and (XII) to give the corresponding σ-alkyl complexes [79, 103].

However, when strong acids such as fluoroboric, perchloric, or hexafluorophosphoric acids are used, a mixture of products is obtained, one of which is the cationic ethylene compound [79].

Some related cleavage reactions are the conversion of $\pi$-C$_5$H$_5$Fe(CO)$_2$-σ-CO$_2$CH$_3$ (XIII) to the [79], and the formation of [(diene)PdCl$_2$] (XV; $M = Pd$) [21, 151] and [(diene)PtCl$_2$] (XV; $M = Pt$) [20] complexes from the corresponding methoxy-substituted compounds (XIV; $M = Pd, Pt$).
A reaction of rather a different nature may be suitably mentioned here, since it too involves cleavage of a metal-$\sigma$-alkyl bond. Reaction of dichlorohexamethyl Dewar benzeneplatinum, $C_6H_{12}\cdot PtCl_2$, with stoichiometric sodium methoxide yields a dimeric dehydro complex ($C_6H_{12}\cdot Pt\cdot CH_2\cdot CH_3$)  which is found to have a bridging dehydrohexamethyl Dewar benzene ligand consisting of both a Dewar benzene bond and two Dewar benzene bonds. This reaction is reversible, in that exposure to hydrogen chloride gas causes the $\sigma$-bond to generating the starting complex [122].

3. $\sigma$-Acyl complexes

The first transition metal-carbene complexes prepared by acidification of acylethylene complexes [($C_8H_{18}$)$_2$N] [W(CO)$_5$(OCH$_3$)$_2$]$_2$ followed by reaction with diazomethane to give $W$(CO)$_5$(OCH$_3$)$_2$C$_6$H$_5$) [60]. X-ray studies [133, 134] of $W$(CO)$_5$(OCH$_3$)$_2$C$_6$H$_5$ has shown this to have an $\eta^1$-carbon structure similar to the type (X). $W$(CO)$_5$(OCH$_3$)$_2$L$_2$ (L = CO, (C$_6$H$_3$)$_2$P) can be protonated with dry hydrogen chloride to form the metal-carbene complexes (XVIII; L = CO, (C$_6$H$_3$)$_2$P) [78].

4. Non-electron ligands

Saturation of a chloroform solution of Rh$_2$Cl$_2$(CO)$_2$C$_6$H$_5$$_2$ (XIX) with dry hydrogen chloride, followed by addition of light petroleum, yields a yellow Rh-$\sigma$-ethyl complex of the approximate composition...
A reaction of rather a different nature may be suitably mentioned here, since it too involves cleavage of a metal-\(\sigma\)-alkyl bond. Reaction of dichlorohexamethyl Dewar benzeneplatinum, \(\text{C}_{12}^1\text{H}_{18}\text{PtCl}_2\)
, with methanolic sodium methoxide yields a dimeric dehydro complex \((\text{C}_{12}^1\text{H}_{17}\text{PtCl})_2\) which is said to have a bridging dehydrohexamethyl Dewar benzene ligand containing both a Pt-\(\sigma\)-C bond and two olefin bonds. This reaction is reversible, in that dry hydrogen chloride gas cleaves the \(\sigma\)-bond regenerating the starting complex [130].

3. \(\sigma\)-Acyl complexes

The first transition metal-carbene complex was prepared by acidification of the \(\sigma\)-acyl complex \([\text{(CH}_3^3\text{)}_4\text{N}] [\text{W(CO)}_5 (\text{COC}_6^6\text{H}_5^6)]\)
 followed by reaction with diazomethane to give \(\text{W(CO)}_5 [\text{C(OCH}_3^3\text{)}_6^6\text{H}_5^6]\) [60]. X-ray studies [133,134] of \(\text{W(CO)}_5 [\text{C(OCH}_3^3\text{)}_6^6\text{H}_5^6]\), its chromium analogue [61], and \(\text{Cr(CO)}_4 [\text{P(C}_6^6\text{H}_5^5\text{)}_3] [\text{C(OCH}_3^3\text{)}_6^6\text{H}_5^6]\) have shown these to have carbene structures of the type (XVI).

In a similar manner, \(\Pi-\text{C}_5^5\text{H}_5^5\text{Fe(CO)L(COCH}_3^3\text{)}\) (XVII; \(L = \text{CO, (C}_6^6\text{H}_5^5\text{)}_3\text{P}\)) can be protonated with dry hydrogen chloride to form the metal-carbene complexes (XVIII; \(L = \text{CO, (C}_6^6\text{H}_5^5\text{)}_3\text{P}\)) [78].

B. Two-electron ligands

Saturation of a chloroform solution of \(\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{C}_2^2\text{H}_4^4)_2\)
 (XIX) with dry hydrogen chloride, followed by addition of light petroleum, yields a yellow Rh-\(\sigma\)-ethyl complex of the approximate composition
[RhCl\textsubscript{2}C\textsubscript{2}H\textsubscript{5}(CO)]\textsubscript{x}. Treatment of this with dimethylphenylphosphine gives the octahedral compound (XX) [148].

Rhodium-\sigma-ethyl complexes are also intermediates in the dimerisation [27] and isomerisation [28] of olefins using rhodium-olefin complexes. These species have been detected by NMR, and the complex Cs\textsubscript{2}[C\textsubscript{2}H\textsubscript{5}RhCl\textsubscript{3}(H\textsubscript{2}O)]\textsubscript{2} has been isolated.

Reaction between allyl alcohol and palladium salts in acid solution yields \pi-alloy complexes, the \pi-alloy group presumably being formed by protonation of a palladium-olefin complex followed by loss of water [135,156].

C. Three-electron ligands

\pi-Ethoxytetraphenylcyclobutenylpalladium (XXI) and -nickel (XXIII) complexes are converted to the corresponding tetraphenylcyclobutadiene compounds (XXII) and (XXIV), respectively, on reaction with dry hydrogen chloride or hydrogen bromide [14,46,125,128].

This reaction is reversible, the \pi-alloy species being regenerated on treatment of the diene complexes with alkoxide [14, 46,125-128]. In addition, it has been shown that the ethoxy group is exo to the metal [31].

A similar reaction is reported to occur when dry hydrogen chloride is passed into an ethereal solution of bis(chloro-\pi-allylpalladium). Though Hütte [99] claimed to isolate the olefin
complexes (dichloroethylenepalladium), later workers [109] were unable to repeat this work.

An interesting example of the stabilization of carboxonium ions by transition metals is the acid-catalysed alcoholysis of hot ethanolic molar hydrochloric acid, of (XXVII) in which the methoxy is replaced by an ethoxy group, and vice versa. It is suggested that the allyl carboxonium ions of the type (XXVII) may have considerable stability thus facilitating the conversions [150].

D. Four-electron ligands

1. Formation of 5-allyl complexes

Tricarbonylbutadieneiron reacts with dry hydrogen chloride to give the covalent species tricarbonyl-syn-1-methylallylchloroiron (XXVIII) [109, 101, 141], while strong acids such as fluoroboric and perchloric acids yield cationic species in which the methoxy group has been replaced (XXIX) [99, 31]. The action of hydrogen chloride on the phosphine substituted derivative Pa[O(Et)2][(CN)2]Cl, presumably analogous to (XXVIII) is too unstable to characterize [22].

The formation of the syn-isomer (XXVIII) implies that geometrical inversion has taken place. This is confirmed by the fact that tricarbonyl-trans-1,3-dimethyl-allylchloride (XXX) gives solely the syn, syn-dimethyl derivative (XXXI) with hydrogen chlorides.
complex bis(dichloroethylene)palladium, later workers [109] were unable to repeat this work.

An interesting example of the stabilisation of β-carbonium ions by transition metals is the acid-catalysed alcoholysis, using hot ethanolic 10^{-2} molar hydrochloric acid, of (XXV) to (XXVI) in which the methoxy is replaced by an ethoxy group, and vice versa.

It is suggested that Π-allyl carbonium ions of the type (XXVII) may have considerable stability thus facilitating these transformations [150].

D. Four-electron ligands

1. Formation of Π-allyl complexes

Tricarbonylbutadieneiron reacts with dry hydrogen chloride to give the covalent species tricarbonyl-syn-1-methyl-Π-allylchloroiron (XXVIII) [100,101,141], while strong acids such as fluoroboric and perchloric acids yield cationic species in which the methyl group has the anti-configuration (XXIX) [49,51]. The adduct formed by the action of hydrogen chloride on the phosphine substituted complex, Fe(CO)₂[(C₆H₅)₃P]C₄H₆, presumably analogous to (XXVIII), is too unstable to characterise [22].

The formation of the syn-isomer (XXVIII) implies that geometrical inversion has taken place, and this is confirmed by the fact that tricarbonyl-trans-penta-1,3-dieneiron (XXX) gives solely the syn, syn-dimethyl derivative (XXXI) with hydrogen chloride.
The mechanism of this inversion postulates approach of the hydrogen chloride molecule from the side opposite to the iron atom, followed by cis-addition to give the intermediate (XXXI) which undergoes bond rotation with inversion of configuration. It is clear that the chloride remains in a position favourable for bond formation with the iron atom [49].

The 17,17-isomer (XXVIII) can also be prepared from the tetracarbonylbutadieneiron and hydrogen chloride. The mechanism involves a tetracarbonyl-1-methyl-1-methyl-1-allylchloroiron species, which is rather unstable, and the addition-elimination product (XXXII) [40].

The tetracarbonyl-2-methyl-3-allyliron chloride (XXXV) may be prepared in the manner described above [49] or from the novel compound tricarbonyltrimethyleneiron (XXXIV) by reaction in concentrated hydrogen chloride. Attempts to prepare the analogous 1,4-allyl species by reaction with hydrogen chloride proved unsuccessful.

The 17,17-isomer (XXVIII) reacts with various metals to give appropriately substituted iron complexes, while the analogue derived from tricarbonyl-trans-penta-1,3-dieneiron yields pentan-2-one [32]. The mechanism proposed to account for these
The mechanism of this inversion postulates approach of the hydrogen chloride molecule from the side opposite to the iron atom, followed by cis-addition to give the intermediate (XXXII) which undergoes bond rotation, with inversion of the methyl group, in order that the chlorine atom attains a position favourable for bond formation to the iron (XXXIII) [49].

The syn-isomer (XXVIII) can also be prepared from tetracarbonylbutfadieneiron and hydrogen chloride. The mechanism involves a tetracarbonyl-syn-1-methyl-π-allylchloroiron species, which is rather unstable, and rapidly converts to the syn-1-methyl-π-allyl complex (XXVIII) [140].

The tricarbonyl-2-methyl-π-allyliron cation (XXXV) may be prepared in the manner described above [49] or from the novel compound tricarbonyltrimethylenemethaneiron (XXXIV) by protonation in concentrated sulphuric acid [48].

Attempts to prepare the analogous cyclic π-allyl species by protonation of tricarbonylcyclohexa- [11,49] or tricarbonylcyclohepta-1,3-dieneiron [22] complexes by reaction with hydrogen chloride proved unsuccessful.

The cation tricarbonyl-anti-1-methyl-π-allyliron (XXIX) reacts with water to give appreciable quantities of butan-2-one, while the analogue derived from tricarbonyl-trans-penta-1,3-dieneiron yields pentan-2-one [52]. The mechanism proposed to account for these
products involves attack of water to give a substituted π-allyl complex (XXXVI) which isomerises, via a tricarbonyl-π-allylhydroiron intermediate (XXXVII), to an unstable enol complex (XXXVIII) which gives rise to the products observed.

Analogous π-allyl complexes are postulated as intermediates in the facile electrophilic substitution of tricarbonylcyclobutadieneiron (XXXIX) [72]. Using the conventional mechanism for this reaction, it is postulated that an electrophilic species, R⁺, adds to the diene forming the π-allyl complex (XL).

This mechanism is supported by the structure, found by X-ray diffraction [142], for the product (XLI) of the reaction between dichlorotetramethylcyclobutadienenickel and sodium cyclopentadieneide [29,110].

A cation whose structure is probably (XLIII) has been isolated by treatment of the chloride (XLII) with SbCl₅ [73]. It is postulated that such a species is the intermediate in the conversion, using concentrated hydrochloric acid, of the tricarbonylhydroxymethylcyclobutadieneiron complex (XLIV) to the chloride (XLII), and the aqueous solvolysis of the latter to regenerate the alcohol (XLIV). The ease with which the hydrolysis occurs suggests that, as in the previously described acid-catalysed alcoholysis of π-allylpalladium complexes [150], there may well be some interaction between the metal atom and the β-carbon of the organic ligand. In addition, the acids $\text{M-Ch}_2\text{CO}_2\text{H}$ ($\text{M} = \text{Mn(CO)}_5$, $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2$) are unusually weak, having
There are some examples of this apparent stabilisation of $\beta$-carbonium ions, particularly in the ferrocene series where the ease with which $\alpha$-acetoxyferrocenyls (XLIV) undergo acid-catalysed deacetoxylation [94,149] provides strong evidence for $\beta$-carbonium ion stabilisation [16,17].

Similarly, the solvolyses rates of tricarbonyl(benzonitrile)chromium and tricarbonyl(benzonitrile)chromium in 98% aqueous acetone are increased by a factor of about $10^3$ and $10^5$, respectively, as compared to the free ligands, and this is thought to be due to a stabilised intermediate such as (XLVI) being formed in the reaction [95].

In contrast, perhaps, it should be mentioned that solvolysis reactions have shown that tricarbonyl(s-2,3,4,5-tetramethylnitrenyl)cation to be much less stable than the free 7-s-tetramethylnitrenyl cation itself. However, this instability is attributable to the interaction of homoallylic interactions which stabilise the latter species [97].

$\eta^2$-Cyclohexenylpalladium complexes (XLVII) can be obtained from cyclohexa-1,3-dienes using either either either (COCl)$_2$ [69,70], PdCl$_2$ in acetic acid [90,91] or mechanochemical Na$_2$[PdCl$_4$] [149]. The role of proton transfer to the diene molecule with formation of an allylic complex, e.g. cyclohexa-1,3-diene yields stable(chloro-$\eta^2$-cyclohexenyln-palladium) (XLVII), which can also be prepared from cyclohexane and palladium chloride, loss of a hydrogen atom occurring in the latter reaction [98].
pKa values of 6.1 and 6.7, respectively, indicating some interaction between the metal and the carbon atom of the carboxyl group [77]. There are other examples of this apparent stabilisation of β-carbonium ions, particularly in the ferrocene series where the ease with which α-acetoxyferrocenyls (XLV) undergo acid-catalysed deacetoxylation [94,149] provides strong evidence for β-carbonium ion stabilisation [16,17].

Similarly, the solvolysis rates of tricarbonyl(benzylchloride)chromium and tricarbonyl(benzhydrylchloride)chromium in 80% aqueous acetone are increased by a factor of about $10^5$ and $10^3$, respectively, as compared to the free ligands, and this is thought to be due to a stabilised intermediate such as (XLVI) being formed in the reaction [95].

In contrast, perhaps, it should be mentioned that solvolysis reactions have shown the tricarbonyl-π-7-norbornadienyliron cation to be much less stable than the free 7-norbornadienyl cation itself. However, this instability is attributable to the inhibition of homoallylic interactions which stabilise the latter species [97].

π-Cyclohexenylpalladium complexes (XLVII) can be obtained from cyclohexa-1,3-dienes using either $(\text{PdCOC}_2)_2$ [69,70], PdCl$_2$ in acetic acid [98,155], or methanolic Na$_2$PdCl$_4$ [151]. In each case proton addition to the diene occurs with formation of the π-allyl complex, e.g. cyclohexa-1,3-diene yields bis(chloro-π-cyclohexenylpalladium) (XLVII), which can also be prepared from cyclohexene and palladium chloride, loss of a hydrogen atom occurring in this latter reaction [98].
2. Formation of 5-dienyl complexes

The tricarbonyl-1-hydroxy-tri[(5R)-5-dienyl]iron (XLVIII; R = H) with strong acids such as HBF₄ or HClO₄ yields the tricarbonyl-pentadienyl cation (XLIX; R = H) [123, 724]. This same complex can be prepared by hydride abstraction from tricarbonyl-spiro-1,3-dieneiron (L; R = H) using triphenylmethyl silylborate \( \left( \text{III}_{127, 123} \right) \). Each reaction will be further discussed in III.

The analogous transformations (XLVIII and L; R = CH₃) to (XL; R = CH₃) were carried out with equal facility [121, 123].

Although no X-ray data for these 5-dienyl cations are available, it seems probable that the iron atom lies below a plane defined by a cisoid arrangement of the aliphatic carbon atoms. The mechanism of formation of these cationic forms of the alcohol complexes is thought to involve dehydroxylation of the latter to give a hydrated tricarbonyl-vinyl-5-allyliron cation (LI) in which a trans configuration exists about the double bond. Free rotation about the appropriate double bond in (LI) then gives (LII) which undergoes intramolecular displacement of solvent from iron by coordination of the vinyl bond, and the 5-dienyl cation (LIII) is obtained [124].

The reaction of the tricarbonyl-5-dienyl iron with water is interesting in that, for example, the tricarbonyl-5-penta
dienyliron (LIV; R = CH₃) yields only tricarbonyl-trans-hexa-3,5
diene-2,4-dienyliron (XLVII), and, in addition, only one of
2. Formation of $\pi$-dienyl complexes

The acid cleavage of tricarbonyl-1-hydroxy-trans-penta-2,4-dieneiron (XLVIII; $R = H$) with strong acids such as HBF$_4$ and HClO$_4$ yields the tricarbonyl-$\pi$-pentadienyliron cation (IL; $R = H$) [123,124]. This same complex can be prepared by hydride abstraction from tricarbonyl-cis-penta-1,3-dieneiron (L; $R = H$) using triphenylmethyl fluoroborate [124], which reaction will be further discussed in III, C, 1. The analogous transformations (XLVIII and L; $R = CH_3$) to (XL; $R = CH_3$) occur with equal facility [121,123].

Although no X-ray data for these $\pi$-dienyl cations are available, it seems probable that the iron atom lies below a plane defined by a cisoid arrangement of the five carbon atoms. The mechanism of formation of these cations from trans alcohol complexes is thought to involve dehydration of the latter to give a hydrated tricarbonyl-vinyl-$\pi$-allyliron cation (LI) in which a trans configuration exists about the double bond. Free rotation about the appropriate double bond in (LI) then gives (LII) which undergoes intramolecular displacement of solvent from iron by coordination of the vinyl bond, and the $\pi$-dienyl complex (LIII) is obtained [124].

The reaction of these tricarbonyl-$\pi$-dienyliron cations with water is interesting in that, for example, the tricarbonyl-$\pi$-pentadienyliron cation (IL; $R = CH_3$) yields only tricarbonyl-trans-hexa-3,5-diene-2-oliron (LIV) to the exclusion of tricarbonyl-trans, trans-hexa-2,4-diene-1-oliron (XLVIII; $R = CH_3$), and, in addition, only one of
\[
\text{R-CH(OH)CH}_2\text{OH} \xrightarrow{\text{HBF}_4} \text{R-CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{solvent}} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{solvent}} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{solvent}} \text{CH}_3\text{CHCH}_3
\]

\[
\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
\]

\[
\text{OH} \quad \text{OH}_2 \quad \text{OH}_3 \quad \text{OH}_4
\]

\[
\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
\]

\[
\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
\]

\[
\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
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\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
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\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
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\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
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\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
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\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
\]

\[
\text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3 \quad \text{Fe(CO)}_3
\]
the two possible diastereoisomers of (LIV) is formed [121]. The mechanism of this hydrolysis is thought to follow that outlined for the formation of the $\pi$-dienyl cations, described on p.21 but in reverse [124].

