

STUDIES ON UNSATURATED HYDROCARBONS

BOUND TO

TRANSITION METALS

A Thesis submitted

by

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ABSTRACT.

The behaviour of tricarbonyl cyclooctatetraene iron in strong acids has been investigated by proton magnetic resonance spectroscopy. Unlike certain other organometallic compounds, this substance attaches a proton to its organic ring to give a bicyclic carbonium ion which is bound to and stabilised by the metal carbonyl residue. A solid tetrafluoroborate of the protonated species has been obtained, and on reduction this gives a neutral complex in which the bicyclic structure is retained. The protonation of various other metal-olefin complexes has been examined, and it is concluded that the stability of the protonated species depends upon the ability of the organic part of the molecule to distribute the excess positive charge over as many atoms as possible.

Cyclooctatetraene complexes of cobalt and rhodium have been made and examined by proton magnetic resonance spectroscopy using the double irradiation technique, and it is concluded that in them the organic ligand adopts a tub conformation.

Complexes of the various isomeric cyclooctatrienes and tricarbonyl iron, and η -cyclopentadienyl cobalt have been prepared. It is found that whilst cobalt is

indifferent to whether the double bonds to which it becomes attached are conjugated or not, iron will only combine with a butadiene-type of system.

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CHAPTER I.INTRODUCTION.

Although Zeise's salt, $K[PtCl_3(C_2H_4)]$, was discovered as long ago as 1827, and the carbonyl complex (butadiene) $Fe(CO)_3$ was first made¹ in 1930, no satisfactory progress was made in the explanation of their structures until the discovery of ferrocene,^{2,3} the elucidation of its structure, and the digestion of this information. From the first, the investigation of the chemistry of the η -cyclopentadienyl- and arene- metal complexes took two different courses, one of them concerned with the organic reactions of five- and six- membered rings which normally displayed aromatic behaviour, when bound to a transition metal atom. The other dealt with the extension of the range of metals and aromatic systems able to form such compounds. The study of metal-olefin complexes has been confined mainly to the second of these courses, and it is only very recently that the reactions of these compounds, other than the complete replacement of the ligand, have been examined in any detail. Some of these reactions are described in this thesis.

The nature of the bonding in metal-olefin complexes will be discussed later, but a rule which is

frequently obeyed is that each double bond in the olefin contributes two electrons to the metal atom, which itself strives to attain the electronic configuration of the next inert gas in the periodic system. In general, mono-olefins form stable complexes[†] only with metals towards the end of the transition series, and silver and platinum in particular form monodentate and chelated complexes with almost equal facility. Indeed, silver often forms complexes in which a particular silver atom is attached to double bonds in different ligand molecules; it is evident that here the chelating effect does little or nothing to enhance the stability of these complexes.

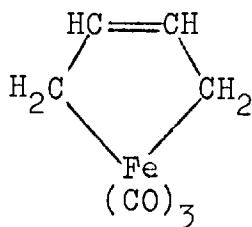
Di- and poly- olefins form complexes with vanadium and all the transition metals from group VI onwards, with the exception of technetium which has been very little investigated. In the case of the poly-olefins (and to some extent of the di-olefins also) the number and choice of the double bonds actually associated with the metal atom depend upon a number of factors: their relative arrangement, the conformational mobility of the olefin, and the orbitals that the metal atom has available. This thesis deals with olefin complexes which

[†] A notable exception is acrylonitrile iron tetracarbonyl, in which the organic part is bound to the iron by the double bond.

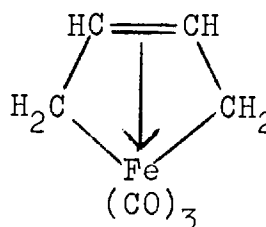
contain other strongly π -bonding ligands such as carbonyl and π -cyclopentadienyl, in addition to the olefin, and other types of olefin complex (e.g. the halide complexes) will not be discussed except for the purpose of comparison.

When a poly-olefin is heated for several hours with any one of the three iron carbonyls $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, or $\text{Fe}_3(\text{CO})_{12}$, displacement of carbon monoxide occurs and a double bond of the olefin takes the place of each displaced CO group. Usually the iron atom remains attached to three carbonyl groups, no matter how many double bonds the olefin may have available, and the only exceptions to this are tetracarbonyl acrylonitrile iron (see footnote on p.2), and polynuclear complexes where there is a possibility of forming a direct Fe - Fe bond.

It was initially suggested¹ that the butadiene complex of iron carbonyl, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$, has the structure shewn in fig. I, but it was pointed out in 1958⁴ that this



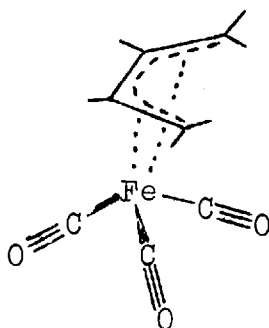
I.



II.

structure is not acceptable as the compound is diamagnetic

(in I the iron atom has 34 electrons and should thus give rise to paramagnetism), and that there is no evidence of a free double bond as the complex is unaffected by catalytic hydrogenation or treatment with maleic anhydride. The structure shewn in fig. II ⁵ does not possess these disadvantages and there is a band in its infra-red spectrum at 1464 cm.^{-1} which can be ascribed to a $\text{C}=\text{C}$ stretching mode lowered by about 150 cm.^{-1} by coordination to the metal. In fact, a single crystal X-ray analysis of the substance confirmed the suggestion of Hallam and Pauson⁴ that the butadiene group retains its planarity (but adopts a cisoid rather than transoid configuration) and is bound to the iron atom by interaction between its π -electron system and the d-orbitals of the metal. See fig. III.

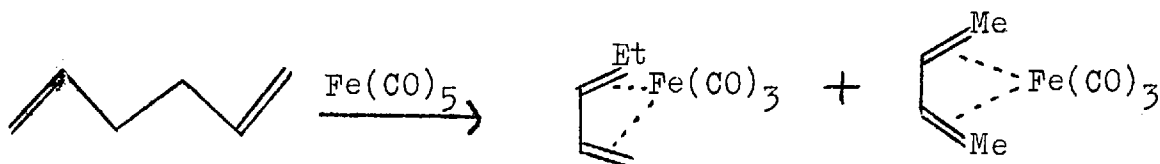


III.

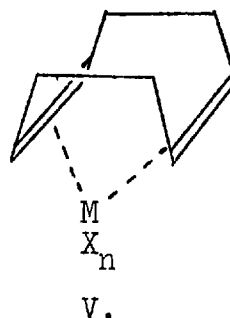
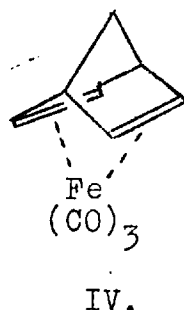
This structure accounts for the proton magnetic resonance observation of two different kinds of methylene proton in the compound; structures I and II should each contain only

one kind.

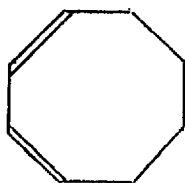
A variety of conjugated dienes, such as penta-1,3-diene, isoprene, cyclohexa-1,3-diene, and 1,2,3,4 tetraphenyl butadiene, which have, or can easily adopt, a cisoid configuration, give complexes with iron carbonyl which have very similar properties. When non-conjugated dienes are heated with an iron carbonyl they usually rearrange to give a complex of a closely related conjugated diene. Thus hexa-1,5-diene gives a mixture of the 1,3- and 2,4- complexes:



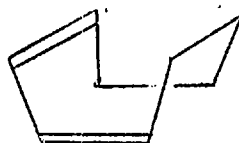
and cyclohexa-1,4-diene gives the cyclohexa-1,3-diene complex. The most stable complex formed between iron and a non-conjugated diene is that obtained from norbornadiene (bicyclo[2,2,1]heptadiene)^{6,7,8} It is an air-sensitive oil, markedly less stable than the butadiene and related compounds, and a large number of by-products are formed during its preparation. Its structure is shown in fig. IV.



Discrepant results have been recorded for the reaction between the various iron carbonyls and the powerful chelating di-olefin cycloocta-1,5-diene, which forms stable complexes of the type indicated in fig. V with a variety of transition metals; but it is agreed that no stable complex exists. Stone and his co-workers^{9,10} obtained an unstable orange liquid which decomposed in a few hours at room temperature in a nitrogen atmosphere, and do not give any n.m.r. data. In contrast, Arnet and Pettit¹¹ state that no organo-metallic compound was to be found in the reaction mixture and that most of the $\text{Fe}(\text{CO})_5$ was recovered unchanged. Furthermore, they found that the 1,5- diene had been converted quantitatively into its 1,3- isomer (fig. VI) and that no trace of any other organic compound could be detected. In the course of the



VI.



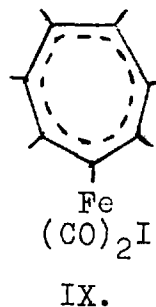
VII.

investigation described in this thesis it was found that when either 1,5- or 1,3- cyclooctadiene was heated with dodecacarbonyl tri-iron extensive decomposition took place and the reaction mixture became pale brown. This brown colour disappeared when the mixture was chromatographed on alumina.

The inability of the 1,5- isomer to form a stable complex with iron carbonyl is probably a consequence of its lack of conjugation and the rather large distance between the centres of the double bonds. This is about 2.9 Å. (in $[\text{C}_8\text{H}_{12}\text{RhCl}]_2$ ³³) which is considerably more than in norbornadiene (2.4 Å. in $\text{C}_7\text{H}_8\text{PdCl}_2$ ¹²) whose iron complex is already rather unstable. The refusal of the 1,3- isomer to give a stable complex may be due to the fact that in the free olefin the double bonds, although adjacent, are not conjugated. This is because the conformational requirements of the saturated part of the molecule impose a twist of approximately 80° about the bond between C_2 and C_3 , so that the molecule appears as in fig. VII rather than as in fig. VI. If the above explanation is correct however, it makes it very difficult to understand the stability of certain compounds to be discussed later.

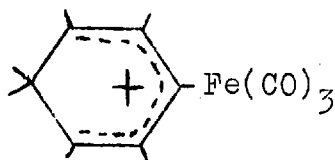
Cycloheptatriene forms complexes $\text{C}_7\text{H}_8\text{M}(\text{CO})_3$ ^{13,14} with the metals of group VI, the most stable being the molybdenum one, in which the alternation of double and single bonds is preserved.¹⁵ It therefore follows that this ligand might be capable of forming complexes in which only two of the double bonds are involved in the bonding to the metal atom, since there is no (pseudo-)aromatic system to be destroyed. This behaviour is in fact observed with iron carbonyl, and provided the reaction time is fairly short the main product

is $C_7H_8Fe(CO)_3$. With longer reaction times reduction of the triene occurs and a complex $C_7H_{10}Fe(CO)_3$, which is a derivative of cyclohepta-1,3-diene (from which the complex can also be made directly) is obtained.^{38,39} Various polymeric complexes have also been observed in this reaction, but the iron atom invariably occurs in association with three carbonyl groups. Dauben and Bertelli¹⁷ found that when the triene complex is treated with strong acids - tetrafluoroboric in particular - the organic part takes up a proton to give the cationic species shown in fig. VIII.

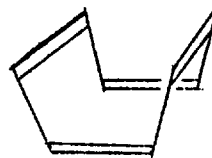


They also found that treatment of the diene complex with the powerful hydride ion abstracting reagent triphenyl-carbonium tetrafluoroborate gave the same cation, which can be regarded as either cycloheptatrienium- or cycloheptadienyl- iron tricarbonyl. These authors also find that when the cation is treated with potassium iodide in acetone for some time, stable maroon crystals of the tropylium complex $\pi-C_7H_7Fe(CO)_2I$ (see fig. IX) are obtained, although their n.m.r. data do not seem to agree very well with this structure.

Tropylium complexes, $\pi\text{-C}_7\text{H}_7\text{M(CO)}_3^+ \text{BF}_4^-$, of the group VI metals can be made by hydride abstraction with trityl tetrafluoroborate from the corresponding cycloheptatriene complex. Fischer and Fischer¹⁸ have found that cyclohexa-1,3-diene tricarbonyl iron will also undergo hydride abstraction to give the cationic species $\text{C}_6\text{H}_7\text{Fe(CO)}_3$, indicated in fig. X.



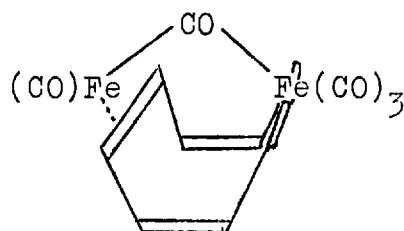
X.



XI.

The hydrocarbon cyclooctatetraene exists in the free state in the tub conformation shown in fig. XI, in which each double bond is twisted out of the plane of its neighbours by about 80° so that the amount of conjugation in the system is almost negligible.^{41a} This is supported by the observed bond lengths in the molecule which are 1.33 and 1.46 Å., not very different from those found in ethylene (1.34 Å.) and to be expected for a single bond between sp^2 hybridised carbon atoms.¹⁹ It is also known that cyclooctatetraene retains its tub conformation in its silver complexes^{20,21} and probably in its complexes with copper and platinum. The reaction of iron pentacarbonyl with cyclooctatetraene was reported by three groups of workers almost simultaneously with essentially the same results.^{22,23,24,25} Three complexes

are obtained from this reaction: their compositions are $C_8H_8Fe(CO)_3$, $C_8H_8[Fe(CO)_3]_2$, and $C_8H_8Fe_2(CO)_7$. All three show strong infra-red absorption in the region ($1900-2100\text{ cm}^{-1}$) normally associated with terminal groups, and the third has an additional strong band at 1802 cm^{-1} which is assigned to a bridging carbonyl group. Accordingly this compound, which is black and insoluble in most solvents, is supposed to be a derivative of di-iron enneacarbonyl, in which the Fe - Fe bond is retained as shown in fig. XLI.



XII.

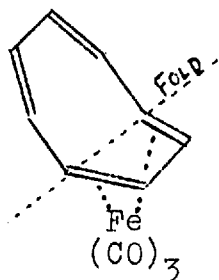
The evidence either for or against this structure is somewhat scanty however, and on the whole the compound has excited little interest.

The mononuclear complex displays a number of surprising properties; it is extremely air-stable, and although it would be expected to contain two free double bonds it is only slowly attacked by bromine (with release of carbon monoxide and disruption of the molecule), is unaffected by catalytic hydrogenation, and does not react with the dienophile

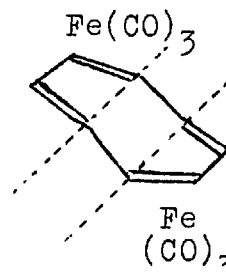
maleic anhydride. Furthermore its infra-red spectrum shews no bands in the region of 1600 cm^{-1} which can be attributed to free double bonds, although there is a band at 1416 cm^{-1} which is assigned to an olefinic stretching frequency modified by coordination to the metal atom. The most puzzling feature of the compound is that its proton magnetic resonance spectrum shews only one sharp line, whereas other diene and olefin complexes of transition metals have spectra with bands over a range of about 2 p.p.m., with unbound olefin groups giving resonances some 0.5 - 1.0 p.p.m. lower. These facts led to a great deal of speculation and a number of structures were proposed, although none proved to be the correct one. The two most popular explanations were firstly, that the C_8H_8 group adopted a tub conformation which was continually inverting, so that no particular double bond spent a continuous period of time next to the iron atom; and secondly that the hydrocarbon ring was planar with complete delocalization of its eight π -electrons, the bonding to the metal atom taking place by overlap of suitable metal orbitals with a symmetrical π -orbital which involved all these electrons.²⁶

In fact, the single crystal X-ray diffraction studies of Dickens and Lipscomb^{27,28} demonstrated that the compound has the unusual structure shewn in fig. XIII. In this structure the conformation of the cyclooctatetraene is

apparently dominated by the desire of the $\text{Fe}(\text{CO})_3$ to be bound to a butadiene-like residue, and by the desire of the unbound diene group to achieve planarity.



XIII.



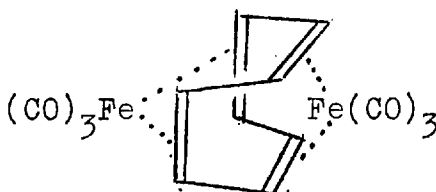
XIV.

The C - C bond lengths within the bound butadiene unit are equal at 1.42 Å., but in the free unit the inner bond is 1.49 Å. and the outer two are 1.34 Å. long. The bonds joining the two halves of the C_8H_8 group are 1.45 Å. long, and the π -overlap integral between the carbon atoms at the ends of these bonds is 0.25, indicating considerable interaction between the π -electrons of the two halves of the molecule. This presumably accounts for the unwillingness of the compound to react with maleic anhydride or to undergo catalytic hydrogenation.

The structure of the dinuclear compound $\text{C}_8\text{H}_8[\text{Fe}(\text{CO})_3]_2$ has been determined by the same workers^{29,30} and is shown in fig. XIV., although different ones (including the inherently probable one shown in fig. XV) had been previously suggested by other workers. The conformation of the ligand is clearly

determined by the formation of two butadiene units as in the case of the mononuclear compound, but in this case the ring is folded along two axes instead of one. There is a somewhat greater difference in length between the inner and outer bonds of each butadiene unit, and the bonds joining the two units are also rather longer in this compound. This is in agreement with the calculation of a π -overlap integral of only 0.04 between the carbon atoms at the ends of these bonds, shewing that the two halves of the molecule are electronically isolated from one another.

Although the dinuclear compound is very stable it is rather insoluble in most solvents, and this has made it rather difficult to obtain a record of its n.m.r. spectrum.

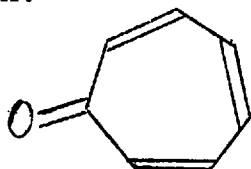


XV.

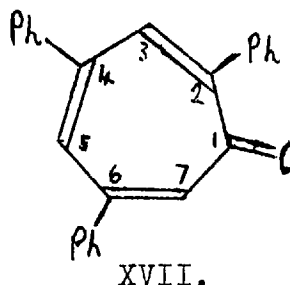
However, Fritz and Keller³¹ state that in deuterio-chloroform two resonances of equal intensity are observed, although they do not say whether any fine structure could be detected. Certainly, the protons in structure XIV would be expected to display considerable spin coupling, but the published spectrum cannot be said to be inconsistent with this structure.

The observation of a single resonance line in the proton magnetic resonance spectrum of $C_8H_8Fe(CO)_3$ has not yet received a satisfactory explanation in terms of structure XIII, but it is generally agreed that some kind of exchange phenomenon is responsible for the anomaly. It can be pointed out here however, that the protons in this structure would normally be expected to give resonances over a range of at least 2 p.p.m. - that is, about 120 c.p.s. at a measuring frequency of 60 mc/s. - so that the individual molecular configurations involved must have life-times of less than 0.01 sec.. Certain n.m.r. experiments performed in the (vain) hope of resolving this difficulty will be described later in this thesis.

Two examples of molecules being bent by coordination to an $Fe(CO)_3$ residue, when they would otherwise be planar, are the complexes of tropone (XVI) and 2,4,6-triphenyl tropone (XVII), both of which have been studied by X-ray diffraction.^{32,33}



XVI.



XVII.

In the second of these complexes, C_4 , C_5 , C_6 , and C_7 form an almost planar butadiene-like unit which is coordinated to

the iron atom. The remainder of the ligand is planar and is bent away from the iron atom along a line joining C_4 and C_7 . The dihedral angles in both this and the unsubstituted complex are about 140° . From the position of the phenyl group attached to C_4 it seems likely that the state of hybridization of the carbon atoms at the ends of the butadiene unit is between sp^2 and sp^3 .

The reaction between cyclooctatriene and transition metal carbonyls is complicated by the existence of a number of isomers of the hydrocarbon. It has been studied by a number of workers with discrepant results, and will be discussed in detail later.

