A Thesis
entitled

A STUDY OF LABILE LIGANDS IN
TRANSITION METAL COMPLEXES.

Submitted by

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This work was supported by a C.A.P.S. studentship.
Felix qui potuit rerum cognoscere causas.

Virgil. (Georgies 11 490.)
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SUMMARY.

The original aim of this research was to prepare a series of metal-olefin complexes, and investigate the effect of the metal on the olefin. In particular, whether sufficient electron density could be withdrawn from the olefin, to make it susceptible to attack by carbon nucleophiles. Initial results with the \( \pi \)-propene cation, \( [\pi-C_5H_5Fe(CO)_2C_3H_6]^+ \), indicated that attack took place on the metal, in preference to the ligand. Attempts, in order to change the steric conditions around the metal, to prepare the analogous phosphine substituted complexes, for example, \( [\pi-C_5H_5Fe(CO)P\_3C_3H_6]^+ \), resulted in unexpected results. As a result the chemistry of the phosphine substituted system was studied in greater detail, particularly the properties of the unknown \( \sigma \)-propyl and \( \sigma \)-allyl derivatives, \( \pi-C_5H_5Fe(CO)P\_3R \). These studies showed that hydride abstraction of the \( \sigma \)-propyl derivative, \( \pi-C_5H_5Fe(CO)P\_3CH_2CH_2CH_3 \), did not give the \( \pi \)-propene cation, \( [\pi-C_5H_5Fe(CO)P\_3C_3H_6]^+ \). This cation was, however, prepared on protonation of the \( \sigma \)-allyl derivative, \( \pi-C_5H_5Fe(CO)P\_3CH_2CH=CH_2 \), but shown to be very unstable, readily losing propene. Similar \( \pi \)-propene cations have been shown to be sensitive to excess acid.

A general mechanism is proposed, in which the \( \pi \)-propene cation loses propene, to give the unsaturated cation, which can then either react further with the nucleophiles, for example the acid anions, to yield covalent products, or, in the case of the tetrafluoroborate or hexafluorophosphate salts, can be isolated.

The reaction of bromocarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron, \( \pi-C_5H_5Fe(CO)P\_3Br \), with Lewis acids, was investigated as a route to the unsaturated cation, \( [\pi-C_5H_5Fe(CO)P\_3]^+ \). The reaction, however, gave a mixture of cationic species. The
three that have been isolated so far are, $[\pi-C_{5}H_{5}Fe(CO)P\Phi_{3}]^{+}$, $[\pi-C_{5}H_{5}Fe(CO)_{2}P\Phi_{3}]^{+}$, and $[\pi-C_{5}H_{5}Fe(CO)_{2}Br-(CO)_{2}Fe(\pi-C_{3}H_{5})]^{+}$. The phosphine lability observed in these reactions was typical of all derivatives in this system, for example, $\sigma$-allylcarbonyl-triphenylphosphine-$\pi$-cyclopentadienyliron, $\pi-C_{5}H_{5}Fe(CO)P\Phi_{3}CH_{2}CH=CH_{2}$ was thermally unstable, yielding triphenylphosphine and $\sigma$-allyl-carbonyl-$\pi$-cyclopentadienyliron, $\pi-C_{5}H_{5}Fe(CO)-\pi-C_{3}H_{5}$. The kinetics of this reaction were studied, and used to suggest a mechanism for the reaction.
CHAPTER I.

HISTORICAL INTRODUCTION.
The organic chemistry of transition metal complexes has rapidly developed, in the last two or three decades, into an important and stimulating branch of chemistry. The beginnings, however, of the subject are many centuries old, for instance, the first metal-olefin complex is reported to be that of the Danish chemist, W.C. Zeise, as far back as 1827. The entirely novel substance, which is now commonly known as "Zeise's salt", was isolated as a crystalline substance, $\text{KCl}.\text{PtCl}_2.\text{C}_2\text{H}_4.\text{H}_2\text{O}$, on boiling an ethanolic solution of chloroplatinic acid, and subsequent addition of potassium chloride.

Controversy about Zeise's conclusions remained until 1868, when Birnbaum succeeded in preparing two analogous compounds, the propene and amyylene platinum compounds. It was not until forty years after Birnbaum that the first di-olefin complex was reported. Hofmann and von Harbut, in 1908, studied the reaction of dicyclopentadiene, in various alcoholic solutions with "potassium platinum chloride". When using propanol as a solvent, a crystalline substance, $\text{C}_{10}\text{H}_{12}.\text{PtCl}_2$, was obtained, in which, it was assumed, a chlorine atom and a platinum chloride radical added across the double bond. The correct structure was not postulated until 1956, when Doyle and Jonassen said that the complex might be a di-olefin complex. Final confirmation came, in 1961, when Baenziger obtained X-Ray structural analysis.

The chemistry of $\sigma$-bonded derivatives, although not really appreciated as such, then, was begun in 1841 by Bunsen's preparation of cacodyl, $(\text{CH}_3)_4\text{As}_2$. About 1900, after a very quiet period, this chemistry made great progress, through the efforts of great men such as Grignard and Schlenk. The latter had much influence on the use of mercury and arsenic compounds for medical purposes.
Reihlen and his coworkers, in 1930, tried to elucidate the structure of mononuclear metal carbonyls, by solving the problem of whether the carbonyls were bonded to the metal through the carbon or through the oxygen atom in, for example, iron pentacarbonyl. When they allowed the latter to react with butadiene in a pressure tube the yellow, air stable, low melting solid, butadieneirontricarbonyl was obtained. It was suggested that a possible stabilising factor was the formation of a five membered ring, formed by the butadiene and the iron atom. This therefore introduces the idea of the iron-carbon sigma (σ) bond.

Thus progress in the first century was very slow, and this may well be associated with the fact that no satisfactory explanation could be found for the bonding of unsaturated organic molecules to a metal atom. However, progress gathered momentum about 1945, when Chatt and his coworkers made significant contributions to the theoretical, as well as the practical, side of the subject.

In 1957 Chatt wrote in a paper, "At present the triangle of elements, Cu(I), Pd(II), Ag(I), Pt(II), Hg(II), is known to form reasonably stable (olefin) complexes. There are also iron complexes of the type butadieneiron tricarbonyl, but their structures are unknown."

Progress within the next four years was rapid, to the extent that metal olefin complexes were prepared (FIG. 1.) for all the transition metals, in the rectangle bonded by the coinage metals, and the Group VI transition metals, except for technetium and gold. More recently, however, gold olefinic complexes have been prepared.
Transition metals forming olefin complexes:

- **Olefin complexes formed by direct reaction of metal halide with olefin.**

- **Olefin complexes formed when other strongly Π-bonding ligands present.**

- **Olefin complexes formed by either possibility.**
Several reasons can be suggested for this sudden expansion, which was accompanied by a general upsurge of interest in all transition metal–carbon bonded compounds; one of the major reasons was the independent discovery of ferrocene, in 1951, by Kealy and Pauson and Millar and his coworkers. This led to intensive research in the field of transition metal complexes containing sandwich bonded aromatic systems such as \((C_5H_5^-)\) and \((C_6H_6)\). This was reinforced by the realisation that chelating cyclic and acyclic conjugated olefins gave metal complexes as well as the mono-olefins. Chatt and his coworkers studied the complex forming ability of unconjugated di-olefins, and were, for example, able to show that cycloocta-1,5-diene forms very stable complexes with some transition metal halides, due to the favourable geometry of the double bonds. Their attempts to prepare cycloocta-1,5-diene-metal carbonyls from cycloocta-1,5-diene remained unsuccessful. About the same time Hallam and Pauson isolated an irontricarbonyl complex analogous to butadieneirontricarbonyl, as prepared by Reihlen, with the cyclic conjugated di-olefin, cyclohexa-1,3-diene. The work of Chatt and Hallam ensured rapid development in the chemistry of di- and oligo-olefin-metal compounds, which in turn promoted research into the complexes of aromatic ligands. In 1958, Fischer prepared \(C_6H_6Cr(CO)_3\), and Wilkinson, by an analogous reaction, prepared \(C_7H_8(Mo)(CO)_3\), this being the first complex of cyclohepta-1,3,5-triene. Twelve months later complexes of cyclooctatetraene and cycloocta-trienes, cyclopentadiene and cyclobutadiene had been prepared.

Another reason for the sudden expansion in 1957 was the
re-examination of the metal carbonyl-acetylene reactions, which, besides their important economic organic synthesis applications, yielded many new metal-olefin and metal-carbon bonded complexes.
CHAPTER 11.

THEORIES OF BONDING

and

THEIR USE IN THE PREDICTION OF STABILITY.
Observations to be explained by bonding theories.

Any theory which aims to explain bonding in transition metal organometallic chemistry must explain the following empirical observations:

(a.) In many cases the total number of valence electrons, in the bonding orbitals of the central metal, is eighteen.

(b.) The majority of stable organometallic complexes are formed with metals in low, or zero, oxidation states, although it must be stressed that it is often difficult to decide exactly what this is, for example, the cyclopentadienyl rings in ferrocene can be regarded as ions, $\text{C}_5\text{H}_5^-$ or radicals $\cdot\text{C}_5\text{H}_5\cdot$ in which case the iron is in oxidation state two or zero, for the respective idea.

(c.) In general pure alkyls ($\text{MR}_n$) and hydrides ($\text{MH}_m$) are very unstable, compared with their non-transition metal counterparts, for example $\text{SnR}_4$.

(d.) Alkyl and hydride complexes of transition metals are stabilised by the presence of certain ligands, usually soft bases.

(e.) $\pi$-olefin metal complexes are more stable than the corresponding $\sigma$-analogues, for example, $\pi$-allyl and $\sigma$-allyl complexes, and that further stabilisation of the complex is enhanced by the presence of good donor-poor acceptor ligands.

Bonding in metal-olefin complexes.

At an early stage metal-olefin complexes were regarded as "organic molecular compounds" rather than organometallic complexes, since it was realised that olefins, unlike most
ligands, do not have any non-bonding electron pairs. However, many structures were postulated, for example that of Kharasch for bis(ethylene-platinum dichloride), containing σ-bonded ethylene bridges, (FIG. 2.)

![Diagram of a molecule with a Pt-C1 bond and two CH2 groups connected to Pt atoms.]

FIG. 2.

Olefin complexes of silver proved very unstable, and most of the information about them was originally obtained from a comparison of the distribution of various olefins, between aqueous silver nitrate and carbon tetrachloride, with that between aqueous potassium nitrate, at the same ionic strength, and carbon tetrachloride. More recently data has been obtained from gas chromatography and from the isolation of stable complexes.

These studies show the following points:

1. usually only one olefin molecule coordinates to each silver ion. A notable exception to this is the bullvalene-silver tetrafluoroborate complex, \((C_{10}H_{10})_3^{+}\)AgBF4.

2. the higher the alkyl substitution on the olefin the lower the stability of the complex.

3. more stable complexes are formed with the cis- than with the trans-olefins.

4. deuteriation of the olefin increases the stability
(5.) for endo-cycloolefins, the stability of the complex increases with ring strain.

The structure and bonding of these compounds provoked many suggestions and arguments. The original representation of Hinstein and Lucas was as a resonance hybrid of three forms (FIG. 3.)

\[
\begin{align*}
\text{C}^+ &\quad \xrightarrow{\text{Ag}} \quad \text{C} \\
\text{C} &\quad \xrightarrow{\text{Ag}^+} \quad \text{C} \\
\text{C} &\quad \xrightarrow{\text{Ag}} \quad \text{C}^+
\end{align*}
\]

FIG. 3.

Pitzer considered that these complexes could be regarded as having an "argenated double bond" in an analogous way to his idea of a "protonated double bond". This would involve the participation of the unoccupied s-orbital of the silver, as with the proton, forming a bond with the olefin.

Dewar and Walsh independently realised the ability of \(\pi\)-electrons to form dative bonds and thus act as donors, with respect to acceptor atoms. Walsh postulated that the metal-olefin bond was closely similar to that of a metal-ammonia bond, basing his arguments for this on the fact that the \(\pi\)-electrons of ethylene occupy an orbital with ionisation potential of 10.45 V., whereas the lone electron pair of ammonia has an ionisation potential of 10.8 V.

These suggested elucidations of the bonding of metal-olefin complexes were, although an improvement, still basically unsatisfactory. A more satisfactory picture was forwarded by Dewar in 1951. This involved the use of a Molecular Orbital
Theory approach. The bonding was assumed to consist of two components, the first was a $\sigma$-bond, formed by the overlap of vacant 5s orbital of the silver atom, with a filled $\pi$-2p orbital of the olefin, and the second a $\pi$-bond formed by the overlap of a filled 4d- orbital of the metal, with a vacant $\pi^*$-2p antibonding orbital of the olefin (FIG. 4.)

![Diagram of bonding](image)

Thus in the Dewar model the $\sigma$-component of the bonding pushes negative charge onto the metal, from the olefin, whilst the $\pi$-bonding restores the equilibrium, by removing the negative charge from the metal.

The bonding model can be modified to explain all metal-olefin bonding, for instance, Chatt and Duncanson\(^\text{43}\) used a similar model to explain the bonding in the square planar olefin complexes of Pt.(II). In this case it was assumed that the $\sigma$-bond was formed from the overlap of a filled $\pi$-orbital, of the olefin, with a vacant 5i6s6p²-hybrid orbital of the platinum, and that of the $\pi$-bond from an overlap of a filled 5i6p-hybrid orbital on the metal with a $\pi^*$-2p antibonding orbital of the olefin (FIG. 5.).
Dewar's theory explains why the majority of the stable metal olefin complexes are formed by metals, at or near the ends of the transition series. These elements have filled d-orbitals, capable of overlapping with olefin antibonding orbitals.

If the Dewar theory is correct, then as complex formation takes place there will be a reduction of the double bond character of the olefin, as the carbon atoms decrease in sp² and increase in sp³ character. The most sensitive indicators of the decrease in double bond character are the infra-red carbon-carbon double bond stretching frequency, and the increase in bond length of the olefin, as observed by X-Ray crystallographic studies.

In the infra-red and Raman studies on silver olefin complexes it was found that the carbon-carbon double bond stretching frequency of a number of olefins, for example, butene, cyclopentene, and cyclohexene, was lowered by between 50 and 70 cm⁻¹. However, similar studies on many platinum-olefin complexes showed that there was a shift, to lower wave numbers of about 145 cm⁻¹, with respect to the corresponding free olefin. This shift represents an elongation of the carbon-carbon bond.
to a length of formal bond order of 5/3. These results can be related to the stability of the platinum and silver complexes, by the fact that the more stable the complexes, the larger the carbon-carbon double bond stretching frequency shift. Assuming this relationship, the shift of the carbon-carbon double bond stretching frequency also proves that di- and oligo-olefin complexes are more stable than mono-olefin complexes, as shown in Table 1.