Reduction of the $\pi$-hexadienyl cation ($IL; R = CH_3$) with sodium borohydride yields four isomeric complexes in the ratio 57:28:13:2, with ($L; R = CH_3$), arising from hydride attack at an unsubstituted carbon, being the major component [124].

$\pi$-Cycloheptadienyliron cations can be prepared by protonation of the uncomplexed double bond of cyclohepta-$1,3,5$-trieneiron complexes with strong acids such as HCl and HBF$_4$, the tricarbonyl ($LV; L = CO$) giving the tricarbonyl-$\pi$-cycloheptadienyliron cation ($LVI; R = H, L = CO$) [15,32,37,39] while the phosphine-substituted complex ($LV; L = (C_6H_5)_3P$) is not protonated under these conditions [22], and dichlorocyclohepta-$1,3,5$-trieneplatinum is decomposed [118].

If triphenylmethyl fluoroborate instead of fluoroboric acid is used, then addition of the triphenylmethyl cation to the free double bond of ($LV; L = CO, (C_6H_5)_3P$) occurs, and the substituted $\pi$-cycloheptadienyl complex ($LVI; R = (C_6H_5)_3C, L = CO, (C_6H_5)_3P$) is obtained

*$\pi$-Cycloheptadienyliron cations can be prepared by protonation of the uncomplexed double bond of cyclohepta-$1,3,5$-trieneiron with strong acids such as HCl and HBF$_4$, the tricarbonyl giving the tricarbonyl-$\pi$-cycloheptadienyliron cation ($LVI; R = H, L = CO$) [15,32,37,39] while the phosphine-substituted complex ($LV; L = (C_6H_5)_3P$) is not protonated under these conditions [22], and dichlorocyclohepta-$1,3,5$-trieneplatinum is decomposed [118].

If triphenylmethyl fluoroborate instead of fluoroboric acid is used, then addition of the triphenylmethyl cation to the free double bond of ($LV; L = CO, (C_6H_5)_3P$) occurs, and the substituted $\pi$-cycloheptadienyl complex ($LVI; R = (C_6H_5)_3C, L = CO, (C_6H_5)_3P$) is obtained.

* The uncoordinated double bond in this and similar compounds is denoted in bold face type (doubly underlined in this copy) in accordance with the suggestion of Wilkinson [131].
Reduction of (LVI; R = H, L = CO) with sodium borohydride gives tricarbonylcyclohepta-1,3-dieneiron (LVII) [15].

Pettit [122] has shown that tricarbonyl-7-methoxycyclohepta-1,3,5-trieneiron is protonated by HBF$_4$ with loss of methanol yielding the tricarbonyltropyliumiron cation (LVIII). The infrared spectrum of this fluoroborate salt indicates the presence of an unsymmetrical seven-membered ring with an uncomplexed cis double bond, while the NMR spectrum shows only one proton resonance signal, and, therefore, it is assumed that the Fe(CO)$_3$ group is rotating rapidly around the ring. This phenomenon is known as valence tautomerism between equivalent structures such as (LVIII) and (LIX) in solution. Other examples of this are \( \Pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{-\Pi-C}_7\text{H}_7 \) [113,114] (see III, E) and \( \text{C}_8\text{H}_8\text{Fe(CO)}_3 \) [122].

In a similar manner, hexacarbonyl-7-methoxy-\( \Pi\)-cyclohepta-trienylidiiron (LX; R = OCH$_3$) loses methanol when treated with HBF$_4$ yielding the \( [\Pi\text{-C}_7\text{H}_7\text{Fe}_2\text{(CO)}_6]^+ \) cation (LXI) which also shows only one proton resonance signal. This is presumably due to valence tautomerism between (LXI) and (LXII) together with rapid rotation of the metal-metal bond about the seven-membered ring [50].

The tropylium cation (LXI) may also be obtained from the unsubstituted complex (LX; R = H) by reaction with triphenylmethyl fluoroborate [50] (see III, E).

The ability to protonate a free double bond in a 1,3,5-trieneiron complex allows the novel preparation of some substituted
Fe\((CO)_2L\) \[\xrightarrow{H^+}\] Fe\((CO)_2\) \[\xrightarrow{NaBH_4}\] Fe\((CO)_3\)

(LV)

(LVI)

(LVII)

Fe\((CO)_3\) \[\xrightarrow{\text{etc.}}\] Fe\((CO)_3\)

(LVIII)

(LIX)

Fe\((CO)_3\) \[\xrightarrow{(CO)Fe \xrightarrow{(CO)Fe}}\] Fe\((CO)_3\)

(LX)

(LXI)

(LXII)

The process is envisaged to involve reversible equilibration of various dicarbonyl iron complexes, via intermediates, an isomer of type (LXII) undergoing rapid and irreversible loss of methoxyl to give, in this case, the salt (LVIII; \(R = \text{CH}_3\)) (17).
tricarbonyl-\(\pi\)-cyclopentadienyliron cations, e.g. tricarbonyl(diphenylfulvene)iron (LXIII) is protonated by hydrogen chloride to the cation (LXIV), the reaction probably being facilitated by the stability of \(\pi\)-cyclopentadienyl compounds [159,160]. If, however, concentrated hydrochloric acid in acetone is used, the cation rearranges to give a mixture of \(\left(\text{C}_6\text{H}_5\right)_2\text{CHC}_5\text{H}_4\text{Fe(CO)}_2\text{Cl}\) and \(\left(\text{C}_6\text{H}_5\right)_2\text{CHC}_5\text{H}_4\text{Fe(CO)}_2\text{J}_2\). This latter dimer can be obtained in 97\% yield using glacial acetic acid [160].

A reaction of rather a different nature is one recently described by Birch [12] involving removal of methoxyl from the 1- or 2-position of substituted tricarbonylcylohexa-1,3-dieneiron complexes to yield tricarbonyl-\(\pi\)-cyclohexadienyliron salts, e.g. (LXV; \(R = \text{H, CH}_3\)) and (LXVI; \(R = \text{H, CH}_3\)) give (LXVII; \(R = \text{H, CH}_3\), respectively). The results indicate that equilibration of the neutral complexes or of a protonated intermediate occurs. Evidence for equilibration is found in the result that a mixture of (LXVIII; \(R = \text{CH}_3\)) (67\%) and (LXIX; \(R = \text{CH}_3\)) (33\%) gives, with 95\% recovery, the same compounds in the ratio 86:14.

The process is envisaged to involve reversible protonation leading to equilibration of various diene complexes, via \(\pi\)-allyl intermediates, an isomer of type (LXX) undergoing rapid and irreversible loss of methoxyl to give, in this case, the salt (LXVII; \(R = \text{CH}_3\)) [12].

Brief mention may suitably be made here of the \(\pi\)-pentalenylidium
Scheme 3
system which may be even more stable than the \( \pi \)-cyclopentadienyl group from which it can be made by the reaction outlined in Scheme 3 [18].

It is reported that tricarbonylcinnamaldehydeiron forms a 1:1 adduct with dry hydrogen chloride [157].

E. Six-electron ligands

Acid hydrolysis of either tricarbonyltropyliumchromium (LXXI) or the malonate substituted complex (LXXII), prepared by the reaction of (LXXI) and diethyl malonate [138,139] (see III, E), leads to dimeric products (LXXIII) and (LXXIV) in which two cycloheptatrienyl units have become linked [139]. This implies that the malonate complex (LXXII) is readily cleaved under these conditions to diethyl malonate and the tropylium complex (LXXI). The latter will be discussed in more detail in III, E.

F. Cyclooctatriene and cyclooctatetraene complexes

Though cyclooctatetraene itself has the tub conformation, it has been established that in \( \text{C}_8\text{H}_8\text{Fe(CO)}_3 \) the ligand has the chair form [41-43]. Protonation with strong acids results in ligand rearrangement and formation of the tricarbonylbicyclo[5.1.0]-\( \pi \)-octadienyliron cation (LXXV) [37,39,40,96,132,154,158]. The bicyclic nature of (LXXV) is confirmed by reduction with sodium borohydride to give mainly tricarbonylbicyclo[5.1.0]octa-2,4-dieneiron (LXXVI),
though a small amount of tricarbonylcycloocta-1,3,5-trieneiron and, under vigorous conditions, the dimer (LXXVII), better obtained by zinc dust reduction of (LXXV), are also formed [39,40,131].

Elegant use of this protonation was made by Pettit in his synthesis of homotropone (LXXVIII) [96].

In the cobalt and rhodium complexes $\Pi\text{-C}_5\text{H}_5\text{MC}_8\text{H}_8$ (M = Co, Rh) the ligand is in the tub conformation and bonded via a 1,5-diene linkage to the metal. Protonation of these compounds with fluoroboric acid gives the cyclooctatrienium cations, $[\Pi\text{-C}_5\text{H}_5\text{MC}_8\text{H}_9]^+$ (M = Co, Rh), which are less stable than $[\Pi\text{-C}_8\text{H}_9\text{Fe(CO)}_3]^+$, presumably the tub conformation of the former precluding any delocalisation of the charge [39,40].

Protonation of the uncomplexed double bond in tricarbonylcycloocta-1,3,5-trieneiron occurs with strong acids such as concentrated sulphuric and fluoroboric acids, delocalisation of the charge then yielding the tricarbonyl-$\Pi$-cyclooctadienyliron cation (LXXIX). Similarly, hexacarbonyl-bis(cycloocta-2,4,6-trienyl)diiron (LXXX) gives the binuclear cation (LXXXI) [131]. In contrast, $\Pi\text{-C}_5\text{H}_5\text{CoC}_8\text{H}_{10}$ gives rise to an unstable protonated species in concentrated sulphuric acid, the instability probably arising from the cycloocta-1,3,5-triene ligand being here also in the tub conformation and complexed as a 1,5-diene, thus prohibiting the delocalisation of the positive charge [131].
reaction of both tricarbonyliron and tricarbonylnickel complexes (LXXII) with sodium borohydride (NaBH₄) to yield the complexes (LXXIV). The reaction proceeds via the intermediate (LXXIII) and the final product (LXXIV) is formed by the addition of the proton to the unsaturated bond in (LXXIII). In fact, the NMR spectrum of Ce⁺(CO)₃ in D₂O shows very clear evidence for the formation of the complex (LXXIV).

Equation 1:  
\[
\text{Fe(CO)₃} + \text{NaBH₄} \rightarrow \text{Fe(CO)₃} + \text{H₂}
\]

Equation 2:  
\[
\text{Fe(CO)₃} + \text{CrO₃} \rightarrow \text{Fe(CO)₃} + \text{CrO}_3^-
\]

Equation 3:  
\[
\text{Fe(CO)₃} + \text{Ce}^{4+} \rightarrow \text{Fe(CO)₃} + \text{Ce}^{3+}
\]

Equation 4:  
\[
\text{Fe(CO)₃} + \text{NiCl} \rightarrow \text{Fe(CO)₃} + \text{NiCl}_2
\]

Equation 5:  
\[
\text{Mo(CO)₃} + \text{Mo(CO)₃} \rightarrow \text{Mo(CO)₃}_2
\]
When hydrogen chloride is passed into a toluene solution of a polymeric cyclooctatetraenenickel complex, \([C_{8}H_{8}Ni]_{x}\), at -80°, chloro-\(\pi\)-cyclooctatrienynickel dimer (LXXXII) is obtained [161].

Reaction of both tricarbonyl- and tetracarbonylcyclooctatetraenemolybdenum with \(D_{2}SO_{4}\) results in formation of the tricarbonyl-homotropyliummolybdenum cation \([C_{8}H_{9}Mo(CO)_{3}]^{+}\), to which the non-classical structure (LXXXIII), has been assigned [108,169]. It is clear that a bicyclic structure as in \([C_{8}H_{9}Fe(CO)_{3}]^{+}\) is excluded, since its NMR has a 1:4:2:2 pattern of proton resonances, whereas (LXXXIII) exhibits the required 5:2:1:1 pattern of the homotropylium cation. In fact the NMR spectrum of \(C_{8}H_{8}Mo(CO)_{3}\) in \(D_{2}SO_{4}\) is very similar to that of the free cation obtained by protonation of cyclooctatetraene in concentrated sulphuric acid, and also shows the addition of the proton to be stereospecific (\(H_{a}\) in (LXXXIII)) [152,169].

III. HYDRIDE ABSTRACTION

A. One-electron ligands

The preparation of olefinic cations by protonation of \(\sigma\)-allyl complexes (LXXXIV) was described in II, A, 1 [83,86].

An alternative route to cations of the type (LXXXV) is by the abstraction of hydride from \(\sigma\)-alkyl complexes, such as (LXXXVI), with triphenylmethyl fluoroborate [85,87]. That hydride is removed from the \(\beta\)-carbon atom is shown by the formation of the 2-deuteropropene
The reaction of the iron carbonyl complexes with ethylene leads to the formation of another complex, which in turn reacts with the other iron carbonyl complex to form a new compound. This process is repeated several times, resulting in the formation of a series of products. The reaction scheme is shown in the diagram.

In summary, the reaction involves the addition of ethylene to the iron carbonyl complex, followed by the formation of a new complex with another iron carbonyl moiety. The cyclic product is obtained in small yield.
cation (LXXXV; R = D) from the 2-deutero-σ-isopropyl complex (LXXXVII). The mechanism of the abstraction reaction is thought to be bimolecular involving a metal-stabilised β-carbonium ion intermediate (LXXXVIII) (see II, A, 1) which then forms the olefin-metal bond [87].

In an analogous manner, $\pi$-C$_{5}$H$_{5}$Mo(CO)$_{3}$-σ-C$_{2}$H$_{5}$ [26] and Mn(CO)$_{5}$-σ-C$_{2}$H$_{5}$ [87] each lose hydride ion with (C$_{6}$H$_{5}$)$_{3}$CBF$_{4}$ to give the $[\pi$-C$_{5}$H$_{5}$Mo(CO)$_{3}$C$_{2}$H$_{4}$]$^+$ and $[\text{Mn(CO)}_{5}C_{2}H_{4}]^+$ cations, respectively, the latter albeit in small yield.

These reactions are reversible in that the olefin cations may be reduced back to σ-alkyl complexes with sodium borohydride, $[\text{MC}_{2}H_{4}]^+$ giving M-σ-C$_{2}$H$_{5}$ (M = $\pi$-C$_{5}$H$_{5}$Mo(CO)$_{3}$ [26], $\pi$-C$_{5}$H$_{5}$W(CO)$_{3}$ [91], $\pi$-C$_{5}$H$_{5}$Fe(CO)$_{2}$ [84,87]). An interesting feature of these reductions is that the propene cations $[\text{MC}_{3}H_{6}]^+$ (M = $\pi$-C$_{5}$H$_{5}$W(CO)$_{3}$ [91], $\pi$-C$_{5}$H$_{5}$Fe(CO)$_{2}$ [84,87]) yield only the M-σ-isopropyl complex, and there is no evidence for the presence of the n-propyl isomer. Attempted reduction of the $[\text{Mn(CO)}_{5}C_{3}H_{6}]^+$ cation gave mainly Mn$_{2}$(CO)$_{10}$ [84].

A reaction of interest is the abstraction of hydride from (CH$_{2}$)$_{3}$$[\pi$-C$_{5}$H$_{5}$Fe(CO)$_{2}$]$^{2}$ (LXXXIX) with (C$_{6}$H$_{5}$)$_{3}$CPF. A crystalline PF$_{6}$ salt is obtained whose NMR spectrum indicates the two $\pi$-cyclopentadienyl groups, and hence the iron atoms, to be equivalent [115]. This is consistent with structure (XCI), in which the positive charge is located on the central carbon of the three carbon chain. However, in view of the stability of $[\pi$-C$_{5}$H$_{5}$Fe(CO)$_{2}$(olefin)]$^+$ cations relative to carbonium ions, already discussed, it is thought that a dynamic
equilibrium between the carbonium ion (XCI) and the two olefin cations (XC) and (XCII) is a better representation of its structure [115].

The manganese complex, \((\text{CH}_2)_3\text{[Mn(CO)]}_2\), reacts very slowly with \((\text{C}_6\text{H}_5)_3\text{CPF}_6\) to give a yellow solid which shows the absence of metal carbonyl groups. This behaviour lends support to the idea that the structure of the manganese complex is different from the iron compound, and is thought to be (XCIII) [111,115].

B. Three-electron ligands

The \(\pi\)-allyl complex dicarbonyltriphenylphosphine-2-methyl-\(\pi\)-cyclopentenonylcobalt (XCIV; \(R = \text{CH}_3\)) is converted to the cyclopentadienone compound (XCV; \(R = \text{CH}_3\)) on reaction with \((\text{C}_6\text{H}_5)_3\text{CBF}_4\) at \(0^\circ\). Although the unsubstituted complex (XCIV; \(R = \text{H}\)) reacts similarly, the resulting cation is too unstable for characterisation [93].

C. Four-electron ligands

1. Acyclic diene complexes

The preparation of tricarbonyl-\(\pi\)-diencyliron cations of the general formula (XCVII) by acid cleavage of the corresponding alcohol complexes (XCVI) with strong acids has already been discussed in II, D, 2. An alternative route to these salts is from the tricarbonyl-cis-cis-dieneiron compounds (XCVIII) by reaction with \((\text{C}_6\text{H}_5)_3\text{CBF}_4\) [123,124].
If the diene ligand is in the trans configuration, however, as in the case in the products of the reaction of pentacarbonyliron with free dienes, then no abstraction occurs.

2. Cyclopentadiene complexes

In a similar manner to that described in the preceding section, cations containing the \( \pi \)-C\(_5\)H\(_5\) group are obtained by abstraction of hydride from the cyclopentadiene complexes with (C\(_6\)H\(_5\))\(_3\)CBF\(_4\) [36,119]. An interesting reaction of these cations is their reduction with sodium borohydride to give, in some cases, compounds other than the starting diene complexes. \([\pi \text-C\(_5\)H\(_5\)Fe(CO)]^+\) yields, under these conditions, both the hydride \( \pi \text-C\(_5\)H\(_5\)Fe(CO)\(_2\) \)H and the dimer \([\pi \text-C\(_5\)H\(_5\)Fe(CO)]_2\) [119], arising from hydride attack on the metal atom [36], while replacement of one of the carbonyl groups by triphenylphosphine, i.e. \([\pi \text-C\(_5\)H\(_5\)Fe(CO)](\text-C\(_6\)H\(_5\))_3\text-P]^+\), causes hydride to add to the \( \pi \)-C\(_5\)H\(_5\) ligand, and the diene complex \( \text-C\(_5\)\text-C\(_6\)\text-H\(_5\)Fe(CO)](\text-C\(_6\)H\(_5\))_3\text-P \) is obtained [36].

Reaction of the \([\pi \text-C\(_5\)H\(_5\)Fe(CO)]^+\) cation with potassium iodide also leads to displacement of a carbonyl group, yielding \( \pi \text-C\(_5\)H\(_5\)Fe(CO)\(_2\)I \) which can be converted to \( \pi \text-C\(_5\)H\(_5\)Fe(CO)\(_2\)\text-CN \) using KCN [92].

Hydride ion can also be removed from the cyclopentadiene ligand in \( \pi \text-C\(_5\)\text-HMC\(_5\)\text-H \) to give the cations \([(\pi \text-C\(_5\)H\(_5\))\(_2\)M]^+\) (M = Co [89], Rh [71,89], Ir [71]). In this series the abstracting agent is 2N.
equation hydrochloric acid though the hydrolyzed cation is formed were rapidly if acid hydroxide is used.