The two carbonyl groups in dicarbonyl π -cyclopentadienyl cobalt, $\pi-C_5H_5Co(CO)_2$, are readily replaced by a variety of ligands, including chelating di-olefins. In this respect the $\pi-C_5H_5Co-$ group is formally analogous to the $-Fe(CO)_3$ group, and many of the cobalt complexes have structures similar to those of their iron analogues. However, the $\pi-C_5H_5Co-$ group shews no tendency to impose a butadiene type of configuration upon dienes which do not already possess it, and in the complexes with both cyclooctatetraene and cycloocta-1,5-diene the ligand appears to retain a tub configuration.^{34,35} Rhodium chloride similarly forms complexes in which a non-conjugated form of the ligand is retained -

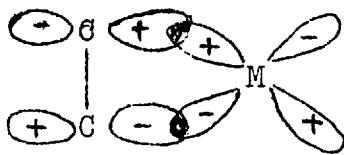
indeed preferred, for when rhodium trichloride in ethanol is treated with cycloocta-1,3-diene, only the 1,5- complex is obtained.³⁶

The bonding between the metal atom and the ligands in these complexes is usually discussed in terms of molecular orbital theory rather than the valence-bond description, and although there is some disagreement about the details, it is generally accepted that both donation to the metal from the ligand, and back donation from the metal via its d-orbitals are involved. Fig. XVIII indicates the way in which the

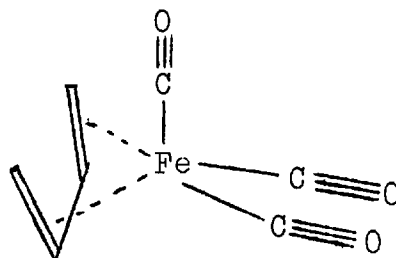


XVIII.

σ -bond from the olefin to the metal is formed. Case (a) is to be regarded as an overlapping of the original bonding π -orbital of the olefin with a suitable vacant metal orbital. In case (b) however, it is considered that a completely new three-centre orbital is formed from the metal orbital and the $2p_z$ orbitals of the olefin. In fig. XIX the nature of the orbitals used in the back donation is shown. This molecular orbital involves suitable filled metal (usually d-) orbitals and the vacant $\pi_z^* 2p$ orbital of the olefin.

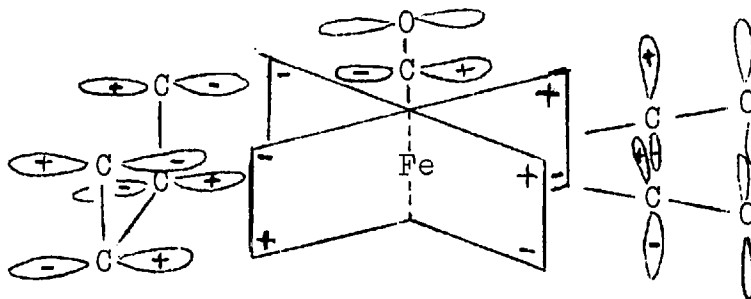


XIX.



XX.

In its tricarbonyl diene complexes the iron atom usually adopts a square pyramidal configuration, as in fig. XX, the centre of each double bond of the diene system being regarded as a coordination position. This can be understood if it is assumed that the orbitals of the iron which are involved in the forward coordination from the diene (and from the carbonyl groups) are hybrids of the $4s$, $4p^3$, and $3d_{xy}$ atomic orbitals. The back donation then involves the anti-bonding orbitals of the carbonyl groups, the lowest anti-bonding orbital of the diene, and the d_{xz} and d_{yz} orbitals of the iron atom. This is shown schematically in fig. XXI.



XXI.

An important feature of this model is that owing to the orthogonality of the d_{xz} and d_{yz} orbitals, electronic effects

arising in either bond of the diene should be transmitted mainly to the carbonyl group trans to that bond, and these effects will be reflected in the infra-red spectrum of the complex in the carbonyl absorption region. Experimentally it is found that the lower carbonyl band (c. 1990 cm^{-1}) is often split in the tricarbonyl iron complexes of unsymmetrically substituted butadienes, and that this splitting is greater in the corresponding substituted norbornadiene complexes. This is to be expected as there will be less interaction between the double bonds in these latter complexes.

The view that the coordination of the iron in these complexes is square pyramidal has been criticised on the grounds that it leads to very small overlap integrals.²⁹ Instead, it has been suggested that the iron is either 6- or 7- fold coordinated. In the first case the ligands are considered to be the three carbonyl groups, and the central bond and terminal carbon atoms of the butadiene unit. In the second case, the three carbonyl groups and all four carbon atoms of the butadiene unit are regarded as ligands.

Comprehensive reviews of the complexes formed between olefins and transition metals have been published by Bennett,⁵⁹ and by Guy and Shaw.³⁷

CHAPTER II.THE PROTONATION OF TRICARBONYL CYCLOOCTATETRAENE IRON.

When this work was begun it was known that treatment of certain arene and π -cyclopentadienyl transition metal complexes led to the formation of species containing metal-hydrogen bonds.^{38,39,40,41b} In view of the apparent inertness of tricarbonyl cyclooctatetraene iron towards reagents which normally attack olefins, and the possible pseudo-aromatic character of the organic part of the compound, it was thought that this complex might also be capable of giving a hydride on treatment with acid. In fact a completely different kind of behaviour was observed, and the proton added to the olefin ligand to give a carbonium ion bound to and stabilised by the metal-carbonyl portion. This kind of behaviour had been previously noticed by Burton et al^{16,41b} in tricarbonyl cycloheptatriene iron. This compound, in which the organic part has a free double bond not involved in the bonding to the metal atom, reacts with halogen acids to give salts of the cation $C_7H_9Fe(CO)_3^+$. The structure and proton magnetic resonance spectrum of this cation will be discussed later.

Tricarbonyl cyclooctatetraene iron dissolves in de-aerated concentrated sulphuric acid with slight evolution of heat to give a deep red solution which is reasonably stable.

If this solution is carefully diluted with ice-cold water a yellow solution is obtained which slowly evolves carbon monoxide and deposits hydrated ferric compounds. Neutralization of the freshly diluted acid solution, followed by extraction with diethyl ether gave variable amounts of the original tricarbonyl cyclooctatetraene iron, but the yields were by no means quantitative. The diluted acid solutions also gave precipitates with the salts of large anions such as hexachloroplatinate, but the solids obtained were impure, and no satisfactory analytical figures could be obtained.

When a solution of tricarbonyl cyclooctatetraene iron in propionic anhydride is treated with an excess of hydrogen tetrafluoroborate in the same solvent (the purpose of the acid anhydride is to remove the water - c.60% - present in commercial fluoroboric acid) an immediate lightening in colour occurs, and if the mixture is poured into a large volume of diethyl ether or tetrahydrofuran a bright yellow precipitate is obtained which is of stoichiometry $C_{11}H_9BF_4FeO_3$. This compound is stable indefinitely in dry air and is soluble in water, acetone, and polar solvents in general, although its aqueous solution slowly decomposes with evolution of carbon monoxide. For this reason it is very important that all traces of acid anhydride be removed from it before storage by thorough washing with ether, otherwise moisture

will be absorbed from the atmosphere and decomposition will ensue.

The mull infra-red spectrum of the compound shews absorption in the region of 3000 cm^{-1} which is assigned to C - H stretching vibrations; there is a strong peak at 1060 cm^{-1} which is assigned to an asymmetric stretching mode of the tetrafluoroborate ion; but there is no absorption in the neighbourhood of 1630 cm^{-1} which is the region normally associated with free double bonds. There are also two intense absorptions at 2108 and 2055 cm^{-1} which are assigned to terminal carbonyl groups. The increase in the wave number of these peaks by about 100 cm^{-1} above that found in the parent compound is to be expected in a complex in which a positive charge becomes associated with the metal atom. This is a result of a decrease in the back donation from the metal atom into the anti-bonding orbitals of the carbonyl groups with a consequent increase in the strength of the C - O bonds.

It is clear from the above evidence that when tricarbonyl cyclooctatetraene iron is treated with strong acids a proton attaches itself either to the ring system or directly to the metal atom. Measurement of the proton magnetic resonance spectrum of a solution of the compound in concentrated sulphuric acid shewed that there were no lines present with

τ -values greater than 9, thus indicating the absence of Fe - H bonds. However, the single line which the compound displays in solvents with which it does not react was replaced by a complex set of lines extending from $\tau=2$ to 9. The proton magnetic resonance spectra of tricarbonyl cyclooctatetraene iron in concentrated sulphuric and dideutero-sulphuric acids are reproduced in plate I, A and C. (p.24)

These spectra proved to be very difficult to interpret until the technique of double irradiation (or double resonance) was used in the examination of the specimen. This is probably the first example of the application of this technique to the solution of a problem in transition metal organic chemistry. In the normal n.m.r. experiment the specimen is placed in a strong magnetic field and is irradiated with radio-frequency radiation whose frequency is varied over the range within which nuclear resonances are expected to occur. However, if the rf. field used is too intense, saturation occurs at the resonant frequency and there are frequent transitions between the magnetic states of the nuclei, so that their lifetime becomes too short to be recorded by the receiver. The observable consequence of this is that the original sharp line loses height and becomes broader and may even vanish.

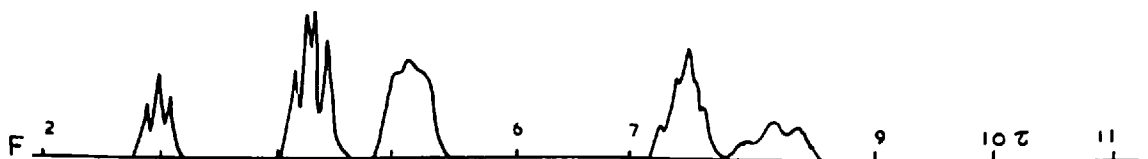
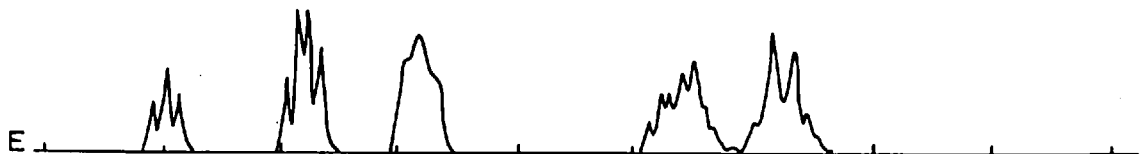
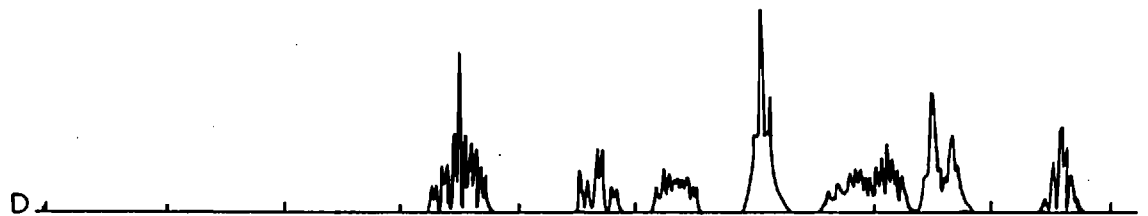
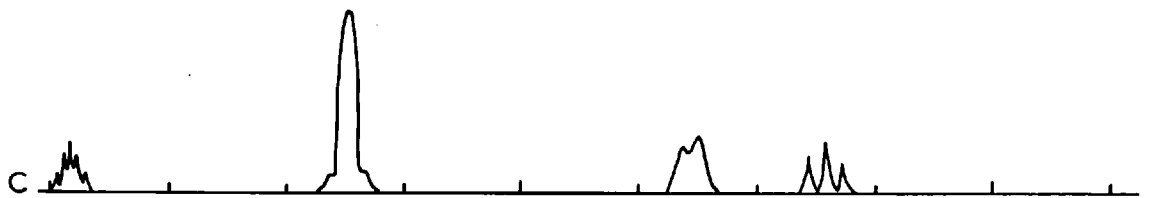
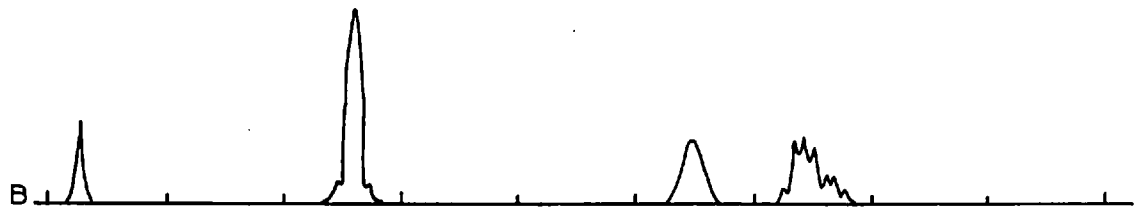
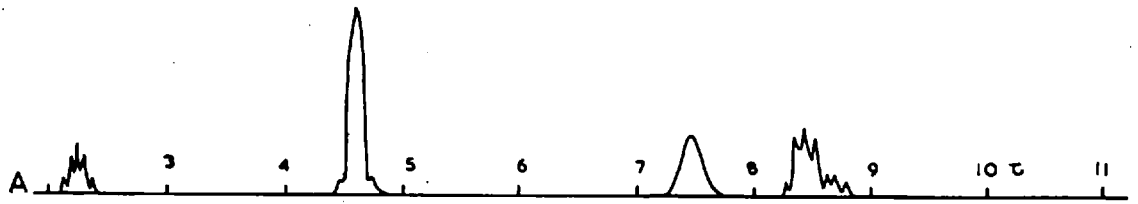
This effect considerably hinders measurements on

LEGEND FOR PLATE I.

- A. $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3$ in H_2SO_4 .
- B. The appearance of the low-field resonance in $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3$ when the resonance at $\tau = 4.62$ is irradiated.
- C. $\text{C}_8\text{H}_8\text{DFe}(\text{CO})_3$ in D_2SO_4 .
- D. Bicyclo[5,1,0]octa-2,4-diene $\text{Fe}(\text{CO})_3$ in benzene. (Solvent line not shewn.)
- E. $\text{C}_7\text{H}_9\text{Fe}(\text{CO})_3$ in H_2SO_4 .
- F. $\text{C}_7\text{H}_8\text{DFe}(\text{CO})_3$ in D_2SO_4 .

The spectra were measured at 56.45 mc/s.

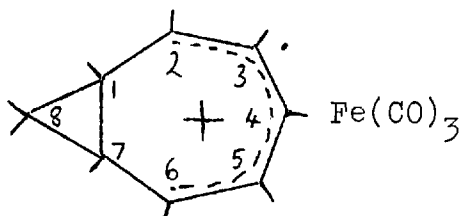
2 hrs.



dilute solutions but it can be turned to good account; for saturation, besides reducing the line height given by a nucleus, also effectively decouples it from the other nuclei of the system. This means that if one line - say A - of a specimen which contains nuclei in three different environments (giving lines A, M, and X) is observed using a radio frequency field of small or moderate intensity, while at the same time the specimen is irradiated with a very strong (saturating) rf. field at the resonant frequency of band M, the only splitting of band A that will be observed will be that due to the coupling to the nuclei which give rise to band X. Similarly, irradiation with a strong field at the resonant frequency of X will mean that the only splitting of A to be observed will be that arising from the coupling to band M. This technique is of great value in the measurement of complex spectra, and the equipment used in this work generates both the measuring and decoupling rf. fields from the same oscillator by means of a special modulation technique.⁴³

The lines of the spectrum of the solution of tricarbonyl cyclooctatetraene iron in concentrated acid are all somewhat broad; this may be due to the presence of small amounts of paramagnetic impurities produced by oxidation of the complex by the acid, or to incomplete averaging of the dipolar broadening in the viscous solutions. A satisfactory

assignment of the lines of the two spectra can be made on the basis of the bicyclic structure shewn in fig. XXII.



XXII.

The line at lowest field is assigned to H_4 and displays quintuplet structure which arises from approximately equal spin coupling to the protons H_2 , H_3 , H_5 , and H_6 . This crucial interpretation was confirmed by the decoupling experiment which shewed that the groups causing the quintuplet structure were chemically shifted 132 c.p.s. to the high-field side of the line, and were therefore coincident with the second band of the spectrum which is assigned to the four protons H_2 , H_3 , H_5 , and H_6 . The appearance of the spectrum during the decoupling experiment is illustrated in plate I, B. The four protons which give rise to the second band appear to be nearly equivalent, and besides being coupled to H_4 should also be coupled to H_1 and H_7 . None of this structure could be observed however, but as the band is 12 c.p.s. wide this is probably not significant.

The band between $\tau = 7$ and 8 is attributed to

the bridgehead protons H_1 and H_7 , and the high-field band is assigned to the non-equivalent methylene protons on C_8 . These two protons can be regarded as an "AB" pair with a coupling constant of 4.86 c.p.s.. This alone would give a quartet but the observed spectrum can be reproduced satisfactorily (as a quartet of overlapping doublets) if allowance is made for the additional coupling from the bridgehead protons H_1 and H_7 . These have different coupling constants to the protons giving rise to the A ($J = 4.5$ c.p.s.) and the B ($J = 8$ c.p.s.) parts of the spectrum, suggesting that the bonds to these protons make different dihedral angles with the bonds to the bridgehead protons. This is likely since the cyclopropane ring will almost certainly be bent either up or down to relieve strain at the bridgeheads. A satisfactory correlation (on the basis of a cosine law for the variation of coupling constant with dihedral angle) with the observed coupling constants is obtained if it is assumed that the dihedral angle between B and either of the bridgehead protons is $0^\circ \pm 5^\circ$, and that the corresponding angle for A is $120^\circ \pm 5^\circ$. The bending of the cyclopropane ring will be discussed again later.

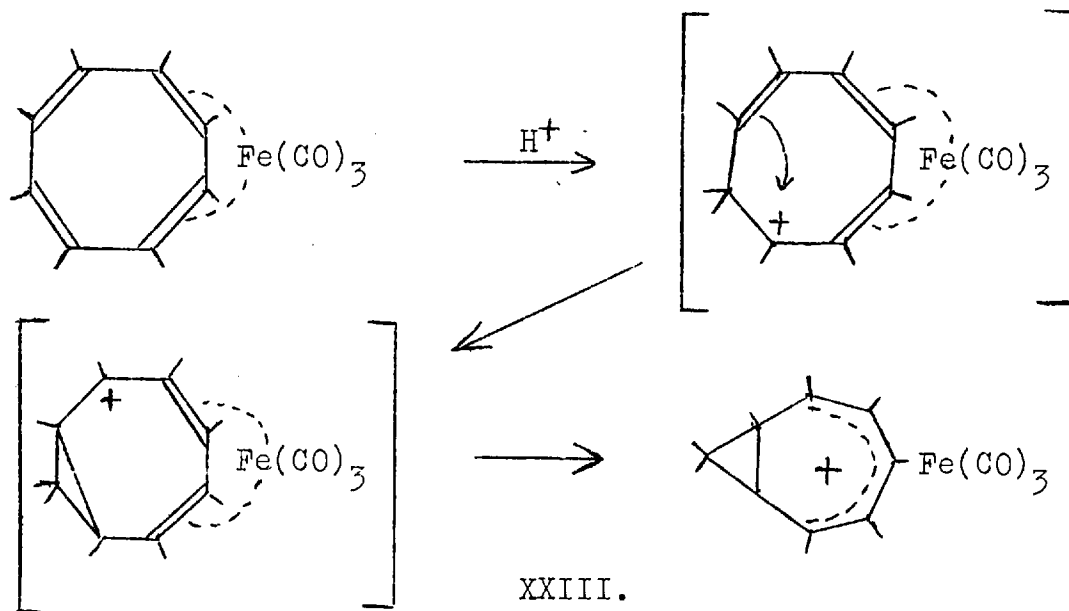
The above assignment of the lines in the spectrum of tricarbonyl cyclooctatetraene iron in concentrated sulphuric acid was confirmed by a measurement in dideuterosulphuric acid

Except for a small solvent effect which alters the line-positions somewhat, the spectrum differs from that of the protonated species only in the appearance of the two lines at highest field. The band due to H_1 and H_7 is now an incompletely resolved unsymmetrical doublet, and the band at highest field is an unsymmetrical triplet. These bands can be regarded approximately as arising from an " AB_2 " grouping, with a value of 7.9 c.p.s. for the coupling constant between the bridgehead protons and the remaining methylene proton. This is sufficiently close to the value of 8 c.p.s. obtained for the coupling constant between B and the bridgehead protons in the protonated species, to shew that the proton taken up by tricarbonyl cyclooctatetraene iron in strong acids becomes proton B on the nomenclature used here.