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\nu_{C=C}(\text{cm}^{-1})$</th>
<th>$\Delta \nu_{C=C}$</th>
</tr>
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<tbody>
<tr>
<td>Free $\text{C}_2\text{H}_4$</td>
<td>1623</td>
<td>112</td>
</tr>
<tr>
<td>$K\left[\text{C}_2\text{H}_4\text{PtCl}_3\right]$</td>
<td>1511</td>
<td>113</td>
</tr>
<tr>
<td>$\pi\cdot\text{C}_5\text{H}_5\text{Mn(C}_2\text{H}_4)\text{(CO)}_2$</td>
<td>1510</td>
<td>113</td>
</tr>
<tr>
<td>Free $\text{C}_4\text{H}_6$</td>
<td>1597</td>
<td>124</td>
</tr>
<tr>
<td>$K_2\left[\text{C}_4\text{H}_6(\text{PtCl}_3)_2\right]$</td>
<td>1473</td>
<td>131</td>
</tr>
<tr>
<td>$\pi\cdot\text{C}_5\text{H}_5\text{Mn(C}_4\text{H}_6)\text{(CO)}$</td>
<td>1466</td>
<td>131</td>
</tr>
<tr>
<td>Free 1,5-cyclooctadiene</td>
<td>1655</td>
<td>135</td>
</tr>
<tr>
<td>$(\text{C}<em>8\text{H}</em>{12})(\text{AuCl})_2$</td>
<td>1520</td>
<td>135</td>
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The weakening of the double bond on coordination has further been shown by X-Ray studies. For example, an X-Ray study of the cyclooctatetraene silver complex, $\text{C}_8\text{H}_8\text{AgClO}_3$, has shown that the cyclooctatetraene retains its "tub" configuration in the complex with alternating single and double bonds of length 1.46 and 1.37 Å, respectively. 52, 53 Similarly in platinum
complexes a lengthening of the carbon-carbon bond is observed, for example, in \( \text{C}_2\text{H}_4\text{PtCl}_2\text{Ni(CH}_3\text{_2)} \) there is an increase in the carbon-carbon double bond length, from 1.34 Å in free ethylene, to 1.47 Å in the complex. In the di- and oligo-olefin metal complexes similar lengthening of the carbon-carbon double bond is observed. The distances, however, are not so great as in the mono-olefin complexes, for example, 1.40 – 1.41 Å for \( (\text{C}_6\text{H}_{12}\text{CuCl})_2 \), 1.44 Å for \( (\text{C}_6\text{H}_{12}\text{RhCl})_2 \), and finally 1.37 Å for norbornadiene palladium dichloride.

Table 1. shows that the class of di- and oligo-olefins must be further subdivided into conjugate and non-conjugate dienes. For the non-conjugated dienes the carbon-carbon double bond may be assumed to be completely independent, and hence they bond to the metal like two separate ethylene moieties. In 1,3-butadiene, however, the double bonds cannot be treated as separate. Reihlen 7 was the first to prepare butadiene tricarbonyliron, but considered it to be a five membered ring, formed by the butadiene and the iron atom. (FIG. 6(i.)). Nearly thirty years later it was realised that delocalisation of the \( \pi \)-electron system could take place.59 (FIG. 6(ii.)) The X-Ray structure 60 showed that the butadiene moiety was planar, with all the bond lengths at 1.45 Å, which is a little shorter than expected for a single bond between two \( sp^3 \) hybridised carbon atoms. The four carbon atoms of the olefin are all shown to be equidistant for the iron atom. (FIG. 6(iii)).
Stability of olefin complexes.

Very few metal olefin complexes contain just the olefin ligands, although complexes such as nickel(olefin)_n and (triene)(iron)(diene) do exist. On the Dewar concept the stability of these complexes is explained by considering the overlap of the bonding π-orbitals of the olefin with vacant metal orbitals, in effect a charge transfer from the donor olefin to the metal, which attains a very slight negative charge. The weakly electronegative transition metals will attempt to transfer back the negative charge to the olefin, thus strengthening the back bonding. This sort of situation is only possible if there is a sufficiently small energy gap between the donor orbitals of the metal, and the lowest vacant orbital of the olefin. Should the gap be too large, then there will only be a charge transfer from the olefin to the metal, and not back again, thus producing very unstable, or non-existent complexes. The back bonding from metal to olefin is really the crucial factor in the stability of olefin complexes.
If, therefore, the energy required can be lowered, that is, reduction of the energy of antibonding orbitals of the olefin, then back bonding will be favoured and more stable complexes obtained.

The easiest way of lowering the energy is to introduce an electron attracting substituent into the olefin moiety. 61 Many examples of this can be found in the literature, for example, cyclopentadienone, quinone, cyclohepta-1,3,5-trienone or cycloocta-1,3,5-trienone form much more stable complexes than the pure di- and oligo-olefins. 62, 63 Similar effects can be obtained by using fluorocarbon-olefins, rather than the hydrocarbon olefins. In these cases the fluorine acts as the electron attracting group.

As stated above not very many stable metal olefin complexes are known that do not contain other ligands. The complexes studied in this work, for instance, contain aromatic ring systems, carbonyl groups, and phosphines. All these ligands are strongly electronegative in character, so that they are perfect for back bonding from the metal, taking all the negative charge away, that has been placed there by the olefin, (compare with the case of triene(iron)diene and nickel(olefin)₄ described above.). Group VIII metals form stable complexes of the type dienometaldihalide, for example, cycloocta-1,5-diene-palladiumdichloride, C₈H₁₂PdCl₂. 16 If the halide is replaced by a ligand with less electronegative character, then the stability of the diene complex decreases. Replacement, thus, by an alkyl group gives a very unstable complex, for example, C₈H₁₂Pd(CH₃)₂. 64 A good barometer of this effect is the dipole moment of the complex; for example the above dihalide complexes will have a
dipole moment with the olefin as the positive end, and the halogen atoms the more negative parts of the dipole.

In the complexes studied in this work metal carboxyls are used mainly because of their stabilising effect. Di- and oligo-olefin metal carboxyls have been prepared, and the infra-red carboxyl stretching frequency of the symmetrical mode is reduced by 40 - 60 cm\(^{-1}\), compared with pure carboxyls. This means that there is a decrease in the carboxyl force constants and the carboxyl bond order. Thus the stronger the bonding of the olefin to the metal the more the d-electrons of the metal can back bond to the carboxyl, thus forming the M-C=O bond, and lowering the carboxyl bond order. (FIG. 7.)

\[
\begin{align*}
\text{Me}^\Theta &\rightarrow \text{C}=\text{O}^\Theta \\
\text{Me} &\rightarrow \text{C}=\text{O}
\end{align*}
\]

Fig. 7.

This shows us why the progressive substitution of carbon monoxide in metal carboxyls must result in stronger bonding of those carboxyl groups remaining. Further evidence is obtained from the observation that as the carboxyl stretching frequency lowers, then there is a corresponding increase in the dipole moment of the complex. X-Ray crystallographic studies have also shown the increase in the bond order between the metal and carboxyl groups. In the cyclohepta-1,3,5-triene molybdenumtricarbonyl and cycloocta-1,3,5-trienechromiumtricarbonyl the metal carboxyl-carbon distances were approximately 0.1 Å shorter than in the unsubstituted metal carboxyl. (Table II.)
The metal olefin bond can be strengthened further if the ligands introduced push electron density onto the metal, but do not accept it back quite so readily. This can be attained by replacing the carbonyl group with a phosphine. The latter, with its 3d-orbitals has acceptor properties, but is a much stronger donor than a carbonyl, thus forcing more electron density onto the metal. An example of this is the contrasting properties of cyclopentadienetricarbonyliron, \( \text{C}_8\text{H}_6\text{Fe(CO)}_3 \), an unstable liquid,\(^{69}\) postulated as an unstable intermediate in the preparation of dicyclopentadienyldiiron-tetracarbonyl,\(^{70}\) from irongpentacarbonyl and cyclopentadiene, and cyclopentadienedi(carbonyltriphenylphosphine)iron, \( \text{C}_5\text{H}_6\text{Fe(CO)}_2\text{PPh}_3 \), a stable crystalline substance.\(^{71}\)

Aromatic ring systems also have stabilising effects on the metal-olefin bond. The most common aromatic system used is the π-bonded cyclopentadienyl ring, for example, complexes of the type π-cyclopentadienyl-metal(olefin) have been made

### TABLE II

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>BOND LENGTH (Å)</th>
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<tr>
<td>( \text{C}_7\text{H}_8\text{Mo(CO)}_3 )</td>
<td>1.936(±0.02); 1.936(±0.02); 1.95(±0.02)</td>
</tr>
<tr>
<td>( \text{Mo(CO)}_6 )</td>
<td>2.03 (± 0.04)</td>
</tr>
<tr>
<td>( \text{C}<em>8\text{H}</em>{10}\text{Cr(CO)}_3 )</td>
<td>1.78(± 0.03); 1.83(±0.03); 1.87(±0.03)</td>
</tr>
<tr>
<td>( \text{Cr(CO)}_6 )</td>
<td>1.94 (± 0.04)</td>
</tr>
</tbody>
</table>
where the metal is cobalt, rhodium, iridium, chromium, and the olefin is \( \text{C}_4\text{R}_4^-, \text{C}_5\text{H}_5\text{R}, \text{C}_5\text{H}_5\text{O}, \text{C}_6\text{H}_8 \), etc.. Complexes with six or seven membered rings are much more scarce, but complexes such as \( \text{C}_6\text{H}_6\text{MeC}_6\text{H}_8 \), where \( \text{M} \) is iron, \( 72 \) ruthenium or \( \text{osmium} 73 \) have been prepared.

It should be noted that there is a tendency to assume that the cyclopentadienyl rings behave as delocalised aromatic systems in all complexes. However Mason and his coworkers 74 indicated that in certain complexes a localised electron density may be observed. It has been shown that the aromatic ring systems tend to form complexes which have essentially a cylindrical symmetry about the metal ion, for example, complexes like \( \pi \)-cyclopentadienylmanganesetricarbonyl, and that the carbon-carbon bond lengths are identical. The idea that this might not always be so was first put forward by Dahl and Wei, 75 in a structural study of \( \text{C}_5\text{H}_5\text{NiC}_6\text{H}_5\text{C}_2(\text{COOC}_3)^2 \) in which they found that the carbon-carbon bond lengths in the cyclopentadienyl ring varied from 1.39\( \text{Å} \) to 1.47\( \text{Å} \). Similar variations in the nickel carbon bond lengths led Dahl and Wei to suggest, in valence bond terms, that the distribution was due to the tendency of nickel(II) to form square planar complexes, using \( \text{d}^{2} \) hybrid orbitals. Mason and his coworkers 74 approached the problem from a Molecular Orbital point of view, by considering that the six electrons in the cyclopentadienyl anion are distributed among the three molecular orbitals \( \text{a}^-, \text{e}^-, \) and \( \text{e}^- \). (FIG. 8.). Only when \( \text{e}^+ \) and \( \text{e}^- \) are equally occupied does one get uniform electron density, and hence cylindrical symmetry. The degeneracy of the \( \text{e}^+ \) and \( \text{e}^- \) orbitals could be removed by the removal of the degeneracy of the \( d_{xy} \) and \( d_{yz} \) orbitals.
of the metal, the normal orbitals of bond formation.

\[ a \quad e^+ \quad e^- \]

\textbf{Fig. 8.}

Thus, as shown in FIG. 9., carbon \( C_1 C_2 C_3 \) are joined by bonds of relatively low bond order compared with \( C_4 C_5 \), and thus will always be trans to strong field ligands, on the other side of the molecule, for example, one carbonyl in \( C_5 H_5 Mo(CO)_3 CH_2 CH_3 \).

Another excellent example of this non-symmetric bonding to the cyclopentadienyl ring is that of tris(cyclopentadienyl) nitrosylmolybdenum, \( (C_5 H_5)_3 Mo(NO) \). In this complex the NMR spectrum 76 was originally interpreted to show that there was one ring \( \sigma \)-bonded, one bonded through three carbons, and one through five carbons to the central metal. In terms of the Cotton notation \( (h_1-C_5 H_5)(h_3-C_5 H_5)(h_5-C_5 H_5) Mo(NO) \). An X-Ray
crystallographic study 77 showed that one ring was σ-bonded, but that the other two rings were identically arranged with respect to the metal: two carbon atoms at 2·32 - 2·35 Å, one at 2·43 Å, and two at 2·59 - 2·68 Å, from the metal. Churchill 78 has shown that, in general, the carbon atoms of the cyclopentadienyl ring are between 2·26 and 2·40 Å from the metal. Thus the bonding of two carbon atoms in the ring is diminished, but they are still close enough to interact, to some extent with the metal. Thus, instead of the delocalised aromatic system, it is possible for there to be a localised system, formed by either electrostatic effects, π-bonding, or both, perturbing the 'δ' orbitals, which, in turn, remove the degeneracy over and above the normal crystal field splitting.

Bonding of σ-alkyl complexes.

So far it has been shown that back bonding or dative bonding tends to stability in π-bonded organometallic complexes, especially when electronegative ligands are attached to the metal, to push electron density back onto the metal, and hence back onto the π-olefin or π-allyl bond. In the case of σ-alkyl complexes back bonding is impossible, resulting in most of the transition metal σ-alkyl derivatives being very unstable, and impossible to isolate in the pure state. The latter is, in general, because the alkyls are thermally unstable, usually existing only at very low temperatures, and are very sensitive to oxygen and atmospheric moisture, for example, Ti(CH₃)₄ 79 or Ti(C₆H₅)₄. 80 Recently a few transition metal alkyls have been prepared, that are stable, for example, zirconium 81 or titanium 82 tetrabenyl, M(CH₂C₆H₅)₄. However these are the exception rather than the rule.
Difficulty arises in distinguishing between high reactivity and instability, as in the alkali metal alkyls. The tetramer, methyl lithium is quite stable, but reacts rapidly on exposure to moisture, to give methane and lithium hydroxide. Not all metal alkyls, however, are as sensitive as this; for instance stable compounds can be made for mercury, tin and lead.