The cyclopentadiene complexes, while HBF_4 allows the preparation of the mononuclear compounds Fe(CO)_3 (4 = Co, Rh) (55),...}

...molecules complex, while HBF_4 allows the preparation of the mononuclear compounds Fe(CO)_3 (4 = Co, Rh) (55),...}

...molecules complex, while HBF_4 allows the preparation of the mononuclear compounds Fe(CO)_3 (4 = Co, Rh) (55),...}

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aqueous hydrochloric acid though the rhodicenium cation is formed more rapidly if acid hydrogen peroxide is used. Reduction of these species with NaBH$_4$ or LiAlH$_4$ regenerates the cyclopentadiene complexes, while LiAlD$_4$ allows the preparation of the monodeutero compounds $\Pi$-$\text{C}_5\text{H}_5\text{MC}_5\text{H}_5\text{D}$ (M = Co, Rh) [55,89,162,163]. Reaction with nucleophiles other than hydride ion yields a series of substituted cyclopentadiene complexes, e.g. $\Pi$-$\text{C}_5\text{H}_5\text{CoC}_5\text{H}_5\text{R}$ ($\text{R} = \text{CH}_3$, $\text{C}_6\text{H}_5$, $\text{CCl}_3$, etc.) (IC) [1,55,89]. That the substituent $\text{R}$ is in the exo position relative to the metal atom has been shown by the X-ray structure determination [23,24] of the phenyl-substituted complex (IC; $\text{R} = \text{C}_6\text{H}_5$), prepared from $[(\Pi$-$\text{C}_5\text{H}_5)\text{Co}]^+$ and phenyl-lithium [1,163]. A comparison of the X-ray diffraction powder photographs of (IC; $\text{R} = \text{C}_6\text{H}_5$) and its rhodium analogue shows the two compounds to be isomorphous [1].

A pentadienium species that may conveniently be described here is the benzenepentadienium cation (CI), obtained by hydride abstraction with $(\text{C}_6\text{H}_5)_3\text{CBF}_4$ from tricarbonyl-1,2-benzocycloheptatrieneiron (C) [9]. Since the proton NMR spectrum shows the benzene protons in the cation (CI) essentially unchanged compared to the starting diene complex, unlike the free benzotropenium cation where there is a downfield shift of about 1.5 ppm [8], it is thought that the positive charge is localised on the five carbon atoms of the seven-membered ring in a benzenepentadienium system [9].

An interesting reaction that indicates the stability of
the $\pi$-cyclopentadienyl grouping is the sodium borohydride reduction of tricarbonyl(diphenylfulvene)chromium (CII) to the substituted $\pi$-cyclopentadienyl anion, $[\pi-C_5H_4CH(C_6H_5)_2Cr(CO)_3]^{-}$ (CIII), isolated as its thallium salt [25].

The reduction of $\pi$-cyclopentadienyl-transition metal complexes does not always give rise to compounds containing the cyclopentadiene group, as has already been indicated in the case of the $[\pi-C_5H_5Fe(CO)_3]^+$ cation (see III, C, 2), though products other than metal hydrides are formed in some reactions, e.g. sodium amalgam reduces $\pi-C_5H_5Ni$ to the $\pi$-allyl complex $\pi-C_5H_5Ni-\pi-C_5H_7$ (CIV) [44], earlier erroneously formulated as $(C_5H_6)_2Ni$ [68,170]. Reduction of $(\pi-C_5H_5)_2Cr$ with hydrogen and carbon monoxide at low temperatures and pressures gives the hydride $\pi-C_5H_5Cr(CO)_3H$, while at high pressure a $\pi$-cyclopentenyl complex, analogous to (CIV), $\pi-C_5H_5Cr(CO)_2-\pi-C_5H_7$, is formed [67], originally thought to be $(C_5H_6)_2(CO)_2$ [66]. A third example of the conversion, under reducing conditions, of the $\pi-C_5H_5$ group to the $\pi-C_5H_7$ species is the hydrogenation, using platinum, of the bis($\pi$-cyclopentadienyl)rhenium-substituted dimethyl maleate (CV) formed from the hydride $(\pi-C_5H_5)_2ReH$ and dimethylacetylene dicarboxylate. In addition to the formation of the $\pi$-cyclopentenyl group, the dicarboxylate ligand is converted to the fumarate configuration (CVI) [45].

3. Cyclohexa- and cyclohepta-1,3-diene complexes

Tricarbonyl-$\pi$-cyclohexadienyliron cations are generally
Cyclometalated cations 

\[
\text{Fe(CO)}_3\text{R}^1\text{R}^2\text{L} 
\]

Cyclometalated anions 

\[
\text{Fe(CO)}_3\text{L}^{-} 
\]

Complexes of tricarbonyliron 

\[
\text{Fe(CO)}_3 
\]

Soluble in polar solvents such as water and dimethylformamide, the tricarbonyliron-cyclopentadiene salts (CIX) exhibit interesting electronic and magnetic properties.
prepared by reaction of \((\text{C}_6\text{H}_5)_3\text{CBF}_4\) with the corresponding diene complexes of the general formula \(\text{C}_6\text{H}_7\text{RFe}(\text{CO})_2\text{L}\) (CVII). Fischer first demonstrated this reaction in the case of the parent tricarbonylcyclohexa-1,3-dieneiron complex (CVII; \(\text{R} = \text{H}, \text{L} = \text{CO}\)) [53], and the series has since been extended to include such tricarbonyliron compounds as (CVII; \(\text{R} = \text{OH}\) [11], \(\text{OCH}_3\) [11,92], \(\text{CN}\) [11,92], \(\text{CH(COCH}_3\)\(_2\) [11,120], \(\text{L} = \text{CO}\)) and the triphenylphosphine-substituted analogue (CVII; \(\text{R} = \text{H}, \text{L} = (\text{C}_6\text{H}_5)_3\text{P}\)) [22].

Cyclohepta-1,3-diene complexes (CVIII; \(\text{L} = \text{CO}, (\text{C}_6\text{H}_5)_3\text{P}\)) react in a similar manner, both the tricarbonyl [32] and dicarbonyl-triphenylphosphine [22] compounds giving the corresponding \(\pi\)-cycloheptadienyl cations (CIX; \(\text{R} = \text{H}, \text{L} = \text{CO}, (\text{C}_6\text{H}_5)_3\text{P}\)) discussed in II, D, 2. Attempted hydride abstraction from tricarbonylcyclohepta-1,3,5-trieneiron results in addition of the triphenylmethyl cation to the uncomplexed double bond with formation of the substituted \(\pi\)-cycloheptadienyl cation (CIX; \(\text{R} = (\text{C}_6\text{H}_5)_3\text{C}, \text{L} = \text{CO}\)) [32,143].

Tricarbonylbicyclo[5.1.0]octa-2,4-dieneiron (CX) also loses hydride to yield the bicyclic \(\pi\)-octadienyl cation (CXI) which behaves essentially as a substituted \(\pi\)-cycloheptadienyl complex in that \(\text{NaBH}_4\) reduction regenerates the diene complex (see II, D, 2) [39].

Most of the cations described form stable diamagnetic crystals soluble in polar solvents such as water and dimethylsulphoxide, though the tricarbonyl-1-methoxy-\(\pi\)-cyclohexadienyliron salts (CXII; \(\text{R}_1 = \text{H},\)
\( \text{CH}_3, \text{R}_2 = \text{H} \) and \((\text{CXII}; \text{R}_1 = \text{H}, \text{R}_2 = \text{OCH}_3)\) are hydrolysed by water to yield the novel tricarbonylcyclohexadienoneiron complexes \((\text{CXIII}; \text{R}_1 = \text{H}, \text{CH}_3, \text{R}_2 = \text{H})\) and \((\text{CXIII}; \text{R}_1 = \text{H}, \text{R}_2 = \text{OCH}_3)\), respectively, in which the ligands may be regarded as tautomers of the corresponding phenols, stabilised by coordination \([10,11]\).

The reactions of nucleophiles such as hydride, methoxide, cyanide, etc. with these cations \((\text{CXIV})\) \([11,12,32,33,92]\) follows the same course as that described for the cobalticenium cation \((\text{II}, \text{C}, 2)\), e.g. fluoroborate salts \((\text{CXIV}; \text{R} = \text{OCH}_3, \text{L} = \text{CO})\) and \((\text{CXIV}; \text{R} = \text{H}, \text{L} = \text{CO})\) yield the 5-cyano-substituted complexes \((\text{CXV}; \text{R}_1 = \text{OCH}_3, \text{R}_2 = \text{CN})\) \([11]\) and \((\text{CXV}; \text{R}_1 = \text{H}, \text{R}_2 = \text{CN})\) \([92]\), respectively. The cation \([\text{\Pi-C}_6\text{H}_7\text{Fe(CO)}_3]^+\) \((\text{CXIV}; \text{R} = \text{H}, \text{L} = \text{CO})\) can be converted to the iodide \(\text{\Pi-C}_6\text{H}_7\text{Fe(CO)}_2\text{I}\) \((\text{CXIV}; \text{R} = \text{H}, \text{L} = \text{I})\) with potassium iodide, in the same manner as that described for the \([\text{\Pi-C}_5\text{H}_5\text{Fe(CO)}_3]^+\) species in \(\text{III}, \text{C}, 2\), which in turn yields the cyanide \((\text{CXIV}; \text{R} = \text{H}, \text{L} = \text{CN})\) with KCN and the dimer \((\text{CXVI})\) with sodium cyclopentadienide \([92]\).

This series of reactions is also followed by the tricarbonyl-\(\Pi\)-cycloheptadienyliron cation \([32,33,92]\).

By analogy with the cobalticenium \([23,24]\) and tricarbonyltropylium chromium (see \(\text{III}, \text{E}\)) cations, it is assumed that anions attack the ligand from the side remote from the iron atom, and therefore in the adducts \((\text{CXV})\) the group \(\text{R}_2\) has the \text{exo} configuration.

That the stereochemistry of electrophilic attack by the triphenylmethyl cation on the ligand is the same as that of nucleo-
philic attack on the \( \pi \)-dienyl cations is demonstrated by the complete removal of deuterium from the 5-deutero derivative (CXV; \( R_1 = \text{OCH}_3 \), \( R_2 = \text{D} \)) by \( (\text{C}_6\text{H}_5)_3\text{CBF}_4 \) [11].

The analogous tricarbonyl-2-methoxy-\( \pi \)-cyclohexadienylruthenium cation may similarly be prepared from tricarbonyl-2-methoxycyclohexa-1,3-dieneruthenium by reaction with triphenylmethyfluoroborate [102].

In some cases \( (\text{C}_6\text{H}_5)_3\text{CBF}_4 \) abstracts two hydride ions from the complexed cyclohexa-1,3-diene ligand giving rise to doubly-charged benzene cations: \( \text{C}_6\text{H}_6\text{RuC}_6\text{H}_8 \) yields \( [(\text{C}_6\text{H}_6)_2\text{Ru}]^{2+} \) [105] while \( \pi\text{-C}_5\text{H}_5\text{CoC}_6\text{H}_8 \) gives the \( \pi\text{-C}_5\text{H}_5\text{CoC}_6\text{H}_6 \) \( ^{2+} \) cation [54].

If the diene ligand is not conjugated, then the positive charge resulting from hydride abstraction cannot be delocalised over five carbon atoms to give a \( \pi \)-dienyl species, but only over three, and a \( \pi \)-allyl complex is the product: tricarbonylbicyclo[3.2.1]octa-1,4-dieneiron (CXVII) gives the bicyclic \( \pi \)-octadienyl cation (CXVIII) [129].

Although \( \pi\text{-C}_5\text{H}_5\text{MC}_6\text{H}_8 \) (CXIX; \( M = \text{Co}, R_1 = R_2 = \text{H} \)), in which the diene is bonded via a 1,5-linkage, reacts in a similar manner to give the \( \pi \)-allyl complex (CXX; \( M = \text{Co}, R_2 = \text{H} \)), the rhodium analogue (CXIX; \( M = \text{Rh}, R_1 = R_2 = \text{H} \)) undergoes substitution of the \( \pi \)-cyclo-pentadienyl ring when treated with one mole of \( (\text{C}_6\text{H}_5)_3\text{CBF}_4 \) giving (CXIX; \( M = \text{Rh}, R_1 = \text{H}, R_2 = (\text{C}_6\text{H}_5)_3\text{C} \)), while a second mole abstracts a hydride ion from the diene ligand to yield the cation (CXX; \( M = \text{Rh}, R_2 = (\text{C}_6\text{H}_5)_3\text{C} \)) [120].
Both cations (CXX; M = Co, R₂ = H) and (CXX; M = Rh, 
R₂ = (C₆H₅)₃C) react with nucleophiles in the manner already described 
giving neutral complexes of the general formula (CXIX; M = Co, R₁ = H,
CN, CH(COCH₃)₂, R₂ = H) and (CXIX; M = Rh, R₁ = (CH₃)₂N, R₂ = (C₆H₅)₃C),
respectively [120].

D. Five-electron ligands

Winkhaus first reported the existence of the π-cyclohexadienyl 
system as a ligand in the compound π-C₆H₇Mn(CO)₃, obtained by the 
reaction of Mn₂(CO)₁₀ and cyclohexa-1,3-diene [168], and showed that 
not only (C₆H₅)₃CBF₄, but also carbon tetrachloride, abstracts hydride 
from the complex to give the tricarbonylbenzenemanganese cation [166,
168]. In a similar manner, CCl₄ reacts with the substituted rhenium 
analogue, C₆(CH₃)₆HRe(CO)₃ to generate [C₆(CH₃)₆Re(CO)₃]⁺ [167].

Tricarbonyl-1-methyl-π-cyclohexadienylmanganese is obtained 
by reaction of the [C₆H₆Mn(CO)₃]⁺ with methyl lithium, and is considered 
to have a structure in which the methyl is exo to the metal [107].

Reduction of [C₆H₆Mn(CO)₃]⁺ with NaBH₄ or LiAlH₄ [165, 166,
168], or of [C₆(CH₃)₆Re(CO)₃]⁺ with LiAlH₄ [167] regenerates the starting 
π-cyclohexadienyl complexes, though in the former case a metal hydride,
C₆H₈Mn(CO)₃H, is formed as a by-product [165].

In a similar manner LiAlH₄ reduces [C₆H₆MnC₆(CH₃)₆]⁺ to 
π-C₆H₇MnC₆(CH₃)₆, addition to the unsubstituted ring having occurred
[65], and {[C₆(CH₃)₆]₂Re}⁺ is reduced by LiAlH₄ or sodium in liquid 
ammonia to C₆(CH₃)₆Re-π-C₆(CH₃)₆H [64].
Although hydride cannot be abstracted from \( [\pi-C_6H_7Fe(CO)_3]^+ \), hydrochloric acid converts \( \pi-C_5H_5Fe-\pi-C_6H_7 \) (CXXI) to the \( [\pi-C_5H_5FeC_6H_6]^+ \) cation [90, 105] which can be reduced back to (CXXI) with LiAlH\(_4\) [90].

Other cations which can be reduced to \( \pi \)-cyclohexadienyl species are \( [(C_6H_6)_2Re]^+ \) to \( C_6H_6Re-\pi-C_6H_7 \) with LiAlH\(_4\) [105, 106] and \( [C_6H_6V(CO)_4]^+ \) to \( \pi-C_6H_7V(CO)_4 \) using sodium borohydride [19]. An interesting feature of the latter reaction is that in the reduction of the mesitylene cation (CXXII) addition of hydride again takes place predominantly at an unsubstituted carbon atom (cf. the reduction of the syn-\( \pi \)-hexadienyliron (see II, D, 2) and previously mentioned \( [C_6H_6MnC_6(CH_3)_6]^+ \) cations) to give the 2,4,6-trimethyl-substituted cation (CXXIII) [19].

The doubly-charged species \( [(C_6H_6)_2Ru]^2+ \) reacts in a different manner under these reducing conditions in that addition of two hydrides occurs, when NaBH\(_4\) is used, to give \( C_6H_6RuC_6H_8 \), while this complex, together with \( (\pi-C_6H_7)_2Ru \), are the products from LiAlH\(_4\) reduction [105].

The cations \( [\pi-C_5H_5MoC_6H_6CO]^+ \) (\( M = Mo, W \)) react with hydride ion to give the complex \( \pi-C_5H_5MoC_6H_8 \) [56, 57] and the metal hydride \( \pi-C_5H_5WC_6H_8(CO)H \) [57], respectively.

It may be conveniently mentioned here that the neutral complex \( [(C_6(CH_3)_6)_2Co] \) may be prepared by reduction of the \( [(C_6(CH_3)_6)_2Co]^+ \) cation [59] by sodium in liquid ammonia, while the analogous rhodium compound \( [(C_6(CH_3)_6)_2Rh]^+ \) is obtained when
the doubly-charged cation \([\{C_6(\text{CH}_3)_6\}_2\text{Rh}\}]^{2+}\) is reduced with zinc in acid solution \([58]\).

Maitlis \([46,47]\) found that although triphenylmethyl fluoro-borate would not abstract hydride from the \(\pi\)-cyclohexadienyl complexes \((CXXIV; R = \text{H, n-butyl}), \text{N-bromosuccinimide (NBS)}\) in methanol effected the abstraction to give the corresponding benzene cations \((CXXV; R = \text{H, n-butyl})\). Similarly, the \(\pi\)-cycloheptadienyl compound \((CXXVI; R = \text{H})\) yields the cycloheptatriene cation \((CXXVII)\).

The two cations \((CXXV; R = \text{H})\) and \((CXXVII)\) show some similarities and some differences in their reactions towards nucleophiles. Though both react with sodium borohydride and n-butyllithium to give \((CXXIV; R = \text{H, n-butyl})\) and \((CXXVI; R = \text{H, n-butyl})\), only the cycloheptatriene species \((CXXVII)\) is attacked by sodium methoxide and methylmagnesium iodide, giving \((CXXVI; R = \text{OCH}_3, \text{CH}_3)\) \([46,47]\).

Consideration of these and other \([125,127]\)(see II, C) reactions led Maitlis to propose an order of susceptibility of complexed ligands in metal \(d^8\) complexes toward nucleophilic attack, namely, cycloheptatriene > benzene > tetraphenylcyclobutadiene > \(\pi\)-cyclopentadienyl, the last being the most resistant.

E. Six-electron ligands

The cycloheptatriene complexes \(C_7H_8M(\text{CO})_3\) \((M = \text{Cr, Mo, W})\) all react with \((\text{C}_6\text{H}_3)_3\text{CBF}_4\) to give the tropylium cations \([C_7H_7M(\text{CO})_3]^+\).
(M = Cr [35,137,145], Mo [34,137,145], W [35,117]), as does hexacarbonylbicycloheptatrienyldichromium [139]. The methyl-substituted tropylium cation \( \text{[C}_{7}\text{H}_{6}\text{CH}_{3}\text{Cr(CO)}_{3}]^{+} \) can be obtained in a similar manner from tricarbonyl-7-endo-methylcycloheptatrienechromium (CXXIX; \( R = \text{CH}_{3} \)); the 7-exo-methyl complex (CXXVIII; \( R = \text{CH}_{3} \)) remains unattacked [146].

Attempted preparation of a tropylium-platinum complex from \( \text{C}_{7}\text{H}_{8}\text{PtCl}_{2} \) by reaction with triphenylmethyl fluoroborate resulted only in decomposition to cycloheptatriene and platinic acid [118].

The reactions of nucleophiles with tricarbonyltropylium chromium is of interest in that they can proceed in three different ways.

(a) With anions such as hydride, methoxide, diethylmethylmalonate, hydrogen sulphide or tert-butylcyclopentadienide, a so-called "normal" reaction occurs, i.e. analogous to that of the cobalticenium and \( \pi \)-cyclohexadienyl cations, with formation of the 7-substituted cycloheptatriene complexes \( \text{C}_{7}\text{H}_{7}\text{RCr(CO)}_{3} \) (CXXVIII) [138,139].

An X-ray examination of \( \text{C}_{6}\text{H}_{5}\text{C}_{7}\text{H}_{5}\text{Cr(CO)}_{3} \) (CXXVIII; \( R = \text{C}_{6}\text{H}_{5} \)) indicates that these additions occur from the side remote from the chromium atom, and that in (CXXVIII; \( M = \text{Cr}, \text{Mo} \)) the R group has the exo configuration [5,146].