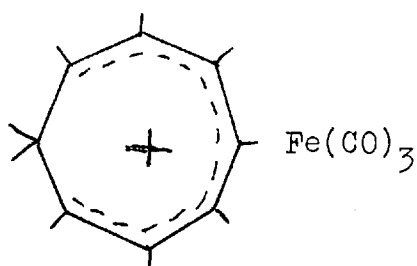
The spectrum of the compound in strong acid was re-examined after three days and found to be unchanged apart from a slight broadening of the lines (presumably a result of the formation of paramagnetic materials), shewing that the other protons in the compound do not undergo exchange with the solvent. Fig. XXIII on p. 29 indicates a possible reaction path for the formation of the bicyclic protonated species.

Some time after a preliminary account of the above had been published⁴⁴ Schrauzer reported essentially

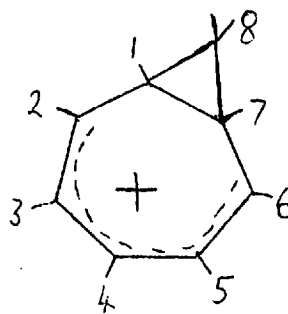
the same experimental results⁴⁵, but suggested that the protonated species could be represented best by the structure shewn in fig. XXIV. In this structure it is postulated that



the six π -electrons of the ring are distributed over seven carbon atoms, but that only four of them are involved in the bonding to the iron atom. This is not compatible with the



XXIV.



XXV.

n.m.r. evidence, since in such a structure one would expect

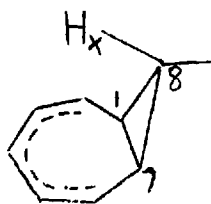
to find the resonances of seven rather than five of the protons at low-field, and only the two methylenic protons should give rise to high field lines. Later Schrauzer⁶⁸ suggested that it was not possible to distinguish between his structure and the one described in this work, and proposed that the actual structure was probably a hybrid with an 85% contribution from the bicyclic structure. Clearly only a measurement of the distance between C_1 and C_7 can settle the matter finally.

Although the bonding of the metal atom to the ligand in protonated tricarbonyl cyclooctatetraene iron will enhance its stability by helping to distribute the surplus positive charge, cyclooctatetraene itself gives a reasonably stable solution in concentrated sulphuric acid.

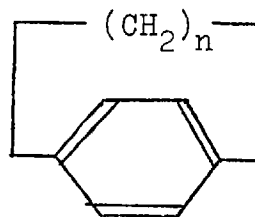
This spectrum has also been obtained by von Rosenberg et al, but these authors did not observe the fine structure found in this work.⁴⁷ These authors also succeeded in making a salt $C_8H_9 SbCl_6^-$ by treating the olefin with hydrogen chloride and antimony pentachloride. A satisfactory interpretation of the spectrum can be made on the basis of the structure shewn in fig. XXV. The lowest band in this spectrum is assigned to the protons of the delocalised system H_2 , H_3 , H_4 , H_5 , and H_6 , and the next group of lines is assigned to the bridgehead protons H_1 and H_7 . This group is a quadruplet

(really a double doublet) because the bridgehead protons have different coupling constants to the two (different) methylene protons on C_8 . One of these protons gives rise to a quartet (really two overlapping triplets arising from the coupling to the other proton C_8 and the bridgehead protons) at high-field, and the other to a pair of overlapping triplets. These two protons have different coupling constants to the bridgehead protons which indicates that the bonds from them to C_8 make different dihedral angles with the bonds to the bridgehead protons.

There is a very large difference (almost 6 p.p.m.) between the chemical shifts of the two protons attached to C_8 . This can be understood if it is assumed that the system is folded along the $C_1 - C_7$ bond as shown in fig. XXVI.



XXVI.



XXVII.

This means that one of the protons (H_x in the diagram) will be held in a position directly above the system of delocalised π -electrons, and will therefore experience considerably increased screening from the ring currents, with a consequent

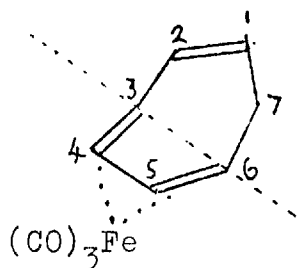
shift of its resonance to a higher field value. This situation is analogous to that which has been observed in the 1,4-polymethylenebenzenes⁴⁸ (see fig. XXVII) in which some of the protons are held in a position directly above the ring. The resonance lines from these protons are in fact found to be shifted to high-field relative to the normal methylene position.

The above argument has considerable relevance to the geometrical configuration of the protonated species derived from tricarbonyl cyclooctatetraene iron, in which the chemical shift between the two methylene protons is small. In general, when a delocalised system of π -electrons is spread over n successive sp^2 hybridised carbon atoms, not only are these atoms all held in the same plane, but so also are two more atoms - one at each end of the chain - so that $n + 2$ atoms in all are maintained coplanar. If the constraints of the remainder of a molecule containing such a system of carbon atoms oppose this effect sufficiently strongly, the delocalised system of π -electrons will usually split into two (or more) such systems, which are twisted about the single bond (still between sp^2 hybridised atoms) joining them, rather than give a single deformed π -system. This is exemplified in cyclooctatetraene where there is no conjugated system, but each double bond is associated with

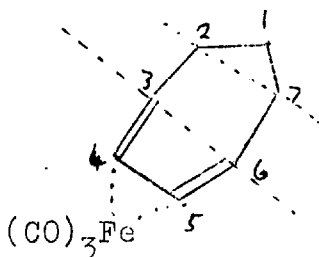
four coplanar carbon atoms.

There is a growing body of evidence that this rule does not apply to unsaturated systems when they are bound to transition metals. Instead the terminal carbon atoms of the chain have a certain degree of sp^3 hybridization, and in a system where the π -electron density is distributed over n carbon atoms, only n carbon atoms need be coplanar. Thus in the case of tricarbonyl cyclooctatetraene iron itself, the butadiene unit which is bound to the metal atom is associated with only four coplanar carbon atoms, whereas the free butadiene unit maintains six carbon atoms in a condition of coplanarity.^{27,28} In the dinuclear species $C_8H_8 Fe(CO)_3$ however, there is no free butadiene unit and there are two folds in the molecule so that the carbon atoms fall into two groups, each containing only four coplanar carbon atoms. This phenomenon is also to be observed in the tricarbonyl iron complexes of tropone and 2,4,6-triphenyl tropone,^{32,33} where C_4 , C_5 , C_6 , and C_7 of the bound butadiene unit form one plane, and C_7 , C_1 , C_2 , C_3 , and C_4 form another. The planarity of the second group of atoms is maintained by the free double bond between C_2 and C_3 , and by the sp^2 hybridization of C_1 which is bound to the ketonic oxygen atom. In all cases so far studied it has been found that the uncoordinated part of the molecule is bent away from the metal atom.

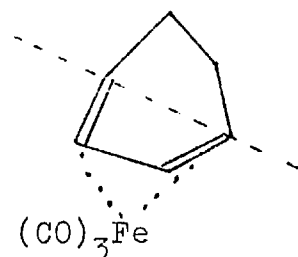
On the preceding hypothesis it can be predicted that the molecular configurations of the tricarbonyl iron complexes of cycloheptatriene, cycloheptadiene and cyclohexa-1,3-diene should be as shewn in figs. XXVIII, XXIX, and XXX, respectively. In the cycloheptatriene complex the



XXVIII.



XXIX.

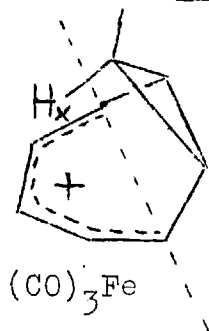


XXX.

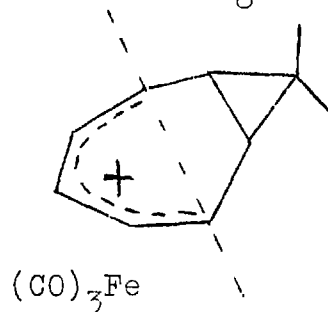
ligand will be folded along a line joining C_3 and C_6 , and the atoms C_3 , C_3 , C_1 , and C_7 (but not necessarily C_6) will be maintained coplanar by the free double bond between C_1 and C_2 . In the cycloheptadiene complex there will again be a fold along $C_3 - C_6$, but there will be no need for the uncoordinated carbon atoms to lie all in the same plane, and one possible conformation for this part of the molecule is indicated in the diagram. The ligand in the cyclohexadiene complex will be folded in a similar way, and its conformation will be not unlike that of free cyclohexene.

It is reasonable to suppose that the organic part in the protonated species derived from tricarbonyl cyclooctatetraene iron will be folded away from the metal

atom along a line joining C_2 and C_6 . In addition to this the cyclopropane ring will be bent either one way or the other in order to minimise the strain at the bridgehead carbon atoms. The two possibilities are illustrated in figs. XXXI and XXXII. In XXXI one (H_x) of the protons on C_8 is



XXXI.



XXXII.

held above the part of the ring which is bound to the iron atom, and is almost embedded in the π -electron cloud, where it would be expected to be exposed to the ring currents and to experience a large shielding effect. The consequence of this should be a large difference between the chemical shifts of the two protons on C_8 - probably greater than that found in protonated cyclooctatetraene itself - but this is not in fact observed. In fig. XXXII the cyclopropane ring is bent in the opposite direction so that neither proton on C_8 is close to the delocalised π -electron system, so that only a small difference between the chemical shifts of the two protons is to be expected. This is what is observed,

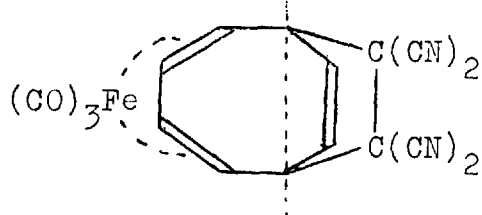
($\Delta \sim 0.2$ p.p.m.) so that it can be concluded that the configuration of the protonated species of tricarbonyl cyclooctatetraene iron is that shown in fig. XXXII.

CHAPTER III.COMPARISON OF THE CYCLOOCTATETRAENE DERIVATIVES
OF IRON, COBALT AND RHODIUM.

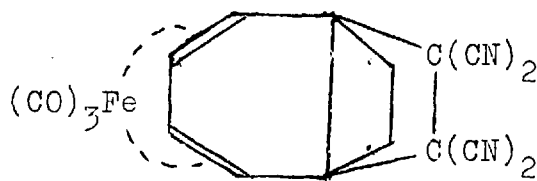
It is evident from its reaction with strong acids that under suitable circumstances tricarbonyl cyclooctatetraene iron can exhibit chemical behaviour shewing that the organic part contains a 1,3-diene system which is not involved in the bonding to the metal atom. This is in spite of previous reports to the contrary.²³ A further example of this kind of behaviour is provided by the reaction of the compound with tetracyanoethylene. Although $C_8H_8Fe(CO)_3$ fails to react with such dieneophiles as maleic anhydride²³ and acetylene dicarboxylic acid (this work), it readily forms a pale yellow diamagnetic adduct with tetracyanoethylene. This adduct contains $C_2(CN)_4$ and $C_8H_8Fe(CO)_3$ in a 1 : 1 ratio, is stable in air, and appears to be insoluble in almost all solvents except concentrated sulphuric acid, in which it gives a deep brown paramagnetic solution with very broad n.m.r. lines. This makes its constitution rather difficult to determine, but it appears that the $C_8H_8Fe(CO)_3$ grouping has not been greatly altered, as the original iron complex can be recovered by reducing a suspension of the adduct in

anhydrous tetrahydrofuran with sodium borohydride.

The mull infra-red spectrum of the adduct shews strong absorption at 2072 and 2012 cm^{-1} which can be attributed to terminal carbonyl stretching modes shifted to higher wave-numbers by the association of the iron with a ligand of greater electron withdrawing power. There is also a weak band at 2250 cm^{-1} which arises from a stretching vibration of the CN groups; these might have been expected to give strong absorption, but the bands from tetracyanoethylene itself in this region are rather weak, and the presence of oxygen in a molecule often markedly reduces the intensity of cyanide absorptions. The weak band at 1670 cm^{-1} is assigned to a free double bond stretching mode, and the weak bands above 2950 cm^{-1} are assigned to tertiary C - H stretching vibrations. The absence of strong absorption near 2860 and 1455 cm^{-1} suggests that the adduct does not contain any methyl or methylene groups. These results indicate that the structure is that of a normal Diels Alder adduct as in fig. XXXIII rather than the tricyclic arrangement of fig. XXXIV where there is no free double bond.



XXXIII.



XXXIV.

The adduct is therefore designated as tricarbonyl 9,9,10,10-tetracyano-bicyclo[4,2,0]deca-2,4,7-triene iron.

The reaction between π -cyclopentadienyl dicarbonyl cobalt and cyclooctatetraene gives the complex $\pi\text{-C}_5\text{H}_5\text{CoC}_8\text{H}_8$ ³⁴ in which the cyclooctatetraene part is believed to adopt a tub conformation, and it was thought to be of interest to prepare the rhodium analogue for the purposes of comparison. π -cyclopentadienyl rhodium complexes of di-olefins can often be made by treating the corresponding halide complex with sodium cyclopentadienide. It happens however, that the cyclooctatetraene complex of rhodium chloride, although known⁴⁹, is rather unstable and difficult to prepare. Accordingly the reaction between cyclooctatetraene and dicarbonyl π -cyclopentadienyl rhodium was used, and the complex was obtained as an air-stable, low-melting solid which was deep yellow in colour - in marked contrast to its cobalt analogue which is dark brown in colour. The absorption band at 1640 cm^{-1} in the infra-red spectrum of the compound indicates that it contains double bonds not involved in the bonding to the rhodium atom.

The proton magnetic resonance spectra of the cobalt and rhodium complexes are shewn in plate II, A and B. They are very similar, and each shews three resonances with intensities in the ratios 4 : 5 : 4. The central line is

LEGEND FOR PLATE II.

The proton magnetic resonance spectra of the π -C₅H₅MC₈H₈ (M = Co or Rh) complexes in CCl₄ at 56.45 mc/s.

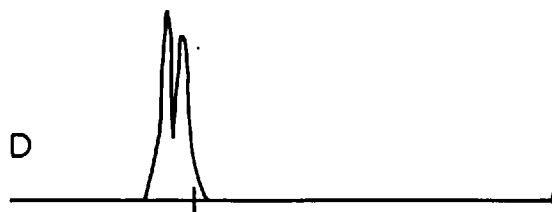
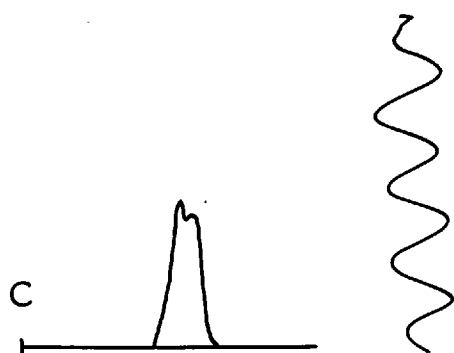
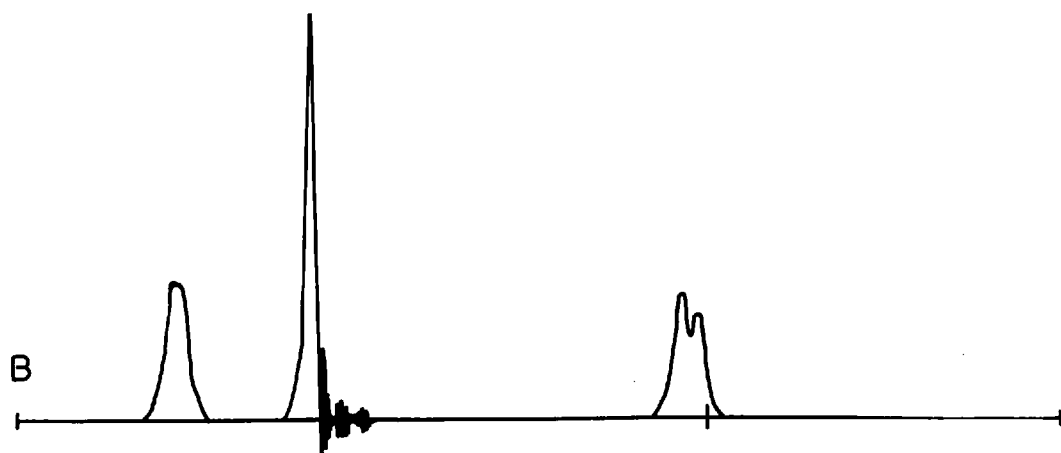
A. π -C₅H₅CoC₈H₈.

B. π -C₅H₅RhC₈H₈.

C. Appearance of the low-field resonance in

π -C₅H₅RhC₈H₈ when the high-field resonance is irradiated.

D. Appearance of the high-field resonance when the low-field resonance is irradiated.

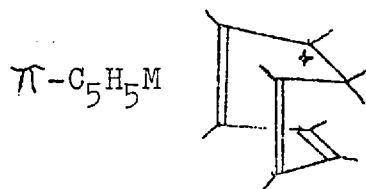


very sharp and is assigned to the protons of the π -bonded C_5H_5 ring. This line is a singlet in the cobalt compound and a closely spaced doublet in the rhodium complex. This splitting arises from the fact that the nucleus of the most abundant isotope has a spin of $\frac{1}{2}$ and is coupled ($J = 0.7$ c.p.s.) to the protons of the π - C_5H_5 ring via the C - H bonds. Larger splittings are found in compounds in which a proton is directly bound to a rhodium atom. The other bands, which are somewhat broad, arise from the protons of the cyclo-octatetraene ring. In contrast to the behaviour observed in the parent olefin the protons in the complex occur in two non-equivalent groups, each containing four protons. This non-equivalence can be understood on the basis of a tub conformation of the bonded olefin ligand. The resonances of the four non-bonded olefinic protons H_3 , H_4 , H_7 , and H_8 occur on the low-field side of the π - C_5H_5 resonance, and the protons H_1 , H_2 , H_5 , and H_6 of the olefin bonds associated with the metal atom give lines on the high-field side. The width of the lines is due in part at least, to spin coupling between the protons of the two groups. This was demonstrated by means of a spin decoupling experiment. In both complexes irradiation at the frequency of one of the groups of intensity 4 produced sharpening of the other, and vice-versa. In the case of the rhodium complex, the sharpening of the low-field

group produced by irradiation of the high-field band revealed a residual doublet structure; this is due to the coupling ($J \sim 1.4$ c.p.s.) between the non-bonded olefinic protons and the ^{103}Rh nucleus. The high-field resonance shows a larger doublet structure, which can be detected in the normal spectrum, which arises from the coupling ($J \sim 2.4$ c.p.s.) of the rhodium nucleus to the four protons of the bonded olefin groups. Irradiation of the specimen at the resonant frequency of the low-field protons, which removes their spin coupling to the high-field ones, made the high-field doublet better resolved without altering the separation of its component lines. Although the coupling constants between the protons of the two different groups in these two compounds could not be measured, they were clearly less than 1 c.p.s.. This is an unusually small coupling constant for protons on adjacent sp^2 hybridised carbon atoms connected by a single bond, and is probably a result of the geometry of the molecule, for there is a twist about each single bond which effectively prevents conjugation and produces a dihedral angle of about 80° between the C - H bonds.