The strength of the covalent bond between the alkyl moiety and a transition metal is governed by the extent of the overlap of the bond forming orbitals. This is the key to the instability of transition metal alkyls, since the 3d, and also the 4s and 4d orbitals of the metal are small, and hence give only a small overlap with the typical σ-orbitals of the ligands. (FIG. 10.)

Confirmation of this is obtained from the observation that formation of metal alkyl derivatives is possible, giving better stability, with those metals with d orbitals of larger dimensions.

It cannot, however, be assumed that the size of the overlap integrals is the only factor affecting the stability of the metal-alkyl bond, because the overlap integrals, even in the more stable complexes, are not very large. It is therefore possible that the instability, rather than being a purely thermodynamic phenomenon, may be due to the extremely high reactivity of the complexes.

There is little quantitative data on thermodynamic stability of transition metal complexes, although it would seem probable that even some of the more "thermally stable" complexes are thermodynamically unstable, with respect to some decomposition products. The first step in the decomposition of many σ-organo complexes is postulated to be a unimolecular
Interaction between carbon \((s, p_z \text{ and } p_x)\) and metal \((s, p_z, p_x, d_{xz}, \text{ and } d_{z^2})\) orbitals in the \(xz\)-plane.
homolytic or heterolytic breaking of the metal–carbon bond. This will give either a carbon radical or an ionic species, which, being very reactive will immediately dimerise or polymerise. (FIG. 11.)

In 1926 it was suggested by von Grosso \(^{83}\) that the instability of transition metal alkyl complexes was due to the fact that the valence electrons of the transition metal are derived from shells of different principal Quantum Number. Jaffe \(^{84}\) showed, by the use of Mulliken's formula, that there is little chance of the transition metals forming strong \(\sigma\)-bonds with carbon in its usual hybridisation states. Mulliken's formula \(^{85}\) is an equation expressing the energy of a chemical bond, in terms of overlap integral, and the ionisation potentials of those atoms concerned. Jaffe brought in a term for ionic resonance energy, calculated from the electronegativity differences, thus dividing the energy of the bond into two basic components, an ionic and a covalent component. Since exact calculations, using this formula require the use of specific complexes, various assumptions were made, so that a general study could be made. This limits the accuracy of the predictions, but some meaningful results can be drawn. It was shown that the covalent contribution, involving ionisation potentials and the overlap integral, for bonds from \(sp^3\) hybridised carbon atoms, to metals of the first transition series, was only 50 – 60 \% of that for neighbouring non-transition metals, and furthermore the ionic component, was only about one quarter of that which stabilises the bonds to alkaline earth metals.

Expansion of this work, by the calculation of the relevant overlap integrals, \(^{86}\) showed that the bond energies, in general, decreased as the atomic weight increased, with any group in the Periodic system. This is in agreement with empirical evidence. \(^{87}\) Jaffe also found that the mean metal–carbon bond dissociation
Thermal decomposition of a $\sigma$-bonded organometallic complex by a unimolecular dissociation of the M-R bond.
energy is very dependent on the organic radical, which can effect the mean dissociation energy in the following ways:

i.) The state of hybridisation of the carbon atom.

ii.) The $\pi$-electron resonance energy.

iii.) The rearrangement energy of the organic radical.

When the 's' character of the carbon hybrid orbitals is enhanced, the overlap integrals, the ionic resonance energy, and the ionisation potential of the carbon atom, are all changed, in such a way that there is an increase in the strength of the carbon-metal bond. This explains why, in general, $\sigma$-aryl complexes are more stable than $\sigma$-alkyl complexes, for in aryls the hybridisation is $sp^2$, whilst in alkyls, it is $sp^3$. The effects of the $\pi$-electron resonance energy and rearrangement energy are small, but both contribute to a more stable bond. The first two factors above show that $\sigma$-bonded, unsaturated derivatives, (such as vinyl, ethynyl etc.), should be quite stable. This is seen, for example, in copper chemistry, where pure copper alkyls decompose below $-40^\circ C.$, copper phenyl about $80^\circ C.$, and copper acetylide explodes at $120^\circ C.$.

The conclusion that the instability of many transition metal-carbon bonds was due to the abnormally low ionic character led some workers to conclude that this could be remedied by the use of fluorocarbon derivatives. The effective electronegativity of $CF_3$ being approximately $3.3$, on the Pauling scale, which compares to fluorine ($4.0$) and chlorine ($3.0$). Likewise the electronegativity of the pentafluorophenyl group is similar to that of the bromine at $2.8$. This increase in ionic character does stabilise the complexes markedly, drawing the bonding electrons towards the fluorocarbon group, hence decreasing the charge.
on the metal. This is confirmed by spectroscopic data, supporting the importance of a structure shown in FIG. 12.

\[
\begin{array}{c}
\text{F} \\
\text{F}^- \\
\text{F} \\
\end{array}
\]

\[
\text{F} = \text{M}^+
\]

Fig. 12.

Jaffe, thus showed that it was possible to make transition metal complexes, with alkyls and aryls, although they would be unstable. However he, in no way, provided reasons why the transition metal complexes should have such little ionic and covalent strength in their bonds to carbon, as compared to the alkali metals. Chatt and Shaw 92 considered that the peculiarity of the transition metals was that the d-orbitals of the penultimate layer were energetically close to their s and p valence orbitals. This, they argued, meant that there was now the possibility of either an easy transition of non-bonding electrons from the higher occupied d-orbitals to the antibonding orbitals of the metal-carbon bond, or, when the d-orbital was vacant, the reverse transition from the orbital of the metal-carbon bond to this vacant orbital. In both cases the transfer of electrons from the bond weakens the bond, hence preventing the formation of the complex, or giving a very unstable one. This led to the postulation that stable organometallic complexes are only formed when there is a certain minimum energy difference ($\Delta E_*$) between the highest energy occupied orbital, and the lowest energy vacant orbital. (FIG. 13.)
Vacant orbitals:

\( \text{L.V.O.} \) - \( \sigma \)-antibonding orbitals and \( d \)-orbitals, not used in bonding.

\( \Delta E \)

Occupied orbitals:

\( \text{H.O.O.} \) - \( d \)-orbitals and the \( \sigma \)-bonding orbitals.

Orbitals associated with the metal.

\( \text{L.V.O.} \) - Lowest-energy vacant orbital.

\( \text{H.O.O.} \) - Highest-energy occupied orbital.

FIG. 13.

Chatt and Shaw\(^{92}\) prepared several alkyl and aryl derivatives of Group VIII, in which tertiary organic phosphines were used to stabilise the metal–carbon bond, by virtue of their ability to form strong dative bonds with the metal, using the non-bonding electrons of the highest occupied level. This led to the lowering of the level, and then to an increase in the critical value of \( \Delta E \). A ligand field theory approach to this problem would, therefore, be that where \( d \)-orbitals are used in the formation of \( \sigma \)-alkyl or aryl bonds ligands are required with a strong field, for example, phosphines, which will cause sufficiently large ligand field splitting in the energy levels of the \( d \)-shell.
This theory also agrees with the earlier observation that the heavier transition metals form more stable \( \sigma \)-complexes. This is so because the double bonding and ligand field splitting are much greater for the heavier transition metals, the complexes having occupied non \( \sigma \)-bonding \( d \)-orbitals. This is an important point, because it is completely the reverse situation to all other groups, with the exception of the group zinc, cadmium, and mercury. This group probably has some transition metal character in it, as is shown in some of its other properties.

New ideas have been put forward since the Chatt-Dewar hypothesis, but the latter is generally used for qualitative discussion of the situation. It would, however, be very interesting if more details of the critical energy factor, such as a rough order of magnitude for various series of organometallic compounds, could be determined.

In conclusion bonding, in transition metal \( \sigma \)-complexes, is very weak, but the complexes can be stabilised by the use of strong electron donating ligands, such as phosphines, or by the strong back bonding ligands, for example, aromatic systems, carbon monoxide, cyanide, etc. Thus the metal-carbon \( \sigma \)-bond is stabilised by exactly the same coordinated ligands as stabilise the metal-olefin complexes.

**Bonding in Allyl complexes.**

There are three different types of metal-allyl complex. The two types studied in this work are the \( \sigma \)-allyl and the \( \pi \)-allyl complexes, although bridging or \( \mu \)-allyl exist.

The first identified allyl complexes were reported in the late 1950's, and were all stabilised by other ligands. Heck and Breslow were the first to show the
symmetrical nature of the allyl moiety in π-allylcobalttricarbonyl

This was confirmed by NMR. studies, 98, 99 which also showed
that it was possible to distinguish between the π- and σ-allyl
complexes.

The reaction of allylic halides with nickel tetracarbonyl,
resulting in coupling of the allylic groups 100 was known for
many years before the isolation of the intermediate π-allyl
nickel complexes. 101

\[
\text{CH}_2=\text{CHCH}_2\text{Br} + \text{Ni(CO)}_4 \rightarrow \pi\text{C}_3\text{H}_5\text{NiBr(CO)} + 3\text{CO}
\]

\[
\begin{align*}
\pi\text{C}_3\text{H}_5\text{NiBr(CO)} & \xrightarrow{\cdot} \text{CH}_2=\text{CHCH}_2\text{Br} \\
\left[\pi\text{C}_3\text{H}_5\text{NiBr}\right]_2 + 2\text{CO} & \rightarrow \text{C}_6\text{H}_{10} + \text{NiBr}_2 + \text{CO}
\end{align*}
\]

Many good reviews on the synthetic use of allyl complexes
exist 102, 103 and these, in general show that the stability of
allylmetal complexes increase with atomic number, for example,
Ni<Pd<Pt<Cr<Mo<W and Ti<Zr<Th. The colour intensity
of the compound falls in a reverse order.

In general most pure π-allyl complexes are thermally
stable, many palladium complexes up to 200°C, but are
unstable to hydrolysis and atmospheric oxygen, especially when
in solution.

\[
\left[\text{C}_3\text{H}_5\text{Fe(CO)}_3\right]^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COCH}_3 + \text{CO}
\]

+ iron hydroxides etc.
In \( \sigma \)-allyl complexes the bonding is considered to be the straightforward bonding of an allyl radical, \( \cdot \text{CH}_2=\text{CH.CH}_2 \), contributing one electron to the metal-allyl bond in the normal way, giving the conventional carbon-metal electron pair bonding. \( \sigma \)-Allyls are subjected to the same problems of instability, as were observed for the \( \sigma \)-alkyl complexes. It is usually found, and has been confirmed with all the complexes used in this work, that the \( \sigma \)-allyls are more unstable than the corresponding \( \sigma \)-alkyl metal complexes. This is probably because the \( \sigma \)-allyl complex can decompose by two routes. One of these routes is the same as for the alkyl analogue, that of homolytic or heterolytic breakage of the metal-carbon bond; and the second is by the formation of the more thermodynamically stable \( \pi \)-allyl complex. This is illustrated by the fact that all known \( \sigma \)-allyl metal carbonyl complexes lose carbon monoxide on irradiation, usually under mild conditions, to give the \( \pi \)-allyl. The production of the \( \pi \)-allyl is probably made much more energetically favourable by the \( \beta \) effect, which has already been shown to be a possible route for the dissociation of metal-alkyl bonds.

When an unsaturated group \( X \), (where \( X \) is \( \text{CN}, \text{CH}_2=\text{CH}_2, \text{CHO} \), etc.) is in the \( \beta \) position, then there is an even more pronounced effect due to the empty \( \pi^* \) orbitals, which, being in the \( \beta \) position, with respect to the metal, have room to manoeuvre the empty orbitals into such a position that they overlap weakly with suitable d-orbitals on the metal.

In the \( \pi \)-allyl complexes one can regard the allyl moiety bonding to the metal as an allyl radical, anion, or even a cation. For instance, in the complex, \( (\pi-\text{C}_3\text{H}_5)\text{Ni} \), depending on whether one considers the allyl moiety as a radical, contributing three
electrons to the metal-allyl bond, or an allyl anion contributing four electrons, then the nickel may be regarded as being in either oxidation state (II) or oxidation state (0). In the allyl group the carbon atoms are approximately $sp^2$ hybridised, and there is one bonding, one anti-bonding, and one non-bonding orbital, in which the electrons, that will be transferred to the vacant metal orbitals, can be placed. In the allyl anion there will be two electrons each in the bonding and anti-bonding orbital; whereas in the allyl radical there will be two electrons in the bonding, and only one in the antibonding orbital. The three $2p$ atomic orbitals of the allyl carbon atoms will give rise to three molecular orbitals, normally represented as shown in FIG. 14.

![Fig. 14.](image-url)
When deciding with which metal orbitals these molecular orbitals can interact one must make several approximations. Brown 105, 106 and Orgel 107 made the assumption that the metal electrons can be classified under the local symmetry of the attached ligands. The local symmetry of the π-C₃H₅M grouping is C₃v, which is a very low symmetry, and does not limit the possible combination of orbitals very much. It does allow, however, the possible bonding and non-bonding orbitals to be separated, (TABLE. III.), since only orbitals of the same symmetry can combine.

### TABLE III.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Metal orbitals</th>
<th>Ligand orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>s, pₓ, pᵧ, pₓ, dₓ²₋ᵧ², dₓ², dᵧz</td>
<td>ψ₁, ψ₃</td>
</tr>
<tr>
<td>A''</td>
<td>pₓ, dₓᵧ, dₓz</td>
<td>ψ₂</td>
</tr>
</tbody>
</table>

The strongest metal-ligand bonds can be estimated from the symmetry allowed orbital combinations by looking at the pictorial representations of the orbitals of the metal, which can combine with the ligand. For example, one can eliminate the dₓᵧ and the dₓ²₋ᵧ² orbitals as these lie well below the allyl plane. There is no evidence to show, however, which combination of orbitals is preferred, although a consideration of the symmetry, if the π-allyl group is considered to be linear, 108 or an equilateral triangle, 109 can provide the guide to which metal orbitals will interact with the ligand orbitals.
The Chatt and Shaw hypothesis indicated that, to obtain a stable \( \sigma \)-complex the energy (\( \Delta E \)) of the transition from the highest filled \( d \)-orbitals into the lowest anti-bonding orbitals should be a maximum (FIG. 13.), and the best way to attain this was to lower the energy of the \( d \)-non-bonding orbitals, by combining them with the \( \pi \)-type orbitals of a suitable ligand. However in \( \pi \)-complexes \( \Delta E \) is further increased by the interaction of the \( \pi \) antibonding orbitals on the ligand and the non-bonding metal orbitals. (FIG. 15.).