Pauson [146] found that some of these complexes (CXXVIII; \( R = \text{CH(CO}_{2}\text{Et)}_{2}, \text{CH}_{3}, \text{C}_{6}\text{H}_{5} \)) can also be obtained by displacement of methoxide from (CXXVIII; \( R = \text{OCH}_{3} \)) by other anions. The fact that
the products of this reaction have the same stereochemistry as the starting material suggests that an $S_N$ mechanism is probably operative.

The 7-endo substituted cycloheptatriene complexes (CXXIX) may be obtained by heating the appropriate triene with hexacarbonylchromium in an inert solvent, or treating the ligand with tricarbonyltripyridinechromium and boron trifluoride in ether [147].

An interesting feature of the sodium borohydride reduction of the methyltropylium species (CXXX) is that the predominant component of the mixture of isomeric complexes obtained is the 1-methyl derivative (CXXXI); this is another example of hydride addition occurring mainly at an unsubstituted carbon atom [146].

(b) The second route that nucleophilic attack may follow is one that occurs with diethyl malonate and sodium cyclopentadienide, and involves ring contraction to tricarbonylbenzenechromium [136,138]. The coordinated benzene ring is derived entirely from the tropylium ligand and not from the $\pi$-cyclopentadienyl group, since only $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ is obtained from $[\text{C}_7\text{H}_7\text{Cr(CO)}_3]^+$ and $\text{C}_5\text{H}_4\text{CH}_3\text{Na}$, and only $\text{C}_6\text{H}_5\text{CH}_3\text{Cr(CO)}_3$ from $[\text{C}_7\text{H}_7\text{CH}_3\text{Cr(CO)}_3]^+$ and $\text{C}_5\text{H}_5\text{Na}$. Experiments with labelled tropylium complexes confirm these results [138].

The mechanism suggested for this contraction is shown below [147], and differs from that suggested earlier [138] in that the by-product is $\text{CHY=CX}_2$, containing the attacking $Y^-$ species, rather than $\text{CH}_2=\text{CX}_2$. 
This mechanism accounts for the observation that both the exo- and endo-malonate complexes (CXXXII; CHX₂ = exo- or endo-CH(CO₂Et)₂) rearrange to C₆H₆Cr(CO)₃, since the difference between these isomers disappears in the first step.

(c) With basic reagents, such as KCN, NaHCO₃, NaOAc, NaNH₂, C₆H₅Li and C₆H₅CONH₂, an "abnormal" reaction occurs, and the dimeric products (CXXXIII) and (CXXXIV), together with some of the "normal" adduct C₇H₇RCr(CO)₃ (CXXVIII), are obtained [139]. In a typical experiment, using potassium cyanide, 18% C₇H₇CNCr(CO)₃ (CXXVIII; R = CN), 17% (CXXXIII) and 46% (CXXXIV) were obtained. The structure of (CXXXIV) is confirmed by its formation on reduction of [C₇H₇Cr(CO)₃]+ with zinc dust.

In contrast to the dimer formed from Π-C₈H₈Fe(CO)₂⁺ and sodium cyclopentadienide [92], discussed in III, C, 3, C₇H₇Mo(CO)₂⁺ [7] gives the diamagnetic complex Π-C₅H₅Mo(CO)₂-Π-C₇H₇ (CXXXV) [113, 114] in which the Π-C₇H₇ group must be functioning as a 3-Π-electron donor, i.e. as a substituted Π-allyl group, in order that molybdenum attains the rare gas configuration. However, the complex shows only two signals in its proton NMR spectrum in a 5:7 intensity ratio, the latter being broadened on cooling to -40°C [112] and resolved into two signals of intensity ratio 4:3 at -105°C [6], while the former remains unchanged. The spectrum is therefore analogous to that of C₈H₈Fe(CO)₃⁺ [122] and Π-C₇H₇Fe(CO)₃⁺ (n = 1,2), discussed in II, D, 2, and it is assumed that valence tautomerism between equivalent structures such as (CXXXV) and (CXXXVI) must be occurring.
The complex $\pi$-C$_5$H$_5$CrC$_7$H$_8$ and the cation [C$_5$H$_5$CrC$_7$H$_7$]$^+$ are related in the same manner as are C$_7$H$_8$Cr(CO)$_3$ and [C$_7$H$_7$Cr(CO)$_3$]$^+$. $\pi$-C$_5$H$_5$CrC$_7$H$_8$ is formed in good yield from $\pi$-C$_5$H$_5$CrC$_1$, THF, isopropylmagnesium iodide and cycloheptatriene in ether. Oxidation of this complex with atmospheric oxygen yields the cation [C$_5$H$_5$CrC$_7$H$_7$]$^+$, while the neutral complex $\pi$-C$_5$H$_5$CrC$_7$H$_7$ can be obtained from it by catalytic dehydrogenation [62].

The preparation of [C$_7$H$_7$Fe$_2$(CO)$_6$]$^+$ [122] and [C$_7$H$_7$Fe$_2$(CO)$_6$]$^+$ [50] has already been discussed in II, D, 2, however, it is appropriate to mention here that the latter species is also formed by hydride abstraction from C$_7$H$_8$Fe$_2$(CO)$_6$ with triphenylmethyl fluoroborate. Reduction of the [C$_7$H$_7$Fe$_2$(CO)$_6$]$^+$ species with sodium borohydride reverses this abstraction reaction with the formation of C$_7$H$_8$Fe$_2$(CO)$_6$ [50].

The complex tricarbonylcyclooctatetraenemolybdenum does not react with triphenylmethyl fluoroborate [63].

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PART A

THE ABSTRACTION OF HYDRIDE FROM
TRICARBONYLCYCLOHEXA-1,3-DIENEIRON COMPLEXES

Introduction

Although a description of the preparation and reactions of tricarbonyl-\(\pi\)-cyclohexadienyliron fluoroborate complexes has already been presented in Part III, it is useful to consider here the actual structure of these cations.

The proton resonance spectrum of tricarbonyl-\(\pi\)-cyclohexadienyliron fluoroborate (1; \(R = H\)) in liquid sulphur dioxide solution has five resonance lines: a triplet at 2.66\(\tau\) assigned to \(H_3\); an overlapping double doublet at 4.08\(\tau\) for \(H_2\) and \(H_4\); a second overlapping double doublet at 5.66\(\tau\) for \(H_1\) and \(H_5\); a double triplet at 6.86\(\tau\) and 7.09\(\tau\) for \(H_\alpha\); and two single sharp bands at 7.85\(\tau\) and 8.11\(\tau\) for \(H_\beta\). The difference in structure of the bands assigned to \(H_\alpha\) and \(H_\beta\) suggests that they are coupled in different ways to \(H_1\) and \(H_5\). If the \(\pi\)-cyclohexadienyl ring were not planar, but the methylenic carbon atom, C-6, were bent out of the plane containing the other five carbon atoms, either away from (2) or towards (3) the metal atom, then \(H_\alpha\) would make a dihedral angle of approximately 90° with \(H_1\) and \(H_5\), and hence there should be no coupling between them. Coupling between \(H_\beta\) and these two protons would be expected, since \(H_\beta\) would make a dihedral angle of about 30° with each of them.
Birch found the spectrum of the 2-methoxy analogue (1; \( \text{R} = \text{OCH}_3 \)) to be very similar, and concluded that in this case too the \( \Pi \)-cyclohexadienyl is non-planar.

It is interesting, and a little surprising, that although the hydride abstraction reaction has been known and used for some time, no attempt has been made to investigate it systematically with a view to discovering whether any general principles govern the mode of abstraction. It was with this end in view that the reaction of triphenylmethyl fluoroborate with a wide range of substituted tri-carbonylcyclohexa-1,3-dieneiron complexes was studied.
Discussion

The isolation of tricarbonyl-1,3-dieneiron complexes \( \text{Fe(CO)}_3 \) (4; \( R = \text{CH}_3 \)) and \( \text{Fe(CO)}_3 \) (5; \( R = \text{H} \)), respectively, gave rise to a new and interesting observation, namely, that the two carbon atoms, C-5 and C-6, from which the protons can theoretically be abstracted, are no longer equivalent in contrast to the simple cyclohexa-1,3-diene case. In fact it has been reported that triphenylmethyl fluoroborate abstracts solely from C-5 of these two complexes, giving the tricarbonyl-1-methoxy and -2-methoxy-7-cyclohexa-1,3-dieneiron cations (6; \( R = \text{H} \)) and (1; \( R = \text{OCH}_3 \)), respectively. The evidence that reaction (2) yields only (6; \( R = \text{H} \)) did not seem entirely conclusive, and a reinvestigation of the reaction was carried out to find that hydrates from C-5 and C-6 were formed in equal proportions.

Subsequently the reaction of a number of substituted tricarbonyl-1,3-dieneiron complexes with triphenylmethyl fluoroborate was investigated. The complexes were prepared by now known method involving pentacarbonyliron with the substituted cyclohexa-1,3-dienes, produced by reduction of aromatics with metal-ammonia solutions, in di-\( \alpha \)-butyl ether. The products
Discussion

The preparation of tricarbonyl-1-methoxy and -2-methoxy-cyclohexa-1,3-dieneiron complexes (4; R = H) and (5; R = H), respectively, gave rise to a new and interesting situation, namely, that the two carbon atoms, C-5 and C-6, from which hydride can theoretically be abstracted, are no longer equivalent in contrast to the simple cyclohexa-1,3-dieneiron case. In fact it has been reported that triphenylmethyl fluoroborate abstracts solely from C-5 of these two complexes, giving the tricarbonyl-1-methoxy and -2-methoxy-cyclohexa-dienyliron cations (6; R = H) and (1; R = OCH₃), respectively. The evidence that (4; R = H) yields only (6; R = H) did not seem entirely conclusive, and prompted a reinvestigation of the reaction when it was found that loss occurs from C-5 and C-6 in equal proportions.

In a similar manner, it was found that hydride is abstracted from C-5 and C-6 of tricarbonyl-1-methoxy-4-methylcyclohexa-1,3-dieneiron (4; R = CH₃) in the ratio 1:4, and not exclusively from C-6 to give only (7). Subsequently the reaction of a number of substituted tricarbonylcyclohexa-1,3-dieneiron complexes with triphenylmethyl cation was investigated. The complexes were prepared by the now standard method of Cais and Maoz which involves refluxing pentacarbonyliron with the substituted cyclohexa-1,4-dienes, produced by reduction of benzenes with metal-ammonia solutions, in di-n-butyl ether. The products
of the hydride abstraction reaction, and their ratio, were determined by isolation, characterisation, and proton magnetic resonance, details of which are contained in the Experimental Section.

The results of these hydride abstraction reactions are contained in Table 1 on p. 72 from which a number of conclusions may be drawn. Firstly, it appears that whether hydride is lost from C-5 or C-6 of these complexes depends on the structure of the resulting cations: those bearing alkyl substituents on C-1 and/or C-5 of the \( \pi \)-dienyl moiety being favoured. That this occurs is perhaps to be expected if we compare the structures of the \( \pi \)-dienyls that could result from, say, (16), namely (24) and (25), by abstraction of hydride from C-5 and C-6, respectively. For the purpose of this comparison the mesomeric formulation\(^3,7\) in which an arrow denotes donation of two electrons by each double bond of the diene to give the metal atom an inert-gas configuration, will be used. Thus (24) may be formulated as (26) and (27), while (28) and (29) represent (25). It can be seen that only in (26) is the positive charge located on a tertiary carbon atom, and, hence, this structure would traditionally be considered the most stable form.

A consideration of the results in Table 1 shows this directing effect to be an extremely strong one. For example, among the tricarbonyl-methoxycyclohexa-1,3-dieneiron complexes, (9) loses hydride predominantly, and (11) exclusively, from C-6, giving cations containing tertiary carbon atoms, whereas abstraction occurs from C-5 of (10) to yield the
The same situation is seen to exist in the group of complexes containing solely alkyl substituents, e.g. (16) loses hydride predominantly, and (17) and (20) exclusively, from C-3. Since abstraction of hydride from either C-5 or C-6 of (19) would not give cations containing tertiary carbon atoms, it is not surprising that loss from these two positions occurs in equal proportions. It has been reported that a mixture of (17) and (20) gives only the tricarbonyl-2-ethyl-2-cyclohexadienyl fluoride salt (25) on reaction with triphenylmethyl fluoroborate.

In (18) abstraction from both C-5 and C-6 would lead to cations containing tertiary carbon atoms, (31) and (32), respectively. Although the greater inductive effect of the iso-propyl group will tend to stabilise the latter salt to a greater degree, this effect would not be expected to cause the dramatic shift on abstraction from C-5 of (17) to C-6. A second consideration to be taken into account when dealing with bulky groups such as iso-propyl is the use of steric hindrance. It would seem reasonable that this effect may become important when it is the large triphenylmethyl cation that is attempting to approach the adjacent carbon atom, and hence abstraction at C-6 may be preferred.
tricarbonyl-1,5-dimethyl-3-methoxy-\pi\text{-cyclohexadienyl}iron cation (30) in which both C-1 and C-5 bear methyl groups.

Similarly, (14) loses hydride from C-5, while (15) gives the stable salt (30) by abstraction from C-6.

The same situation is seen to exist in the group of complexes containing solely alkyl substituents, e.g. (16) loses hydride predominantly, and (17) and (20) exclusively, from C-5. Since abstraction of hydride from either C-5 or C-6 of (19) would not give cations containing tertiary carbon atoms, it is not surprising that loss from these two positions occurs in equal proportions. It has been reported\(^3\) that a mixture of (16) and (20) gives only the tricarbonyl-2-methyl-\pi\text{-cyclohexadienyl}iron salt (25) on reaction with triphenylmethyl fluoroborate.

In (18) abstraction from both C-5 and C-6 would lead to cations containing tertiary carbon atoms, (31) and (32), respectively. Although the greater inductive effect of the iso-propyl group will tend to stabilise the latter salt to a greater degree, this effect would not be expected to cause the dramatic shift of abstraction from C-5 of (17) to C-6 of (18). A second consideration to be taken into account when dealing with bulky groups such as iso-propyl is the one of steric hindrance. It would seem reasonable that this effect may become important when it is the large triphenylmethyl cation that is attempting to approach the adjacent carbon atom, and hence abstraction at C-6 may be promoted.
That steric considerations may be of some importance is confirmed by the contrasting behaviour of complex (21) with trimethylmethyl fluoroborate. Although (20) shows the expected hydride loss from C-3 described earlier, the site at which the substituent at C-5 is an alkoxyl group and hence would be expected to be the more reactive, does not yield a W-dienyl salt.

If we employ the same argument as in the previous example, we would expect the hindrance to abstraction at C-3 to be greater, since this carbon atom is the one now bearing the neo-propyl group. In addition, as in (18), C-5 would also be hindered to abstraction in the either position is blocked.

A second conclusion to be drawn from Table 1 is that abstraction cannot give rise to W-dienyl salts bearing alkyl substituents at C-1 or C-3, then formation of 2-alkoxy-substituted cations occurs in preference to those bearing an alkoxy group at C-2. For example, (12), (13), and (23) lose hydride exclusively from C-3, as does the previously mentioned complex (14). The reason for this preference is not at all obvious, since the carbonyl-3-alkoxy-3-cyclohexenyliron cation, described in Part 3, is found to be as stable as the methoxy analogue, and does not rearrange under equilibrium conditions.

Where the possibility of obtaining 1-alkoxy-substituted salts exists the situation is not too clear. It appears from the
That steric considerations may be of some importance is to some extent confirmed by the contrasting behaviour of (20) and (21) with triphenylmethyl fluoroborate. Although (20) shows the now expected loss of hydride from C-5, described earlier, (21), in which the substituent at C-5 is an iso-propyl group, and hence would be expected to be the more reactive, does not yield a \( \Pi \)-dienyl salt.

If we employ the same argument as in the previous example, we would expect the hindrance to abstraction at C-5 to be even greater, since this carbon atom is the one now bearing the iso-propyl group. In addition, as in (18), C-6 would also be hindered, thus abstraction from either position is blocked.

A second conclusion to be drawn from Table 1 is that where abstraction cannot give rise to \( \Pi \)-dienyl salts bearing alkyl substituents at C-1 or C-5, then formation of 2-alkoxy-substituted cations occurs in preference to those bearing an alkoxy group at C-3. For example, (12), (13), and (23) lose hydride exclusively from C-5, as does the previously mentioned complex (14). The reason for this preference is not at all obvious, since the tricarbonyl-3-methoxy-\( \Pi \)-cyclohexadienyliiron cation, described in Part B, is found to be as stable as the 2-methoxy analogue, and does not rearrange under equilibrating conditions.

Where the possibility of obtaining 1-alkoxy-substituted salts exists the situation is not too clear. It appears from the
reaction of triphenylmethyl fluoroborate with (8) that the methoxyl group has no effect on the course of the reaction, since equal proportions of the 1- and 2-methoxy-π-cyclohexadienyliiron cations are obtained. However, a consideration of their mesomeric formulations (33)-(35) and (36)-(37), respectively, would lead one to expect the 1-methoxy analogue to be the more stable. Two factors would contribute to this increase in stability, namely, structure (34) contains a tertiary carbon atom, and, in addition, the existence of three rather than two forms would tend to reduce the energy of the system, and hence increase its stability.

Indeed the situation is further complicated when the reaction of triphenylmethyl cation with the 1-iso-propoxy complex (22) is considered. This compound is found to lose hydride preferentially from C-6 which would be considered to be sterically hindered. The stabilisation due to the iso-propoxy group is greater than that of the methoxyl from a mesomeric point of view, and hence the 1-isopropoxy-substituted salt would be expected to predominate. In fact, the reverse situation is found to occur!

From these results it is possible to construct a tentative order of the substituent effect on π-dienyl structures which seems to govern the course of the hydride abstraction reaction: 1- and/or 5-alkyl > 2-methoxy > 3-methoxy and ≥ 1-methoxy.
Six reporters for sample calculations of % absorption.

Figures rounded to nearest 5%.
Experimental

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

Infra-red and ultra-violet spectra were measured on Perkin Elmer P.E. 257 and Unicam SP. 800 machines, respectively.

Proton magnetic resonance spectra were determined on a Varian Associates HA 100 high resolution machine, while mass spectral measurements were carried out on a G.E.C.-A.E.I. MS.902 mass spectrometer.

Preparation of tricarbonyliron complexes

A mixture of the cyclohexa-1,4-diene (0.2 moles) and pentacarbonyliron (0.4 moles) in di-n-butyl ether (400 ml) was refluxed for 16-18 hrs. under nitrogen. The mixture was cooled, filtered through Celite 545, and solvent and unreacted starting materials removed on the rotary evaporator. Distillation of the residual liquid under reduced pressure gave pure tricarbonyliron complexes, details of which are given below.

Since the structure of these compounds is well established, and in some cases already reported, only those NMR details relevant to the calculation of the proportions of isomers are included. This has been calculated from the ratio of the integrated intensities of absorptions of two or more regions of the proton resonance spectrum,
and this ratio will be given in brackets following the assignment of protons to these transitions.

**1-methoxycyclohexa-1,4-diene**

Gave tricarbonyl-1-methoxycyclohexa-1,3-dieneiron (8) and tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (12) (57%)₃, bp. 70⁰/0.5mm. τ(CDC₃) 6.45s(OCH₃ of 12), 6.58s(OCH₃ of 8) (33:67).

**1-methoxy-4-methylcyclohexa-1,4-diene**

Gave tricarbonyl-1-methoxy-4-methylcyclohexa-1,3-dieneiron (9) and tricarbonyl-2-methoxy-5-methylcyclohexa-1,3-dieneiron (14) (33%)₃, bp. 78-80⁰/2.5mm. τ(CDC₃) 6.44s(OCH₃ of 14), 6.65s(OCH₃ of 9) (54:46).