Chemical confirmation of the different structures of, on the one hand the π -cyclopentadienyl cobalt and rhodium complexes of cyclooctatetraene, and on the other the tricarbonyl iron complex of that ligand, is provided by their behaviour

with strong acids. Unlike $C_8H_8Fe(CO)_3$ the cobalt and rhodium complexes give very unstable solutions in strong acids, and most of the lines in the n.m.r. spectra of these solutions are broad, so that only tentative interpretations can be given. The most striking feature of these spectra is that although most of the lines are broad, the line which in each case is assigned to the five protons of the $\pi-C_5H_5$ group is sharp, and so is one other line which is of unit intensity and occurs very close to the $\pi-C_5H_5$ line. It seems most probable that the species present in these acid solutions is that shown in fig. XXXV, and that the sharp line of unit intensity arises from the proton attached to the carbon atom which carries the localised positive charge. It was also



XXXV.

found that certain of the lines in the spectrum of the rhodium complex appeared to display more fine structure than the corresponding lines of the cobalt complex, but it is not possible to say whether this is due to splitting by the ^{103}Rh nucleus, or to somewhat better resolution because less paramagnetic material was produced by the decomposition

of the rhodium complex. Treatment of η -cyclopentadienyl cyclooctatetraene cobalt with hydrogen tetrafluoroborate in acetic or propionic anhydride gave an unstable yellow solid which quickly turned brown. The infra-red spectrum of this solid indicated that it was an ionic tetrafluoroborate, since it showed a strong absorption at 1050 cm^{-1} due to the BF_4^- ion, and there were also some of the peaks characteristic of a η -bonded C_5H_5 group. Further evidence of the absence of a non-bonded 1,3-diene system in the neutral complexes $\eta\text{-C}_5\text{H}_5\text{MC}_8\text{H}_8$ ($\text{M} = \text{Co}$ or Rh) is their inability to give stable Diels Alder adducts with tetracyanoethylene. Instead, slow decomposition occurred.

The instability of these cobalt and rhodium complexes in strongly acid media is presumably due to the inability of the carbonium ion initially formed to rearrange to a form in which the positive charge is delocalised, without first breaking the bonds to the metal atom and thus disrupting the complex. Clearly a mechanism such as that proposed on p. 29 for the protonation of tricarbonyl cyclooctatetraene iron is quite impossible when the metal is bound to the 1,5- positions of the ligand.

It was pointed out in the introduction that there is a discrepancy between the structure of tricarbonyl cyclooctatetraene iron obtained by an X-ray investigation^{27,28}

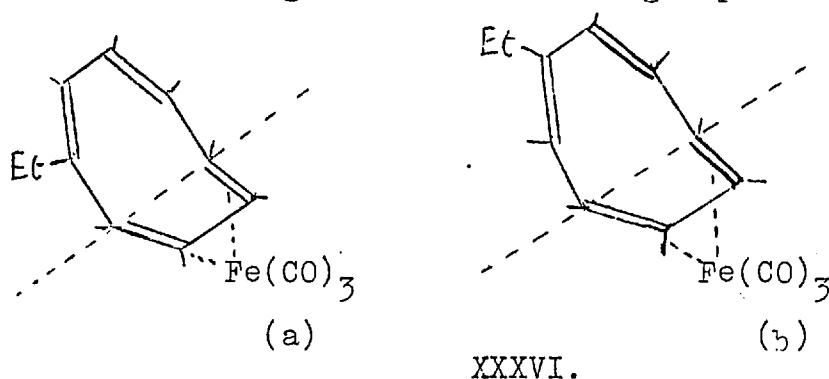
of the solid, and that which would be expected from n.m.r. measurements of solutions of the compound. It is generally supposed that some kind of exchange phenomenon is responsible, and in the hope of reducing the rate of this process sufficiently for the protons in the different environments to give separate resonances, the spectrum of a solution of the compound in carbon disulphide was measured at -60° . The only change noticed was that the width of the single line became about 2 c.p.s.; this was probably due to the difficulty in maintaining the field adequately homogeneous at this temperature. The measurement was made at a radiofrequency of 40 mc/s. and if it is assumed that in the absence of exchange, protons in the environments found by X-ray diffraction would give signals over a range of at least 2 p.p.m., it follows that the lifetime of the individual species is less than $1/80$ sec. at -60° . This means that the lifetime at ordinary temperature will probably be less than $1/20,000$ sec., so that in order to observe more than one line at 20° it would be necessary to use a measuring frequency of at least 10^4 mc/s. and a magnetic field strength of more than $1\frac{1}{2}$ million gauss.

The proton magnetic resonance spectrum of tricarbonyl cyclooctatetraene iron has been measured in a wide variety of solvents, and in none has more than one resonance line been observed, so it seems unlikely that the solvent plays a major

part in the exchange process. However, in order to test this, the spectrum of the pure substance was measured at 100° at which temperature it is molten. Of course, the rate of any exchange processes will be greatly increased at this temperature, but fortunately it was possible to super-cool the melt to below its normal freezing point of 98° and to obtain a spectrum down to 35° . Once again only one line was observed.

The reaction between dodecacarbonyl tri-iron and ethyl cyclooctatetraene was investigated to determine whether tricarbonyl iron complexes of substituted cyclooctatetraenes shewed a similar apparent equivalence of protons in their n.m.r. spectra. Two products were obtained from the reaction which could be separated by fractional crystallization, but not by chromatography. One of these was a yellow powder which gave very variable analytical results, but which appeared from spectral data to contain carbonyl and ethyl groups. The other, and major product was an air-stable red oil which froze at -20° , and whose analysis agreed with the formulation $C_2H_5C_8H_7Fe(CO)_3$. The infra-red spectrum of this compound has intense bands in the region of 2000 cm^{-1} in the pattern characteristic of $Fe(CO)_3$ groupings; there was no absorption near 1630 cm^{-1} which is normally associated with free olefinic bonds. The proton magnetic resonance spectrum of the parent ethyl cycloocta-

tetraene shows lines due to the ethyl group at high-field, and only a single rather broad line at low-field which arises from the protons of the ring. This approximate equivalence of the ring protons is destroyed in the tricarbonyl iron complex, and the low-field protons give resonances over a range of about 2 p.p.m.. The spectrum is reproduced in plate III, A., and is interpreted on the basis of one of the structures shown in fig. XXXVI. The two groups of lines



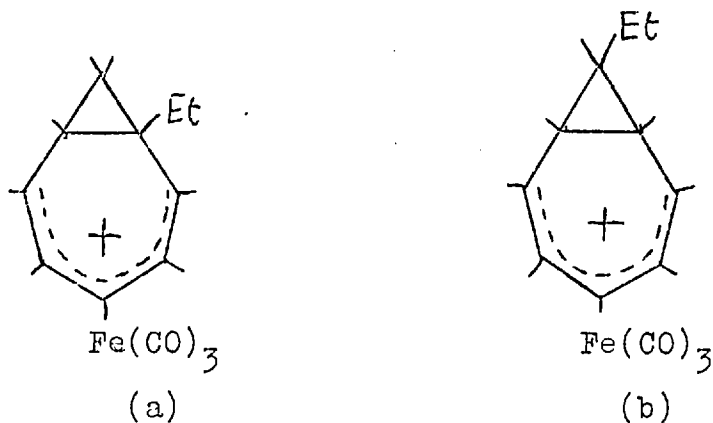
at highest field arise from the ethyl group, and the coupling between the methylene protons of this group and the adjacent ring protons is very small. The group of lines at lowest field arises from the three protons associated with the non-bonded diene system; the other two groups arise from the inner and outer protons of the bonded diene system. It was not possible to distinguish on the basis of this spectrum between structures (a) and (b).

The chemical properties of tricarbonyl ethylcyclooctatetraene iron are similar to those of its unsub-

stituted cyclooctatetraene analogue. It reacts with tetracyanoethylene to give a 1 : 1 adduct which is rather less insoluble than that obtained from $C_8H_8Fe(CO)_3$, although no n.m.r. spectrum could be recorded. A band in the infra-red spectrum of the adduct at 1660 cm^{-1} indicates the presence of a free double bond, and there is also absorption near 2845 cm^{-1} shewing that methylene or methyl protons are also present. Treatment of the neutral complex with tetrafluoroboric acid in propionic anhydride gives a yellow solid which is reasonably stable in dry air. The infra-red spectrum of this solid indicates that it is an ionic tetrafluoroborate like that which can be made by the protonation of $C_8H_8Fe(CO)_3$, since there is a band at about 1050 cm^{-1} , and the carbonyl absorptions shew the increase in wavenumber to be expected in a positively charged complex.

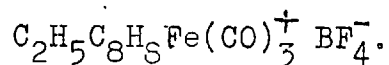
The proton magnetic resonance spectrum of a solution of the salt in liquid sulphur dioxide is the same as that of the original complex in concentrated sulphuric acid. It shews a line of unit intensity at low-field which can be attributed to the middle proton of the delocalised system, a band near $\tau = 5$ which arises from the other protons of the delocalised system, and an extended band at high-field which is due to the protons of the cyclopropane ring overlapping those of the ethyl group. It is not possible to tell from

the spectrum which of the structures shewn in fig. XXXVII is adopted by the protonated system, and possibly both are present.



XXXVII.

The rather low stability of this compound, compared with that derived from $C_8H_8Fe(CO)_3$, prevented a completely satisfactory analysis from being obtained, but the results agreed fairly well with the formulation

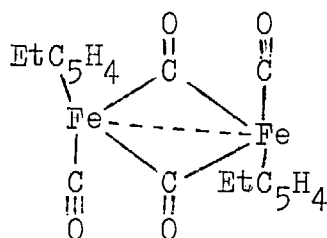


CHAPTER IV.THE PROTONATION OF VARIOUS METAL-OLEFIN COMPLEXES.

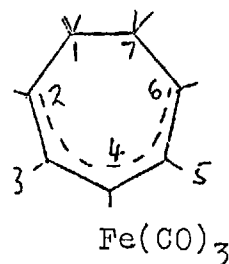
The behaviour with strong acids of a variety of metal-olefin complexes besides the derivatives of cyclo-octatetraene has also been investigated, although in most cases the results have been less definite.

The reaction of tricarbonyl cycloheptatriene iron with halogen acids to give the cation $C_7H_9Fe(CO)_3^+$ was first noted by Burton *et al*¹⁶. This cation was subsequently prepared by Dauben *et al*¹⁷ as a tetrafluoroborate salt, both by the protonation of tricarbonyl cycloheptatriene iron with hydrogen tetrafluoroborate in propionic anhydride, and by hydride abstraction from tricarbonyl cycloheptadiene iron with triphenylmethyl tetrafluoroborate in dichloromethane. In the course of this work it has been found that this last reaction is reversible, for treatment of a suspension of the tetrafluoroborate in anhydrous tetrahydrofuran with sodium borohydride gave a solution from which it was possible to isolate the cycloheptadiene complex. A sparingly soluble purple compound was also obtained in this reaction, and although insufficient was obtained for analysis it appeared to be a super-sandwich type of compound like that indicated in

fig. XXXVIII, since its infra-red spectrum shewed the presence of both terminal and bridging carbonyl groups, and its n.m.r. spectrum shewed resonances characteristic of ethyl and substituted η -cyclopentadienyl groups. Furthermore the compound dissolved in concentrated sulphuric acid to give a stable solution whose n.m.r. spectrum shewed a resonance with a τ -value of about 36. This behaviour resembles that displayed by a number of species containing metal - metal bonds.³⁹



XXXVIII.



XI..

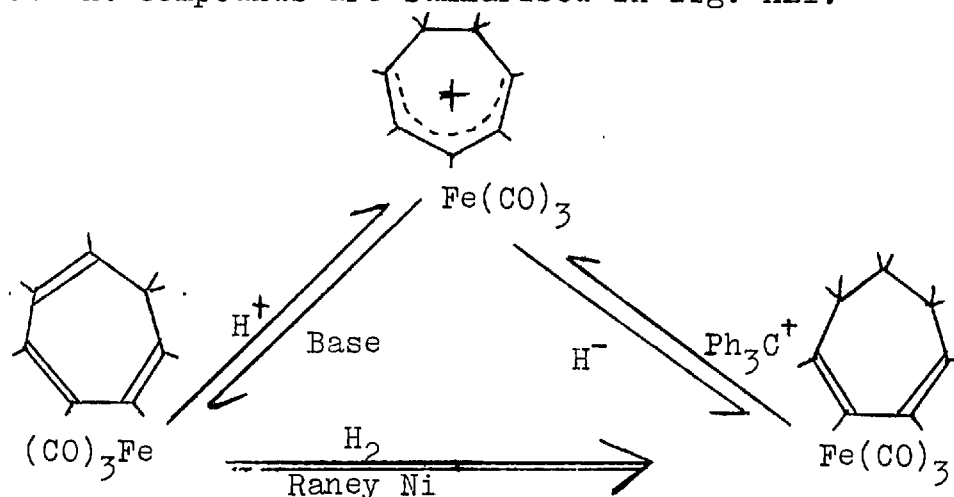
The formation of a substituted η -cyclopentadienyl super-sandwich type of compound has also been observed in the course of this work during the preparation of tricarbonyl cycloheptatriene molybdenum from cycloheptatriene and hexacarbonyl molybdenum, and a number of similar compounds have been reported by Singh.⁵⁰ In the present case a metal hydride is probably involved as an intermediate.

The proton magnetic resonance spectra of solutions of tricarbonyl cycloheptatriene iron in trifluoroacetic and concentrated sulphuric acids, and of the complex tetrafluoro-

borate salt in liquid sulphur dioxide are identical, except for small solvent shifts of the line positions. This spectrum and that of the complex dissolved in dideuterosulphuric acid are shown in plate I, E and F, and can be interpreted on the basis of the structure shown in fig. XL. The three bands at lowest field are identical in the protonated and deuterated species and arise from the protons H_4 , H_3 and H_5 , and H_2 and H_6 , respectively. The two bands at high field are assigned to the methylene protons on C_1 and C_7 . In the deuterio-species the lower of these two bands shows less fine structure than in the protonated species, and the higher band is of unit intensity and remains so for several hours.

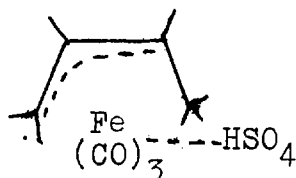
This means that the proton (deuteron) which becomes attached by protonation (deuteration) of the free double bond of $C_7H_8Fe(CO)_3$ to give one of the methylene groups is not involved in chemical exchange with the protons (deuterons) of the solvent. Since the parent $C_7H_8Fe(CO)_3$ is not regenerated when the solutions in concentrated acid are diluted, but only when they are neutralized by base, (cf. the behaviour of the tricarbonyl bicyclo[5,1,0]octadienyl iron cation in concentrated sulphuric acid) it is unlikely that exchange occurs on dilution. This was confirmed by diluting a solution of the $C_7H_9Fe(CO)_3$ ion in concentrated sulphuric acid to about 1N with deuterium oxide

and allowing the mixture to stand for 30 mins.. Ammonium hexafluorophosphate was then added and it was found that the n.m.r.spectrum of a solution in liquid sulphur dioxide of the complex hexafluorophosphate which precipitated was identical with that of the original protonated cation in the acid. Similarly, the hexafluorophosphate obtained from a solution of $C_7H_8DFe(CO)_3$ in dideuterosulphuric acid which had been diluted with water and allowed to stand, had a spectrum identical with that of $C_7H_8DFe(CO)_3$ in D_2SO_4 . Thus the protonation is irreversible in acid media and is stereospecific. Tricarbonyl cycloheptatriene iron can also be converted into the diene complex without the intervention of a cationic intermediate by reduction with hydrogen in the presence of a Raney nickel catalyst, and the relations between the compounds are summarised in fig. XLI.

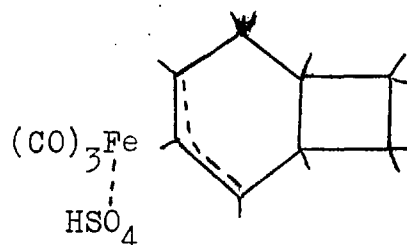


XLI.

The proton magnetic resonance spectrum of a solution of tricarbonyl butadiene iron in concentrated sulphuric acid shews a series of bands at low field, and also a line of relative intensity 3 with the unusually high γ -value of 16.9. At first it was thought that this might be due to the formation of a hydridic species, although this seemed unlikely in view of the large intensity of the band, and the fact that in trifluoroacetic acid it occurs at a γ -value of about 12. It is now clear from the work of Impastato and Ihrman⁵¹ and others⁵² on the reaction between hydrogen chloride and $C_4H_6Fe(CO)_3$ that the species involved is a π -allylic derivative of iron with the structure shewn in fig. XLII.



XLII.



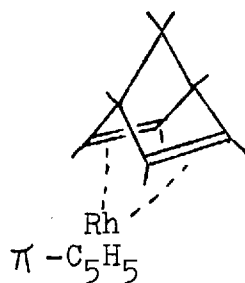
XLIII.

The unusually high γ -value observed for the resonance of the methyl protons in the sulphuric acid solution, compared with the more normal value found by the above workers in the chloro-complex, is probably due to the lower coordinating power of the HSO_4^- ion which results in a certain deficit of electronic charge on the iron atom and so leads

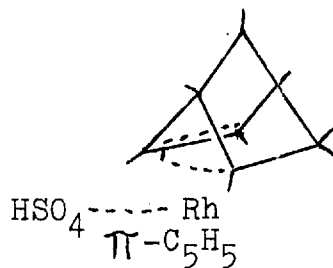
to slight paramagnetism. Tricarbonyl bicyclo[4,2,0]octa-2,4-diene iron can be regarded as a substituted butadiene complex, and the n.m.r. spectrum of its solution in concentrated sulphuric acid also shews a line at unusually high field. The spectrum can be interpreted on the basis of the structure shewn in fig. XLIII.

Other complexes whose reactions with strong acids were examined included the cycloheptatriene complexes of the group VI metal carbonyls, and the norbornadiene complexes of these metals and iron. In all cases n.m.r. spectra were obtained whose lines were so broad that they gave little information about the protonated species. As it was thought that the stability of the protonated species might depend upon the presence of a strongly π -bonding ligand in the molecule, the complex π -cyclopentadienyl norbornadiene rhodium was prepared by treatment of the norbornadiene rhodium chloride dimer with sodium cyclopentadienide. The compound is an air-stable yellow solid whose n.m.r. spectrum is consistent with the structure shewn in fig. XLIV. The line at highest field is a triplet and is assigned to the pair of methylene protons split by the bridgehead ones. The resonances of the remaining protons of the norbornadiene part overlap to give a complex band, and the protons of the π -C₅H₅ ring give a closely spaced doublet as a result of coupling to

the ^{103}Rh nucleus. The spectrum of a solution of the complex



XLIV.



XLV.

in concentrated sulphuric acid was very poorly resolved and no definite conclusions about the nature of the protonated species could be drawn. However, the shape of the high-field triplet was unchanged from its appearance in the uncharged complex, indicating that the methylene protons and the bridgehead protons (which cause the splitting) are unaffected by protonation. The probable structure of the protonated species is therefore that shown in fig. XLV. in which a π -allylic system is formed from three of the original olefinic carbon atoms.

In general, it seems that the stability of protonated metal olefin complexes depends upon the ability of the complex to distribute the positive charge which it acquires over as many atoms (including the metal and other ligand atoms) as possible. This ability is increased by the presence in the molecule of strongly π -bonding ligands, and

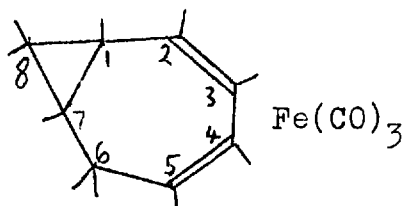
so is often paralleled by the air-stability of the complex: it is lower when the geometry of the olefin (in the complex) is such as to prevent electronic interaction between those double bonds which are involved in the bonding to the metal atom and those which are not.

CHAPTER V.CYCLOOCTATRIENE COMPLEXES OF IRON AND COBALT.

Confirmation of the bicyclic structure assigned to the cation $C_8H_9Fe(CO)_3^+$ was obtained by reducing it with sodium borohydride. When this reaction was performed in anhydrous tetrahydrofuran under fairly mild conditions it was possible to isolate from the reaction mixture a yellow, somewhat air-sensitive crystalline complex of composition $C_8H_{10}Fe(CO)_3$. The infra-red spectrum of this compound has absorptions in the region $3100 - 2700\text{ cm}^{-1}$ which can be ascribed to secondary and tertiary C - H groups, but there is no absorption in the region of 1630 cm^{-1} which is normally associated with free double bonds. The very strong bands in the neighbourhood of 2000 cm^{-1} are attributed to the terminal C - O stretching vibrations of the $Fe(CO)_3$ -grouping.