The \( \sigma \)- to \( \pi \)- rearrangement can, therefore, be considered to occur when the \( \sigma \)-complex loses a ligand, thus reducing the value of \( \Delta E \), and allowing the rearrangement to a \( \pi \)-complex, in which the back bonding will stabilise the complex. The reverse process, the \( \pi \)- to \( \sigma \)- rearrangement can similarly be enhanced by the addition of a ligand, preferably one with a large donor capacity, such as a phosphine. This will push more electron density onto the metal, thus causing the energy of the \( d \)-orbital to rise, hence pushing more negative charge back onto the \( \pi \)-group as the metal tries to get rid of the excess negative charge. A relationship between the ligands effecting these \( \pi \)- and \( \sigma \)-rearrangements and the trans effect series \(^{110}\) has been put forward, and also that the rearrangements can be regarded in terms of "hard" and "soft" acids. \(^{111}\) In this approach the \( \sigma \)-bonded groups are considered hard, due to the greater polarisability of the delocalised \( \pi \) electron cloud, compared to the localised \( \sigma \)-orbitals. \(^{112}\)

Both of these approaches, however, lead to the same conclusion, that \( \pi \)- to \( \sigma \)- rearrangements result from the addition
Energy levels for organotransitionmetal complexes, (a) without $\pi$-bonding, (b) with $\pi$-bonding.

Fig. 15.
of strong π-bonding ligands, such as carbonyl, cyanide, phosphine, and dimethyl sulfoxide, whilst the reverse rearrangement results from the removal of one of these groups.

Influence of bonding theories on the choice of system.

The major aim of the research project, proposed as a basis for this thesis, was a detailed study of the attack of a series of carbon nucleophiles on olefins coordinated to metal systems, in the hope of finding an easy, selective, and even catalytic way of forming new carbon-carbon bonds. This would be of great interest in organic and industrial chemistry. As the research proceeded the proposed objective gave way to a more detailed study of the interesting reactions which appeared in the process of preparing the starting π-olefin and σ-alkyl derivatives. The choice of system, however, was dictated by the initial aim to form stable π-olefin complexes, which could be converted into stable σ-alkyl complexes by nucleophilic attack on the coordinated olefin.

In any research topic it is essential to first spend time in choosing the actual system to be studied, for the particular effect required. This means consideration of the stability of the starting material, the final product, and, of course, any intermediates that might be formed, as well as consideration of the electronic effects of the rest of the system on the groups under investigation.

It has been shown, in the preceding survey of bonding theories, that certain groups can stabilise σ-alkyl, allyl and π-olefin groups. The first essential is, therefore, to find a system in which both the σ- and π-bonded complexes are stable:
Many examples are known, for example nickel and platinum phosphines give stable complexes. Another system in which the type of complexes to be studied here have been made is the dicarbonyl-π-cyclopentadienyliron π-C₅H₅Fe(CO)₂X, in which the σ-alkyl, σ-allyl, and π-propene and ethylene complexes are known. This system has many advantages over, for instance, the nickel and platinum phosphines. Firstly the presence of the cyclopentadienyl ring gives the complex an electron "sink" into which to push excess electrons from the metal and secondly the ring protects the whole of one face of the metal from attack by any nucleophile, or other reagent. The presence of the carbonyl groups is also very important, as they act as electron "sinks," being both good donors and acceptors of electron density. In addition the carbonyl groups are very useful in that they give one a "handle," with which to follow any reaction, in the infra-red carbonyl stretching frequencies. The infra-red carbonyl stretching frequencies of the carbonyl groups attached to the metal, are not only very intense, so that only minute quantities of material are needed, but are, as is seen in the discussion of bonding theories, very sensitive to the substituent attached to the metal, as shown in TABLE IV.

The choice of metal is also important, since obviously the amount of charge that the metal can accommodate controls the amount of back bonding that can take place. In the literature there are three metals that can form this type of complex. They are tungsten, molybdenum, and iron. The stability of tungsten and molybdenum complexes is, in general, greater than that of the iron analogues. In this research all these three systems were investigated, to a certain
extent, but the iron system was explored in the greatest depth. The original intention was to compare the complexes of these three metals. The initial work was on the iron complexes, and as the chemistry of these proved so complex, in the time available, it was impossible to do as much work on tungsten and molybdenum complexes, as one would have liked.

**TABLE IV.**

<table>
<thead>
<tr>
<th>Complex.</th>
<th>Solvent.</th>
<th>$\nu_{\text{C=O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$</td>
<td>$\text{CCl}_4$</td>
<td>2016, 1955</td>
</tr>
<tr>
<td>$\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_2\text{CH}_3$</td>
<td>$\text{CCl}_4$</td>
<td>2010, 1950</td>
</tr>
<tr>
<td>$\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{C}_6\text{H}_5$</td>
<td>$\text{CCl}_4$</td>
<td>2020, 1960</td>
</tr>
<tr>
<td>$\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{Cl}$</td>
<td>$\text{CHCl}_3$</td>
<td>2060, 2010</td>
</tr>
<tr>
<td>$\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{Br}$</td>
<td>$\text{CHCl}_3$</td>
<td>2055, 2010</td>
</tr>
<tr>
<td>$[\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3\text{CN}]^+$</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>2080, 2035</td>
</tr>
<tr>
<td>$[\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{C}_3\text{H}<em>6]</em>+$</td>
<td>$\text{HCB}$</td>
<td>2089, 2055</td>
</tr>
</tbody>
</table>

A further advantage of this particular system is the ease with which a range of analogous phosphine substituted systems may be prepared, for example $\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}\left[\text{P(C}_6\text{H}_5\right]_3X$. This allows one to change, selectively, three different parameters; the steric nature around the metal, the ability to back bond, and the ability to force electrons onto the metal. The ability to alter the steric nature around the metal was found, in this work, to be an advantage. Much research has been carried out on the
changes in carbonyl stretching frequencies, on phosphine substitution, for example work on cobalt nitrosyl carbonyls resulted in a "spectrochemical series". 119 A more systematic study was made by Tolman, 120 in which spectral properties of tricarbonylphosphine nickel complexes were investigated for seventy different phosphines. In an extension of this work the apex angle of the cone extended by the phosphine was calculated. 121 The method of calculation was very empirical, but it gives a better approximation than previous estimates. These results indicated that the bulkiest phosphine is the o-tolyl phosphine, \( P(o-\text{C}_6\text{H}_4\text{CH}_3)_3 \), with a minimum cone angle of 194°. The bulkiest series of phosphines, with approximately the same angle, but differing in electronic effects was shown to be tris(pentafluorophenyl)phosphine, tricyclohexyl-phosphine, and triphenylphosphine, with cone angles of 184, 179, and 145° respectively.
CHAPTER III.

ASPECTS OF NUCLEOPHILIC ATTACK

on

ORGANOMETALLIC COMPLEXES.
Nucleophilic attack in transition metal complexes.

In the chemistry of olefins it is well established that electrophilic attack on the double bond is preferred to that of nucleophilic attack. The reason for this is that the cylindrical \( \pi \)-electron cloud, which is formed by the combination of the 2p orbitals on the two carbon atoms, acts as a repulsive force on the negatively charged nucleophile, and an attractive force for the electrophile. Even halogen addition involves initial electrophilic attack on the olefin to give an intermediate carbonium, or bromonium ion, in the case of bromine. The presence of the bromonium ion has been demonstrated by Olah (see FIG. 16(i)).

![Fig. 16(i)](image)

The second step in the reaction is nucleophilic attack by \( Br^- \) on the ionic species, to give the \( \text{vic-dibromide} \).

![Fig. 16(ii)](image)
The reason for the nucleophilic attack being allowed, in the second step of this reaction, is that the bromonium ion produced has effectively withdrawn a large part of the electron density from the double bond. It is clear that formation of a more stable system, in which the electrons are partly withdrawn from the double bond would facilitate nucleophilic attack. One section of this work deals with the properties of propene, when it is coordinated to a transition metal to give an organometallic complex analogous to the organic bromonium ion.

This is not the first study of this type of complex, since many important industrial processes, such as catalytic hydrogenation, hydration of acetylene, Ziegler-Natta process, and metal catalysed hydrolytic oxidation of olefins, have shown to involve intermediates of this type. An example of the latter being the Wacker process, which converts ethylene into acetaldehyde, acetone and methylethylketone. It is postulated that the important steps in this process are the following:

\[
PdCl_4^- + CH_2=CH_2 \rightleftharpoons [PdCl_3(\text{CH}_2=\text{CH}_2)]^- + Cl^-
\]

\[
[PdCl_3(\text{CH}_2=\text{CH}_2)]^- + H_2O \rightleftharpoons [PdCl_2(\text{H}_2\text{O})\text{CH}_2=\text{CH}_2] + Cl^-
\]

\[
[PdCl_2(\text{H}_2\text{O})\text{CH}_2=\text{CH}_2] + H_2O \rightleftharpoons [PdCl_2(\text{OH})\text{CH}_2=\text{CH}_2] + H_3O^+
\]

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 &\rightarrow \text{CH}_2\text{CH}_2\text{OH} &\rightarrow \text{CH}_3\text{CHO} \\
\text{Pd} &\rightarrow \text{Pd-H} &\rightarrow \text{CH}_3\text{CHO}.
\end{align*}
\]

Kinetic studies show agreement with this mechanism of an intramolecular nucleophilic attack.
Attack of nucleophiles, on transition metal complexes, can occur at different sites on the molecule, either at the metal, or at one or more of the ligands. Attack at the metal will not be considered here, in any detail, except to say that it can be a very good synthetic technique:

\[ \pi-C_5H_5Fe(CO)_2X + RLi \rightarrow \pi-C_5H_5Fe(CO)_2R + LiX \]

and that it is possible that many examples of nucleophilic attack on the ligands may involve initial attack on the metal followed by an intramolecular rearrangement. Investigation of this problem is in its early stages, and has not yet been studied in any great detail. The ligands on the metal must have some effect, for example, tricarbonyl(norbornadiene)iron protonates on the metal \(^{126}\) whereas similar complexes of other dienes protonate on the ligand \(^{127}\). The other important factor, in determining the site of attack, is the nature of the attacking nucleophile.

In the complexes dieneplatinum (or palladium)dichloride attack by halide or thiocyanate displaces the chloride atoms, \(^{128}\) but ethyl malonate or ethyl acetoacetate attack the diene \(^{129, 130}\). This could be due to the thermodynamic stability of the metal-chloride bond, or to the fact that the halide groups have a much lower base strength than oxygen or nitrogen atoms.

In the last few years investigation of nucleophilic attack on ligands, in transition metal chemistry, has become much more common. Paiaro and his coworkers \(^{131}\) have shown that nucleophilic attack by amines on \(\pi\)-bonded olefins, in the type of complex, cis(PtCl\(_2\))(olefin)(PR\(_3\)), give stable \(\sigma\)-bonded complexes. Similar results have been observed in the reaction of strong acids...
The attack of nucleophiles at the carbonyl-carbon in transition metal-carbonyl systems has been investigated. The most studied nucleophile, in these reactions, being the methoxide anion, which will, for example, react with the cationic species, $\left[ \text{Mn(CO)}_4\left[\text{P(} \text{C}_6\text{H}_5\text{)}_3\right]_2 \right]^+$ to give the ester, $\text{Mn(CO)}_3\left[\text{P(} \text{C}_6\text{H}_5\text{)}_3\right]_2(\text{CO}_2\text{CH}_3)$.

It has also been shown that ironpentacarbonyl and $\pi$-cyclopentadienyliron carbonyl cations are attacked at the carbonyl carbon atom by various amines. Busetto and his coworkers extended their work on $\pi$-cyclopentadienyliron tricarbonyl cation, $[\pi-\text{C}_5\text{H}_5\text{Fe(CO)}_3]^+$, to include other nucleophiles, which may be classified roughly into three groups.

The first group includes hydrazine and azide anions which attack the carbonyl carbon through the nitrogen atom. This gives an unstable intermediate of the type:

\[
\begin{align*}
\pi-\text{C}_5\text{H}_5\text{Fe} & \xrightarrow{\text{CO}} \text{O}\xrightarrow{\text{C-NHNH}_2} \\
\pi-\text{C}_5\text{H}_5\text{Fe(CO)}_3 & \xrightarrow{\text{O}} \text{C-N}_3
\end{align*}
\]

An intramolecular rearrangement, with the expulsion of ammonia or nitrogen respectively, gave the stable complex $\pi-\text{C}_5\text{H}_5\text{Fe(CO)}_2(\text{NCO})$. The second group includes amines and alkoxide anions. With these nucleophiles a stable adduct is formed, for instance, an amine will attack the carbonyl group to give a carboxamido group:

\[
\begin{align*}
\pi-\text{C}_5\text{H}_5\text{Fe(CO)}_3^+ + \text{RNH}_2 \rightarrow & \pi-\text{C}_5\text{H}_5\text{Fe(CO)}_2 + \text{H}^+ \\
& \text{C}=\text{O} \\
& \text{NHR}
\end{align*}
\]
The last group is made up of CN, NCO, and NCS. These nucleophiles displace one of the carbonyl groups to give, for example, the cyanodicarbonyl-π-cyclopentadienyliron complex. It was originally thought that the cyanate ion attacked the carbonyl carbon atom with nitrogen, in a similar fashion to the isoelectronic azide ion, but Angelici showed, by using 14C labelled cyanate, that at least 99% of the reaction proceeded by direct substitution of the cyanate, with expulsion of one of the carbonyl groups originally attached to the metal. The reaction rates were increased by increasing the solvent polarity, which suggested that there was considerable charge separation in the activation process.

Nucleophilic attack on the corresponding thiocarbonyl, \([\pi-C_5H_5Fe(CO)\text{CS}]^+\), prepared from acidifying the product of the reaction of sodium dicarbonyl-π-cyclopentadienylferrate and ethyl chlorothioformate, with the three groups of nucleophiles outlined above, proceeded in similar fashion to that on \([\pi-C_5H_5Fe(CO)_3]^+\). The reactions were considerably faster under the same conditions, for the thiocarbonyl species, and from the single pathway of the reaction, it is obvious that the electrophilic nature of the carbon atom in the CS group is greater than in the carbonyl group, since no attack is reported on the carbonyl.