**1-methoxy-3,5-dimethylcyclohexa-1,4-diene**

Gave tricarbonyl-1-methoxy-3,5-dimethylcyclohexa-1,3-dieneiron (10) and tricarbonyl-2-methoxy-4,6-dimethylcyclohexa-1,3-dieneiron (15), together with some starting material (21%), bp. 63-64⁰/0.2mm.

**1-methoxy-2-methyl- and 1-methoxy-6-methylcyclohexa-1,4-dienes**

Gave tricarbonyl-1-methoxy-2-methylcyclohexa-1,3-dieneiron, tricarbonyl-1-methoxy-6-methylcyclohexa-1,3-dieneiron (11) and tricarbonyl-2-methoxy-3-methylcyclohexa-1,3-dieneiron (13) (31.1%), bp. 65⁰/1mm. τ(CDC₃) 6.38s(OCH₃ of 13), 6.57s(OCH₃ of 1-methoxy-2-methyl isomer), 6.62s(OCH₃ of 11) (13:20:8).
l-methylcyclohexa-1,4-diene

Gave tricarbonyl-1-methylcyclohexa-1,3-dieneiron (16) and tricarbonyl-2-methylcyclohexa-1,3-dieneiron (19) (29.9%)\(^3\), bp. 103-4°/3mm. \(\tau(CDCl_3) 4.80d(H-2, H-3\text{ of } 16\text{ and } H-3\text{ of }19),\ 6.80m\ (H-4\text{ of }16\text{ and }H-1, H-4\text{ of }19)(1:1).\)

1,4-dimethylcyclohexa-1,4-diene

Gave tricarbonyl-1,4-dimethylcyclohexa-1,3-dieneiron and tricarbonyl-2,5-dimethylcyclohexa-1,3-dieneiron (20) (36%)\(^3\), bp. 58-60°/0.3mm. \(\tau(CDCl_3) 4.85d(H-3\text{ of }20),\ 5.05s(H-2, H-3\text{ of }1,4\text{-dimethyl isomer})\ (1:1).\)

2-methyl-5-isopropylcyclohexa-1,3-diene (a-pheillandrene)

Gave tricarbonyl-1-isopropyl-4-methylcyclohexa-1,3-dieneiron (18) and tricarbonyl-2-methyl-5-isopropylcyclohexa-1,3-dieneiron (21) (41%), bp. 93°/0.25mm. \(\tau(CDCl_3) 4.79d(H-3\text{ of }21),\ 5.01s(H-2, H-3\text{ of }18)\ (8:1).\)

1-isopropoxycyclohexa-1,4-diene

Gave tricarbonyl-1-isopropoxycyclohexa-1,3-dieneiron (22) and tricarbonyl-2-isopropoxycyclohexa-1,3-dieneiron (23) (45%), bp. 80°/0.5mm. \(\tau(CDCl_3) 4.92m(H_3\text{ of }23\text{ and }H-2, H-3\text{ of }22),\ 6.91m(H-1, H-4\text{ of }23\text{ and }H-4\text{ of }22)(17:13).\)
Reaction of complexes with triphenylmethyl fluoroborate

The procedure used was identical to that described by Birch. Triphenylmethyl fluoroborate (0.011 moles) in methylene dichloride (minimum volume) was added to the mixture of complexes (0.01 moles) in a similar volume of the same solvent. After 30 minutes the mixture was poured into ether, and the yellow precipitate filtered off and analysed. In the case of methoxy-substituted complexes, a portion of the mixture was dissolved in hot water, cooled, and then extracted with ether. The ether layer was then examined for the presence of tricarbonylcyclohexadienoneiron complexes, while addition of a 10% solution of ammonium hexafluorophosphate to the aqueous solution after ether extraction precipitated any water stable salts.

Tricarbonyl-1-methoxy-(8) and -2-methoxycyclohexa-1,3-dieneiron (12) (67:33)

Gave the tricarbonyl-1-methoxy-\(\pi\)-cyclohexadienyliron (6; \(R = \text{H}\)) and tricarbonyl-2-methoxy-\(\pi\)-cyclohexadienyliron cations (1; \(R = \text{OCH}_3\)) (93%) \(^3\). \(\tau((\text{CD}_3)_2\text{CO})5\cdot70s\) (OCH\(_3\) of 6; \(R = \text{H}\)), 6.05s (OCH\(_3\) of 1; \(R = \text{OCH}_3\)) (3:7).

From the complex mixture (2.5g., 0.01 moles) tricarbonylcyclohexadienoneiron (0.71g), mp.104-105° (lit. \(^3\) 104-104.5°), and tricarbonyl-2-methoxy-\(\pi\)-cyclohexadienyliron hexafluorophosphate (2.44g) \(^3\) were obtained.
Tricarbonyl-1-methoxy-4-methyl-(9) and -2-methoxy-5-methylcyclohexa-1,3-dieneiron (14)

Gave the tricarbonyl-1-methoxy-4-methyl-π-cyclohexadienyiron (6; R = CH₃) and tricarbonyl-2-methoxy-5-methyl-π-cyclohexadienyiron cations (7) as a gum. From the complex mixture (0.6g) tricarbonyl-4-methyl-cyclohexadienoneiron (0.45g) and the tricarbonyl-2-methoxy-5-methyl-π-cyclohexadienyiron cation (0.74g) were obtained. The ketone was recrystallised from pentane, mp. 88-90°. (Found: C, 48.41; H, 3.31. C₁₀H₈O₄Fe requires C, 48.30; H, 3.26%); ν max (nujol) 2076, 2055, 1988, 1664 cm⁻¹; λ max 230μ (ε 14,540); τ(CDCl₃) 4.02d (1H, J₂,₃ = 6c./sec., H-3), 6.84m (2H, H-2 and H-5), 7.80m (2H, 2H-6), 7.94s (3H, CH₃); mass spectral peaks at m/e 248, 220, 192, 164, 146, 136, 135 (breakdown typical of this type of complex).

Tricarbonyl-1-methoxy-3,5-dimethyl- (10) and -2-methoxy-4,6-dimethylcyclohexa-1,3-dieneiron (15)

Gave the tricarbonyl-1-methoxy-3,5-dimethyl-π-cyclohexadienyiron and tricarbonyl-3-methoxy-1,5-dimethyl-π-cyclohexadienyiron cations (30) as a gum. Hydrolysis and work-up gave tricarbonyl-3,5-dimethylcyclohexadienoneiron, mp. 54.5-55°. (Found: C, 50.11; H, 4.01. C₁₁H₁₀O₄Fe requires C, 50.39; H, 3.82%); ν max (nujol) 2077, 2057, 1990, 1665 cm⁻¹; λ max 231μ (ε 14, 480); mass spectral peaks at m/e 262,234,206,178. Also obtained was tricarbonyl-3-methoxy-1,5-dimethyl-π-cyclohexadienyiron hexafluorophosphate (Found: C, 34.42; H, 4.83. C₁₂H₁₃O₆FePF₆ requires C, 34.13; H, 3.08%).
\( \nu_{\text{max}} (\text{CH}_2\text{Cl}_2) \) 2156, 2126, 2055 cm\(^{-1}\); \( \tau(\text{CF}_3\text{CO}_2\text{H}) \) 4.20s (2H, H-1 and H-3), 5.81s (3H, OCH\(_3\)), 7.05d and 7.50d (1H each, \( J_{\text{gem}} = 17\text{c.}/\text{sec.}, 2\text{H-6} \)), 8.10s (6H; 2CH\(_3\)).

Tricarbonyl-1-methoxy-2-methyl-,-1-methoxy-6-methyl- (11), and -2-methoxy-3-methylcyclohexa-1,3-dieneiron (13) (13:20:8)

Gave the tricarbonyl-1-methoxy-2-methyl-, -1-methyl-2-methoxy-, and -2-methoxy-3-methyl-\( \Pi \)-cyclohexadienyliron cations (95%). Hydrolysis and work-up gave tricarbonyl-2-methylcyclohexadienoneiron, mp. 73-4\(^0\). (Found: C, 48.21; H, 3.25. \( \text{C}_{10}\text{H}_{18}\text{O}_4\text{Fe} \) requires C, 48.30; H, 3.26%); \( \nu_{\text{max}} \) (nujol) 2074, 2054, 1987, 1665 cm\(^{-1}\); \( \lambda_{\text{max}} \) 230 (\( \epsilon \) 13,800); \( \tau(\text{CDCl}_3) \) 4.18d (1H, \( J_{3,4} = 5.5\text{c.}/\text{sec.}, \text{H-3} \)), 4.50t (1H, \( J_{4,5} = 5.5\text{c.}/\text{sec.}, \text{H-4} \)), 6.90m (1H, H-2), 7.44 double doublet (1H, \( J_{5,6} = 4\text{c.}/\text{sec.}, \text{H-6} \)), 7.80d (1H, \( J_{\text{gem}} = 18\text{c.}/\text{sec.}, \text{H-6} \)), 8.54 (3H, CH\(_3\)); mass spectral peaks at m/e 248,220,192,164,146,136, 135 (breakdown typical of this type of complex) 26,27.

Also a mixture of tricarbonyl-1-methyl-2-methoxy-\( \Pi \)-cyclohexadienyliron and tricarbonyl-2-methoxy-3-methyl-\( \Pi \)-cyclohexadienyliron was obtained.

hexafluorophosphates / (Found: C, 31.86; H, 2.60. \( \text{C}_{11}\text{H}_{11}\text{O}_4\text{FePF}_6 \) requires C, 32.35; H, 2.76%). \( \tau(\text{CF}_3\text{CO}_2\text{H}) \) 5.87s (OCH\(_3\) of 1-methyl-2-methoxy isomer), 6.24s (OCH\(_3\) of 2-methoxy-3-methyl isomer), 7.20s (CH\(_3\) of 2-methoxy-3-methyl isomer), 8.24s (CH\(_3\) of 1-methyl-2-methoxy isomer).
Tricarbonyl-1-methyl- (16) and -2-methylcyclohexa-1,3-dieneiron (19)(1:1)

Gave tricarbonyl-1-methyl- (24), -2-methyl- (25), and 3-methyl-\(\pi\)-cyclohexadienyliron fluoroborates (93%). \(\tau (\text{CF}_3\text{CO}_2\text{H}) 7.16s\) (CH\(_3\) of 3-methyl isomer), 7.79s (CH\(_3\) of 2-methyl isomer), 8.13s (CH\(_3\) of 1-methyl isomer) (c.5:7:9).

Tricarbonyl-2-methylcyclohexa-1,3-dieneiron (19)

(The preparation of this pure complex is given in Part B.)

Gave the tricarbonyl-2-methyl-\(\pi\)-cyclohexadienyliron and tricarbonyl-3-methyl-\(\pi\)-cyclohexadienyliron fluoroborates (95%). \(\tau (\text{CF}_3\text{CO}_2\text{H}) 2.82d\) (H-3 of 2-methyl isomer), 4.20d (H-2, H-4 of 3-methyl isomer and H-4 of 2-methyl isomer) (7:19).

Tricarbonyl-1,4-dimethyl- and -2,5-dimethylcyclohexa-1,3-dieneiron (20)(1:2)

Gave tricarbonyl-1,4-dimethyl-\(\pi\)-cyclohexadienyliron fluoroborate (91%). (Found: C, 33.58; H, 2.80. \(\text{C}_{11}\text{H}_{11}\text{O}_3\text{FeBF}_4\) requires C, 33.67; H, 2.30%; \(\nu_{\text{max}} (\text{CH}_2\text{Cl}_2) 2155, 2128, 2058 \text{ cm}^{-1}\); \(\tau (\text{CF}_3\text{CO}_2\text{H}) 3.05d\) (1H, J\(_{2,3} = 5.5\text{c./sec.}, \text{H-3})), 4.62d (1H, H-2), 5.99d (1H, J\(_{5,6} = 5.5\text{c./sec.}, \text{H-5})), 6.90m and 8.00m (2H-6), 7.80s (3H, CH\(_3\) on C-4), 8.16s (3H, CH\(_3\) on C-1).

Tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (17)

(The preparation of this pure complex is given in Part B.)
Gave tricarbonyl-1,3-dimethyl-\(\pi\)-cyclohexadienyliron fluoroborate (89%). (Found: C, 33.47; H, 2.61. \(\text{C}_{11}\text{H}_{11}\text{O}_{3}\text{FeBF}_4\) requires C, 33.67; H, 2.30%); \(\nu_{\text{max}}\) (CH\(_2\)Cl\(_2\)) 2153, 2127, 2055 cm\(^{-1}\); \(\tau\) (CF\(_3\)CO\(_2\)H) 4.06\(d\) (1H, \(J_{4,5} = 6.5\text{c.}/\text{sec.},\ H-4\)), 4.44\(s\) (1H, H-2), 5.88\(t\) (1H, H-6), 7.02 double doublet (1H, \(J_{1,6} = 16\text{c.}/\text{sec.},\ H-6\)), 7.17s (3H, CH\(_3\) on C-3), 7.71d (1H, H-6), 8.09s (3H, CH\(_3\) on C-1).

Tricarbonyl-1-methyl-4-isopropyl- (18) and -2-methyl-5-isopropylcyclohexa-1,3-dieneiron (21)(1:8)

Gave tricarbonyl-1-isopropyl-4-methyl-\(\pi\)-cyclohexadienyliron fluoroborate (32) (10%) which was converted to the hexafluorophosphate. (Found: C, 36.80; H, 2.96. \(\text{C}_{13}\text{H}_{15}\text{O}_{3}\text{FePF}_6\) requires C, 37.10; H, 3.57%); \(\nu_{\text{max}}\) (CH\(_2\)Cl\(_2\)) 2155, 2129, 2055 cm\(^{-1}\); \(\tau\) (CF\(_3\)CO\(_2\)H) 2.78\(d\) (1H, \(J_{3,4} = 6.0\text{c.}/\text{sec.},\ H-3\)), 4.15\(d\) (1H, H-4), 5.65\(d\) (1H, J = 6.0c./sec., H-1), 6.30\(m\) (1H, CH(CH\(_3\))\(_2\)), 7.02\(m\) (1H, H-6), 7.65s (3H, CH\(_3\)), 8.90\(m\) (6H, (CH\(_3\))\(_2\)CH).

Tricarbonyl-1-isopropoxy- (22) and -2-isopropoxycyclohexa-1,3-dieneiron (23)(7:3)

Gave the tricarbonyl-1-isopropoxy-\(\pi\)-cyclohexadienyliron and tricarbonyl-2-isopropoxy-\(\pi\)-cyclohexadienyliron fluoroborates (94%). \(\tau\) (CF\(_3\)CO\(_2\)H) 2.88\(m\) (H-3 of 1-isopropoxy isomer and H-3 of 2-isopropoxy isomer), 3.95\(m\) (H-2, H-4 of 1-isopropoxy isomer and H-4 of 2-isopropoxy isomer)(13:16).
PART B

THE REACTION OF CONCENTRATED SULPHURIC ACID WITH TRICARBONYLCYCLOHEXA-1,3-DIENEIRON COMPLEXES

Introduction

The reaction of alkyl-substituted cyclohexa-1,4-dienes with iron carbonyls invariably yields mixtures of complexes, e.g. 1-methyl-cyclohexa-1,4-diene gives (16) and (19). Treatment of these mixtures with triphenylmethyl fluoroborate gives tricarbonyl-\(\Pi\)-cyclohexadienyliron cations which cannot be separated, the former complex mixture yielding tricarbonyl-1- and -2-methyl-\(\Pi\)-cyclohexadienyliron fluoroborates, (24) and (25), respectively, as described in Part A.

It seems desirable, therefore, both from intrinsic and synthetic points of view, to discover a method whereby these, and other, salts may be prepared in pure form. Success in this may also lead to pure neutral complexes obtained by sodium borohydride reduction of these cations.
Discussion

It has been reported\(^3\) that reaction of tricarbonyl-1,4-
dimethoxycyclohexa-1,3-dieneiron (4; \(R = \text{OCH}_3\)) with triphenylmethyl fluoroborate yields solely the tricarbonyl-1,4-dimethoxy-\(\pi\)-cyclo-
hexadienyliron cation which is hydrolysed by water to tricarbonyl-1-
4-methoxycyclohexa-2,4-dienoneiron\(^{38}\). However, closer examination of
the aqueous solution showed the presence of the tricarbonyl-2-methoxy-
\(\pi\)-cyclohexadienyliron cation in 6% yield.

Treatment of a solution of (4; \(R = \text{OCH}_3\)) in acetic anhydride
with a fluoroboric acid/acetic anhydride mixture increased this yield
to 10% while that of the ketone (38) fell from 51 to 11%. On the basis
of these two results it seemed reasonable to assume that demethoxylation
with triphenylmethyl fluoroborate was due to small quantities of
fluoroboric acid formed by the presence of moisture. Investigation
of the methylene chloride/ether solution, after removal of all salts,
failed to show any trace of the methyl ether of triphenylmethanol,
indicating that the methoxyl group had not been removed from an
intermediate such as (5; \(R = \text{OCH}_3\)) by the triphenylmethyl cation.

This demethoxylation reaction was then extended to complexes
containing only a single methoxyl group. Hence, after confirming that
tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (40) gave purely the
tricarbonyl-2-methoxy-\(\pi\)-cyclohexadienyliron salt with triphenylmethyl
fluoroborate\(^3\), the neutral complex in acetic anhydride was treated
with the same fluoroboric acid/acetic anhydride mixture, and
tricarbonyl-\textit{\Pi}-cyclohexadienyliniron fluoroborate (45) was isolated, as the only product, in 48\% yield.

The proportions of acid and acetic anhydride are such that the reagent may be considered to act as an anhydrous fluoroboric acid/acetic anhydride mixture. It was, therefore, thought feasible that concentrated sulphuric acid may act as a demethoxylating agent. Thus, tricarbonyl-2-methoxycyclohexa-1,3-dieneiron was dissolved in this acid, when rapid demethoxylation was found to occur, and the cation (45) isolated in 70\% yield as the hexafluorophosphate.

The reaction is an extremely simple one in that it entails allowing the acid solution of the complex to stand for about ten minutes, after which it is carefully saturated with sodium-dried ether. This results in the precipitation of any salts in the form of a gum, and decantation of the supernatant solution, followed by repeated trituration with sodium-dried ether removes any neutral complexes and much of the acid, allowing investigation of the cationic products.

It was found that a 67/33 mixture of the tricarbonyl-1- and -2-methoxycyclohexa-1,3-dieneiron complexes (39) and (40), respectively, gives the same salt (45) also in 70\% yield, indicating probable equilibration of either the neutral compounds or of protonated intermediates.

A possible mechanism for this demethoxylation is outlined in Scheme 1. The first step involves protonation of C-4 of (39) and
Scheme 1

In order to gain a further insight into the mechanism, attempts were made to slow the reaction by forming the unreacted species. However, the demethylation was found to occur too rapidly with concentrated sulphuric acid to allow this to be done. Longer periods of fluorosulphonic acid mixture were tested using a very large excess of anhydride and found to be satisfactory.

It was found that pure (40) or the 67/33 mixture of (39) and (40) yielded, in the former case only pure (40), and in the latter both complexes in the same ratio as the unreacted species.
C-1 of (40) to give the intermediate π-allyl complex (41), analogous to the acyclic π-allyl salts of Pettit\textsuperscript{8,9} already discussed in Part A,\textsuperscript{1} in which the oxygen atom is probably involved in the bonding. This species could undergo a 1,4-proton shift to yield (42) which can give the neutral intermediate (43) by loss of a proton.