The proton magnetic resonance spectrum of the compound shews seven complex bands and is reproduced in plate I, D. A satisfactory assignment can be made on the basis of the formulation of the compound as tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron as in fig. XLVI. The bonding of the iron atom to the conjugated diene leads to a separation of the proton resonances of the coordinated olefin into high- and low-field groups; their positions are close to those which

have been previously observed in similar diene complexes of iron.⁴¹ The band at lowest field arises from the two central protons H_3 and H_4 of the diene group. These protons are almost equivalent. The terminal diene protons are not equivalent:

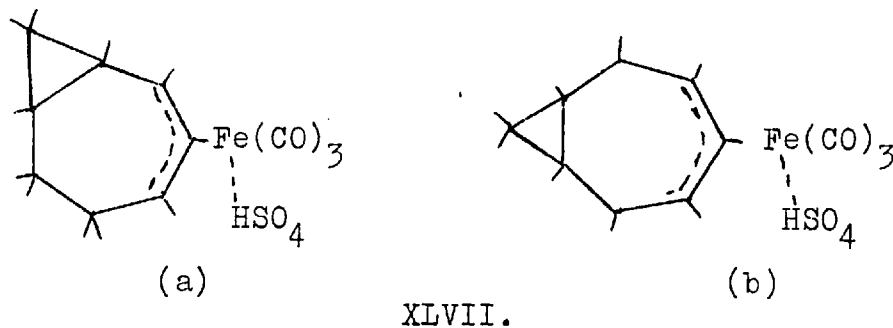


XLVI.

one of them (H_2 , at $\tau = 6.7$) is next to the single bridgehead proton H_1 and shews less fine structure than the other (H_5 , at $\tau = 7.3$) which is adjacent to the methylene group of C_6 . This methylene group gives the band at $\tau = 8.06$, and the bands at highest field arise from the bridgehead and methylene protons of the cyclopropane ring. Some of these assignments were confirmed by spin decoupling experiments, but the electronic formation of strong sidebands of the resonance line from the benzene used as solvent confused the spectrum and made a complete check impossible.

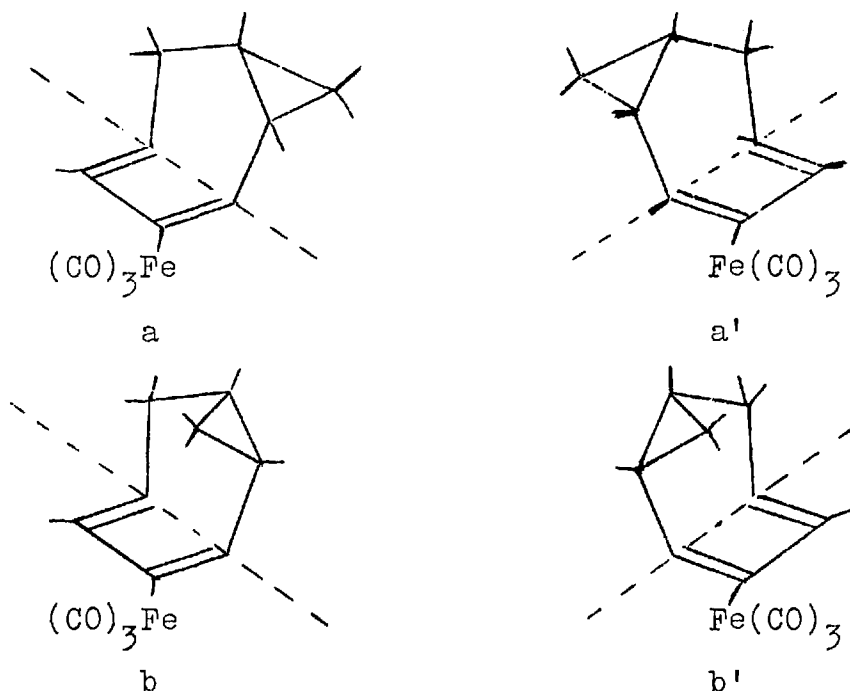
The n.m.r. spectrum of the complex dissolved in trifluoroacetic or concentrated sulphuric acid shewed that in these media it behaves like tricarbonyl butadiene iron and forms a π -allylic system. The spectra were insufficiently well resolved to enable a distinction between structures

(a) and (b) of fig. XLVII to be made, although the second seems to be less likely as its higher symmetry is not reflected in the observed spectrum.



As in the case of the protonated species derived from tricarbonyl cyclooctatetraene iron, it is possible to visualize two geometrical isomers of the complex according as the cyclopropane ring is bent towards or away from the coordinated diene system of the ligand. Furthermore, the ligand in this neutral complex will enjoy a greater degree of conformational mobility than in the charged species, since the fold will now be along a line joining C_2 and C_5 , so that the range of positions that C_6 can take up will be less restricted. It is not possible to say with certainty which of the two structures is in fact adopted, but the closeness of the nuclear magnetic resonance lines from the cyclopropane ring is in favour of structure (a) of fig. XLVIII in which this ring is bent away from the bonded diene group. Each geometrical isomer will exist in two enantiomorphous forms

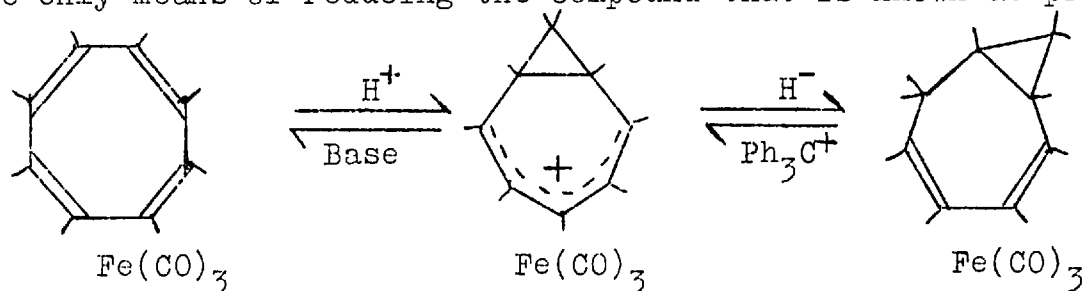
and these are all illustrated in the diagram; no attempt at resolution was made.



XLVIII.

Treatment of tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron with triphenylmethyl tetrafluoroborate in dichloromethane results in the gradual precipitation of tricarbonyl bicyclo[5,1,0]octadienyl iron as pale yellow crystals whose infra-red and n.m.r. spectra were identical to those of an authentic specimen of the salt prepared by the protonation of tricarbonyl cyclooctatetraene iron. Since the cationic species can be converted into the original $C_8H_8Fe(CO)_3$ by treatment with base, the processes shewn in fig. XLIX constitute a two-stage stereospecific reversible

hydrogenation of tricarbonyl cyclooctatetraene iron. It has been shown²³ that this compound, unlike tricarbonyl cycloheptatriene iron, cannot be hydrogenated to give organometallic compounds directly, and the following processes are the only means of reducing the compound that is known at present.



XLIX .

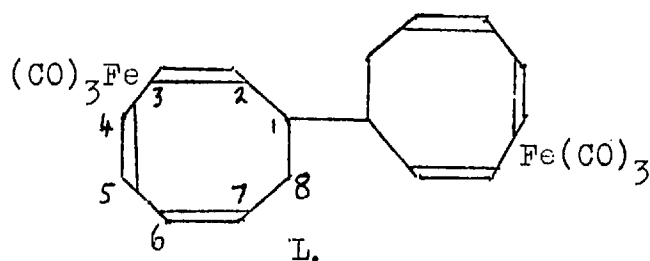
When the reduction of tricarbonyl bicyclo[5,1,0]octadienyl iron is performed under rather more severe conditions, e.g. in the presence of lithium chloride and/or water, the yield of tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron falls markedly, and in addition a variety of other organometallic derivatives of iron are produced. These include the tricarbonyl iron complexes of cyclooctatetraene itself, of bicyclo[4,2,0]octa-2,4-diene, and of a cyclooctatriene which will be discussed later; and a compound of stoichiometry $\text{C}_{22}\text{H}_{18}\text{Fe}_2\text{O}_6$. This last compound has also been found as one of the products of the reactions between the complex tetrafluoroborate and methyl lithium and phenyl lithium. These two reactions were performed in the hope of obtaining complexes such as

$\text{RC}_8\text{H}_9\text{Fe}(\text{CO})_3$ ($\text{R} = \text{Me}$ or Ph) but although they probably formed, their isolation was prevented in the first case by decomposition, and by polymerization in the second. Another route to this kind of complex which was investigated was the reduction with sodium borohydride of tricarbonyl ethylcyclo-octatetraenium iron tetrafluoroborate, but the product again decomposed.

The dimeric compound which was formed in these reactions is an air-stable yellow solid which decomposes without melting, and which is sparingly soluble in common organic solvents. Its infra-red spectrum has bands in the region of 2000 cm^{-1} in the pattern to be expected from a complex containing two (or any other number) of symmetrically disposed tricarbonyl iron residues. There is no absorption in the bridging carbonyl region, but there is a weak band at 1640 cm^{-1} which indicates the presence of free double bonds. These properties suggest that the complex might be formed by coupling together two $\cdot\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3$ groups (considerable amounts of biphenyl were formed in the reaction between PhLi and $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+ \text{BF}_4^-$), and this was confirmed by its formation in fair yield when a mixture of the complex tetrafluoroborate and zinc dust were refluxed in tetrahydrofuran for several hours.

The proton magnetic resonance spectrum, which is

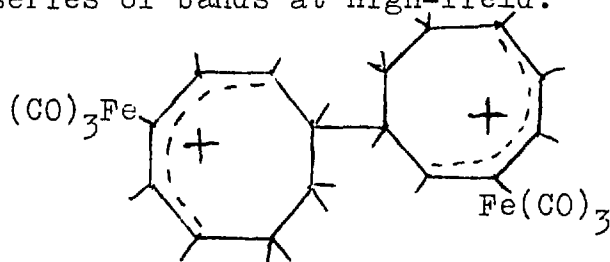
reproduced in plate III, B, is in agreement with this, and the complex can be formulated as hexacarbonyl bi(cycloocta-2,4,6-trienyl) di-iron as shewn in fig. L. (The nomenclature used will be explained later.) The band at lowest



field is assigned to the free olefinic protons and is in the normal position; the next band is complex and arises from the inner protons of the bound diene group. The outer bound diene protons are non-equivalent and give separate signals. H_2 is adjacent to the single proton on C_1 (the bridging carbon atom) and its resonance therefore displays less fine structure than that of H_5 which is coupled to the free olefinic protons. The tertiary proton H_1 and the methylene protons on C_8 give rise to the part of the spectrum at highest field.

This dimeric complex gave reasonably stable solutions in trifluoroacetic and concentrated sulphuric acids, but no protonated species could be isolated by the usual method as the compound was insufficiently soluble in propionic anhydride. The proton magnetic resonance spectrum of the acid solution is in agreement with the structure shewn in fig. LI

for the protonated species. The triplet at lowest field arises from the central proton of the delocalised system; the remaining protons of this system give the other two bands at low field. The protons attached to C₁, C₇, and C₈ give a complex series of bands at high-field.

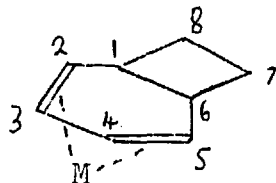


LI.

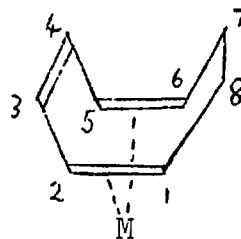
The complexes so far described in this chapter can be regarded as derivatives of cyclooctatriene, and since discrepant results had been reported for the direct reactions between this ligand and various metal carbonyls, it seemed worthwhile to reinvestigate some of these reactions. The reduction of cyclooctatetraene with zinc dust and sodium hydroxide gives a mixture of cycloocta-1,3,5-triene, cycloocta-1,3,6-triene, and bicyclo 4,2,0 octa-2,4-diene in amounts which vary from preparation to preparation and which depend upon the duration and vigour of the reaction. The exact proportions of the constituents of the mixture are not important in the present context since isomerization takes place readily when the mixture is heated with metal carbonyl compounds. Fig. LII shews some of the complexes that might

be formed when one of these cyclooctatrienes becomes associated with a metal able to combine with a di-olefin.

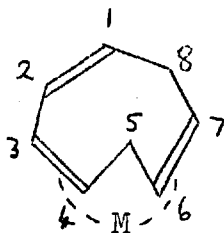
($M = -Fe(CO)_3$ or $\eta-C_5H_5Co-$).



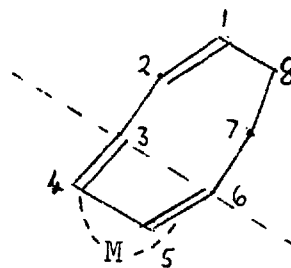
i. Bicyclo[4,2,0]octa-2,4-diene-.



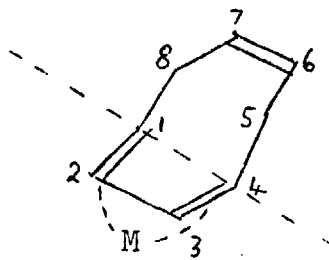
ii. Cycloocta-1,3,5-triene-.



iii. Cycloocta-1,3,6-triene-.



iv. Cycloocta-1,3,5-triene-.



v. Cycloocta-1,3,6-triene-.

LII.

All but one of these complexes have a free double bond which is not involved in the bonding to the metal atom, and the following nomenclature has been devised

for distinguishing in such cases between the bound and free double bonds:⁵³ (a) The ring is numbered in accordance with the standard organic procedure for such systems; (b) The number corresponding to the free double bond is underlined or printed in bold-faced type; (c) Where there is no conflict with rule (a) the number in bold-faced type is made as small as possible; (d) If a choice still remains the sum of the numbers in bold-faced type is minimised. According to this nomenclature the cyclooctatetraene derivative of $-\text{Fe}(\text{CO})_3$ is tricarbonyl cycloocta-1,3,5,7-tetraene iron, and the derivative of $\pi\text{-C}_5\text{H}_5\text{Co-}$ is π -cyclopentadienyl cycloocta-1,3,5,7-tetraene cobalt.

In contrast to previous work,⁵⁴ it has been found that the reaction between the cyclooctatriene mixture and π -cyclopentadienyl dicarbonyl cobalt gives two products, which can be separated by chromatography, in proportions which depend on the temperature and duration of the reaction. Under mild conditions or with short reaction times the principal product is the deep red solid with structure (i) ($\text{M}=\pi\text{-C}_5\text{H}_5\text{Co-}$) of fig. LII which was obtained by the previous workers, although the proton magnetic resonance spectrum they obtained was poorly resolved and not wholly conclusive. The present measurements confirm that the structure of the compound is indeed that shown in (i), for

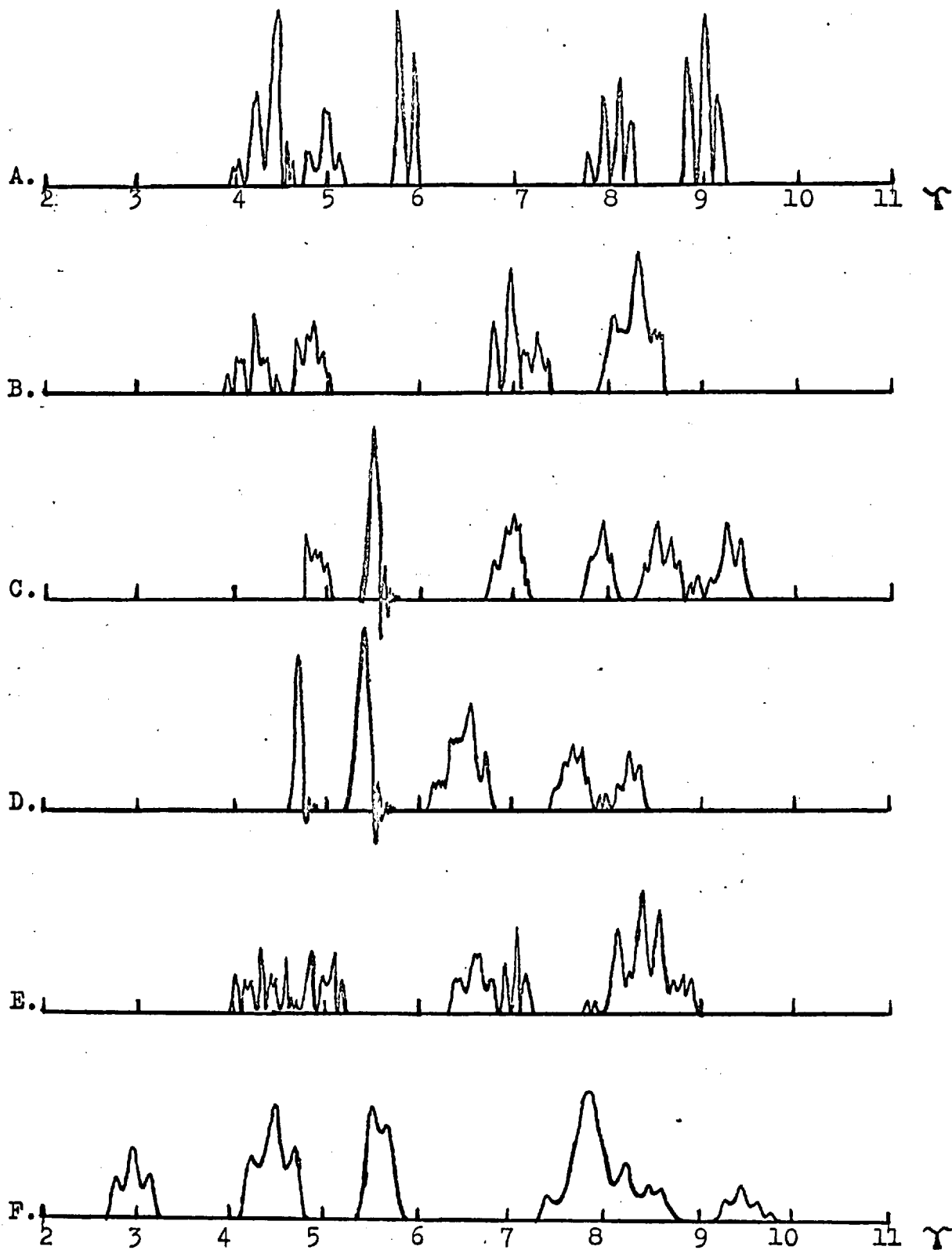
the n.m.r. spectrum is almost identical with that of the corresponding tricarbonyl iron complex,¹⁶ with the addition of an extra line of relative intensity 5 due to the $\pi\text{-C}_5\text{H}_5$ group. This spectrum is reproduced in plate III, C. The resonances from the bound diene system are divided into two groups which correspond to the inner and outer protons, and the line from the $\pi\text{-C}_5\text{H}_5$ group falls between them. The resonance from the bridgehead protons lies at $\tau=7.7$, and the high-field band arises from the methylene protons of the cyclobutane ring. This assignment is confirmed by the infra-red spectrum of the compound which shews no absorption in the region normally associated with free olefin groups.

If the reaction is allowed to proceed for a longer time, or the conditions are more severe, the main product is a golden brown air-stable solid, whose infra-red spectrum shews a weak band at 1618 cm^{-1} which can be ascribed to the presence of a free double bond in the molecule. The analysis of the compound is in agreement with its formulation as a cyclooctatriene complex of cyclopentadienyl cobalt, $\pi\text{-C}_5\text{H}_5\text{CoC}_8\text{H}_{10}$. The proton magnetic resonance spectrum is reproduced in plate III, D, and a satisfactory assignment of the lines can be made on the assumption that the complex is π -cyclopentadienyl cycloocta-1,3,5-triene cobalt as in fig. LII, (ii). The line at lowest field arises from the

LEGEND FOR PLATE III.

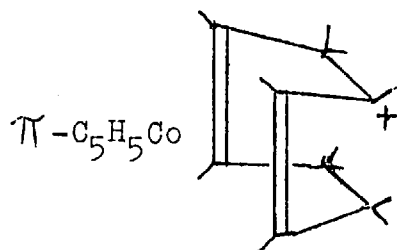
Proton magnetic resonance spectra of various metal-olefin complexes recorded at 56.45 mc/s..