Busetto followed this work by studying the reactions of nitrogen and oxygen nucleophiles with the coordinated ethylene in \([\pi-C_5H_5Fe(CO)_2C_2H_4]^+\) cation. In this case the reaction took place on the ethylene, rather than a carbonyl carbon atom, which is not very surprising, because the metal is withdrawing, from the double bond, a considerable amount of electron density, which is distributed by back bonding in the orbitals of the carbonyl group. Nucleophilic attack by methoxide and amines resulted in
attack on the olefin to give, for example, the σ-methoxyethyl derivative. Both products are easily converted back to the ethylene cation by treatment with anhydrous hydrogen chloride in ether. Attack by azide, however, gave the cyanato derivative, \( \pi-C_5H_5\text{Fe}(CO)(C_2H_4)(NCO) \) which was formed by attack at the carbonyl carbon followed by an intramolecular rearrangement, with expulsion of nitrogen (cf. \( \pi-C_5H_5\text{Fe}(CO)_3 \)). The product is possibly thermodynamically controlled, as the azido adduct, \( \pi-C_5H_5\text{Fe}(CO)_2(C_2H_5N_3) \) would be unstable. Cyanide and isocyanate both displace ethylene, presumably by a similar process to that outlined above for \( \pi-C_5H_5\text{Fe}(CO)_3 \) to give the cyano and cyanato dicarbonyl-π-cyclopentadienylniron complexes.

Very recently Busetto and Angelici \(^{141}\) have reported on the nucleophilic attack of primary and secondary amines on the two systems, \( \pi-C_5H_5\text{Fe}(CO)_3 \) and \( \pi-C_5H_5\text{Fe}(CO)_2\text{Ph}_3 \). The workers showed that amines attack at the carbonyl carbon to form carboxamido complexes, of the type \( \pi-C_5H_5\text{Fe}(CO)\text{Ph}_3(\text{CONHR}) \), which on treatment with hydrogen chloride removed the -NHR group from the carboxamido group. These results with \( \pi-C_5H_5\text{Fe}(CO)_2\text{Ph}_3 \) contrast to those obtained by Treichel and Shubkin, \(^{142}\) which show attack takes place at the metal and at the π-cyclopentadienyl ring.

Factors influencing nucleophilic attack.

A survey of reported nucleophilic attacks on metal complexes shows that the following points have the most influence on the course of the reaction:

1. Charge on the substrate.

This is very important because no anionic species has
has been reported which undergoes nucleophilic attack, although many neutral complexes do. Cationic species are attacked readily by nucleophiles, the electrostatic forces between the ions probably assisting the reaction. It is possible to visualise the incoming nucleophiles displacing the counter ion of the cation species, forming an ion pair complex, which then collapses to give the product. It has also been shown that charge is important in isoelectronic complexes; for example $[\text{C}_6\text{H}_5\text{Mn(CO)}_3]^+$ is susceptible to attack, whereas $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ is not.

2.) Oxidation state of the metal.

From theoretical considerations, one would expect that, for easy nucleophilic attack to take place, the metal atom involved should be able to change its oxidation state to a stable state two units lower. Thus one could generalise that nucleophilic reactions are enhanced by substrates in which the metal is in a high oxidation state.

3.) Coordination number of the metal.

The coordination number could be of importance, if the nucleophilic attack is considered to be initial attack on the metal, followed by an intramolecular rearrangement. All of the reaction products which have been studied by X-Ray analysis, so far, show that the incoming nucleophile takes up an exo-position, attack therefore, coming from the side remote from the metal. Examples of this are $\text{C}_7\text{H}_7\text{PhCr(CO)}_3$ and $\text{C}_5\text{H}_5\text{PhCoC}_5\text{H}_5$. It was found that this result held not only for phenyl anions, but also for hydride and methoxide, thus ruling out the possibility of steric factors influencing the result.

4.) Nature of the ligands.

Nucleophilic attack at the ligand will be greatly enhanced by the presence of electron withdrawing substituents on
the ligand. Fluorine, for example, makes tricarbonyl(perfluorocyclohexa-1,3,diene)iron susceptible to nucleophilic attack, whereas the pure hydrocarbon complex is not. Some ligands can cause competition to the expected pathway, and even give a completely different product, for example, azide does not attack the ethylene ligand in \([\pi C_5H_5Fe(CO)C_2H_4]^+\), but the carbonyl carbon atom, which, after rearrangement gives \(\pi C_5H_5Fe(CO)C_2H_4(NCO)\). A steric factor also presents itself here. Large ligands, such as phosphines or an aromatic cyclic ligand, for example, the cyclopentadienyl ring can protect a metal from direct nucleophilic attack.

5.) Nature of the nucleophile.

The two important features of the nucleophile are its steric and nucleophilic properties. The steric nature has already been dealt with in connection with the coordination number where, in the examples studied so far, it has been shown that it is relatively unimportant. Rates of reactions, however, are not quoted.

No details are available on the effect of variation of the nucleophilicity of the attacking reagent. For example, nucleophilicity falls, in the order methyl lithium, methylmagnesium bromide, and methyl cadmium. One might expect that, by correct choice of the nucleophilicity of the attacking reagent, it would be possible to attack certain ligands specifically.
Abbreviations.

The following abbreviations are used in the text of this thesis:

I. Abbreviations relating to Spectral Details.

A. Infra-red Spectra.

I.R. - Infra-red.

ν (cm⁻¹) - Frequency of absorption maxima, in wave numbers.

s., m., w. - strong, medium, and weak absorption.

B. Ultra-violet Spectra.

U.V. - Ultra-violet.

λ max. (nm.) - Wavelength of absorption, in nanometers.

ε molar - Molar extinction coefficient.

C. Nuclear Magnetic Resonance Spectra.

NMR. - Nuclear magnetic resonance.

ppm. - parts per million.

TMS. - Tetramethylsilane.

τ - Tau values of peaks, based on TMS. = 10.00.

J (c/s) - Spin-spin coupling constant, in cycles per second.

s., d., m., and q. - singlet, doublet, multiplet, and quartet.

Methods of obtaining spectra.

Infra-red spectra were recorded on Perkin Elmer 257, 457, or 621 instruments, calibrated with polystyrene and phenyl acetylene.

Ultra-violet spectra were recorded using a Unicam SP800 spectrophotometer.

NMR. spectra were recorded, at 60 Mc/s. on Perkin Elmer R10 and R12 spectrometers, and at 220 Mc/s. at I.C.I. Runcorn.

II. Abbreviations of a more general nature.

m.p. - melting point. - these were uncorrected.

b.p. - boiling point.
M. Wt.  -  molecular weight.
G., mg.  -  gram, milligram.
mMole.  -  millimole.
ml.    -  millilitre.
μl.    -  microlitre.
CHAPTER IV

EXPERIMENTAL.
General notes on experimental conditions.

All the reactions detailed in the following pages involved the use of dry solvents. Those reactions performed under nitrogen used nitrogen that had been dried by passing slowly through potassium hydroxide pellets, and then concentrated sulphuric acid. Only in special cases was the nitrogen scavenged for oxygen, in which case the nitrogen was either passed through a solid BTS catalyst, or through a self-generating reagent, prepared as follows:

Mercury (100g.) and granulated zinc (15g.) were shaken together to produce a zinc amalgam. To this was added chromium chloride hexahydrate (10g.) and dilute hydrochloric acid (100ml.), made up from water and concentrated hydrochloric acid, in the ratio 9:1. The mixture was shaken well, under nitrogen, and then saturated with nitrogen, until a bright clear blue solution was obtained. The scavenger became ineffective when it was bright green.

Preparation of ligands.

Dicyclopentadiene used in the preparation of the complexes studied was distilled at 88°C. and 35 mm. of Hg. pressure. The monomer, cyclopentadiene, was prepared by dripping the dimer into tetralin at 180°C., and collecting the distillate coming over below 40°C. The distillate was collected at -78°C. and used immediately. This prevented any reversal to the dimer, the rate of dimerisation of cyclopentadiene being 0.05% per hour at -20°C. and 1% per hour at 10°C.
Preparation of sodium cyclopentadienide.

Of the two standard methods of preparing the complex, 146, 147 that of reacting cyclopentadiene with sodium hydride in THF, at 0°C, was preferred to that using sodium sand. This was because sodium sand is inconvenient to make, and because the reaction proceeded much smoother the other way.

The clear red solution of sodium cyclopentadienide was always used immediately.

The triphenylphosphine used was supplied by BDH Chemicals Ltd., and was used without further purification. Triphenylphosphite was supplied by BDH Chemicals Ltd. and was purified by distillation at 234°C at 18 mm Hg pressure. Tricyclohexylphosphine was prepared as detailed below, and was purified by the formation of the carbondisulphide adduct.

Preparation of Tricyclohexylphosphine.

Procedure.

Refluxing of distilled cyclohexanol, concentrated hydrochloric acid, and anhydrous calcium chloride, gave, after work up, cyclohexyl chloride (70%) b.p. 141 - 143°C. 148

A Grignard reagent was prepared from dried magnesium turnings (20g.) and cyclohexyl chloride (81.2g. 685 mmole.), using anhydrous ether (250ml.) under nitrogen in dry apparatus. Phosphorus trichloride (27g. 215 mmole.), in absolute ether (50ml.), was added dropwise, very slowly under pure nitrogen, with vigorous stirring, over a period of four hours, the mixture being kept at about -30°C throughout the addition. The initial dark brown Grignard solution showed white spots, every time the phosphorus trichloride hit the surface. At half addition the suspension began to go grey, and by completion was pure white.
The mixture was then stirred for three hours at 0°C., one hour at room temperature, and finally refluxed on a water bath for three hours. The white suspension was cooled to -10°C. and ammonium chloride solution (250 ml.), prepared by dissolving ammonium chloride (40 g.) in water (240 ml.), was added slowly, with vigorous stirring. The yellow ethereal layer was syphoned off from the colourless aqueous layer, under a positive pressure of nitrogen. Concentration of the dried ethereal solution to about 30 ml. gave a very viscous liquid, which on addition of carbonyl sulphide (7.5 ml.) gave an immediate red colour. On shaking a deep rust red coloured precipitate (about 30 g.) was produced, which was washed with petroleum ether (30 - 40°C. fraction) (3 x 50 ml.), and then dissolved in refluxing absolute ethanol (200 ml.). The alcohol was slowly distilled off, removing the carbonyl sulphide at the same time, to yield a white solid. This was recrystallised from acetone, to give the pure white waxy solid, tricyclohexyl-phosphine (7.2 g., 20%), m.p. 73 - 75°C., infra-red: (K.C.B.) 2930 (s.), 2855 (s.), 1447 (m.), 1221 (w.), 889 (m.).

Yields from these reactions were very low, possibly due to the presence of minute traces of oxygen in the reaction vessel.

Preparation of Tris(pentafluorophenyl)phosphine.

Procedure.

A stock solution of methyl lithium was prepared from methyl iodide (40.7 g., 334 mmole.) in sodium dried ether (150 ml.) and lithium metal (4.0 g., 679.7 mmole.) in ether (100 ml.) and then standardised by hydrolysing a sample, and titrating with standard hydrochloric acid. The freshly prepared methyl lithium (200 ml.) was cooled slowly to -78°C. with vigorous stirring, to prevent a solid mass forming. Pentafluorobenzene (19.5 g., 116 mmole.)
in sodium dried ether (45 ml.) was added dropwise to the vigorously stirred suspension, which effervesced, as methane was evolved. On complete addition the reaction mixture was stirred for a further fifteen minutes, to give a white suspension in a light brown solution. The pentafluorophenyl lithium (20.16g. - assuming 100 % reaction.) was cooled to -78°C. and freshly distilled phosphorus trichloride (6.6g. 47.6 mmole.), in anhydrous ether (150 ml.) was added dropwise. The first drop of phosphorus trichloride caused a colour change in the solution, from pale brown to intense gold, which progressively went orange, chocolate brown and finally orange again. The mixture was hydrolysed with cold dilute hydrochloric acid (150 ml.), and the deep orange ethereal layer separated from the yellow aqueous layer. The aqueous layer was washed with ether (3 x 50 ml.), and the combined extracts dried over anhydrous calcium sulphate. Removal of the solvent, under reduced pressure, gave an orange solid which was extracted with hexane (5 x 75 ml.). The extracts were reduced to a small volume ( about 35 ml.) and cooled. An off-white solid was obtained, which on sublimation at 130° and 10⁻³ mm. gave pure crystalline Tris(pentafluorophenyl)phosphine m.p. 114 - 117°C. (lit. value 116 - 117°C.)¹⁴⁹

Preparation of organic reagents used for ligand formation.

A.) Preparation of tosylate derivatives.

Two methods of preparation were used. For alkyl derivatives it was found that pyridine, as the base gave best yields, whereas, for allyl derivatives, this method gave very low yields, and it was necessary to use a sodium hydroxide solution.
(i.) Typical procedure for butyl tosylates.

An excess of pyridine (300 ml.) was dried by refluxing, and then distilling from barium oxide, directly into the reaction vessel. Butyl alcohol (47 g. 635.2 mmole.) was added and the mixture cooled to -5°C., with a salt-ice bath. p-Toluenesulphonylchloride (100 g. 525 mmole.) was recrystallised from light petrol (40 - 60°C fraction.) and added in small aliquots, over three hours to the mixture, which was stirred for a further hour after complete addition, and then left overnight at 0°C. The reaction mixture, cream lower layer and orange upper layer, was poured into ice (500 g.) and water (150 ml.) and vigorously stirred. The lower layer of orange oil was taken up in benzene : hexane 1 : 3 (50 ml.) and washed with 2N. hydrochloric acid, water 10%, sodium bicarbonate, and finally water. Low boiling impurities were removed under high vacuum, and then the yellow viscous liquid distilled. This proved to be very difficult, due to easy decomposition.

Yields approximately 60%. infra-red:— Iso-butyl tosylate (neat film.) 2970(s.), 2940(m.), 2882(m.), 1602(m.), 1498(w.), 1399(m.), 1360(vs.), 1309(w.), 1293(w.), 1260(vw.), 1214(w.), 1191(vs.), 1178(vs.), 1121(w.), 1098(s.), 1040(vw.), 1020(m.), 977(vs.), 947(s.), 910(m.), 845(s.), 812(vs.), 790(s.), 705(w.), 686(m.), 662(vs.).

Sec-butyl tosylate (neat film.) 2980(s.), 2941(m.), 2835(m.), 1601(m.), 1499(w.), 1464(m.), 1401(w.), 1386(s.), 1360(vs.), 1310(w.), 1292(w.), 1264(w.), 1213(w.), 1190(vs.), 1180(vs.), 1095(s.), 1026(w.), 1020(m.), 995(w.), 960(m.), 900(vs.), 851(s.), 816(vs.), 775(w.), 740(s.), 706(m.), 684(m.), 661(vs.).
(ii.) Preparation of allyl tosylate.