This complex, after oxygen-protonation to yield (44), may undergo irreversible loss of methanol to yield the cation (45). This final step is analogous to Olah's\textsuperscript{10} mechanism for the formation of stable carbonium ions in strong acid media by hydroxyl loss from alcohols. He found that at -60°C primary and secondary alcohols are protonated by a fluorosulphonic acid/antimony pentachloride/sulphur dioxide mixture to [ROH\textsubscript{2}]\textsuperscript{+} species which, at higher temperatures, lose a hydroxonium ion.

In order to gain a further insight into the mechanism, attempts to slow the reaction were made with a view to examining the nature of the unreacted species. However, the demethoxylation was found to occur too rapidly with concentrated sulphuric acid to enable this to be done, but use of a fluoroboric acid/acetic anhydride mixture containing a very large excess of anhydride was found to be satisfactory.

It was found that pure (40) or the 67/33 mixture of (39) and (40) yielded, in the former case, only pure (40), and in the latter both complexes in the starting ratio as the unreacted species.
A possible explanation of these results is that all the equilibria outlined in Scheme 1 are very much favoured in the direction of the forward reactions, i.e. essentially all of the initial protonated intermediate (41) is rapidly converted to product.

That equilibration can occur is shown by the conversion, with 92% recovery, of a 50/50 mixture of tricarbonyl-1- and -2-methylcyclohexa-1,3-dieneiron complexes (16) and (19), respectively, to one containing these compounds in the ratio 33:67. Similarly, a 33/67 mixture of tricarbonyl-1,4- and -2,5-dimethylcyclohexa-1,3-dieneiron (46) and (20), respectively, gives, with 95% recovery, the same compounds in the ratio 86:14, while the mixture of complexes from 1,5-dimethylcyclohexa-1,4-diene (47) and pentacarbonyliron, containing approximately 40% tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48), yields exclusively this species after 88% recovery.

The method of calculating the ratio of tricarbonylmethylcyclohexa-1,3-diene isomers, (16) and (19), involves a comparison of the integrated intensities of the transitions in the 5 and 7τ regions of the proton magnetic resonance spectrum. It is not possible to use the transitions due to the methyl groups at 7·93 and 8·40τ as these occur in the same region as those of the protons on the methylenic carbon atoms. In the case of the tricarbonyldimethylcyclohexa-1,3-dieneiron complexes, (46) and (20), the observation that the 1,4-dimethyl isomer (44) gives a sharp singlet at 5·04τ due to the protons on C-2 and C-3, while the C-3 proton in the 2,5-dimethyl complex (20)
appears as a doublet centred at 4.85\tau, was used to calculate their relative proportions.

A consideration of the possible electronic and steric factors does not shed light on the reason for this differing stability of the neutral complexes. However, analysis of the possible \( \pi \)-allyl species, formed by protonation, does seem to indicate that the thermodynamic equilibria observed are those of charged species.

Protonation of tricarbonyl-1-methylcyclohexa-1,3-dieneiron (16) would yield the \( \pi \)-allyl complexes (49; \( R = H \)) and (50), while the 2-methyl analogue (19) gives (49; \( R = H \)) and (51; \( R = H \)). In addition (52) may be formed from (50) via a 1,4-proton shift. It has been reported\(^1\) that bis(\( \pi \)-2-methylallyl)nickel is more stable than the unsubstituted bis(\( \pi \)-allyl)nickel complex. Application of this observation to the group of compounds studied here may imply that the substituted \( \pi \)-allyl species (49; \( R = H \)) and (51; \( R = H \)) would be the most stable, and hence the major components of the mixture.

Since both of these can give rise to the 2-methyl-substituted complex (19) by simple loss of a proton, while the 1-methyl analogue (16) can only be formed from the former, (19) may be expected to be the major component of the mixture of recovered complexes.

Similarly, both (49; \( R = CH_3 \)) and (51; \( R = CH_3 \)) give rise to the 2,5-dimethyl isomer (20), while only the former can yield the 1,4-dimethyl complex (46), and hence (20) is found to predominate in the mixture of these two compounds after this acid equilibration.
of this stabilisation of the substituted α-allyl carbene. Due to the inductive effect of the α-allyl group, these complexes are generally expected to be more stable, provided of course this effect is not outweighed by any destabilising effects such as steric clash of the substituents. Evidence in support of this is the isolation of pure tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48) from a mixture of dimethyl-substituted isomers.

Consideration of the substituted α-allyl structures (53)-(55), resulting from protonation of this mixture, shows that were disubstituted α-allyls to be the more stable, (54) would be the major component in any equilibrium involving these complexes, and, hence, work-up would give almost exclusively (48).

A useful application of the demethoxylation reaction is the preparation of pure salts not accessible by the hydride abstraction procedure. For example, a 46/54 mixture of tricarbonyl-1-methoxy-4-methyl- and -2-methoxy-5-methylcyclohexa-1,3-dieneiron complexes, (56) and (57), respectively, gave in 77% yield the pure tricarbonyl-2-methyl-α-cyclohexadienyliiron cation (58). Similarly, the mixture of isomers, obtained from 39 of 1-methyl-5-methylcyclohexa-1,4-diene (59) and perchloric acid in di-methyl ether, resulted in the formation of the 1-methyl isomer (60) in 72% yield.

In contrast, the complexes from 1-methylcyclohexa-1,4-diene give a mixture of these two salts, together with the 1-methyl salt, on reaction with triphenylmethyl fluoroborate, described in Part A.
If this stabilisation of substituted π-allyl complexes is due to the inductive effect of the methyl group, then one may expect disubstituted species to be even more stable, provided, of course, this effect is not outweighed by any destabilising effects such as steric clash of the substituents. Evidence in support of this is the isolation of pure tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48) from a mixture of dimethyl-substituted isomers.

Consideration of the substituted π-allyl structures (53)-(55), resulting from protonation of this mixture, shows that were disubstituted π-allyls to be the more stable, (54) would be the major component in any equilibrium involving these three complexes, and, hence, work-up would give almost exclusively (48).

A useful application of the demethoxylation reaction is the preparation of pure salts not accessible by the hydride abstraction procedure. For example, a 46/54 mixture of tricarbonyl-1-methoxy-4-methyl- and -2-methoxy-5-methylcyclohexa-1,3-dieneiron complexes, (56) and (57), respectively, gave in 77% yield the pure tricarbonyl-2-methyl-π-cyclohexadienyliron cation (58). Similarly, the mixture of isomers, obtained from the reaction of 1-methoxy-5-methylcyclohexa-1,4-diene (59) and pentacarbonyliron in di-n-butyl ether, resulted in the formation of the 3-methyl isomer (60) in 72% yield.

In contrast, the complexes from 1-methylcyclohexa-1,4-diene give a mixture of these two salts, together with the 1-methyl salt, on reaction with triphenylmethyl fluoroborate, described in Part A.
Consideration of both the overall mechanism and relative stabilities of W-allyl species makes it possible to rationalise the absence of isomer (53). The W-allyl complexes (54)-(56) can be formed by protonation of the mixture of neutral complexes, the first, bearing a methyl group on the W-allyl moiety, being presumably the most stable, and hence the major component. Protonation of (54) then, via a 1,4-proton shift, and subsequent loss of a proton from the formation of the intermediate (55).

Reduction of (56) with sodium borohydride yields pure tricarbonyl-2-methylecyclohexa-1,3-dieneiron (57), obtainable only as one component of a mixture of complexes from 1-methylecyclohexa-1,4-diene, while (58) gives a 50/50 mixture of (19) together with the 1-methyl analogue (see Part C) under the same reducing conditions.

The reaction of concentrated sulphuric acid with a 32/50/18 mixture of tricarbonyl-1-methoxy-2-methyl-, 1-methoxy-6-methyl, and -2-methoxy-3-methylecyclohexa-1,3-dieneiron cations (59)-(60), respectively, yields almost exclusively the tricarbonyl-2-methyl-W-cyclohexadienyliron cation (58) together with a trace (<5%) of the 3-methyl isomer of the W-allyl intermediate (71)-(73), formed by protonation of this mixture, the first two would be the most stable,
In these two examples one can again postulate reversible protonations leading to isomers such as (61) and (62) which can undergo irreversible loss of methoxyl to yield the respective salts (58) and (60).

Consideration of both the overall mechanism and relative stabilities of π-allyl species makes it possible to rationalise the absence of isomer (63). The π-allyl complexes (64)-(66) can be formed by protonation of the mixture of neutral complexes, the first, bearing a methyl group on the π-allyl moiety, being presumably the most stable, and hence the major component. Rearrangement of (64) to (67), via a 1,4-proton shift, and subsequent loss of a proton results in the formation of the intermediate (62).

Reduction of (60) with sodium borohydride yields pure tricarbonyl-2-methylcyclohexa-1,3-dieneiron (19), obtainable only as one component of a mixture of complexes from 1-methylcyclohexa-1,4-diene, while (58) gives a 50/50 mixture of (19) together with the 1-methyl analogue (see Part C) under the same reducing conditions.

The reaction of concentrated sulphuric acid with a 32/50/18 mixture of tricarbonyl-1-methoxy-2-methyl-, -1-methoxy-6-methyl, and -2-methoxy-3-methylcyclohexa-1,3-dieneiron complexes, (68)-(70), respectively, yields almost exclusively the tricarbonyl-2-methyl-π-cyclohexadienyliron cation (58) together with a trace (< 5%) of the 3-methyl isomer (60). Of the π-allyl intermediates (71)-(73), formed by protonation of this mixture, the first two would be the most stable,
but only (61) can rearrange to a metalacyclic complex of the type (59), via methyl-substituted 7-allyl species, hence allowing formation of the cation (60) to occur by loss of the methoxy group. Any rearrangement of the present 3-methylsubstituted 7-allyl complex cannot be based on a rearrangement of the 2-methyl isomer (58), since this latter species is stable and may be recovered unchanged from a concentrated sulphuric acid solution. A rationalisation of the formation of the trace cation involves both rearrangement together with a 1,2-hydride shift during the demethoxylation, as shown in (66). A possible reason for the operation of this mechanism in the case of (75), but not in (61) or (62), is that there is a conceivable steric interaction between the methoxy group and the two intermediates, where steric models of these two complexes show significant steric strain between these two groups in (75). This interaction may cause the leaving methanol molecule to pass closer to the hydrogen atoms on C-6, and could promote the observed migration.

This demethoxylation was then extended to complexes bearing two oxygen substituents, namely, tricarbonyl-1,3- and -1,4-dimethoxycyclohexa-1,3-,dienes (77) and (78), respectively. The former could only be obtained in approximately 6% yield as a component of an inseparable mixture formed by reaction of 1,5-dimethoxycyclohexa-1,4-diene with pentacarbonyliron. The two dienes were tricarbonyl-1- and -2-methoxycyclohexa-1,3-dienes. Treatment of this mixture with concentrated sulphuric acid gave a mixture of the
but only (71) can rearrange to a neutral complex of the type (75), via methyl-substituted π-allyl species, hence allowing formation of the cation (58) to occur by loss of the methoxyl group.

Any explanation of the presence of the 3-methyl salt (60) cannot be based on a rearrangement of the 2-methyl isomer (58), since this latter species is stable and may be recovered unchanged from a concentrated sulphuric acid solution. A rationalisation of the formation of this trace cation involves bond rearrangement together with a 1,2-hydride shift during the demethoxylation, as shown in (76). A possible reason for the operation of this mechanism in the case of (75), but not in (61) or (62), is that there is no conceivable steric interaction between the methyl and methoxyl groups in the latter two intermediates, whereas Dreiding models show there to be significant steric strain between these two groups in (75). This interaction may cause the leaving methanol molecule to pass closer to the hydrogen atoms on C-6, and could promote the observed migration.

This demethoxylation was then extended to complexes bearing two oxygen substituents, namely, tricarbonyl-1,3- and -1,4-dimethoxycyclohexa-1,3-dieneiron, (77) and (78), respectively. The former could only be obtained in approximately 6% yield as a component of an inseparable mixture formed by reaction of 1,5-dimethoxycyclohexa-1,4-diene with pentacarbonyliron. The two other components were tricarbonyl-1- and -2-methoxycyclohexa-1,3-dieneiron. Treatment of this mixture with concentrated sulphuric acid gave a mixture of the
(68) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(69) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(70) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(71) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(72) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(73) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(74) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)

(75) \( \text{Fe}(	ext{CO})_3 \) \( \text{OCH}_3 \) \( \text{CH}_3 \)
expected products: the tricarbonyl-W-cyclooxadienyliron cation, from the 1-methoxy complex, and the tricarbonyl-W-cyclooctadienyliron salt (83), prepared via the -allyl intermediates (80)-(82). The reaction of tricarbonyl-1,4-dimethoxycyclooctadiene-1,5-dieneiron (78), however, is not a straightforward one, since in addition to the expected cation (86; 87-88), formed albeit in only 15% yield, presumably via (84) and (85), the well-known \(^3\) ketone (89), obtained by hydrolysis during work-up from the 1-methoxy salt (88), is isolated in a yield of 90%.

The mechanism involving bond rearrangement with a 1,2-hydride shift, as described above, would also account for the formation of this salt, but it is not possible to see how the same steric arguments could be applied here.

A consideration that may be of some importance in this case is that in order to obtain the intermediate (85) a proton must be lost from C-6 of the 1-methoxy-W-allyl species (84). In all previous examples the final W-allyl intermediate, formed from a 1-methoxy-W-allyl species, has been stabilised at either a methyl group at C-1 or C-6 or (as in this case) at C-2. However, in this case, loss of a proton from C-6 does not yield a more stabilised allyl species, and hence there may be a certain reluctance of this reaction to occur, resulting in promotion of an alternative route such as the four-centre reaction described in (90).
expected products: the tricarbonyl-\(\pi\)-cyclohexadienyliron cation, from the latter monomethoxy complexes, and the tricarbonyl-3-methoxy-\(\pi\)-cyclohexadienyliron salt (83), presumably via the \(\pi\)-allyl intermediates (80)-(82).

The reaction of tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron (78), however, is not a straightforward one, since in addition to the expected cation (86; \(R = H\)), formed albeit in only 15\% yield, presumably via (84) and (85), the well-known ketone (89), obtained by hydrolysis during work-up from the 1-methoxy salt (88), is isolated in a yield of 40\%.

The mechanism involving bond rearrangement together with a 1,2- hydride shift, outlined above, would also account for the formation of this salt, but it is not possible to see how the same steric arguments could be applied here.

A consideration that may be of some importance in this case is that in order to obtain the intermediate (85) a proton must be lost from C-6 of the 1-methoxy-\(\pi\)-allyl species (84). In all previous examples the final \(\pi\)-allyl intermediate, formed from a 1-methoxy-\(\pi\)-allyl species, has been stabilised by either a methyl group at C-1 or C-2 or a methoxyl group at C-2. However, in this instance, loss of a proton from (84) does not yield such a stabilised \(\pi\)-allyl complex, and hence there may be a certain reluctance for this reaction to occur, resulting in promotion of an alternative route such as the four-centre reaction outlined in (90).
In conclusion, it may be said that in this demonstration reaction, we have not only a new and convenient method for the synthesis of triene-π-cyclohexadienyl complexes, but also an one which leads to rapid equilibration of π-allyl complexes, those substituted by methyl or methoxyl groups being the most stable. The second stage seems general, as well as of a product from such intermediates to give neutral complexes in which the methoxyl group is now on a tetrahedral carbon atom. Finally, protonation of the oxygen-negative leads to irreversible loss of this group, and formation of cationic species.

A preliminary communication of some of these results has already been reported.
In conclusion, it may be said that in this demethoxylation reaction we have not only a new and facile method for the preparation of tricarbonyl-$\pi$-cyclohexadienyliron cations, but also one that is useful in that the starting materials are readily available, the products are independent of the mixed nature of the original complexes, and, in addition, pure cations, and hence pure complexes, are sometimes obtained.

The mechanism seems to involve, initially, protonations which lead to rapid equilibration of $\pi$-allyl complexes, those substituted by methyl or methoxyl groups being the most stable. The second stage sees generally the loss of a proton from such intermediates to give neutral complexes in which the methoxyl group is now on a tetrahedral carbon atom. Finally, protonation of the oxygen function leads to irreversible loss of this group, and formation of cationic species.

A preliminary communication of some of these results has already been reported.\textsuperscript{12}
Experimental

Preparation of tricarbonyliron complexes

Three further complex mixtures were prepared by the method described in Part A.

1-methoxy-5-methylcyclohexa-1,4-diene (59)

Gave a mixture of complexes whose composition it was not possible to determine (34%), bp. 81-2°/3.5mm.

1,4-dimethoxycyclohexa-1,4-diene

Gave tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron (78) (32%), bp. 82-3°/2mm.

1,5-dimethoxycyclohexa-1,4-diene

Gave tricarbonyl-1,3-dimethoxycyclohexa-1,3-dieneiron (77) and tricarbonyl-1- and -2-methoxycyclohexa-1,3-dieneiron (c.6%), bp. 76-80°/2mm. \(\tau(CDCl_3)\) 6.46s (OCH\(_3\) of 77 and 2-methoxy isomer), 6.60s and 6.63s (OCH\(_3\) of 77 and 1-methoxy isomer).

1,5-dimethylcyclohexa-1,4-diene (47)

Gave tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48) (c.40%), tricarbonyl-1,5-dimethylcyclohexa-1,3-dieneiron, and tricarbonyl-2,6-dimethylcyclohexa-1,3-dieneiron (33.2%), bp. 64-5°/0.25mm. \(\tau(CDCl_3)\) 7.92s (CH\(_3\) on C-2 of 2,6-dimethyl isomer), 7.96s (CH\(_3\) on C-3
of 17), 8.41s (CH$_3$ on C-1 of 17), 8.46s (CH$_3$ on C-1 of 1,5-dimethyl isomer), 9.07d (CH$_3$ on C-5 of 1,5-dimethyl isomer), 9.14d (CH$_3$ on C-6 of 2,6-dimethyl isomer).

Reaction of methoxy-substituted tricarbonyliron complexes with concentrated sulphuric acid

The general procedure described below was used in all cases. To the complex or mixture of complexes (0.005 moles) was added concentrated sulphuric acid (1-2 ml.) dropwise, and the solution allowed to stand, with occasional swirling, for 10-15 min. It was then carefully saturated with dry ether (50-100 ml.), causing any cations to be precipitated in the form of a gum. Repeated trituration with dry ether (3 × 50 ml.) removed any neutral complexes, together with much of the acid, and these ethereal washings may then be further investigated.

The salts were then dissolved in a small volume of cold water (20 ml.), and any tricarbonylcyclohexadieneoneiron complexes, fromed by hydrolysis of tricarbonyl-1-methoxy-π-cyclohexadienyliron cations, extracted with ether. To the aqueous solution was added 10% ammonium hexafluorophosphate solution when the water stable salts were precipitated.

**Tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (40)**

Gave the tricarbonyl-π-cyclohexadienyliron cation (45) (70%) identical to an authentic sample.
Tricarbonyl-1- (39) and -2-methoxycyclohexa-1,3-dieneiron (40) (2:1)

Gave the above cation (45) (70%).

Tricarbonyl-1-methoxy-4-methyl- (56) and -2-methoxy-5-methylcyclohexa-
1,3-dieneiron (57) (46:54)

Gave tricarbonyl-2-methyl-7f-cyclohexadienyliron hexafluoro-
phosphate (58) (77%). (Found: C, 31.78; H, 2.43. \( \text{C}_{10} \text{H}_{9} \text{O}_{3} \text{FePF}_6 \)
requires C, 31.75; H, 2.38). \( \nu \)\text{max}\ (\text{CHCl}_2) 2158, 2127, 2058 cm\(^{-1}\);
\( \tau \)(\text{CF}_3 \text{CO}_2 \text{H}) 2.78d (1H, \( J_{3,4} = 5.5c./\text{sec.}, \text{H-3} \)), 4.13t (1H, \( J_{4,5} = 6c./\text{sec.}, \text{H-4} \)), 5.78m (2H, H-1, H-5), 6.94 doublet of triplets (1H, 
\( J_{1,6} = J_{5,6} = 7c./\text{sec.}, \text{H-6} \)), 7.71s (3H, \text{CH}_3), 7.81d (1H, \( J_{\text{gem}} = 17c./\text{sec.}, \text{H-6} \)).