- A. Tricarbonyl ethylcyclooctatetraene iron in CCl_4 .
- B. Hexacarbonyl bi(cycloocta-2,4,6-trienyl) iron in CS_2 .
- C. π -cyclopentadienyl bicyclo[4,2,0]octa-2,4-diene cobalt in CCl_4 .
- D. π -cyclopentadienyl cycloocta-1,3,5-triene cobalt in CCl_4 .
- E. Tricarbonyl cycloocta-1,3,5-triene iron in CS_2 .
- F. Tricarbonyl cyclooctadienyl iron tetrafluoroborate in liquid SO_2 .

PLATE III.

protons of the free double bond, and is sharp because of the small value of the coupling constant between these protons and the adjacent protons of the bound olefinic groups. This small coupling constant arises in the same way as that observed in the cyclooctatetraene complexes of cobalt and rhodium, and is a consequence of the large (c. 80°) dihedral angle between the C - H bonds at opposite ends of the C - C single bonds. The π -C₅H₅ group gives rise to the sharp singlet at $\tau = 5.45$, and the resonance of the bound olefinic protons occurs at $\tau = 6.46$, thus shewing the increase in shielding expected from the association with the metal atom. The high-field part of the spectrum arises from the methylene protons on C₇ and C₈.

The complex is very soluble in concentrated sulphuric acid to give a moderately stable solution, although no salts could be isolated. The n.m.r. spectrum of this solution is consistent with the protonated species having the structure shewn in fig. LIII. As in the cases of π -C₅H₅CoC₈H₉⁺



LIII.

and $\pi\text{-C}_5\text{H}_5\text{RhC}_8\text{H}_9^+$, the lines arising from the $\pi\text{-C}_5\text{H}_5$ group and the proton attached to the carbon atom which carries the positive charge are much sharper than the remainder of the spectrum. The refusal to give a stable protonated species containing a delocalised π -electron system is again probably due to the need to partially destroy the bonding to the metal atom in order to accomplish this.

The reaction between the cyclooctatriene mixture and iron carbonyl was first described by Fischer and co-workers⁷⁴ who obtained an orange oil of composition $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$ and yellow crystals of stoichiometry $\text{C}_{15}\text{H}_{12}\text{Fe}_2\text{O}_6$. Very recently King⁵⁶ has reported that a complex of composition $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_6$ can be obtained from this reaction, and it seems likely that this is identical with the compound described by the earlier workers, in spite of the discrepancy in the analytical data. It is claimed that this dinuclear species contains an Fe - Fe bond, but the evidence upon which this is based is not available at the time of writing.

On the basis of a comparison of the infra-red spectra of the complex and the free ligand it was suggested that the compound $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$ was a derivative of cyclo-octa-1,3,6-triene, although it was not stated whether structure (iii) or (v) of fig. LII was envisaged. It was pointed out by Manuel and Stone however,²³ that the compound does not

absorb hydrogen or bromine, and that its infra-red spectrum had no bands which could be attributed to a free double bond. It was therefore proposed that the complex was a derivative of bicyclo[4,2,0]octa-2,4-diene which is the isomer of cyclooctatriene whose stability is greatest at higher temperatures. This suggestion was confirmed by Burton et al¹⁶ who gave a complete interpretation of the proton magnetic resonance spectrum.

Manuel and Stone⁵⁷ found that under certain conditions the reaction between the cyclooctatriene mixture and dodecacarbonyl tri-iron gave a complex of composition $C_8H_{10}Fe(CO)_3$ which could be hydrogenated in the presence of a catalyst. This suggested that the complex had a free double bond in its structure, and since cycloocta-1,3,5-triene is thermodynamically more stable than the 1,3,6-isomer, it was proposed that this complex was a derivative of the isomer with adjacent double bonds. This argument seems to be of doubtful validity in view of the work described earlier in this chapter which shews that the cycloocta-1,3,5-triene complex of ~~cyclopentadienyl~~ cobalt is more stable than the bicyclooctadiene derivative, although the stabilities of the free olefins are in the opposite order. Furthermore, studies of certain olefin complexes of silver have shewn that the stability of the complex increases with decreasing stability of the ligand.^{58,60}

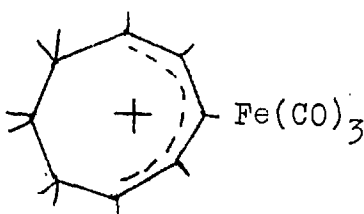
In this work it has been found that the products of the reaction between dodecacarbonyl tri-iron and the cyclo-octatriene mixture are critically dependent on the temperature and duration of the reaction, and probably also upon the particle size and freshness of the carbonyl used. At temperatures greater than 110° or with reaction times longer than $\frac{1}{2}$ hour the main product is tricarbonyl bicyclo[4,2,0]octa-2,4-diene iron; under milder conditions a somewhat air-sensitive yellow-orange oil is obtained which has the same stoichiometry as the bicyclic compound, but which can be separated from it by chromatography. The infra-red spectrum of this complex has the usual pattern of bands near 2000 cm^{-1} to be expected from an $-\text{Fe}(\text{CO})_3$ group, and there is also a weak band at 1636 cm^{-1} indicating the presence of a double bond which is not associated with the metal atom.

The proton magnetic resonance spectrum of the complex is reproduced in plate III, E and is consistent with the formulation tricarbonyl cycloocta-1,3,5-triene iron as in fig. LII (iv) with $\text{M} = -\text{Fe}(\text{CO})_3$. The resonances from the free olefinic protons and the inner bound diene protons overlap slightly in the range $\tau \approx 4 - 5$. The two non-equivalent outer protons of the bound diene group give separate resonances which shew different amounts of fine structure. The low-field part of the spectrum described above makes it

possible to distinguish between the structures in which the double bonds associated with the metal atom are conjugated and the structures in which they are not. In the latter case the resonances of the bound olefinic protons would all occur close together in the region $\tau=6 - 6.5$. Structures (ii) and (iii) of fig. LII can thus be eliminated. In structure (v) the outer protons of the bound diene system are in identical environments, so the observed non-equivalence of these protons eliminates this structure. The assignment of the spectrum to structure (iv) was confirmed by a spin decoupling experiment in which it was demonstrated that one of the outer bound diene protons (H_3) is coupled to the free olefinic protons but not to the methylene protons. It was also shown that the other outer proton (H_6) of the bound diene system is not coupled to the protons of the free double bond, but is coupled to one of the methylene protons on C_7 . This last feature can be understood when a model of the system is examined, for it is found that the bond $C_6 - H_6$ makes a dihedral angle of almost 90° with one of the $C_7 - H$ bonds (thus giving a very small coupling constant), and a fairly small angle with the other. The complex band in the high-field part of the spectrum arises from the methylene protons on C_7 and C_8 .

Solutions of the complex in trifluoroacetic and

concentrated sulphuric acids are stable, and a stable tetrafluoroborate can be obtained by treatment with tetrafluoroboric acid in propionic anhydride in the usual way. The infra-red spectrum of this salt shewed that the carbonyl frequencies are raised by about 70 cm^{-1} as expected for the influence of the positive charge on the complex ion. The proton magnetic resonance spectrum of a solution of the tetrafluoroborate in liquid sulphur dioxide is the same as that of the neutral complex in strong acids, and is reproduced in plate III, F. It resembles the spectrum of the protonated species derived from hexacarbonyl bi(cyclo-2,4,6-trienyl) di-iron and is consistent with protonation of the free double bond followed by delocalisation of the positive charge to give the tricarbonyl cyclooctadienyl iron ion shewn in fig. LIV.



LIV.

It was hoped that reduction of this ion with sodium borohydride would provide a route to tricarbonyl cycloocta-1,3-diene iron which cannot be obtained from the direct interaction of an olefin and iron carbonyl, but extensive decomposition occurred and no organometallic compounds could be isolated from the reaction mixture.

CHAPTER VI.EXPERIMENTAL PART.

General. Micro-analyses and molecular weight determinations (ebullioscopic in benzene) were performed by the Micro-analytical Laboratory of Imperial College. Melting points are uncorrected.

Solvents were freed from air by passing a rapid stream of nitrogen through them for 10 - 15 mins.; concentrated sulphuric acid was degassed under vacuum. The alumina used for chromatography was acid-washed Brockman Grade III. Dideuterosulphuric acid was made by condensing the stoichiometric amount of heavy water onto sulphur trioxide obtained by heating oleum under vacuum.

Infra-red spectra were measured on Perkin Elmer Model 21 and Infracord spectrophotometers with sodium chloride optics unless otherwise stated.

Proton magnetic resonance spectra were measured on solutions contained in 5 mm. outside-diameter spinning pyrex tubes at $23^{\circ} \pm 1^{\circ}$ on a Varian Associates Model 4311 spectrometer operating at 56.45 mc/s. and fitted with field homogeneity coils. The tubes containing the solutions were usually centrifuged for 5 - 10 mins. before measurement as

this markedly improved the resolution by removing colloidal paramagnetic substances produced by the partial oxidation of some of the specimens. Line positions were measured by conventional side-band techniques relative to tetramethylsilane as an internal reference, except in the case of solutions in concentrated sulphuric acid when dimethyl sulphate was used. The γ -value of this reference was found to be 5.97 by a measurement in trifluoroacetic acid. The proton-proton spin decoupling experiments were performed using the single side-band apparatus constructed by Dr D.W. Turner of Imperial College.⁴³ The solutions in liquid sulphur dioxide were prepared under vacuum by condensing distilled sulphur dioxide onto the solid contained in a thick walled pyrex tube (o.d. 5 mm.) and then sealing off. After the tubes had reached room temperature they were centrifuged for a short time in an inverted position so that any excess solute was driven to the top of the tube where it would not interfere with the measurement.

Preparations. Many of the starting materials used in this work were made by standard methods, but in several instances improved procedures were used.

Dodecacarbonyl tri-iron. This was prepared initially by the method of Hieber and Leutert⁶¹ but an adaptation of the procedure of Case and Whiting^{62,63} proved to be much more

satisfactory. Pentacarbonyl iron (110 ccs., 0.82 mol.), triethylamine (84 ccs., 0.60 mol.) and water (240 ccs.) were stirred at $83^{\circ} \pm 5^{\circ}$ under nitrogen for 15 hrs.. The mixture was cooled, and the deep red lower layer of solid $\text{Et}_3\text{NH}^+[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$ which separated was thoroughly washed with cold water and dissolved in 900 ccs. of methanol. 600 ccs. of 1 : 1 hydrochloric acid were then added and the solution was heated on a steam bath for about 5 hrs., until evolution of hydrogen had ceased and all signs of purple or red colour had vanished. The insoluble dense dodecacarbonyl tri-iron was filtered off, washed successively with water, methanol, and light petroleum, and dried under vacuum. The yield was 91 g.. The material obtained in this way is sometimes so finely divided as to be pyrophoric, but comparatively large crystals can be made by extracting the product (in a nitrogen atmosphere) with petroleum ether (b.p. $40 - 60^{\circ}$) in a soxhlet apparatus. Experiments which involve large quantities of the compound should be conducted in an efficient fume cupboard as appreciable amounts of pentacarbonyl iron are often produced.

Tricarbonyl cyclooctatetraene iron. This compound was first made by the interaction of cyclooctatetraene and pentacarbonyl iron,^{45, 47, 48} but the following procedure has been found to give higher yields and a purer product.

Dodecacarbonyl tri-iron (8.4 g., 16.7 m.mol.) and cyclo-octatetraene (5.5 ccs., 52 m.mol.) were refluxed in light petroleum (30 ccs., b.p. 100 - 120°) for 30 mins. under nitrogen. The mixture was cooled, filtered, and evaporated at 50°/0.1 mm. and the residue was recrystallized from hot ethanol and sublimed at 80°/0.01 mm.; small amounts of $C_8H_8[Fe(CO)_3]_2$ were also formed. The yield varied from 9 to 11g. according to the reaction time and the state of subdivision of the $Fe_3(CO)_{12}$.

Dicarbonyl π -cyclopentadienyl cobalt. The following modification of the method of Piper and Wilkinson was found to give satisfactory results.⁶⁴ Octacarbonyl dicobalt (7.23 g., 21 m. mol.) and freshly distilled cyclopentadiene (3.5 ccs., 42 m.mol.) in petroleum ether (20 ccs., b.p. 100 - 120°) were maintained at 100° under nitrogen for 1 hr.. The resulting solution was then cooled, filtered, and chromatographed on a 7 X 75 cm. column of alumina. Light petroleum eluted a deep red band which on evaporation under vacuum gave 5.7 g. (76 %) of the compound.

π -cyclopentadienyl cyclooctatetraene cobalt. This was prepared as described by Nakamura and Hagihara³⁴ except that the filtered reaction mixture was chromatographed on alumina, and yields of 25 - 30 % were obtained.

π -cyclopentadienyl cyclooctatetraene rhodium. Dicarbonyl

π -cyclopentadienyl rhodium (prepared from 4.6 g. of chlorodicarbonyl rhodium, 4.6 g. of sodium, and 18 ccs. of freshly distilled cyclopentadiene by the method of Fischer and Bittler⁶⁵) was refluxed under nitrogen with cyclooctatetraene (4 ccs.) in petroleum ether (50 ccs., b.p. 120 - 160°) for 18 hrs.. The solution was then cooled, filtered, and maintained at 40°/0.1 mm. for several hours. A small amount of light grey solid material which separated was discarded and the brown liquid was chromatographed on a 7 X 75 cm. column of alumina. Light petroleum (b.p. 40 - 60°) eluted two bands, the first of which consisted of unreacted π -C₅H₅Rh(CO)₂ and was treated with more cyclooctatetraene. The second band was evaporated under vacuum and the solid which separated was recrystallised twice from light petroleum (b.p. 30 - 40°) at -78° and sublimed at 75°/0.01 mm. to give deep yellow crystals of the compound, m.p. 106°. (Yield: 0.7 g., 11 %.) (Found: C, 57.5; H, 5.4. C₁₃H₁₃Rh requires: C, 57.4; H, 4.8 %.) The compound is soluble in petroleum ether; very soluble in ether, acetone, carbon tetrachloride, carbon disulphide, chloroform, and benzene; and is insoluble in water. It is stable in air for indefinite periods. A narrow light grey band which remained at the top of the chromatographic column was not investigated.

Tricarbonyl bicyclo[5,1,0]octadienyl iron tetrafluoroborate.

Tricarbonyl cyclooctatetraene iron (12.2 g., 50 m.mol.) in acetic anhydride (75 ccs.) was treated with 40 % aqueous hydrogen tetrafluoroborate (40 ccs. 0.3 mol.) in ice-cold acetic anhydride (125 ccs.). The mixture at once became pale yellow and hot, and after a delay of 15 secs. was poured into diethyl ether (1500 ccs.). A yellow precipitate formed immediately and this was washed with ether (8 X 100 ccs.) and dried under vacuum to give a pale yellow powder (10.3 g., 62 %) of the compound, decomp. 150° , which was analysed immediately. (Found: C, 39.75; H, 3.0; F, 22.4. $C_{11}H_9BF_4FeO_3$ requires: C, 39.8; H 2.7; F, 22.9 %.) The compound is stable in dry air when it is pure, but this depends very much on how effectively the ether washes have removed all traces of acid anhydride. It is soluble in water, in which solvent it slowly decomposes with evolution of carbon monoxide, and in acetone, liquid sulphur dioxide, and trifluoroacetic and concentrated sulphuric acids. It is sparingly soluble in dichloromethane, and is insoluble in light petroleum, ether, benzene, chloroform, carbon tetrachloride, and tetrahydrofuran. A small quantity of the compound was dissolved in air-free water and the solution was treated with aqueous potassium hydroxide in slight excess. Extraction of the mixture with diethyl ether gave some tricarbonyl

cyclooctatetraene iron, but yields were variable owing to the instability of the aqueous solution, and organic materials and hydrated ferric compounds were also produced.

η -cyclopentadienyl cyclooctatetraenium cobalt tetrafluoroborate. η -cyclopentadienyl cyclooctatetraene cobalt was treated with hydrogen tetrafluoroborate in the same way as $C_8H_8Fe(CO)_3$, but the precipitate which separated was brownish yellow and too unstable for a satisfactory analysis to be obtained. However the infra-red spectrum indicated the presence of a BF_4^- group.

Tricarbonyl bicyclo[5.1.0]octa-2,4-diene iron. The entire preparation was performed under nitrogen. The salt $C_8H_9Fe(CO)_3^+BF_4^-$ (10g., 30 m.mol.) was suspended in de-aerated anhydrous tetrahydrofuran (75 ccs.) and powdered sodium borohydride (3 g., excess) was added in small portions over 1 hr.. There was vigorous effervescence, and when all the tetrafluoroborate had dissolved petroleum ether (100 ccs., b.p. 60 - 80°) was added. The tetrahydrofuran and excess borohydride were removed by repeated washing with water, and the filtered petroleum solution was dried overnight over calcium chloride and chromatographed on a 5 X 75 cm. column of alumina. Two bands were eluted with light petroleum (b.p. 40 - 60°), the second giving the complex $C_8H_8Fe(CO)_3$ (0.5 g., 6 %). The first fraction was evaporated under vacuum and

gave, after recrystallization from light petroleum (b.p. 30 - 40°) at -78° and sublimation at 25°/0.01 mm., deep yellow crystals of the complex, m.p. 36.5°. (Yield: 1.2 g., 16 %) (Found: C, 53.5; H, 4.2. $C_{11}H_{10}FeO_3$ requires: C, 53.7; H, 4.1 %). The complex is insoluble in water, but is very soluble in petroleum ether, benzene, carbon disulphide, acetone, and chlorinated organic solvents to give solutions which decompose in air, although the solid itself is fairly stable. When the above reaction was performed in the presence of aquated lithium chloride (2 g.) it was complete in a much shorter time, but the yield of the desired product was much lower and a variety of other organo-iron compounds was produced. These could be separated by chromatography on a 7 × 75 cm. column of alumina and included tricarbonyl bicyclo[4,2,0]octa-2,4-diene iron, cycloocta-1,3,5-triene iron, hexacarbonyl bi(cycloocta-2,4,6-trienyl)di-iron, and on one occasion a purple compound with intense infra-red absorptions at 2040, 2005, 1980, and 1715 cm^{-1} . The last of these was probably a super-sandwich type of compound containing alkyl substituted η -cyclopentadienyl groups.

Hydride abstraction from tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron. Solutions of triphenylmethyl tetrafluoroborate (0.62 g., 1.9 m.mol.) in dichloromethane (4 ccs.) and the iron complex (0.464 g., 1.9 m.mol.) in dichloromethane (2 ccs.)

were mixed at room temperature. The initial dark colour faded in about 30 secs. and after 1 hr. the yellow crystals which had formed were removed, washed with diethyl ether (2 X 50 ccs.) and dried under vacuum. Their proton magnetic resonance spectrum was identical with that of an authentic specimen of tricarbonyl bicyclo[5,1,0]octa-2,4-dienyl iron tetrafluoroborate made from $C_8H_8Fe(CO)_3$ and hydrogen tetrafluoroborate.

Tricarbonyl 9,9,10,10-tetracyano-bicyclo[4,2,2]deca-2,4,7-triene iron. Benzene solutions of tricarbonyl cyclooctatetraene iron (0.52 g., 2.1 m.mol. in 10 ccs.) and tetracyanoethylene (0.27 g., 2.1 m.mol. in 25 ccs.) were mixed at room temperature. The red colour changed to yellow in about 1 min. and after 1 hr. the pale yellow crystals which slowly formed were collected, washed with benzene and then light petroleum (b.p. 30 - 40°), and dried under vacuum. The diamagnetic adduct (Yield: 0.75 g., 95 %.) (Found: C, 55.25; H, 2.8; Fe, 15.2; N, 15.5; O, 12.6. $C_{17}H_8FeN_4O_3$ requires: C, 55.0; H, 2.2; Fe, 15.1; N, 15.1; O, 12.9 %.) darkens at 150°, and slowly turns brown if stored for several months in air. It is insoluble in water, petroleum ether, benzene, alcohol, carbon tetrachloride, chloroform, and diethyl ether; very sparingly soluble in dichloromethane and acetone; sparingly soluble in dimethyl sulphoxide; and soluble in concentrated

sulphuric acid to give an unstable dark brown solution.