The pyridine method, used for the alkyl derivatives was tried, but this proved unsuccessful, probably due to the formation of allyl pyridinium salts. Attempts to prevent the formation of the pyridinium complex, by hydrolysing with ice-water, half an hour after complete addition, also failed; also attempts to salt out the tosylate with sodium chloride, or to decompose any pyridinium complexes, with 20 % potassium hydroxide solution failed.

Procedure (A.)

Allyl alcohol (40g. 690 mmole.) and p-toluenesulphonylchloride (100g. 525 mmole.) were mixed at 0°C., and 20 % sodium hydroxide solution (about 300 ml.) added slowly enough to keep the temperature at 0°C. On addition of the alkali the mixture was tested for alkalinity with litmus and then stirred vigorously for one hour. The tosylate was extracted with a benzene : hexane mixture (1 : 3) (3 x 30 ml.) and the washed with 10 % sodium carbonate solution (3 x 50 ml.), 2N. hydrochloric acid (2 x 25 ml.) and finally with water (3 x 25 ml.). The organic solution was dried over magnesium sulphate, the solvent removed by distillation under reduced pressure, and finally the product distilled.

(69.6g., 46 %.) b.p. 135 - 136°C. at 0.4 mm. Hg pressure (the literature value b.p. 135 - 140°C. at 0.5 - 1.0 mm. Hg)

Infra-red: (film.) 3102(w.), 3080(w.), 3064(w.), 2998(w.), 2962(w.), 2938(w.), 1658(w.), 1602(s.), 1500(m.), 1458(m.), 1428(m.), 1365(vs.), 1311(m.), 1296(m.), 1218(m.), 1190(vs.), 1176(vs.), 1124(w.), 1100(s.), 1085(m.), 1022(m.), 971(vs.), 945(vs.), 918(vs.), 836(vs.), 812(vs.), 668(vs.).
Sodium hydride (50% dispersion in oil) (5.8 g, 414 mmole.) was washed with pentane (4 x 50 ml.) and the sodium hydride reweighed. Anhydrous ether (250 ml.) was added, under nitrogen, followed by an ethereal solution of allyl alcohol (5.8 g, 100 mmole.), causing a change in colour from grey to yellow. Addition of an ethereal solution of p-toluenesulphonylchloride (15 g, 79 mmole.) gave a white precipitate. The mixture was stirred for a further hour, filtered under nitrogen, and the filtrate fractionally distilled to give the tosylate (1.3 g, 58%) b.p. 138-137°C. at 0.8 mm.

Procedure (B.)

B.) Preparation of lithium reagents.

Unless otherwise stated the methyl, ethyl, propyl, butyl, and phenyl lithium reagents used in this work were prepared by reacting the alkyl or aryl halide with lithium in anhydrous ether. It was found advantageous, especially in the case of propyl to use small pieces of sheets of lithium, which were chopped even smaller by the use of a wire Hershberg stirrer. The reaction was then so vigorous at 0°C. to -10°C. as to need a carbon dioxide-acetone condenser to retain the refluxing ether.

Methyl lithium, used in the nucleophilic attack on π-propene salts, was prepared by the reaction of dimethylmercury on lithium.

Procedure - for the preparation of methyl lithium.

Methylmagnesium iodide was prepared from magnesium turnings (10 g, 412 mmole.) and methyl iodide (60 g, 410 mmole.), by standard techniques. The Grignard was filtered under nitrogen, and into it was introduced mercuric chloride (33.5 g, 123 mmole.) by
Soxhlet extraction. This method of adding mercuric chloride was used to prevent clogging, which occurred when it was added directly to the reaction mixture. The mixture was cooled in a salt-ice bath and wet ether (100 ml.) added slowly, followed by water (100 ml.), to destroy any excess Grignard reagent. The two layers were separated, the aqueous layer was washed with ether (3 x 25 ml.) and the combined ether fractions dried over calcium chloride. The ether was removed by distillation, through a Dufton column, and the clear solution remaining, distilled at 54°C. and 250 mm. Hg. A cream solid was left, which from its infra-red appeared to be methylmercuric iodide. The distilled dimethyl mercury (14·1g.) in absolute ether (50 ml.) was shaken with very small pieces of lithium (2·5g. 357 mole.) for three hours. The suspension gradually turned dark grey, and the lithium gradually sank as an amalgam was formed. The mixture was filtered under nitrogen, to yield methyl lithium.

Allyl lithium was prepared by the standard method of cleaving allylphenyl ether with lithium in anhydrous ether at \(-15^\circ\text{C.}\) This procedure, however, suffered from the disadvantage that lithium phenoxide was produced, and could not be removed from the mixture. Therefore there was competition of phenoxide and alkyl for the reaction with the organometallic complexes.

Preparation of Grignard reagents.

All the Grignard reagents were prepared from carefully dried magnesium, which was always stirred for 10 - 15 minutes in the nitrogen flushed apparatus, before starting the reaction. Dibromoethane was used to activate the reaction, rather than a
crystal of iodine. The preparation of allylmagnesium chloride was the only one requiring very strictly controlled temperature. When the magnesium had been activated with dibromomethane the apparatus was cooled to \(-15^\circ C\) to \(-20^\circ C\). This temperature was maintained throughout the addition of allyl chloride. On complete addition the mixture was stirred for a further thirty minutes, filtered and then stored at \(-20^\circ C\).

**Preparation of bis-allyl magnesium.**

Allylmagnesium chloride was prepared as above, and then standardised by adding standard hydrochloric acid and back titrating the excess acid with standard sodium hydroxide. The standard allylmagnesium chloride was then treated, under nitrogen, with an equivalent amount of dioxan. An immediate white precipitate formed, which was centrifuged off, and the clear colourless supernatant used without further standardisation.

**Handling Techniques.**

Since most of the organometallic derivatives prepared in this research were sensitive to air or moisture they were handled, in general, in Schlenk tubes. (FIG. 17.) in conjunction with a vacuum line and nitrogen line.

All the organometallic oils were purified by distillation using a Molecular distillation apparatus (FIG. 18.), usually with a very short pathlength of about 2 cm.
Fig. 17.

Schlenk tube.

Filtration unit.

Double Schlenk tube.

sinter.
Molecular distillation apparatus.
IRON SERIES.

All the organometallic complexes used in this part of the work have been prepared from derivatives obtained from dicyclopentadienyldiirontricarbonyl, \([\pi-C_5 H_5 Fe(CO)]_2\). This dimer was prepared using ironpentacarbonyl and dicyclopentadiene, by the standard procedures. It was, however, found that yields were improved by using petroleum spirit (135 - 145°C fraction.) as solvent, rather than excess dicyclopentadiene, as this improved the ease of crystallisation of the crude product from the reaction vessel. Recrystallisation from hexane, or benzene - hexane, gave deep purple - red crystals. (60 %.) m.p. 194 - 195°C. (literature value 192°C.) Infra-red: (in carbondisulphide.) 2958(w.), 2924(w.), 2870(w.), 2856(w.), 2000(vs.), 1961(vs.), 1926(w.), 1786(vs.).

Iodo-, bromo-, and chloro- dicarbonyl-\(\pi\)-cyclopentadienyliiron were prepared from the dimer by the usual methods. It was found, however, that in the preparation of the bromide yields were vastly improved, and crystallisation much easier when the dimer was oxidised with bromine, and not hydrobromic acid.

Reaction of chloroform with \([\pi-C_5 H_5 Fe(CO)]_2\)

In the preparation of the chloride concentrated hydrochloric acid was added to chloroform solutions of dicyclopentadienyldiirontricarbonyl. It was found that the acid was not really needed in this reaction, although it was catalytic.

Dicyclopentadienyldiirontricarbonyl (501 mg, 1.4 mmole.) was stirred in ethanol free chloroform (20 ml.) under nitrogen. Monitoring by infra-red spectroscopy showed that the reaction was
complete after five hours. (565 mg., 95 %.) m.p. 89 - 90°C. (dec.)
(literature value 84 - 87°C.) 153
Infra-red (in carbon tetrachloride): 3110(m.), 2050(vs.), 2010(vs.), 1425(m.), 1365(w.), 1120(w.),
1070(w.), 1003(s.), 874(s.), 837(s.). Ultra-violet: 338 μμ.
ε_max. 1000(± 150.).

Repeat of this experiment, using chloroform that had had anhydrous hydrogen chloride passed through it for a few seconds, to give a very weakly acidic solution cut the reaction time by half. The reaction also proceeded in the dark, eliminating the photolytic pathway observed by Noack. 155

Following logically from this result the reaction of dicyclopentadienyldiiron tetracarbonyl with bromoform and iodoform was studied.

Reaction with bromoform.

Dicyclopentadienyldiiron tetracarbonyl (497 mg. 1.4 mmole.) was dissolved, under nitrogen, in distilled bromoform (20 ml.)
The deep red solution was shaken for two hours, by which time the infra-red spectrum showed the presence of no starting dimer, but two bands corresponding to the carbonyl stretching frequencies of the bromide. The mixture was evaporated to dryness under high vacuum, to give a red-brown solid residue, which was recrystallised from a benzene : hexane (4:1.) mixture, to give a deep red-brown crystalline product of the bromodicarbonyl-n-cyclopentadienyliron (648mg., 90 %.) m.p. 100 - 101°C. (literature value 98 - 102°C.) 154
Infra-red (in chloroform): 3019(m.), 2964(vw.), 2055(vs.), 2010(vs.), 1428(s.), 1075(w.), 1008(s.). Ultra-violet: 352 μμ.
ε_max. 2200(± 150.).
Reaction with iodoform.

Dicyclopentadienylidirdiiron tetracarbonyl (511 mg., 1.5 mmole.) was dissolved in sodium dried benzene (20 ml.) under nitrogen. Excess iodoform (3.8 g., 10 mmole.) was added and the deep red mixture was refluxed for half an hour, giving a yellow brown solution. The mixture was allowed to cool, and n-pentane (15 ml.) was added. The precipitated excess iodoform was filtered off under nitrogen. The filtrate was evaporated to dryness, and the brown solid recrystallised from a chloroform : petrol (30 - 40° fraction.) (5 : 1 ) mixture, to give dark brown - black crystals. (832 mg., 95 %.) m.p. 118 - 119°C. (literature value 117 - 118°C.)

Infra-red (in chloroform): 2918(\nu), 2770(\nu), 2035(vs.), 1994(vs.), 1962(\nu), 1427(m.), 1005(s.). Ultra-violet \( \lambda_{\text{max}} \) 353 m\( \mu \) \( \epsilon \) molar 2400 (7150.)

Thus it can be seen that this method gives good yields for the bromide, and the iodide, the iodide being the better of the two. Previous preparations of the iodo derivative involved the treatment of chlorodicarbonyl-\( \pi \)-cyclopentadienyliron with sodium iodide in refluxing acetone for twenty four hours.

Attempts to prepare fluorodicarbonyl-\( \pi \)-cyclopentadienyliron by the treatment of dicyclopentadienylidirdiiron tetracarbonyl with 40 % hydrofluoric acid, or by treatment of bromodicarbonyl-\( \pi \)-cyclopentadienyliron with silver tetrafluoroborate and sodium fluoride both gave red oils. It has so far proved impossible to isolate a pure crystalline material - recrystallisation and sublimation having been tried. The carbonyl stretching frequencies of the product, at 2061 and 2021 cm\(^{-1}\) (neat oil.) do not eliminate or prove the presence of \( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)Fe(CO)\(_2\). Another possible product is the cation, [\( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)-F-(CO)\(_2\)Fe(\( \pi \)-C\(_5\)H\(_5\))]\(^+\).
Preparation of carbonylphosphine-π-cyclopentadienyliron halide complexes. (FIG. 19.)

(A.) Preparation of bromocarbonyltriphcnylphosphine-π-cyclopentadieny1iron.

Method (i.)

Two procedures were used for the preparation of this bromide, both based on the work of Treichel, who reported that the reaction of bromodicarbonyl-π-cyclopentadienyliron (1 mole.) with triphenylphosphine (0.95 mole.) in refluxing benzene under nitrogen for 18 hours produced only π-C₅H₅Fe(CO)P₃Br in 51% yield. When this experimental procedure was used it was found that two products were formed, π-C₅H₅Fe(CO)P₃Br in 45–55% yield, and π-C₅H₅Fe(CO)₂P₃Br in 30–40% yield. Furthermore, by following the infra-red spectrum of the reaction mixture it was possible to show that maximum yield of the covalent bromide, π-C₅H₅Fe(CO)P₃Br was formed after one and a half hours.

The second procedure was similar to the first in method, except that the reaction was performed in refluxing n-pentane, rather than benzene. This change was made because it was seen that in benzene at temperatures of 80°C and above some decomposition of π-C₅H₅Fe(CO)P₃Br occurred.

Procedure:

Triphenylphosphine (7g. 34.3 mmole.) was dissolved in n-pentane (150 ml.) under nitrogen, and to this stirred, refluxing solution was added bromodicarbonyl-π-cyclopentadienyliron (5g. 20.5 mmole.) by Soxhlet extraction, using the refluxing pentane. This addition avoided the use of vast volumes of solvent needed to keep the reactants in solution, and also enabled there always to be an excess of triphenylphosphine in the reaction mixture. The mixture was refluxed gently for twenty-four hours.
The green precipitate of the covalent bromide was filtered off from the pale yellow supernatant, washed well with n-pentane (3 x 100 ml.) and ether (3 x 50 ml.) and finally recrystallised from a chloroform - petroleum (40 - 60°C. fraction.) mixture. (7.66 g., 80 %) m.p. 143 - 144°C. Infra-red (in chloroform.):
3055(w.), 2984(m.), 1965(vs.), 1593(vw.), 1482(w.), 1438(m.), 1176(m.), 1120(s.), 1091(m.), 1070(w.), 1028(w.), 999(v.).

NMR: (in dimethyl sulphoxide.) 2.52(m.)(1H.); 5.41(s.)(5H.)
(in deuterochloroform.) 2.54(m.)(1H.); 5.52(s.)(5H.)

It was later found that better yields of the covalent product could be obtained, free from the ionic bromide, by using hexane as solvent, rather than n-pentane. This also reduced the reaction time to six hours. Similar reactions could be carried out with the chloride and the iodide.

Method (ii.).

Preparation from dicyclopentadienyldiiron-tetracarbonyl.

It has been established that the dimer, dicyclopentadienyldiirontetracarbonyl was oxidised by very weakly acidic chloroform, to the chloro derivative, which was then able to react with triphenylphosphine. The following experiment was therefore carried out.