Tricarbonyliron complexes from 1-methoxy-5-methylcyclohexa-1,4-diene
(59)

Gave tricarbonyl-3-methyl-7f-cyclohexadienyliron hexafluoro-
phosphate (60) (72%). (Found: C, 31.62; H, 2.27. \( \text{C}_{10} \text{H}_{9} \text{O}_{3} \text{FePF}_6 \)
requires C, 31.75; H, 2.38). \( \nu \)\text{max}\ (\text{CHCl}_2) 2158, 2128, 2058 cm\(^{-1}\);
\( \tau \)(\text{CF}_3 \text{CO}_2 \text{H}) 4.11d (2H, \( J_{1,2} = J_{4,5} = 7c./\text{sec.}, \text{H-2, H-4} \)), 5.79t (2H, 
\( J_{1,6} = J_{5,6} = 6c./\text{sec.}, \text{H-1, H-5} \)), 7.1m (1H, H-6), 7.12s (3H, \text{CH}_3), 8.0d (1H, \( J_{\text{gem}} = 19c./\text{sec.}, \text{H-6} \)).

Reduction of the cation with sodium borohydride in the manner
described in Part C gave tricarbonyl-2-methylcyclohexa-1,3-dieneiron
(19) (85%). \( \nu \)\text{max}\ (film) 2040, 1960 (broad) cm\(^{-1}\); \( \tau \)(\text{CDCl}_3) 4.79d (1H,
Tricarbonyl-1-methoxy-2-methyl- (68), -1-methoxy-6-methyl- (69), and -2-methoxy-3-methylcyclohexa-1,3-dieneiron (70)(13:20:8)

Gave tricarbonyl-2-methyl-π-cyclohexadienyliron hexafluorophosphate (58) together with a trace (< 5%) of tricarbonyl-3-methyl-π-cyclohexadienyliron hexafluorophosphate (60)(82%). \( \tau(CF_3CO_2H) \) as pure (58) given above together with 7.11s (CH₃ of 60).

Tricarbonyl-1,3-dimethoxy- (77), -1-methoxy- (39) and -2-methoxycyclohexa-1,3-dieneiron (40)

Gave the water stable tricarbonyl-3-methoxy-π-cyclohexadienyliron hexafluorophosphate (83) and tricarbonyl-π-cyclohexadienyliron hexafluorophosphate (45)(78%). \( \tau(CF_3CO_2H) \) 2.71d (H-3 of 45), 4.10m (H-2, H-4 of 45 and 83), 5.77s (OCH₃ of 83), 5.90m (H-1, H-5 of 45 and 83), 7.0m and 7.9m (2H-6 of 45 and 83).

Tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron (78)

Gave tricarbonyl-2-methoxy-π-cyclohexadienyliron hexafluorophosphate (86; R = H)³ (15%) and tricarbonylcyclohexadienoneiron (89)³ (40%).

Reaction of methoxy-substituted tricarbonyliron complexes with a fluoroboric acid/acetic anhydride mixture

To the complex or complexes (0.0005 moles) in acetic
anhydride (2ml.) was added dropwise a solution of 43% aqueous fluoro­
boric acid (2ml.) in acetic anhydride (4ml.), the temperature being
kept below 10°C. After allowing the solution to stand for 30 min.,
the mixture was poured into dry ether (100ml.). The yellow precipitate
was washed thoroughly with dry ether, then treated with a small volume
of water, and any water stable salts and/or neutral complexes investi­
gated in the manner described earlier.

Tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron (4; R = OCH₃)

Gave tricarbonyl-2-methoxy-7π-cyclohexadienyliron hexafluoro­
phosphate₃ (10%) and tricarbonylcyclohexadienoneiron₃ (11%).

Tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (40)

Gave tricarbonyl-7π-cyclohexadienyliron hexafluorophosphate
(45)₃ (48%).

Slowing the reaction by using a diluted fluoroboric acid
(2ml.)/acetic anhydride (c.15ml.) mixture for 10 min. gave, in addition
to the cation (45) (10%), only tricarbonyl-2-methoxycyclohexa-1,3-
dieneiron as the recovered complex.

Tricarbonyl-1- (39) and -2-methoxycyclohexa-1,3-dieneiron (40)(2:1)

Gave tricarbonyl-7π-cyclohexadienyliron hexafluorophosphate
(45)₃ (50%).

Slowing the reaction in the manner described above yielded
the cation (45)(5%), and (39) and (40) in the same ratio of 2:1.
Equilibration of alkyl-substituted tricarbonyliron complexes using concentrated sulphuric acid

The equilibration reaction involved addition of concentrated sulphuric acid (1-2ml.) to the mixture of complexes (0.005 moles), and allowing the solution to stand for 10-15 min. After careful saturation with ether (50ml.), the solution was washed with water (3 × 20ml.), saturated Na₂CO₃ solution (3 × 20ml.), water (20 ml.), and dried. Evaporation of the solvent then gave the mixture of complexes which was analysed again by proton magnetic resonance.

Tricarbonyl-1- (16) and -2-methylcyclohexa-1,3-dieneiron (19)(1:1)

The above complexes, described in Part A, gave (16) and (19) (92% recovery). τ(CDCl₃) 4.80d (H-2, H-3 of 16 and H-3 of 19), 6.90m (H-4 of 16 and H-1, H-4 of 19)(4:5).

Tricarbonyl-1,4- (46) and -2,5-dimethylcyclohexa-1,3-dieneiron (20)(1:2)

Gave (46) and (20) (95% recovery). τ(CDCl₃) 4.91d (H-3 of 20), 5.11s (H-2, H-3 of 46)(3:1).

Tricarbonyliron complexes from 1,5-dimethylcyclohexa-1,4-diene (47)

Gave pure tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48) (88% recovery). Vₘₜₚ (film) 2042, 1970 (broad) cm⁻¹; τ(CDCl₃) 4.87s (1H, H-2), 6.92s (1H, H-4), 7.95s (3H, CH₃ on C-3), 8.4m and 8.41s (7H, 2H-5, 2H-6, CH₃ on C-1).
PART C

NUCLEOPHILIC ATTACK ON TRICARBONYL-$\pi$-CYCLOHEXADIENYL IRON CATIONS

Introduction

The tricarbonyl-2-methoxy-$\pi$-cyclohexadienyliron cation (86; $R = H$) is attacked by nucleophiles such as hydride and cyanide solely at C-5, while the former reagent reacts at C-1 and C-5 of the 2-methoxy-5-methyl analogue (86; $R = CH_3$) in equal proportions. Whether the authors feel these results imply that the latter cation has a mesomeric nature while the positive charge in the former is more localised, or whether the C-5 methyl group hinders attack at this position, is not stated. That the latter factor may be an important consideration is illustrated by a number of examples, already outlined, in which hydride adds exclusively or predominantly to the less substituted carbon atom of a cation. Also, Pauson has recently found that the addition of hydride to halogen- and methoxy-substituted arenecyclopentadienyliron cations occurs at ring positions ortho to the halogen substituent, but mainly meta to the methoxyl group.

These few results made it desirable, therefore, to investigate in detail the mode of nucleophilic attack on the tricarbonyl-$\pi$-cyclohexadienyl iron cations to discover whether some coherent pattern of reaction existed.
Discussion

A number of tricarbonyl-$\pi$-cyclohexadienyliron cations were prepared both in the pure form (see Part B) and as mixtures (Part A). These were then either reduced with sodium borohydride in aqueous solution, and/or treated with hydroxide from aqueous sodium bicarbonate solution and morpholine in the standard way. The products, as well as the starting mixtures of salts, were identified by isolation and characterisation and/or proton resonance spectra, details of which are to be found in the Experimental Section.

(a) Sodium borohydride reduction

Table 2 contains details of these reductions, cations$^3$ (97) and (98) being included for completeness. (See p.110.)

Consideration of the mesomeric formulations, (99; $R = H$) and (100; $R = H$) of the tricarbonyl-1-methyl-$\pi$-cyclohexadienyliron salt (91) would lead one to expect attack of hydride to occur at the tertiary C-1 rather than secondary C-5 carbon atom. However, in the series of 1-methyl-substituted $\pi$-dienyl cations (91)-(93), addition occurs exclusively at the less substituted secondary carbon atom, C-5, to give pure complexes.

It appears, therefore, that the steric hindrance caused by the methyl group on C-1 is the more important factor, and outweighs any electronic effects. That this is so for these complexes, and generally not for simple organic carbonium ions, is perhaps not too
The series of 5-substituted tricarbonyl-2-methyl-3-cyclohexadienyliron salts (94)-(96) lends support to the validity of this approach. Although the positive charge on C-5 of (101) becomes stabilised to an increasingly greater degree by the increase in inductive effect of the R in the series hydroxy, methyl, isopropyl, the steric effect of the increasing bulk of these substituents is seen to outweigh formal considerations, the percentage in the percentage addition of hydride to this tertiary position to fall from 50% to 20% to zero in the above series.

The two examples (97) and (98) reported by Birch\(^3\) seem to confirm this tendency. In the latter cation C-5 is a tertiary carbon atom whereas it is a secondary one in the former case, and hence it is now not surprising to see that attack occurs no longer exclusively at this position, but also at C-1.

Comparison of the 2-methyl (94) and 2-methoxy (97) salts seems to indicate that a methoxy substituent at C-1 causes greater steric hindrance at the adjacent carbon atom C-1 than does a methyl group. For example, while addition to C-1 and C-5 of (94) occurs in equal proportions, hydride attacks the 2-methoxy salt (97) exclusively
surprising, since in the former cases the approach of the reducing species is probably restricted to the exo side of the molecule due to the presence of the tricarbonyliron moiety, and hence any additional steric restrictions, such as substitution at the reactive site, may be expected to play a more important role in the course of the reaction.

The series of 5-substituted tricarbonyl-2-methyl-π-cyclohexadienyliron salts (94)-(96) lends support to the validity of this approach. Although the positive charge on C-5 of (101) becomes stabilised to an increasingly greater degree by the increase in inductive effect of the group R, in the series hydrogen, methyl, isopropyl, the steric effect of the increasing bulkiness of these substituents is seen to outweigh this electronic consideration, and results in the percentage addition of hydride to this tertiary position to fall from 50% to 20% to zero in the above series.

The two examples (97) and (98) reported by Birch seem to confirm this tendency. In the latter cation C-5 is a tertiary carbon atom whereas it is a secondary one in the former case, and hence it is now not surprising to see that attack occurs no longer exclusively at this position, but also at C-1.

A comparison of the 2-methyl (94) and 2-methoxy (97) salts seems to indicate that a methoxyl substituent at C-2 causes greater steric hindrance at the adjacent carbon atom C-1 than does a methyl group. For example, while addition to C-1 and C-5 of (94) occurs in equal proportions, hydride attacks the 2-methoxy salt (97) exclusively
at C-5. Similarly, the percentage addition at C-1 of the 2,5-dimethyl cation (95) is 80% while that of the 2-methoxy-5-methyl salt (98) is 50%.

In summary, it appears that the course of the sodium borohydride reduction of tricarbonyl-π-cyclohexadienyliron cations is governed mainly by the steric effects of substituents on the π-dienyl moiety. In addition, an order of hindrance to hydride attack may be constructed in which CH₃ or OCH₃ at C-1 > OCH₃ at C-2 > CH₃ at C-2 > OCH₃ or CH₃ at C-3. Also the expected order of steric hindrance CH(CH₃)₂ > CH₃ > H applies to this class of compounds.
TABLE 2

<table>
<thead>
<tr>
<th>R</th>
<th>C-1</th>
<th>C-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>---</td>
<td>100</td>
</tr>
<tr>
<td>CH₃</td>
<td>---</td>
<td>100</td>
</tr>
<tr>
<td>OCH₃</td>
<td>---</td>
<td>100</td>
</tr>
<tr>
<td>CH₃</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>OCH(CH₃)₂</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>CH₃</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The results of these reactions, together with those relating to the hydrate attack from Table 1, are presented in Table 2.

As should perhaps be stated at the outset that it is realised that the odds of reaction of the form (a) are not independent. Using the same isoelectric species with selected groups on the cationic side of the anionic species the reaction factors and the reaction factors in the anionic side of the cationic species are determined. The reaction factors in the anionic side of the cationic species are determined to be in proportion to the reaction factors in the anionic side of the cationic species. As should perhaps be stated at the outset that it is realised that the odds of reaction of the form (a) are not independent. Using the same isoelectric species with selected groups on the cationic side of the anionic species the reaction factors and the reaction factors in the anionic side of the cationic species are determined. The reaction factors in the anionic side of the cationic species are determined to be in proportion to the reaction factors in the anionic side of the cationic species.
(b) Reaction with hydroxide and morpholine

Three 1-methyl-substituted cations (92), (95) and (98), in which steric hindrance at C-5 is progressively increased by substitution at C-4, were examined with regard to their reaction towards hydroxide (from aqueous sodium bicarbonate) and morpholine. The results of these reactions, together with those relating to hydride attack from Table 2, are embodied in Table 3, p.113.

It should perhaps be stated at the outset that it is realised that the mode of reaction of the three nucleophiles may be different, since hydroxide is an anionic species while morpholine is neutral with the reactive centre as the lone pair of electrons on the nitrogen atom. In contrast, to these two whether attack by hydride occurs initially on the metal atom or directly on the organic moiety is open to question. However, although these reactions may differ, approach of a nucleophilic species to the reactive sites of a W-dienyl group must occur at some stage, and hence a comparison on the basis of steric considerations alone may be justified.

On this basis hydroxide appears to be sufficiently small to allow the electronic factors to outweigh those of steric hindrance, and attack occurs exclusively at the tertiary carbon atom of all three salts. In addition, it seems that morpholine is intermediate in size between hydroxide and borohydride, since it does not react at C-1, but only at C-5, of (92), and its degree of addition to C-1 of (95)
is less than hydroxide but more than borohydride. Also, like hydroxide, it adds exclusively to the tertiary position of (98).

Comparison of the results in another manner leads to the same conclusion. While hydroxide adds exclusively to the substituted position C-1 in all three cations, the percentage addition of morpholine increases along this series, (92), (95) to (98), from zero to 60% to 100%, which should be compared to zero, 20% and 50% for hydride.

That hydride appears to be larger than morpholine is not too surprising when consideration is taken of some of the aspects of the reduction. It is generally assumed that the borohydride reduction involves the transfer of a hydride from a tetrahedral BH$_4$ species$^{20}$ which is probably solvated to a greater extent than the neutral morpholine molecule.
TABLE 3

<table>
<thead>
<tr>
<th>Reaction Product</th>
<th>Neopentyl 1,2-diol</th>
<th>Monoalkyl 1,2-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>B</td>
<td>92</td>
<td>---</td>
</tr>
<tr>
<td>C</td>
<td>95</td>
<td>60</td>
</tr>
<tr>
<td>D</td>
<td>98</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Note: The values represent the percentage yields or other relevant metrics.
(c) Reaction with enamines

The reaction of tricarbonyl-\(\pi\)-cyclohexadienyliron cations with species containing an active methylene group is well documented\(^3,21\), e.g.

tricarbonyl-\(\pi\)-cyclohexadienyliron fluoroborate gives the neutral species \((103; R = \text{CH(CO}_2\text{C}_2\text{H}_5)_2, \text{CH(COCH}_3)_2)\) on treatment with diethyl malonate and acetylacetone, respectively.

With the view to generalising this reaction to include less active methylene groups, cyclohexanone and the tricarbonyl-2-methoxy-\(\pi\)-cyclohexadienyliron cation were refluxed in methyl cyanide for varying lengths of time. The maximum yield was obtained after ten to twelve hours, and the expected complex \((104)\) was isolated in \(10\%\) yield, and characterised by formation of the 2,4-dinitrophenylhydrazone.

In order to increase this yield it was decided to prepare the pyrrolidine enamine \((105)\)\(^22\) of cyclohexanone, and react this species in the normal way\(^22\) with the cation. In this manner, the yield rose to \(50\%\).

Encouraged by the reactivity of the enamine towards the salt, and with possible synthetic applications in mind, the pyrrolidine-dieneamines \((107)\) of testosterone \((106; R_1 = \text{CH}_3, R_2 = \text{H}, R_3 = \text{OH})\) and 4-estrene-3,17-dione \((106; R_1 = \text{H}, R_2, R_3 = 0)\) were prepared by the standard method\(^23\).
In principle, reactions with cations can take place at either the nitrogen (103), β-carbon (105) or δ-carbon atoms (106). For example, the morpholine and pyrrolidine dienesines (111; \( R = \text{methyl iodide}^{24} \) and ethyl acrylate\(^{25} \) to give the products (112) \( R = \text{CH}_3 \) after hydrolysis, (benzene\(^{12} \text{H}_2 \)). In contrast the pyrrolidine dienesines of \( \Delta^4 \)-3-ketosteroids give N-alkylated products with methyl iodide in benzene\(^{23} \), though more polar solvents give the 4-methylated \( \Delta^4 \)-3-ketosteroids\(^{25} \).

Reaction of both dienesines (107; \( R_1 = \text{CH}_3, R_2 = \text{H} \), \( R_3 = \text{OH} \); \( R_1 = \text{H}, R_2, R_3 = \text{H} \)) with tricarbonyl-2-methoxy-7-cyclohexadienyliron hexafluorophosphate in acetonitrile solution however, only gives quaternary nitrogen salts (113; \( R_1 = \text{CH}_3, R_2 = \text{H} \); \( R_1 = \text{H}, R_2, R_3 = \text{H} \)) in yields of 57 and 95\%, respectively.

\[ \begin{align*}
\delta & : \equiv C - C - C = O - N \\
\gamma & : \equiv C - C - C = O - N \\
\beta & : \equiv C - C - C = O - N \\
\alpha & : \equiv C - C - C = O - N
\end{align*} \]
In principle, reactions with cations can take place at either the nitrogen (108), β-carbon (109) or δ-carbon atoms (110). For example, the morpholine and pyrrolidine dieneamines (111; R = morpholine and pyrrolidine) are attacked at the β-carbon atom by methyl iodide\(^2^4\) and ethyl acrylate\(^2^5\) to give the products (112; \(R = \text{CH}_3\) after hydrolysis, \((\text{CH}_2)_2\text{CO}_2\text{H}\)). In contrast the pyrrolidine dieneamines of \(\Delta^4\)-3-ketosteroids give N-alkylated products with methyl iodide in benzene\(^2^3\), though more polar solvents give the 4-methylated \(\Delta^4\)-3-ketosteroids\(^2^5\).

Reaction of both dieneamines (107; \(R_1 = \text{CH}_3, R_2 = \text{H}, R_3 = \text{OH}; R_1 = \text{H}, R_2, R_3 = \text{O}\)) with tricarbonyl-2-methoxy-\(\pi\)-cyclohexadienyliron hexafluorophosphate in acetonitrile solution afforded, however, only the quaternary nitrogen salts (113; \(R_1 = \text{CH}_3, R_2 = \text{H}; R_3 = \text{OH}; R_1 = \text{H}, R_2, R_3 = \text{O}\)) in yields of 57 and 45%, respectively.
Experimental

The preparation of the cations used for the non-saponification reactions has already been described in Parts A and B, except for that of the tricarbonyl-1-methyl-1,3-methoxy-n-cyclohexadienyliron salt (111) which was obtained in the manner described in Part A from the mixture of complexes discussed in Part B.