The mixture of isomeric cyclooctatrienes. This mixture was prepared by the method of Jones⁶⁶ by the reduction of cyclooctatetraene with zinc dust and sodium hydroxide, but the reaction mixture was not steam distilled. The proton magnetic resonance spectrum of the product shewed that it contained less than 5 % of unreacted cyclooctatetraene, and this was most conveniently removed (as metal complex) by chromatography after the reactions were complete.

Tricarbonyl cycloocta-1,3,5-triene iron. All of the following operations were performed under nitrogen. Dodecacarbonyl tri-iron (6.36 g., 13 m.mol.) was refluxed in petroleum ether (50 ccs., b.p. 100 - 120°) with the cyclooctatriene mixture (5 ccs., 38 m.mol.) for 35 mins.. The brown solution was cooled, filtered, and chromatographed in light petroleum (b.p. 40 - 60°) on a 5 X 75 cm. column of alumina. The first (containing pentacarbonyl iron) and fourth (containing $C_8H_8Fe(CO)_3$) bands to be eluted were rejected. The second and third bands, which were often poorly separated, were evaporated down under vacuum and recrystallized from light petroleum (b.p. 30 - 40°) at -78° to give respectively tricarbonyl bicyclo[4,2,0]octa-2,4-diene iron, and tricarbonyl cycloocta-1,3,5-triene iron (Yield: 1.9 g., 20 %) as a somewhat air-sensitive yellow-orange oil, freezing at -10°.

(Found: C, 54.3; H, 4.1 %; M, 241.3. $C_{11}H_{10}FeO_3$ requires: C, 53.7; H, 4.1 %; M, 245.0) The yield is very sensitive to variations in the reaction conditions, and if either the stated time or temperature is exceeded the main product is the bicyclic isomer.

The interaction of dicarbonyl η -cyclopentadienyl cobalt and the cyclooctatriene mixture. Dicarbonyl η -cyclopentadienyl cobalt (14 g., 78 m.mol.) and the mixture of cyclooctatrienes (10 ccs., 76 m.mol.) were refluxed together in petroleum ether (100 ccs., b.p. 120 - 130°) under nitrogen for 15 hrs. The solution was then cooled, filtered, and chromatographed on a 7 X 75 cm. column of alumina. Light petroleum (b.p. 40 - 60°) eluted two bands. The first was deep red, and on evaporation and recrystallization at -30° (to remove a small amount of unreacted η -C₅H₅Co(CO)₂) from light petroleum (b.p. 30 - 40°) gave η -cyclopentadienyl bicyclo[4,2,0]octa-2,4-diene cobalt (Yield: 1.4 g., 8 %) as dark red needles, m.p. 46°, which were very soluble in organic solvents and decomposed in air over a period of months. The second band was evaporated at 30°/0.1 mm., recrystallized from light petroleum (b.p. 40 - 60°) at -78° and sublimed at 60°/0.01 mm. to give golden-brown crystals, m.p. 98°, of η -cyclopentadienyl cycloocta-1,3,5-triene cobalt. (Yield: 2.2 g., 11.5 %) (Found: C, 67.0; H, 6.8 %; M, 225. $C_{13}H_{15}Co$ requires C, 67.8;

H, 6.5 %; M, 230.1.) The compound is stable in air for indefinite periods, is moderately soluble in petroleum ether, and is soluble in benzene, carbon disulphide, acetone, carbon tetrachloride and chloroform. It is insoluble in water, but dissolves in concentrated sulphuric acid to give a somewhat unstable solution.

Tricarbonyl cyclooctadienyl iron tetrafluoroborate. This compound was made in 70 % yield from tricarbonyl cycloocta-1,3,5-triene iron by treating it with hydrogen tetrafluoroborate in the same way as $C_8H_8Fe(CO)_3$. It is an air-stable powder, decomp. 120° , which is soluble in water (with decomposition), acetone, liquid sulphur dioxide, and trifluoroacetic and concentrated sulphuric acids. It is insoluble in petroleum ether, benzene, carbon tetrachloride, chloroform, diethyl ether, and tetrahydrofuran; and is sparingly soluble in dichloromethane. (Found: C, 40.0; H, 3.5; F, 23.0. $C_{11}H_{11}BF_4FeO_3$ requires: C, 39.6; H, 3.3; F, 22.8 %.) An attempt to reduce the compound with sodium borohydride in anhydrous tetrahydrofuran led to extensive decomposition, and no organo-iron compounds could be isolated from the reaction mixture.

Hexacarbonyl bi(cycloocta-2,4,6-trienyl) di-iron. Zinc dust (6.5 g., 50 m.mol.) and tricarbonyl bicyclo[5,1,0]octadienyl iron tetrafluoroborate (3.22 g., 10 m.mol.) were

suspended in de-aerated tetrahydrofuran which was then refluxed and stirred vigorously under nitrogen. The tetrafluoroborate slowly dissolved, and after 10 hrs. the mixture was filtered and the filtrate was evaporated at $25^{\circ}/0.1$ mm.. The oily residue was triturated with light petroleum (b.p. $30 - 40^{\circ}$) and the solid which separated was crystallized from benzene to give deep yellow crystals of the compound. (Yield: 0.98 g., 40 %.) (Found: C, 54.0; H, 3.6; O, 19.3 %; M, 485. $C_{22}H_{18}Fe_2O_6$ requires: C, 53.9; H, 3.7; O, 19.1 %; M, 490.1.) The compound is stable in air and is soluble in carbon tetrachloride, carbon disulphide, and dichloromethane; moderately soluble in benzene; and sparingly soluble in light petroleum. It dissolves in trifluoroacetic and concentrated sulphuric acids to give brown unstable solutions, and an attempt to make a tetrafluoroborate by treatment with hydrogen tetrafluoroborate failed. The complex decomposes at $120 - 130^{\circ}$ without melting.

The reaction between tricarbonyl bicyclo[5,1,0]octadienyl iron tetrafluoroborate and phenyl lithium. The following operations were all performed under an atmosphere of nitrogen. An ethereal solution of phenyl lithium⁶⁷ (lithium - 0.25 g., 36 m.mol. - and bromobenzene - 3.75 ccs., 38 m.mol.) was added to a stirred suspension of the tetrafluoroborate (12.5 g., 38 m.mol.) in ether. A deep green colour developed

immediately and faded over the course of 15 hrs. until the supernatant liquid was brownish-red. Filtration, then removal of the ether under vacuum, and finally chromatography on alumina in light petroleum (b.p. 40 - 60°) gave $C_8H_8Fe(CO)_3$, $[-C_8H_9Fe(CO)_3]_2$, and a mixture of biphenyl and a reddish oil which polymerized to a brown gum on attempts to crystallize it. The reaction was repeated at 0° and -25° but this only altered the relative proportions of the products and the time the green colour took to develop. When the tetrafluoroborate was treated in the same way with methyl lithium, similar behaviour was observed except that decomposition rather than polymerization prevented the isolation of the product.

-cyclopentadienyl norbornadiene rhodium. Norbornadiene rhodium chloride dimer (1.1g., 2.2 m.mol.) was stirred at room temperature under nitrogen with sodium cyclopentadienide (from 0.102 g. of sodium and 0.267 g. of freshly distilled cyclopentadiene, i.e. 4.5 m.mol.) in de-aerated tetrahydrofuran (100 ccs.) for 15 hrs.. The mixture was then filtered and evaporated under vacuum, and the residue was extracted with boiling petroleum ether (3 X 40 ccs., b.p. 60 - 80°). Recrystallization from light petroleum (b.p. 30 - 40°) at -78°, followed by sublimation at 70°/0.001 mm. gave the complex, m.p. 74°. (Yield: 0.83 g., 70 %) (Found: C, 55.1; H, 5.1.

$C_{12}H_{13}Rh$ requires: C, 55.4; H, 5.04 %.) The compound is a bright yellow powder which is soluble in petroleum ether, and is very soluble in carbon disulphide, carbon tetrachloride, chloroform, dichloromethane, acetone, and benzene. It is stable in air for long periods, but its solutions in chlorinated solvents tend to decompose on standing.

Tricarbonyl ethylcyclooctatetraene iron. Ethylcyclooctatetraene was prepared by the method of Cope⁶⁸ from ethyl lithium and cyclooctatetraene, but was not purified by means of its silver nitrate adduct. The proton magnetic resonance spectrum of the fraction which distilled in the range 65 - 75°/20 mm. shewed that it consisted principally of the desired product together with a few per cent of cyclooctatetraene and ethyl-cyclooctatriene.

Dodecacarbonyl tri-iron (25 g., 50 m.mol.) and the olefin (20 ccs., 150 m.mol.) were refluxed together under nitrogen in petroleum ether (150 ccs., b.p. 100 - 120°) for about an hour until the original green colour had changed to brown. The mixture was then cooled, filtered, and chromatographed on a 7 X 75 cm. column of alumina in light petroleum (b.p. 40 - 60°). The first and third bands contained pentacarbonyl iron and $C_8H_8Fe(CO)_3$ respectively and were discarded; The second band, which was very broad and incompletely separated from the third, was evaporated under vacuum to

about 100 ccs. when 2 g. of golden-yellow crystals which were moderately soluble in light petroleum were obtained. These crystals melted at $115 - 122^{\circ}$ and were stable in air, but their analysis was very variable from one preparation to another. The dark red mother liquor was further evaporated and maintained at $40^{\circ}/0.01$ mm. for 2 hrs.. It was then mixed with light petroleum (b.p. $30 - 40^{\circ}$, 30 ccs.) and cooled to -78° when a mixture of the yellow substance and some dark red crystals which easily melted to an oil was obtained. The two components were separated by fractional crystallization from light petroleum (b.p. $30 - 40^{\circ}$) at -78° , and the red oil, f.p. -20° was sublimed at $95^{\circ}/0.001$ mm.. (Yield: 11g., 28 %) (Found: C, 57.1; H, 4.3; O, 17.8 %; M, 262. $C_{13}H_{12}FeO_3$ requires: C, 57.4; H, 4.46; O, 17.6 %; M, 272.) The compound is stable indefinitely in air but slowly decomposes in the presence of chlorinated organic solvents.

When a solution of the complex in benzene was treated with an equivalent amount of tetracyanoethylene in the same solvent an immediate loss of colour occurred and pale yellow-green crystals of the adduct were slowly deposited. They were filtered off, washed with benzene and light petroleum (b.p. $30 - 40^{\circ}$) and dried. (Found: C, 57.0; H, 3.2; N, 14.4; O, 12.5. $C_{19}H_{12}FeN_4O_3$ requires: C, 57.0; H, 3.1; N, 14.0; O, 12.0 %.) The adduct is insoluble

in water, petroleum ether, carbon disulphide, carbon tetrachloride, and chloroform; very sparingly soluble in dichloromethane; and sparingly soluble in dimethyl sulphoxide to give a deep yellow solution which slowly turned brown in the air.

INFRA-RED ABSORPTION SPECTRA.

Unless otherwise stated, spectra were measured on solutions in carbon disulphide and carbon tetrachloride. Where mulls are specified the mulling agents were nujol and hexachlorobutadiene.

Key to assignments: (a)- C—H stretching vibration; (b)- C≡N stretching vibration; (c)- terminal C≡O stretching vibration; (d)- C=C stretching vibration; (e)- degenerate asymmetric BF_4^- deformation mode.

Tricarbonyl bicyclo[5,1,0]octadienyl iron tetrafluoroborate:

Mull: 3087(sh)^a, 3060(w)^a, 3011(sh)^a, 2055(vs)^c, 2018(vs)^c, 1060(vs)^e.

Tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron: 3040(sh)^a, 2935(s)^a, 2900(ms)^a, 2855(m)^a, 2820(ms)^a, 2025(vs)^c, 1965(vs)^c, 1920(vs)^c, 1460(sh), 1435(m), 1416(m), 1375(sh), 1362(m), 1340(sh), 1320(m), 1242(w), 1226(m), 1198(w), 1162(w), 1120(m), 1035(s), 1020(m), 993(s), 966(ms), 937(sh), 928(m), 896(ms), 872(m), 850(m), 828(s), 802(m), 758(m), 722(m), 710(ms), 673(ms).

π-cyclopentadienyl cyclooctatetraene rhodium: 3015(s)^a, 2985(s)^a, 1640(m)^d, 1405(w), 1380(w), 1340(ms), 1140(w), 1120(ms), 1100(w), 1006(m), 980(m), 948(w), 908(s), 836(w), 822(sh), 803(vs), 783(vs), 752(m), 722(m).

Tricarbonyl 9,9,10,10-tetracyano bicyclo[4,2,2]deca-2,4,7-triene iron: Mull: 3030(w)^a, 2995(w)^a, 2978(w)^a, 2950(w)^a, 2250(w)^b, 2072(vs)^c, 2012(vs)^c, 1670(w)^d, 1405(w), 1344(w), 1320(m), 1306(sh), 1286(w), 1270(w), 1240(w), 1222(w), 1180(w), 1139(w), 1113(m), 1080(sh), 1062(w), 1024(w), 985(w), 960(m), 928(m), 898(ms), 855(m), 838(w), 827(m), 774(ms), 750(m), 693(w).

π -cyclopentadienyl cycloocta-1,3,5-triene cobalt: 3090(w)^a, 2960(s)^a, 2895(m)^a, 2845(w)^a, 2812(w)^a, 1618(w)^d, 1425(w), 1402(w), 1365(w), 1342(w), 1180(w), 1160(sh), 1121(w), 1107(w), 1009(w), 989(w), 952(w), 929(w), 885(sh), 861(m), 843(w), 809(sh), 800(s), 781(m), 748(w).

Tricarbonyl cycloocta-1,3,5-triene iron: 3045(m)^a, 2970(s)^a, 2941(s)^a, 2846(m)^a, 2065(vs)^c, 1980(vs)^c, 1945(sh)^c, 1673(sh)^d, 1636(w)^d, 1442(m), 1428(w), 1385(w), 1362(w), 1330(m), 1310(m), 1256(m), 1225(w), 1215(sh), 1194(w), 1168(w), 1133(w), 1088(w), 1044(m), 999(m), 962(w), 956(w), 934(w), 914(w), 890(vw), 863(m), 847(m), 828(w), 809(m), 776(m), 722(s), 704(s).

Hexacarbonyl bi(cycloocta-2,4,6-trienyl) di-iron: 2995(s)^a, 2910(ms)^a, 2870(m)^a, 2040(vs)^c, 1980(vs)^c, 1965(sh)^c, 1640(w)^d, 1442(m), 1370(m), 1322(m), 1308(m), 1258(w), 1220(w), 1192(m), 1094(m), 1058(m), 1023(m), 956(w), 932(m), 904(w), 872(w), 848(ms), 832(m), 798(ms), 705(s).

Tricarbonyl cyclooctadienyl iron tetrafluoroborate: Mull:

3080(w)^a, 3030(m)^a, 2925(w)^a, 2880(w)^a, 2840(w)^a, 2105(vs)^c,
2040(vs)^c, 1442(m), 1432(ms), 1420(m), 1333(w), 1282(w),
1231(w), 1199(w), 1144(w), 1080(sh)^e, 1060(vs)^e, 1046(vs)^e,
1032(vs)^e, 950(w), 928(w), 896(w), 872(w), 843(m), 828(w), 776(w).

Tetracyanoethylene: Mull: 2250(m)^b, 2215(w)^b, 1160(s), 1112(m),
1082(w), 1018(vw), 958(ms), 934(w), 916(w), 803(w).

π -Cyclopentadienyl cyclooctatetraenium cobalt tetrafluoro-
borate: Mull: 1410(m), 1050(vs)^e, 899(m), 842(ms), 787(w),
746(w).

Tricarbonyl ethylcyclooctatetraenium iron tetrafluoroborate:
Mull: 3055(sh)^a, 3030(w)^a, 2940(w)^a, 2100(vs)^c, 2030(vs)^c,
1277(vs), 1053(vs)^e, 874(w).

Tetracyanoethylene adduct of ethylcyclooctatetraene tricarbonyl
iron: Mull: 2950(mw)^a, 2920(mw)^a, 2845(vw)^a, 2225(w)^b, 2040(vs)^c,
1985(vs)^c, 1660(w)^d, 1396(w), 1340(vw), 1320(w), 1300(vw),
1278(w), 1264(w), 1245(sh), 1222(vw), 1200(w), 1150(w),
1112(mw), 1085(w), 1056(m), 1036(w), 1008(w), 992(vw), 982(w),
952(ms), 927(mw), 894(ms), 860(mw), 848(m), 800(mw), 774(s),
738(m), 724(w).

Tricarbonyl ethylcyclooctatetraene iron: 2995(s)^a, 2945(s)^a, 2925(ms)^a, 2850(m)^a, 2040(vs)^c, 1965(vs)^c, 1935(vs)^c, 1500(m), 1464(s), 1430(ms), 1410(ms), 1370(m), 1306(m), 1256 (ms), 1210(w), 1190(w), 1048(ms), 954(w), 938(vw), 923(vw), 898(w), 884(w), 848(w), 764(m), 720(ms), 704(s), 675(m).

"Golden-yellow crystals" from reaction between $C_2H_5C_8H_7$ and $Fe_3(CO)_{12}$: 3000(w)^a, 2930(s)^a, 2850(sh)^a, 2020(vs)^c, 1970(vs)^c, 1936(s)^c, 1503(w), 1490(w), 1454(ms), 1406(s), 1372(m), 1360(m), 1318(vw), 1304(vw), 1250(w), 1172(m), 1136(w), 1078(w), 1054(m), 1012(m), 998(m), 980(m), 943(ms), 935(sh), 908(w), 885(m), 876(w), 835(w), 778(w), 700(w), 680(m).

π -cyclopentadienyl norbornadiene rhodium: 3120(sh)^a, 3075(m)^a, 3025(s)^a, 2960(ms)^a, 2930(ms)^a, 2860(m)^a, 1435(w), 1412(m), 1377(s), 1305(s), 1265(mw), 1255(sh), 1177(s), 1160(m), 1107(ms), 1062(s), 1022(sh), 1010(ms), 995(ms), 928(w), 914(ms), 896(m), 862(mw), 850(w).

HIGH RESOLUTION PROTON MAGNETIC RESONANCE SPECTRA.

Line positions are given in τ -values, i.e. in parts per million above a zero which is defined as being 10 p.p.m. below the resonance of tetramethylsilane.

The tricarbonyl bicyclo[5,1,0]octadienyl iron cation in concentrated sulphuric acid: Band A, 2.26; quintuplet; assigned to H_4 , coupled to H_2 , H_3 , H_5 , and H_6 , with $J \sim 3.8$ c.p.s.. Band B, 4.62; poorly resolved, intensity 4; assigned to H_2 , H_3 , H_5 , and H_6 , which form an " A_2B_2 " group further coupled to H_4 , and H_1 and H_7 .

Band C, 7.48; broad, intensity 2; assigned to the bridgehead protons H_1 and H_7 , coupled to the two protons on C_8 , to H_2 and H_6 , and probably to H_3 and H_5 .

Band D, 8.56; complex, intensity 2; assigned to the methylene protons on C_8 , being an "AB" pair with $\Delta_{AB} = 4.8$ c.p.s. and shewing additional splitting; "A" component centred at 8.47 and coupled to H_1 and H_7 with $J \approx 4.5$ c.p.s., "B" component centred at 8.65 and similarly coupled with $J = 8$ c.p.s..

Irradiation of the specimen at the frequency of band B made band A collapse to a singlet, thus confirming that H_4 is coupled to H_2 , H_3 , H_5 , and H_6 . The cation gave spectra identical to the above in trifluoroacetic acid and in liquid sulphur dioxide.

The tricarbonyl 8-deutero-bicyclo[5,1,0]octadienyl iron cation in dideuterosulphuric acid: Band A, 2.18; assigned to H_4 as above.

Band B, 4.55; assigned to H_2 , H_3 , H_5 , and H_6 , as above.