Procedure:

Dicyclopentadienyldiirontetracarbonyl (0.179 g., 0.5 mmole.) was dissolved in chloroform together with triphenylphosphine (0.591 g, 1 mmole.) in a Schlenk tube under nitrogen. The stoppered tube was shaken for two days at room temperature. The initial red solution turned dark green. The
infra-red spectrum (in chloroform.) showed the presence of no starting material, minute traces of chlorodicarbonyl-\(\pi\)-cyclopentadienyliron and large amounts of the phosphine substituted product. The solvent was removed under pressure and the residue chromatographed on a neutral alumina column (10 x 1 cm.). Elution with hexane gave chlorodicarbonyl-\(\pi\)-cyclopentadienyliron and free triphenylphosphine, then elution with benzene gave the chlorocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron (0.49 g., 64\%).

The reaction proceeded much faster when photolysed, and not at all in the dark. A similar reaction has been reported with iodo benzene. 157

(E.). Preparation of bromocarbonyltriphenylphosphite-\(\pi\)-cyclopentadienyliron.

Procedure:

Bromodicarbonyl-\(\pi\)-cyclopentadienyliron (2.056 g., 8 mmole.) and triphenylphosphite (2.24 g., 8.5 mmole.) were refluxed under nitrogen in anhydrous hexane. The solution gradually changed from its deep red colour to brown, at the same time a light brown precipitate was formed. After five hours the supernatant was almost colourless, so the reaction was stopped. The whole reaction mixture was passed through a short fat column of neutral alumina (80 g.). The brown solid was washed with n-pentane (3 x 50 ml.) and then with a n-pentane - ether (8 : 1.) mixture (3 x 50 ml.) to remove all excess bromodicarbonyl-\(\pi\)-cyclopentadienyliron and triphenylphosphite. Finally the brown solid was eluted with chloroform. The chloroform solution was concentrated to approximately 30 ml. and petrol (30 - 40\(^\circ\)C. fraction) added until precipitation began. On standing large
brown crystals formed, these were the bromocarbonyltriphényl-
phosphite-π-cyclopentadienyliron. (4·1g., 95 %) m.p. 141 - 143°C.
Infra-red (in carbon disulphide): 3098(vw.), 3070(w.), 3059(w.),
3042(w.), 3015(w.), 1994(vs.), 1967(w.), 1222(m.), 1214(m.),
1194(s.), 1160(m.), 1069(w.), 1023(m.), 1004(w.), 924(s.), 885(s.),
824(w.), 774(s.), 759(vs.), 732(w.), 720(w.), 690(m.). NMR. (in
deutero-dimethylsulphoxide): 2·55(15H.), 5·65(5H.).

(C.) Attempts to prepare related tricyclohexylphosphine
and tris(pentafluorophenyl)phosphine complexes proved unsuccessful.
Using thermal methods tricyclohexylphosphine did not react at all,
but tris(pentafluorophenyl)phosphine removed all carbonyls to
yield a green product which was not identified. Photolysis, in
the case of tricyclohexylphosphine gave a green solid of similar
infra-red spectrum to π-C₅H₅Fe(CO)P₃Br, but the complex
decomposed rapidly, even at low temperatures. The experiment
could not be repeated.

Preparation of the sodium salts of the cyclopentadienyl metal
carbonyls.

(A.). Preparation of sodium dicyclobonyl-π-cyclopentadienyl-
ferrate.

The preparation was by the standard technique of stirring or shaking a sample of dicyclopentadienyldiiron-
tetracarbonyl at room temperature, under nitrogen, with a 50 %
excess of sodium metal, as a 1 % amalgam. After about an hour
the original red solution became orange-brown. Excess amalgam
was removed and the tetrahydrofuran solution was used
immediately.
(B.). Preparation of sodium carbonylphosphine-π-cyclopentadieny1 ferrates.

Two methods were used to prepare these sodium salts. The first method involved the treatment of bromocarbonylphosphine-π-cyclopentadienyliron with excess 1% sodium amalgam. This gave low yields of the anion, together with large quantities of brown solid, which was shown to contain no carbonyls.

It was found much better to use sodium potassium alloy. A typical procedure was to dissolve the bromide in THF, freshly distilled from lithium aluminium hydride under nitrogen, and then add a slight excess of the potassium alloy. Vigorous shaking dispersed the alloy to give a very fine suspension, and hence a large surface area. When the reaction had finished, usually about half an hour, the suspension was centrifuged, to bring down the excess alloy with the salts formed in the reaction. The anionic species was then removed under nitrogen and used at once.

Preparation of alkyl, aryl, and allyl dicarbonyl-π-cyclopentadienyliron. (FIG. 20.)


(i.) Anion plus alkyl halide.

Sodium dicarbonyl-π-cyclopentadienylferrate solution was prepared as stated above, and after removal of excess amalgam, iso- or sec-butyl iodide was added at 0°C, under nitrogen, in sufficient excess to react with the total amount of sodium used in the generation of the original anion. After stirring the mixture for two hours the solvent was removed to leave, in both cases, a reddish brown solid residue. Direct distillation at 0.01 mm. Hg, and about 40°C, using a 2 cm. pathlength from the reaction flask
Fig. 20.

\[
\begin{align*}
\text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{C}_6\text{H}_5 & \quad \text{CH}_3 \\
\text{CO} & \quad \text{CO} \\
\text{Fe} \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{Br} & \quad \text{CO} \\
\text{Fe} \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{CH}_2\text{CH}=&\text{CH}_2 & \quad \text{CH}_2\text{CH}=&\text{CH}_2 \\
\text{Fe} \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{CO} & \quad \text{CO} \\
\text{Fe} \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{CH}_2\text{CH}=&\text{CH}_3 & \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{Fe} \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} \\
\text{CH}_2\text{CH}=&\text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\]
proved rather slow. The reaction mixture was, therefore transferred to a Soxhlet thimble, and the residue extracted with petrol (30 - 40°C. fraction.). This proved rather unsuccessful, because the temperature needed to reflux the petrol, decomposed the extracted product. Chromatography also proved unsuccessful, and it was therefore necessary to return to the very slow molecular distillation technique.

(ii.) Anion and alkyl tosylate.

Dicyclopentadienyldiirontetracarbonyl (2.21g., 6·25 mmole.) was dissolved in THF., that had been freshly distilled from lithium aluminium hydride, (75 ml.). This solution was added to sodium (31·5 mmole.), as a 1 %, amalgam, in THF. (100 ml.) The resulting mixture was shaken for several hours in a nitrogen atmosphere, and a brown solution of the anion resulted. Iso- or sec-butyl tosylate (4·0g.) in dry THF. (25 ml.) was added in small portions to the mixture at -73°C.

Removal of the solvent gave an orange-red oily solid, from which the butyl derivatives were distilled, at room temperature and 0·03 mm. Hg. This process was slow, but a clear amber oil was obtained, (iso-butyl derivative 0·673g., 23 %. sec-butyl derivative 0·497g., 17 %.). Infra-red(in carbondisulphide.)

Iso-butyl derivative: 2950(m.), 2920(m.), 2870(w.), 2851(w.), 1947(vs.). Sec-butyl derivative: 2959(m.), 2916(m.), 2870(w.), 2859(w.), 2001(vs.), 1954(vs.).

Both the iso- and sec-butyl derivatives proved to be sensitive to air, the secondary derivatives being the more sensitive. In both derivatives the sensitivity to air increased in solution.
(B.). Preparation of \( \text{o'-allyldicarbonyl-} \pi \text{-cyclopentadienyl-iron.} \)

(i.) Anion and alkyl halide.

Following the general route used by Green and Nagy, a THF solution of sodium dicarbonyl-\( \pi \)-cyclopentadienylferrate (5g, 25 mmole.) was treated with a large excess, (4 Molar.) of allyl bromide for one hour, in a nitrogen atmosphere. After removal of the solvent and excess allyl bromide, the red-brown residue was extracted with petrol (30 - 40°C. fraction.) The extracts were concentrated and chromatographed on an acid alumina column, with light petrol.

Yields using the allyl bromide were very low (about 5 %.) but using the allyl chloride were circa 25 %. The low yields, when using the bromide, were accounted for by the elution of large quantities of bromodicarbonyl-\( \pi \)-cyclopentadienyliron from the column.

Yields of the \( \sigma \)-allyl derivative were obtained as high as 35 - 40 %, by replacing the allyl halide by allyl tosylate, and then by using molecular distillation to isolate the pure complex, rather than petrol extractions followed by chromatography. The complex was distilled at 40°C. and 0.01 mm. Hg, with a 2 cm. pathlength onto a cold finger at -78°C. as an amber oil (2.11g., 39 %.) Infra-red (neat film.): 3073(w.), 2960(m.), 2920(m.), 2860(m.), 2010(vs.), 1948(vs.), 1608(s.), 1433(m.), 1419(m.), 1399(w.), 1211(w.), 1190(s.), 1178(s.). (in carbon disulphide.) 2010(vs.), 1952(vs.). (in cyclohexane.) 2010(vs.), 1966(vs.).

NMR. (in cyclohexane.) \( \delta = 7.99 \) ('s.) (2H.) (J(CH₂, H) = 8.5), 5.49 (s) (5H.), 5.3 (m.) (2H.), 3.88 (m.) (1H.).

Exposure of the oil to air caused decomposition, as did heating above 62 - 63°C. The thermolysis might be expected to
give π-allylcarbonyl-π-cyclopentadienyliiron, but this was not observed, due to the latter decomposing at the same temperature.

(ii.) Halide and Grignard.

Bromodicarbonyl-π-cyclopentadienyliiron and allylmagnesium chloride were reacted together, in an atmosphere of nitrogen, using a molar ratio of 1:2. Stirring for two minutes caused a reduction in the redness of the solution giving, finally an amber solution, which was characteristic of the other alkyls in the series. However the extraction of the product proved very difficult. The following methods were used:

(a.) Addition of degassed distilled water, under nitrogen, resulted in an immediate darkening of colour. The ethereal layer and the ethereal extracts were dried over magnesium sulphate. Removal of the solvent gave a red oily solid, which showed in the infra-red spectrum, as the prominent bands those of π-cyclopentadienylicarbonyliiron dimer.

(b.) Addition of ethyl acetate, to destroy the excess Grignard reagent, resulted in poorer overall yields, with the production of large amounts of the dimer, \([\pi-C_5H_5Fe(CO)2]_2\).

(c.) Addition of triethylamine, under nitrogen, to complex the magnesium halides, resulted, on shaking, in a slight darkening in the colour. Subsequent addition of water, followed by extraction with ether gave an amber solution, which after drying and removal of the solvent gave a mixture of an amber - brown oil and red crystals. Infra-red spectra showed this to be a fifty : fifty mixture of the σ-allyl and the dimer, \([\pi-C_5H_5Fe(CO)2]_2\).

(d.) Green and Nagy\(^{158}\) purified the σ-allyl by chromatography on an acid column. This was tried for this reaction mixture, but it was found that elution with n-pentane gave only one fraction, a yellow solution. Removal of the solvent gave an amber oil, whose
infra-red spectrum showed only one carbonyl stretching frequency at 1959 cm\(^{-1}\) (in cyclohexane) and 1950 cm\(^{-1}\) (in carbondisulphide), which was shown by comparison with an authentic sample, to be the \(\pi\)-allylcarbonyl-\(\pi\)-cyclopentadienyliron.

Following the failure of this chromatography it was repeated using rapid chromatography in the dark, with the same result.

(e.) Chromatography on an acid column having failed, a small sample of the reaction product was chromatographed on a basic alumina column, using n-pentane. Removal of the solvent, from the bright yellow fraction, with a slow jet of nitrogen, gave an amber oil, whose infra-red spectrum and NMR. spectrum showed a mixture of two products, the \(\sigma\)- and \(\pi\)-allyl complexes. Only a trace of the dimer was later eluted from the column.

To test that the conversion was actually occurring on the chromatography column, and not as a function of the time of the reaction mixture standing, the product was divided into four, and the portions chromatographed. The first and third on acid alumina and the second and fourth on basic alumina. Although there were twenty four hours between the chromatography of fractions one and two and fractions three and four, the same results as outlined above were observed.

When the basic alumina column size was doubled, thus holding the complexes on the column longer it was found that the ratio of \(\pi\)-allyl to \(\sigma\)-allyl increased. It therefore seems certain that the \(\sigma\)-allyl is converted to the \(\pi\)-allyl on the column, and faster on the acid than the basic alumina column.
Preparation of \( \pi \)-allylcarbonyl-\( \pi \)-cyclopentadienyl iron.

Method (i.).

\( \pi \)-allylcarbonyl-\( \pi \)-cyclopentadienyl iron was prepared by the photolysis of an ethereal solution of \( \sigma \)-allyl-dicarbonyl-\( \pi \)-cyclopentadienyl iron (1g. 4·6 mmole.), in a nitrogen atmosphere, using a 125 Watt ultra-violet lamp, at a distance of 10 cm. The reaction was monitored by infra-red spectroscopy, which showed that it had reached completion after five hours. The ether was then removed and the amber-brown residue dissolved in a minimum of hexane. This solution was chromatographed on a neutral alumina column (10 cm. x 1 cm.), to give an orange solution. After removal of the hexane the yellow solid was sublimed onto a cold finger (-78°C.) from a flask (pathlength 2 cm.) at room temperature under \( 10^{-2} \) mm. Hg pressure. (0·61g., 70 %.) m.p. 19 - 20°C.

Infra-red (in carbondisulphide.): 3105(w.), 3067(s.), 3000(m.), 2850(w.), 1950(vs.), 1485(s.), 1466(m.), 1431(w.), 1419(m.), 1264(w.), 1211(m.), 1200(m.), 1114(s.), 1014(s.), 1007(m.).

Method (ii.).

Similar yields were obtained by chromatography of \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyl iron on an acid alumina column. (See purification of \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyl iron.). This method has the advantage of being much less time consuming. The product was sublimed under the same conditions as above to give yellow crystals. (65 - 75 %.) m.p. 19 - 20°C.

\[ \text{NMR : } \begin{align*} &H' \quad \begin{array}{c} \text{H} \end{array} \quad \begin{array}{c} \text{H} \end{array} \\ &\text{H} \quad \text{C} \quad \text{C} \quad \text{H} \\ &\begin{array}{c} \text{H} \end{array} \end{align*} \] (in deuterobenzene.) \( \delta 9·3 \) (d.,) (2H.)