Reduction with sodium borohydride

To a cooled solution of the cation or mixture of cations (0.0005 moles) in water (20mL.) was added portions of borohydride, the mixture being extracted with ether between additions. After excess had been added, and extracts were no longer coloured, the combined ether extracts were washed with water, dried (MgSO₄), and evaporated to yield small crystals which were analysed by proton magnetic resonance.

Tricarbonyl-1-methyl-1,2-methyl-1,3-methoxy-n-cyclohexadienyliron salt (111)

Gave tricarbonyl-1-methyl-2-methyl-1,3-methoxy-n-cyclohexadienyliron (19) (81%). 1(CDC₃) 4.85 m (H-2, H-3 of 16 and H-3 of 19), 6.85 m (H-4 of 16 and H-1, H-4 of 19) (91%).

Tricarbonyl-2-methyl-1-cyclohexadienyliron (111) gave the same mixture as that above (87%).
Experimental

The preparation of the cations used in the nucleophilic reactions has already been described in Parts A and B, except for that of the tricarbonyl-1-methyl-3-methoxy-\(\pi\)-cyclohexadienyl salt (93) which was obtained in the manner described in Part A from the mixture of complexes discussed in Part B.

Reduction with sodium borohydride

To a cooled solution of the cation or mixture of cations (0.0005 moles) in water (20ml.) was added portions of borohydride, the mixture being extracted with ether between additions. After excess had been added, and extracts were no longer coloured, the combined ether extracts were washed with water, dried (MgSO\(_4\)), and evaporated to yield neutral complexes which were analysed by proton magnetic resonance.

\textbf{Tricarbonyl-1-methyl-} (91), \textbf{-2-methyl-} (94), and \textbf{-3-methyl-}\(\pi\)-\textbf{cyclohexadienyliron cations (1:1:1)}

Gave tricarbonyl-1-methyl- (16) and -2-methylcyclohexadieneiron (19) (91%). \(\tau\)(CDCL\(_3\)) 4.85m (H-2, H-3 of 16 and H-3 of 19), 6.85m (H-4 of 16 and H-1, H-4 of 19) (1:1).

\textbf{Tricarbonyl-2-methyl-}\(\pi\)-\textbf{cyclohexadienyliron (94)}

Gave the same mixture as that above (87%).
Tricarbonyl-1,3-dimethyl-π-cyclohexadienyliron (92)

Gave pure tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (48) (87%) identical to the complex described in Part B.

Tricarbonyl-1-methyl-3-methoxy-π-cyclohexadienyliron (93)

Gave pure tricarbonyl-1-methyl-3-methoxycyclohexa-1,3-dieneiron (90%). ν max (film) 2040, 1965 (broad) cm⁻¹; τ(CDC13) 5.05s (1H, H-2), 6.45s (3H, OCH3), 6.70m (1H, H-4), 8.41s and 8.5m (7H, CH3, 2H-5, 2H-6).

Tricarbonyl-1,4-dimethyl-π-cyclohexadienyliron (95)

Gave tricarbonyl-1,4-dimethyl- and -2,5-dimethylcyclohexa-1,3-dieneiron (90%). τ(CDC13) 4.80d (H-3 of 2,5-dimethyl isomer), 5.00s (H-2, H-3 of 1,4-dimethyl isomer) (1:8).

Tricarbonyl-1-isopropyl-4-methyl-π-cyclohexadienyliron (96)

Gave tricarbonyl-1-isopropyl-4-methylcyclohexa-1,3-dieneiron (85%). ν max (film) 2040, 1970 (broad) cm⁻¹; τ(CDCl3) 4.95s (2H, H-2, H-3), 8.25m and 8.45s (c.8H, 2H-5, 2H-6, CH(CH3)2, CH3), 8.90m (6H, (CH3)2CH).

Reaction of Morpholine

Morpholine (1ml.) in water (5ml.) was added dropwise to an ice-cooled solution of the cation (0.0005 moles) in water (10ml.), and the mixture shaken for five minutes. Extraction with ether, drying
(MgSO₄), and evaporation gave the neutral complex or complexes which were taken up in pentane, filtered through a plug of alumina, evaporated, and analysed in the normal way.

Tricarbonyl-1,3-dimethyl-π-cyclohexadienyliron (92)

Gave tricarbonyl-1,3-dimethyl-5-morpholinocyclohexa-1,3-dieneiron which was recrystallised from pentane, mp. 55-60° (66%).

(Found: C, 54.02; H, 5.87; N, 4.03. C₁₅H₁₉O₄NFe requires C, 54.06; H, 5.71; N, 4.21); νₘₐₓ (nujol) 2042, 1970 (broad) cm⁻¹; τ(CDCl₃) 4.79s (1H, H-3), 6.36t (4H, C₄H₈NO), 6.77 doublet of triplets (1H, 2J₅,₆ = 10c./sec., J₁,₅ = 4c./sec., H-3), 7.15d (fine splitting, 1H, J₁,₃ = 1.5c./sec., H-1), 7.58m (4H, C₄H₈NO), 7.83d (1H, H-5), 7.85s (3H, CH₃ on C-2), 8.00d (1H, H-5), 8.50s (3H, CH₃ on C-4); mass spectral peaks at 333, 305, 277, 275, 249, 247 (characteristic of this type of compound²⁶,²⁷).

Tricarbonyl-1,4-dimethyl-π-cyclohexadienyliron (95)

Gave tricarbonyl-1,4-dimethyl-6-morpholinocyclohexa-1,3-dieneiron and tricarbonyl-2,5-dimethyl-5-morpholinocyclohexa-1,3-dieneiron (72%). τ(CDCl₃) 4.73m (H-2 or H-3 of 1,4-dimethyl isomer and H-3 of 2,5-dimethyl isomer), 4.98d (H-2 or H-3 of 1,4-dimethyl isomer) (5:2).

Tricarbonyl-1-methyl-4-methoxy-π-cyclohexadienyliron (98)

Gave tricarbonyl-2-methoxy-5-methyl-5-morpholinocyclohexa-
1,3-dieneiron which was recrystallised from pentane, mp. 83-4° (60%).

(Found: C, 51.42; H, 5.59; N, 3.77. \( \text{C}_{15} \text{H}_{19} \text{NOFe} \) requires C, 51.58; H, 5.45; N, 4.01). \( \nu_{\text{max}} \) (nujol) 2038, 1970 (broad) cm\(^{-1}\); \( \tau(\text{CDCl}_3) \) 4.79d (fine splitting, \( J_{1,3} = 1.5\text{c.}/\text{sec.}, J_{3,4} = 7\text{c.}/\text{sec.}, \) H-3), 6.33s and 7.25m (8H, OCH\(_3\), H-4, 4H of \( \text{C}_4\text{H}_8\text{NO} \)), 6.79m (1H, H-1), 7.53m (4H, \( \text{C}_4\text{H}_8\text{NO} \)), 7.73d (1H, \( J_{1,6} = 7\text{c.}/\text{sec.}, \) H-6), 8.16m (1H, H-6), 8.80s (3H, CH\(_3\)); mass spectral peaks at 349, 321, 293, 265, 263 (typical of this type of compound\(^{26,27}\)).

**Reaction of Hydroxide**

The cation (0.0005 moles) was dissolved in water (20ml.), and excess NaHCO\(_3\) was added in portions, the temperature being kept below 10°C. The mixture was extracted with ether after each portion, and the combined extracts were worked up as described in the previous section.

**Tricarbonyl-1,3-dimethyl-\( \Pi \)-cyclohexadienyliron** (92)

Gave tricarbonyl-2,6-dimethyl-6-hydroxycyclohexa-1,3-dieneiron which was recrystallised from pentane, mp. 80-1° (85%). (Found: C, 49.75; H, 4.52. \( \text{C}_{11} \text{H}_{12} \text{OFe} \) requires C, 50.00; H, 4.55%); \( \nu_{\text{max}} \) (nujol) 2040, 1980 (broad) cm\(^{-1}\); \( \tau(\text{C}_6\text{D}_6) \) 5.13d (1H, \( J_{3,4} = 7\text{c.}/\text{sec.}, \) H-3), 7.39s (1H, H-1), 7.58m (1H, H-4), 8.23s and 8.25m (6H, CH\(_3\) on C-2, 2H-5, OH), 8.78s (3H, CH\(_3\) on C-6); mass spectral peaks at 264, 246, 236, 218, 216, 208, 190 (characteristic of this type of compound\(^{26,27}\)).
Tricarbonyl-1,4-dimethyl-π-cyclohexadienyliron (95)

Gave tricarbonyl-2,5-dimethyl-5-hydroxycyclohexa-1,3-dieneiron, recrystallised from pentane, mp. 83-4° (75%). (Found: C, 49·87; H, 4·55%; \( \text{V}_{\text{max}} \) (nujol) 2035, 1970 (broad) cm\(^{-1} \); \( \tau \) (CDCl\(_3\)) 4·69d (1H, \( J_{3,4} = 6·5 \) c./sec., H-3), 6·95m (1H, H-4), 7·23d (1H, \( J_{1,6} = 7 \) c./sec., H-1), 7·84s and 7·86m (5H, CH\(_3\) on C-3, H-6, OH), 7·99m (1H, H-6), 8·64s (3H, CH\(_3\) on C-5); mass spectral peaks at 264, 246, 236, 234, 218, 208, 206, 192, 190 (characteristic of this type of compound\(^{26,27}\)).

Tricarbonyl-1-methyl-4-methoxy-π-cyclohexadienyliron (98)

Gave tricarbonyl-2-methoxy-5-methyl-5-hydroxycyclohexa-1,3-dieneiron, recrystallised from pentane, mp. 64-5° (80%). (Found: C, 46·81; H, 4·69. C\(_{11}H_{12}OFe\) requires C, 47·14; H, 4·29%); \( \text{V}_{\text{max}} \) (nujol) 2039, 1980 (broad) cm\(^{-1} \); \( \tau \) (CD\(_6\)D\(_6\)) 5·28d (fine splitting, \( J_{1,3} = 1·5 \) c./sec., \( J_{3,4} = 7 \) c./sec., H-3), 6·84s (3H, OCH\(_3\)), 6·98m (1H, H-1), 7·58s (broad, 1H, OH), 7·68d (1H, H-4), 8·22d (2H, \( J_{1,6} = 4 \) c./sec., 2H-6), 8·80s (3H, CH\(_3\)); mass spectral peaks at 280, 262, 252, 234, 206, 178 (characteristic of this type of compound\(^{26,27}\)).

Reactions of enamines with tricarbonyl-2-methoxy-π-cyclohexadienyliron cation

1(N-pyrrolidinyl)cyclohexene (105)

The above enamine, prepared by the standard method of refluxing the ketone and amine under a Dean Stark head\(^{20}, (1\text{mL})\) and the
hexafluorophosphate salt (analytically pure) (0.890 g.) were refluxed in methyl cyanide for 2.5 hrs. under nitrogen. After distilling off most of the solvent, the residue was diluted with water (20 ml.), and the solution heated on a steam bath for 20 mins. The mixture was then cooled, extracted with ether, and chromatographed on silica using benzene as eluent to give a yellow gum (0.477 g.) (50%). $\nu_{\text{max}}$ (film) 2040, 1980 (broad), 1710 cm$^{-1}$; $\tau$(CDCl$_3$) 7.95d (1H, $J_{3,4} = 6$ c./sec., H-3), 6.41s (3H, OCH$_3$), 6.74m (1H, H-1), 8.0 (very broad, H-4, H-5, 2H-6, C$_6$H$_9$O); mass spectral peaks at 346, 318, 290, 262, 260 (typical for this type of complex).$^{26,27}$

Reaction with Brady's reagent affords a 2,4-dinitrophenyl-hydrazone, recrystallised from methanol, mp. 84-6°C. (Found: C, 50.47; H, 4.52; N, 10.56. C$_{22}$H$_{22}$O$_2$N$_4$Fe requires C, 50.19; H, 4.18; N, 10.65%); $\nu_{\text{max}}$ (nujol) 2040, 1965 (broad), 1620, 1593 cm$^{-1}$; mass spectral peaks at 526, 470, 448 (typical of a tricarbonyliron complex$^{26,27}$).

Reaction of the tricarbonyl-2-methoxy-7-π-cyclohexadienyliron cation with cyclohexanone in the standard way, though the solution was refluxed for 12 hrs. before work-up, gave the same ketone (10%) as above.

$17\beta$-hydroxy-3(N-pyrrolidinyl)androst-3,5-diene (107; $R_1 = CH_3$, $R_2 = H$, $R_3 = OH$)

This enamine was prepared in the standard way$^{23}$, and recrystallised from methanol mp. 136-7°C (46%). (Found: C, 79.69;
H, 10·28. C_{23}H_{35}NO requires C, 80·93; H, 10·27; \nu_{\text{max}} (nujol) 3280, 1635, 1602 \text{ cm}^{-1}; \lambda_{\text{max}} (\text{EtOH}) 279 m\mu (both characteristic of steroidal 3-amino-3,5-dienes).

Reaction of the tricarbonyl-2-methoxy-7-cyclohexadienyliniron hexafluorophosphosphate in the manner described previously, the reflux time having been shortened to one hour, was then carried out.

Recrystallisation from methanol gave the quaternary ammonium hexafluorophosphate (113; R_1 = CH_3, R_2 = H, R_3 = OH), resulting from electrophilic attack by the cation on the nitrogen atom (57%). (Found: C, 53·88; H, 6·02; N, 1·88. C_{33}H_{44}NO_5FePF_6 requires C, 53·88; H, 5·99; N, 1·90%). \nu_{\text{max}} (nujol) 3360, 2040, 1955 (broad), 1625, 840 \text{ cm}^{-1}; \lambda_{\text{max}} (\text{EtOH}) 277·5 m\mu (typical of enamines of \( \Delta^4 \)-3-ketosteroids in acid.23)

17-oxo-3(N-pyrrolidinyl)estra-3,5-diene (107; R_1 = H, R_2, R_3 = 0)

Prepared as above; recrystallisation from methanol gave mp. 189-190\(^o\) (48%). (Found: C, 81·02; H, 9·31; N, 4·08. C_{22}H_{31}NO requires C, 81·23; H, 9·54; N, 4·31); \nu_{\text{max}} (nujol) 1742, 1630, 1605 \text{ cm}^{-1}; \lambda_{\text{max}} (\text{EtOH}) 278 m\mu (both characteristic of 17-keto-steroidal 3-amino-3,5-diienes).

Reaction with the cation, and recrystallisation from methanol gave the quaternary ammonium hexafluorophosphosphate (113; R_1 = H, R_2, R_3 = 0) (48%). Found: C, 53·14; H, 5·64; N, 1·82. C_{32}H_{40}NO_5FePF_6 requires C, 53·40; H, 5·56; N, 1·95%; \nu_{\text{max}} (nujol) 2038, 1955 (broad), 1742, 1625 (broad), 840 \text{ cm}^{-1}; \lambda_{\text{max}} (\text{EtOH}) 275 m\mu (typical of enamines of \( \Delta^4 \)-3-ketosteroids in acid).


reaction of

\[
\begin{align*}
&\text{CH}_3 \\
&\text{H}_1, \text{H}_2, \text{H}_3, \text{H}_4, \text{H}_5 \\
&\text{Fe} \text{(um)}_3 \\
&\text{R} \text{(um)}_3 \\
&\text{CC}_6 \text{H}_{13} \text{F}_3 \\
&\text{Fe} \text{(um)}_3 \\
&\text{CH}_3 \\
&\text{H}_1, \text{H}_2, \text{H}_3, \text{H}_4, \text{H}_5 \\
&\text{Fe} \text{(um)}_3 \\
&\text{CC}_6 \text{H}_{13} \text{F}_3 \\
&\text{Fe} \text{(um)}_3
\end{align*}
\]

\[\text{H-2, H-4 of 3-methyl iron} + \text{H-4 of 2-methyl iron}\]

\[\text{H-3 of 2-methyl iron}\]

2.82
Products from \[ \text{CH}_3 + \text{Fe} (\text{CO})_5 \rightarrow \]

\[ \text{H}_2, \text{H}_3 \text{ of } (16) \]

\[ + \text{H}_3 \text{ of } (19) \]

\[ \text{H}_4 \text{ of } (16) \]

\[ + \text{H}_1, \text{H}_4 \text{ of } (19) \]
Products from \( \text{C}_6\text{H}_5\text{C}_6\text{F}_4^{+} + \text{CH}_3\text{Re}(\text{CO})_3 \rightarrow \text{CH}_3\text{Re}(\text{CO})_3 \) (1:1)

\[ \text{CH}_3\text{Re}(\text{CO})_3 \]

\[ \text{CH}_3\text{Re}(\text{CO})_3 \]
Products from $\text{OCH}_3 + \text{Fe(CO)}_5$
Abstraction from C-5 of (A) would give (C) which can be hydrolysed to (E).
Abstraction from C-6 of (A) would give (D).
Abstraction from (B) occurs only at C-5 to give (D)

From the intensities of the methoxyl transitions in the NMR it is found that

Ratio of (A):(B) = 2:1, and (C):(D) = 3:7.

1. Let fraction of H abstraction from C-5 of (A) = x
   \[ \text{fraction of } H^+ \text{ abstraction from C-6 of (A)} = 1-x \]
   \[ \frac{2x}{2(1-x)+1} = \frac{3}{7} \]
   \[ x = 0.45 \]

M.wt. of complexes (A) and (B) = 250
M.wt. of salts (C) and (D) = 394
M.wt. of ketone (E) = 234

Experimental
Complexes (A) and (B) (0.01 moles) → salt (D) (2.44g) and ketone (E) (0.71g)

2. No. of moles of ketone (E) formed from (A) = \[ \frac{2x}{3} = \frac{71}{234} \]
   \[ x = 0.45 \]
3. No. of moles of salt (D) formed from (A) and (B) = \( \frac{2}{3}(1-x) + \frac{1}{3} = \frac{244}{394} \)

\[ \therefore x = 0.57 \]

Average value of \( x = \frac{1}{3}(0.45 + 0.45 + 0.57) = 0.49 \)

---

**Experimental**

1. Pure (A) \( \rightarrow \) (C) by abstraction from C-6, and (D) by abstraction from C-5.

Let \( \text{ratio of abstraction from C-5 of (A)} = x \)

\[ \therefore \text{From data in experimental section (p.79)} \]

\[ \frac{\text{Intensity of absorption at } 2.82\tau}{\text{Intensity of absorption at } 4.02\tau} = \frac{x}{x+2(1-x)} = \frac{7}{19} \]

\[ \therefore x = \frac{7}{13} \text{ or } 54\% \]
2. (A) and (B) (1:1 from NMR, p. 75) \( \rightarrow \) (C) + (D) + (E) (5:7:9 from CH\text{\textsubscript{3}} intensities in NMR)

Abstraction from C-6 of (B) also gives (D)

Abstraction from C-5 of (B) gives (E)

Let \( \% \) abstraction from C-6 of (A) = \( a \)

Let \( \% \) abstraction from C-5 of (A) = \( b \)

Let \( \% \) abstraction from C-6 of (B) = \( x \)

Let \( \% \) abstraction from C-5 of (B) = \( y \)

\[ \frac{a}{b+x} = \frac{5}{7}, \text{ and } \frac{a}{y} = \frac{5}{9} \]

\[ \frac{9a}{5b} = \frac{y}{b} \]

\[ \frac{a}{b} = \frac{5}{7}, \text{ and } \frac{7a}{5b} = 1 + \frac{x}{b} \]

\[ \frac{9a}{5b} - 1 = \frac{x}{y} \]

But from 1, \( \frac{a}{b} = \frac{6}{7} \)

\[ \frac{6}{5} - 1 = \frac{x}{y} \]

\[ \frac{9 \cdot 6}{5 \cdot 7} \]

\[ \frac{x}{y} = \frac{7}{54} \text{ or } \frac{11}{54} \]

\[ x = 11 \% \]