Band C, 7.44; unsymmetrical doublet (splitting 6.7 c.p.s.), intensity 2; assigned to the bridgehead protons H_1 and H_7 , coupled to the single proton on C_8 , and to H_2 and H_6 , and probably to H_3 and H_5 .

Band D, 8.59; unsymmetrical triplet (splittings 8.5 and 8.3 c.p.s.), intensity 1; assigned to H_8 in the CHD group.

Bands C and D form an 'AB₂' group with $J/\Delta = 0.12$ and $J_{AB} \approx 8.0$ c.p.s..

The tricarbonyl cycloheptadienyl iron cation in concentrated sulphuric acid: Band A, 3.03; unsymmetrical triplet, intensity 1; assigned to H_4 , coupled to H_3 and H_5 with $J = 6.5$ c.p.s..

Band B, 4.81; unsymmetrical quartet (double doublet), intensity 2; assigned to H_3 and H_5 , each coupled to H_4 and to either H_2 or H_6 with $J = 9.9$ c.p.s..

Band C, 5.15; broad, but possibly a triplet, intensity 2; assigned to H_2 and H_6 , coupled to either H_3 or H_5 and the methylene protons on either C_1 or C_7 .

Bands D and E, 7.4 and 8.2; complex, intensity 4; assigned to the methylene protons on C_1 and C_7 , forming an "A₂B₂" further coupled to H_2 and H_6 .

The tricarbonyl 1-deutero-cycloheptadienyl iron cation in dideuterosulphuric acid: Band A, 2.96; unsymmetrical triplet; assigned to H_4 as above.

Band B, 4.07; unsymmetrical quartet; assigned to H_3 and H_5 as above.

Band C, 5.08; broad; assigned to H_2 and H_6 as above.

Band D, 7.4; complex, intensity 2; assigned to two of the methylene protons on C_1 and C_7 , with the remaining proton on C_7 these protons form an "ABC" group which is further coupled to H_2 and H_6 .

Band E, 8.21; incompletely resolved quartet (double doublet) with total and inner splittings of 16.5 and 7.5 c.p.s. respectively, intensity 1; assigned to one of the protons on C_7 , coupled to the other protons on C_1 and C_7 , and also to H_6 .

Tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron in benzene:

Band A, 5.49; complex group of doublets, each of splitting 5.6 c.p.s. and spaced at 5.2 c.p.s. intervals, intensity 2; assigned to the inner bound-diene protons H_3 and H_4 , coupled to H_2 and H_5 .

Band B, 6.68; triplet of doublets with main splitting 5.0 c.p.s., subsidiary splitting 2.0 c.p.s., intensity 1; assigned to the outer bound-diene proton H_2 , coupled to the other diene protons.

Band C, 7.3; complex of width 19 c.p.s., intensity 1; assigned to the outer bound-diene proton H_5 , coupled to the other diene protons and also to the methylene protons on C_6 .

Band D, 8.06; poorly resolved, width 10.4 c.p.s., intensity 2; assigned to the methylene protons on C_6 , coupled to H_5 and H_7 .

Band E, 8.7 - 9.2; very complex, intensity 2; assigned to bridgehead protons H_1 and H_7 , coupled to each other, to the protons on C_6 , and to the methylene cyclopropane ring protons on C_8 .

Band F, 9.4; unsymmetrical doublet (splitting 8.0 c.p.s.) with unresolved fine structure, intensity 1; assigned to one of the methylene protons on C_8 , coupled to the other and to the bridgehead protons H_1 and H_7 .

Band G, 10.61; complex, intensity 1; assigned to the remaining proton on C_8 , coupled to the other proton on C_8 and to the bridgehead protons.

The formation of strong side-bands from the benzene used as solvent made a complete check of these assignments impossible, but the following results were obtained: Irradiation at the frequency of band A removed the triplet structure of band B, but this band was not affected when band D was irradiated. This shews that the proton giving rise to band B is coupled

to H_3 and H_4 but not to the methylene protons on C_6 , and thus confirms its assignment as H_2 . Irradiation at the frequency of Band A also changed band C into a broad doublet, thus demonstrating the expected coupling between H_5 and the inner bound-diene protons.

π -cyclopentadienyl cyclooctatetraene cobalt . in carbon tetrachloride: Band A, 4.56; broad, intensity 4; assigned to the free olefinic protons H_3 , H_4 , H_7 , and H_8 , each coupled to at least (the nearest) two of H_1 , H_2 , H_5 , and H_6 .

Band B, 5.30; sharp singlet, intensity 5; assigned to the equivalent protons of the π -cyclopentadienyl ring.

Band C, 6.50; broad, intensity 4; assigned to the bound olefinic protons H_1 , H_2 , H_5 , and H_6 , each coupled to at least (the nearest) two of H_3 , H_4 , H_7 , and H_8 . The coupling constants between the two groups of protons are less than 1 c.p.s.. This is because of the large dihedral angle between the C - H bonds at opposite ends of the single C - C bonds. Models shew that this is probably greater than 80° .

Irradiation of the specimen at the frequency of either band A or band C produced a marked sharpening of the other, but no residual structure could be detected.

π -cyclopentadienyl cyclooctatetraene rhodium in carbon tetrachloride: Band A, 4.47; broad, intensity 4; assigned to the

free olefinic protons, as in the cobalt compound.

Band B, 4.85; sharp doublet with a separation of 0.71 c.p.s. (measured by the "ringing beat" method), intensity 5; assigned to the equivalent protons of the π -cyclopentadienyl ring, spin-coupled to the ^{103}Rh nucleus which has a spin of $\frac{1}{2}$. Band C, 5.94; incompletely resolved doublet with a splitting of 2.4 c.p.s., intensity 4; assigned to the bound olefinic protons as in the cobalt compound, and further spin-coupled to the ^{103}Rh nucleus. The coupling between the bound and unbound olefinic protons is again small as a consequence of the geometry of the molecule. Irradiation of the specimen at the resonant frequency of band A made the doublet structure displayed by band C much sharper; similarly, irradiation at the frequency of band C made band A sharper, and a small residual doublet splitting became apparent. This is due to the spin-coupling between the free olefinic protons and the ^{103}Rh nucleus, with $J \sim 1.4$ c.p.s..

π -cyclopentadienyl bicyclo[4,2,0]octa-2,4-diene cobalt in carbon tetrachloride: Band A, 4.92; unsymmetrical quartet with total and inner splittings of 6.8 and 2.0 c.p.s. respectively, intensity 2; assigned to the inner bound-diene protons H_3 and H_4 , coupled to each other and to the outer diene protons, and forming the "A" part of an " A_2X_2 " group which could not be analysed completely as the weak outer lines were

invisible.

Band B, 5.34; sharp singlet, intensity 5; assigned to the equivalent protons of the π -cyclopentadienyl group.

Band C, 6.86; incompletely resolved multiplet, intensity 2; assigned to the outer bound-diene protons H_2 and H_5 , coupled to each other and to H_3 and H_4 (this alone would make the band of identical appearance to A), and also to the bridgehead protons H_1 and H_6 .

Band D, 7.96; complex, intensity 2; assigned to the bridgehead protons H_1 and H_6 , coupled to H_2 and H_5 and to the methylene protons on C_7 and C_8 .

Band E, 8.92; complex doublet with broad maxima at 8.24 and 9.02, intensity 4; assigned to the methylene protons on C_7 and C_8 , forming an " A_2B_2 " group with further splitting by the bridgehead protons.

π -cyclopentadienyl cycloocta-1,3,5-triene cobalt in carbon tetrachloride: Band A, 4.62; sharp singlet (splitting < 1 c.p.s.), intensity 2; assigned to the two equivalent protons H_3 and H_4 of the free olefinic bond.

Band B, 5.45; sharp singlet, intensity 5; assigned to the equivalent protons of the π -cyclopentadienyl group.

Band C, 6.46; complex, intensity 4; assigned to the non-equivalent protons H_1 , H_2 , H_5 , and H_6 , of the bound olefinic groups, each coupled to the other proton of the same bond

and to the methylene protons.

Band D, 7.2 - 8.5; complex well-resolved band, intensity 4; assigned to the methylene protons on C₇ and C₈, forming an "A₂B₂" group ("A" part centred at 7.46, "B" at 8.30) with additional splitting from the bound olefinic protons.

Tricarbonyl cycloocta-1,3,5-triene iron in carbon disulphide:

Band A, 4 - 5; complex and well-resolved, intensity 4; alternate lines are split into doublets with a separation of 3.5 c.p.s.; assigned to the non-equivalent free olefinic protons H₁ and H₂, coupled to the adjacent outer bound-diene proton H₃ and to the methylene protons on C₈; and overlapping the inner bound-diene protons H₄ and H₅ which are coupled to H₃ and H₅.

Band B, 6.51; unsymmetrical triplet (splitting 7.2 c.p.s.), shewing further unresolved fine-structure, intensity 1; assigned to the outer bound-diene proton H₆, coupled to the other bound-diene protons and to one of the methylene protons on C₇. (A double irradiation experiment shewed that when the specimen was irradiated at the frequency of the protons on C₇, band B collapsed to a doublet,)

Band C, 6.86; well-resolved unsymmetrical triplet (splitting 8.0 c.p.s.), intensity 1; assigned to the outer bound-diene proton H₃. Double irradiation shewed that this proton is coupled to the free olefinic protons, but not to any of the

methylene protons.

Band D, 7.9 - 8.5; complex, intensity 4; assigned to the methylene protons, one (on C_7) being coupled to the outer bound-diene proton H_6 , and two (on C_8) to the free olefinic protons H_1 and H_2 , in addition to being coupled to each other.

Hexacarbonyl bi(cycloocta-2,4,6-trienyl) di-iron in carbon disulphide: Band A, 4.27; multiplet, intensity 2; assigned to the free olefinic protons H_6 and H_7 , coupled to the outer bound-diene proton H_5 and the methylene protons on C_8 .

Band B, 4.78; multiplet (to a first approximation a quartet with total and inner splittings of 13.6 and 2.5 c.p.s. respectively), intensity 2; assigned to the inner bound-diene protons H_3 and H_4 , coupled to H_2 and H_5 .

Band C, 6.81; unsharp unsymmetrical doublet (separation 7.7 c.p.s.), intensity 1; assigned to the outer bound-diene proton H_2 not adjacent to the free double bond, coupled to the other bound-diene protons (J small) and to the tertiary proton H_1 .

Band D, 7.04; unsymmetrical triplet (splitting 4.3 c.p.s.) shewing unresolved fine structure, intensity 1; assigned to the outer bound-diene proton H_5 adjacent to the free double bond, coupled to the other bound-diene protons and to H_6 and H_7 .

Band E, 8.45; complex, intensity 3; assigned to the protons on C_1 and C_8 , coupled to each other and to H_2 or H_7 .

Tricarbonyl cyclooctadienyl iron tetrafluoroborate in liquid sulphur dioxide: All lines were rather broad.

Band A, 2.73; triplet of splitting 6 c.p.s., intensity 1; assigned to H_4 , coupled to H_3 and H_5 .

Band B, 4.27; unsymmetrical triplet of splitting 7.5 c.p.s., intensity 2, assigned to H_3 and H_5 , coupled to H_4 and to either H_2 or H_6 .

Band C, 5.53; unsymmetrical doublet of separation 8.0 c.p.s. and shewing unresolved fine-structure, intensity 2; assigned to H_2 and H_6 , coupled to either H_3 and the methylene protons on C_1 , or H_5 and the methylene protons on C_7 .

Band D, 7.5 - 8.5; very complex, intensity 5; assigned to the methylene protons on C_1 and C_7 , and one of the protons on C_8 ; all mutually coupled, and also coupled to H_2 and H_6 .

Band E, 9.54; unsymmetrical quartet with total and inner splittings of 35 and 11 c.p.s. respectively, intensity 1; assigned to the remaining proton on C_8 , coupled to the other proton on C_8 and the protons on C_1 and C_7 . The spectrum in trifluoroacetic acid is identical with the above.

Hexacarbonyl bi(cycloocta-2,4,6-trienyl) di-iron in concentrated sulphuric acid: All lines were rather broad.

Band A, 2.71; triplet of separation 6.5 c.p.s., intensity 1; assigned to H_4 coupled to H_3 and H_5 .

Band B, 4.27; poorly resolved quartet of intensity 2, total

and inner splittings of 25 and 6.3 c.p.s. respectively; assigned to H_3 and H_5 , coupled to H_4 and to either H_2 or H_6 . Band C, 5.51 and 6.11; pair of overlapping doublets, each of splitting 8.2 c.p.s., intensity 2; assigned to H_2 and H_6 , coupled to either H_3 and the tertiary proton on C_1 or H_5 and the methylene protons on C_7 .

Band D, 7. - 10; complex, intensity 5; assigned to H_1 and the methylene protons on C_7 and C_8 , coupled to each other and to H_2 and H_6 . The spectrum in trifluoroacetic acid was the same.

Ethylcyclooctatetraene (as pure liquid): Band A, 4.31; narrow (width ~ 3 c.p.s.), intensity 7; assigned to the almost magnetically equivalent ring protons. Toluene displays a similar equivalence of its aromatic protons.

Band B, 8.01; almost regular quartet, intensity 2; assigned to the methylene protons of the ethyl group, coupled to the methyl protons ($J = 7.3$ c.p.s.) and the nearest ring protons ($J < 1$ c.p.s.).

Band C, 9.01; almost regular triplet, intensity 3; assigned to the methyl protons of the ethyl group, coupled to the methylene protons ($J = 7.3$ c.p.s.)

Tricarbonyl ethylcyclooctatetraene iron in carbon tetrachloride:

Band A, 4. - 4.6; complex, intensity 3; assigned to the non-bonded olefinic protons; a measurement at 40 mc/s. showed that some of the splitting was due to spin-coupling and some to chemical shifts.

Band B, 4.93; unsymmetrical triplet with splittings of 12 and 8 c.p.s., intensity 2; assigned to the inner bound-diene protons.

Band C, 5.58; unsymmetrical doublet of splitting 9 c.p.s., intensity 2; assigned to the outer bound-diene protons; a measurement at 40 mc/s. showed that the splitting was independent of the field-strength and therefore due to spin-coupling.

Band D, 8.00; quartet with splittings of 8 c.p.s., intensity 2; assigned to the methylene protons of the ethyl group, coupled to the methyl protons but not ($J < \frac{1}{2}$ c.p.s.) to the ring protons.

Band E, 8.95; triplet of splitting 8 c.p.s., intensity 3; assigned to the methyl protons of the ethyl group.

π -cyclopentadienyl norbornadiene rhodium in carbon tetrachloride;

Band A, 4.97; very sharp doublet, intensity 5; assigned to the π -cyclopentadienyl protons coupled to the ^{103}Rh nucleus ($J = 0.85$)

Band B, 6.86; complex, intensity 6; assigned to the bridgehead protons coupled to the methylene and olefinic protons, and overlapping the olefinic protons.

Band C, 9.08; triplet of splitting 1.3 c.p.s., intensity 2; assigned to the methylene protons coupled to the bridgehead protons.

Cyclooctatetraene in concentrated sulphuric acid: Band A,

1.67 - 1.90; complex, intensity 5; assigned to protons H_2 , H_3 , H_4 , H_5 , and H_6 of the delocalised system.

Band B, 3.70; quartet with total and inner splittings of 21.2 and 7.9 c.p.s. respectively, intensity 2; assigned to the bridgehead protons H_1 and H_7 , coupled to the methylene protons with further structure from the protons of the delocalised system.

Band C, 5.02; quartet (actually a pair of overlapping triplets), intensity 1; assigned to the exo-methylene proton on C_8 , coupled to H_1 and H_7 ($J = 7$ c.p.s.) and to the endo-proton on C_8 ($J = 7$ c.p.s.).

Band D, 10.04; pair of overlapping triplets, intensity 1; assigned to the endo-proton on C_8 , coupled to H_1 and H_7 ($J = 10.3$ c.p.s.) and to the exo-proton on C_8 ($J = 7$ c.p.s.).

The following spectra were rather broad and changed with time because of the presence of paramagnetic materials formed by the oxidation of the specimens during the measurement. In consequence the assignments are incomplete.

Tricarbonyl butadiene iron in concentrated sulphuric acid:

Band A, 5.24; unsymmetrical triplet of splitting 3 c.p.s., intensity 1; assigned to the middle proton of the π -allyl chain.

Band B, 5.74; complex, intensity 1; assigned to either the syn-proton on C_3 of the π -allyl group, or to H_1 (adjacent to the methyl group.)

Band C, 8.49; doublet shewing unresolved fine-structure,

intensity 1; assigned to either H_1 or the syn-proton on C_3 .

Band D, 10.48; double doublet ($J = 12$ and 3 c.p.s.) intensity 1; assigned to the anti-proton on C_3 .

Band E, 16.88; singlet, intensity 3; assigned to the protons of the methyl group attached to C_1 .

Tricarbonyl bicyclo[4,2,0]octa-2,4-diene iron in concentrated sulphuric acid: Band A, 5; broad, intensity 2; assigned to H_4 (the central π -allyl proton) and either H_3 or H_5 .

Band B, 6.5 - 8; broad and complex, intensity 8; assigned to either H_5 or H_3 , the exo-proton on C_2 and the protons of the four-membered ring.

Band C, 14; triplet, intensity 1; assigned to the endo-proton on C_2 .

π -cyclopentadienyl cyclooctatetraene cobalt in concentrated sulphuric acid: Band A, 5.03; triplet of splitting 5 c.p.s., intensity 2; assigned to the protons of the remaining free double bond.

Band B, 5.62; sharp singlet, intensity 5; assigned to the equivalent protons of the π -cyclopentadienyl ring.

Band C, 5.72 (overlapping the previous band); complex and well-resolved, intensity 1; assigned to the proton on the carbon atom carrying the localised positive charge.

Band D, 6.62; poorly resolved multiplet, intensity 2; assigned

to two of the bound olefinic protons.

Band E, 7.47; poorly resolved triplet of splitting 5 c.p.s., intensity 2; assigned to the remaining bound olefinic protons.

Band F, 10.55; doublet of splitting 6 c.p.s., intensity 2; assigned to the methylene protons.

η -cyclopentadienyl cyclooctatetraene rhodium in concentrated sulphuric acid: The assignments of the bands are the same as in the cobalt compound. Bands A, B, and C all overlap in the region 3.3 - 3.6; total intensity 8.

Band D, 4.62; intensity 2, broad.

Band E, 5.56; intensity 2, broad.

Band F, 7.86; intensity 2, complex and broad.

η -cyclopentadienyl cycloocta-1,3,5-triene cobalt in concentrated sulphuric acid: Band A, 5.0; broad, intensity 1; assigned to the proton on the carbon atom carrying the positive charge.

Band B, 6.60; sharp singlet, intensity 5; assigned to the equivalent protons of the η -cyclopentadienyl ring.

Band C, 7.04; complex, intensity 4; assigned to the bound olefinic protons.

Band D, 10.4 - 10.7; complex and broad, intensity 5; assigned to five of the methylene protons.

Band E, 12.35; broad, intensity 1; assigned to the remaining methylene proton.

Tricarbonyl bicyclo[5,1,0]octa-2,4-diene iron in concentrated sulphuric acid: Band A, 5.35; triplet of splitting 5.5 c.p.s., intensity 1; assigned to H_3 - the central π -allyl proton.

Band B, 5.76; poorly resolved multiplet, intensity 1; assigned to H_2 (or possibly H_4).

Band C, 6.31; triplet of splitting 7 c.p.s.; intensity 1; assigned to H_4 (or possibly H_2).

Band D, 6.73; quartet with total and inner splittings of 20 and 3 c.p.s. respectively, intensity 1; assigned to H_1 .

Band E, complex, intensity 1; assigned to other bridgehead proton H_7 .

Band F, 8.9 - 11.5; complex, total intensity about 6; assigned to the various methylene protons.

Tricarbonyl ethylcyclooctatetraene iron in concentrated

sulphuric acid: Band A, 2.82; broad, intensity 1; assigned to the middle proton H_4 of the delocalised system.

Band B, 5.02; complex, intensity 4; assigned to the remaining protons of the delocalised system.

Band C, 7.8 - 10.0; complex; assigned to the protons of the cyclopropane ring and the ethyl group.

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