\( (J_{3,1} = 11) \) 5·85 (m.) (1H.) 5·95 (s.) (5H.) 7·3 (d.,) (2H.) \( (J_{2,1} = 8) \)

(in deuterodimethylsulphoxide.) \( \delta 9·6 \) (d.,) (2H.) \( (J_{3,1} = 11) \)
Preparation of \( \sigma \)-methyldicarbonyl-\( \pi \)-cyclopentadienyl-iron.

Method (i).

\( \pi \)-cyclopentadienylirondicarbonyldimer (1.10 g. 3.1 mmole.) was treated with 5 % sodium amalgam (7.197 g. 15.6 mmole.) in dry THF under nitrogen to give a brown anionic reaction mixture from which the excess amalgam was removed. Addition of methyl iodide at -78°C. (3.0 ml. 6.83 g. 48.06 mmole.) caused an immediate colour change from brown to green-amber. Stirring was continued for a further half an hour, to ensure that the reaction was complete. The pale green precipitate, which settled out, was filtered off, to give a clear orange solution. Removal of solvent gave a yellow-orange waxy solid, which was sublimed at 0.05 mm. Hg pressure at 20°C. onto a cold finger (pathlength 2 cm.) at 0°C. Orange yellow crystals were obtained. (0.669 g., 55 %.) m.p. 77 - 79°C. (literature value 78 - 82°C.)

Infra-red (in carbon tetrachloride): 3890 (s.), 3102 (w'), 2960 (m.), 2900 (m.), 2010 (vs.), 1954 (vs.), 1922 (w.), 1430 (m.), 1420 (m.), 1110 (s.), 1112 (m.), 1063 (w.), 1011 (m.), 825 (vs.), 793 (m.), 636 (s.), 593 (s.), 570 (s.), 560 (s.). NMR. (in deuterobenzene.): \( \gamma \)

5.9 (s.) (5H.) 9.9 (s.) (3H.). Ultra-violet (in cyclohexane.):

\[ \lambda_{\max} = 354 \mu \text{molar} \]

Method (ii).

Halide and methylmagnesium halide.

Treatment of bromodicarbonyl-\( \pi \)-cyclopentadienyliron with a threefold excess of Grignard reagent gave a very low yield of the \( \sigma \)-methyl derivative, the major product.
was $\pi$-cyclopentadienylidicarbonyldimer.

Method (iii.)

Halide and methyl lithium.

This gave a similar result to the Grignard reaction. Yields were slightly improved, but still very low.

(E.). Preparation of $\sigma$-phenyldicarbonyl-$\pi$-cyclopentadienyliron.

Preparation of the $\sigma$-phenyl derivatives from the Grignard reagent in ether with the bromide or iodide gave low yields of 5%. The reaction of the aryl iodide with the sodium salt gave only a 2% yield.

Bromodicarbonyl-$\pi$-cyclopentadienyliron (1.0g, 3.9 mmole.) was dissolved in cyclohexane (60 ml.) under nitrogen at 0°C. The stirred red solution was treated with a twofold molar excess of phenyl lithium. No colour change was observed, but after half an hour stirring a sample of the reaction mixture showed the presence of no carbonyl stretching bands due to the bromide. Excess phenyl lithium was destroyed with cold degassed water (20 ml.) and the organic layer extracted with ether (3 x 15 ml.) to give a dark red solution. This was dried over magnesium sulphate and then the solvent removed. Chromatography of the red residue on a neutral alumina column (15 cm. x 1 cm.) with n-pentane, yielded two bands on the column. One a mixture of two known complexes, the bromide, $\pi$-cyclopentadienyliron dicarbonylbromide, and $\pi$-cyclopentadienyliron dicarbonyldimer; and the other, a yellow solution yielding pale yellow crystals of the $\sigma$-phenyldicarbonyl-$\pi$-cyclopentadienyliron. (0.496.58 %.) m.p. 32 – 33°C. (literature value 35 – 36°C.)
Infra-red (in cyclohexane.): 2021(vs.), 1979(vs.), 1452(m.),
1260(w.), 905(w.), 862(w.). Ultra-violet (in cyclohexane.):
\[ \lambda_{\text{max}}. 227 \text{ m\mu} \epsilon_{\text{molar}} 25,000; \lambda_{\text{max}}. 354 \text{ m\mu} \epsilon_{\text{molar}} 1000. \]

Preparation of \( \sigma \)-derivatives of carbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron. (FIG. 21.)

(A.). Preparation of \( \sigma \)-allylcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron.

(i.). From sodiumcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienylferrate.

The reaction of sodiumcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienylferrate with allyl halides and allyl tosylate was investigated. The reaction, however, gave very low yields, due to the difficulty of preparing the sodium salt.

(ii.). Anion and allyl tosylate.

The reaction of the sodium salt with allyl tosylate produced very slightly improved yields, but the product was very difficult to isolate, no crystals could be obtained from this reaction.

(iii.). Halide and allylmagnesium chloride.

This route to the \( \sigma \)-allyl was preferred to the first two methods because of the higher yields, and the lack of side reactions. However isolation of a pure crystalline product proved very difficult, and could only be achieved by the following procedure:

Solid bromocarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron (1.01g. 2 mmole.) was added very slowly to a twofold molar excess of allylmagnesium chloride, with very efficient stirring.
at 0°C. The resulting red mixture was stirred for a further thirty minutes after complete addition, and then treated with an excess of dioxan (5 ml.). Immediately a dense white precipitate and cherry red supernatant were formed. The precipitate was filtered off, and the filtrate was then washed with degassed cold water (2 x 15 ml.). No decomposition was observed at any stage. The red ethereal layer was dried (magnesium sulphate) and then evaporated to dryness, to remove all traces of dioxan. The red residue was recrystallised from an ether - isopentane (1:3) mixture to give deep red crystals. (0·93g., 90 %.) m.p. 104 - 105°C. Found: C, 70·67; H, 5·73; P, 7·17. C_{27}H_{25}FeOP requires C, 70·96; H, 5·52; P, 7·06 %.

Infra-red (in carbondisulphide): 3076 (w.), 3061 (m.), 3022 (v.), 3004 (wv.), 2930 (vw.), 2959 (w.), 2899 (w.), 2846 (w.), 1917 (vs.), 1200 (m.), 1184 (m.), 1118 (m.), 1090 (s.), 1029 (w.), 1022 (w.), 999 (w.), 859 (m.), 819 (s.), 743 (s.), 698 (s.).

NMR: \[
\begin{array}{c}
H^1 \\
\hline \\
H^3 \\
\hline \\
H^2
\end{array}
\] (in deuterobenzene.)

\[\tau 7·7 (m.) (1H_1) J_{(H_1, P)} = 7; 8·2 (m.) (1H_2) (J_{H_2, P} = 7; 5·96 (s.) (5H_3); 5·11 (d.) and 5·26 (d.) (H^3 and H^4); 3·52 (m.) (H^2).

(in deuterochloroform) \[\tau 7·98 (m.) (H^4); 8·7 (m.) (H^1); 5·84 (s.) (5H_5); 5·65 (m.) (H^3); 5·5 (m.) (H^4); 3·9 (m.) (H^2).

The following variations on this procedure were investigated.

(1.) Mixing of two reagents.

(a.) Addition of the Grignard to the solid bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliiron at room temperature, or at low temperature, gave an amber solution on stirring. After work up the yields were found to be very low. Similar low yields were obtained when the organometallic bromide was in an
ethereal suspension.

(b.). Addition of a green benzene solution of the organometallic halide to a stirred solution of the Grignard produced very rapid reaction, even at temperatures of -60°C and -78°C, to give a bright amber-brown mixture. On hydrolysis of the excess Grignard it was found that there was appreciable decomposition, the product being very unstable, until all the benzene had been removed.

(2.). Effect of temperature.

The reaction was carried out at three temperatures, room temperature, 0°C, and -78°C. Normally, for Grignard and alkyl lithium reagents, it is found that the lower the temperature, down to -78°C, then the "cleaner" the reaction product. In this series, however, it was observed that there was no significant difference between the reactions performed at 0°C and -78°C.

(3.). Methods of isolation.

Treatment of the product with degassed water, saturated aqueous ammonium chloride, or triethylamine followed by degassed water, all failed to give good yields. Chromatography on alumina columns gave a similar result - the major product always being the halide, $\pi$-C$_5$H$_5$Fe(CO)P$_3$X

(4.). Purification.

A sublimation was attempted. Bromocarbonyltriphenylphosphine-$\pi$-cyclopentadienyliron (199·4 mg, 0·4 mmole.) was converted into the allyl derivative by the treatment with a twofold excess of allylmagnesium chloride. The reaction was worked up with dioxan and distilled, degassed water, to give a clear amber ethereal layer, which was dried over magnesium sulphate. The filtered solution was transferred to a 50 ml. round bottom flask, and the ether removed under high vacuum. The flask was then fitted
with a sublimation cold finger, such that the path length was 2 cm. The flask was maintained at 19°C. (± 0.5°C.) for 100 minutes, whilst the cold finger was maintained at -78°C. There was no sublimation at all onto the cold finger at a pressure of 10⁻³ mm Hg. As the temperature of the bath was increased to 25°C., a slight yellowness was noticed on the probe; at 30°C. fine yellow crystals were obtained, leaving behind a mixture of white and brown crystals. The apparatus was allowed to reach thermal equilibrium with the room and then dismantled in an atmosphere of nitrogen. The yellow crystalline material on the probe was dissolved in carbon disulphide and infra-red and NMR. spectra were obtained. These both showed the presence of π-allylcarbonyl-π-cyclopentadienyl iron, with a minute trace of free triphenylphosphine.

(iv.). Halide and Bis(allyl) magnesium.

This reagent was tried, in order to see whether removal of most of the excess magnesium chloride would diminish the amount of decomposition due to Lewis acid attack during the hydrolysis of the reaction with the metal hydride.

Chlorocarbonyltriphenylphosphine-π-cyclopentadienyliron (202.8 mg. 0.4 mmole.) was suspended in ether (15 ml.) in a purged Schlenk tube. Addition of excess bis(allyl)magnesium caused a very rapid amber colouration, and the production of a buff coloured precipitate. The mixture was stirred for a further half an hour, by which time all the bromide had reacted. Triethylamine (1.5 ml.) was added, followed by cautious addition of degassed distilled water (10 ml.), to produce a clear amber ethereal layer, which was removed and dried over magnesium sulphate. Removal of solvent, under high vacuum, gave a chocolate brown coloured low-melting solid. Purification of this material was as difficult as
that prepared from the allyl Grignard, probably due to the production of more magnesium halide during the reaction.

Parallel preparations were carried out in which the amber ethereal layer was filtered from the pale buff precipitate and then the solvent removed under high vacuum. This yielded a mixture of an amber oily material and a white flaky magnesium complex. Exposure of this mixture to the air gave, within three minutes, a green colouration. The infra-red spectrum and melting point showed that this green complex was chlorocarbonyltriphenylphosphine-π-cyclopentadienyliron.

Extraction of the mixture of the amber oil and the white solid, with sodium dried iso-pentane gave an amber solution. Removal of the iso-pentane again gave a mixture, but one that was much richer in the amber oil. If this procedure was repeated twice more all of the magnesium salts could be eliminated. The process was however no better in yield than those methods employing an aqueous work up.


Bromocarbonyltriphenylphosphine-π-cyclopentadienyliron (0.781g, 1.59 mmole.) was added slowly to a stirred two fold excess of methylmagnesium bromide under nitrogen. A reaction rapidly occurred, to give the characteristic red-amber solution of the alkyl in this series.

Attempted decomposition of the excess Grignard by adding "wet" neutral alumina brought about rapid decomposition, giving a deep brown solution and precipitate; neither of which were the c-methyl derivative.

Addition of degassed distilled water (10 ml.) to a similar
reaction product, at room temperature, gave a clear red-amber solution with very little decomposition. The amount of decomposition was lessened by adding a little triethylamine or dioxan to the reaction mixture, before adding the water. Removal of solvent, after drying over magnesium sulphate, gave an orange residue which was recrystallised from an ether:pentane (3 : 1) mixture at 0°C. to give deep orange or red crystals. (0·545), 85 %.) m.p. 150 - 151°C.

Found: C, 70·40; H, 5·21; P, 7·53. C_{25}H_{23}FeOP requires C, 70·42; H, 5·16; P, 7·53 %. Infra-red: (in carbondisulphide.) 3079(m.), 3060(m.), 3021(~.), 3012(w.), 2959(m.), 2924(m.), 2870(m.), 2848(m.), 2798(w.), 1916(vs.), 1308(w.), 1258(w.), 1201(s.), 1185(m.), 1118(s.), 1090(m.), 1078(w.), 1028(w.), 993(w.), 819(m.), 745(m.), 721(s.), 683(s.). NMR: (in deuterobenzene.)

\[ \text{C~2·47 (m.) (6H.) 3·03 (m.) (9H.) 5·98 (s.) (5H.) 9·86 (d.) (3H.)} \]

\[ \text{(JCH}_3\text{P} = 7·5) \]

Infra-red studies of the reaction using methyl lithium showed that, during the course of the reaction a small percentage, (circa. 5 %.) of the \( \sigma \)-methyldicarbonyl-\( \pi \)-cyclopentadienyliiron was formed. This, and many similar results will be discussed later.

(\( \sigma \).) Preparation of \( \sigma \)-benzylcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliiron.

This preparation was performed by the treatment of bromocarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliiron (0·637 g. 1·30 mmole.) with a two fold excess of benzylmagnesium chloride. The reaction was very rapid, but was stirred for half an hour to ensure a complete reaction, giving a bright cherry red solution, which did not decompose at all on the addition of degassed distilled water (10 ml.), at room temperature. The ethereal solution was
removed and dried (magnesium sulphate.). Removal of the solvent gave a red solid residue, which was recrystallised from an ether: isopentane (5: 1 ) mixture, at 0°C. The red-brown crystals obtained were washed thoroughly with ice-cold iso-pentane (5 x 10 ml.) to remove all traces of dibenzyl, which was observed to be present, by its characteristic smell and NMR. spectrum. (0·56g. 95 %.) m.p. 127 - 129°C Found: C, 73 ·81; H, 5 ·39; P, 6 ·51; C_{31}H_{27}FeOP requires C, 73 ·94; H, 5 ·37; P, 6 ·36 %. Infra-red (in carbon-disulphide): 3070(m.), 3059(m.), 3019(w.), 2956(w.), 2921(m.), 2853(m.), 1914(vs.), 1185(m.), 1119(m.), 1089(m.), 1023(w.), 993(v.), 819(m.), 744(m.). NMR. (in deuterobenzene) \( \tau \) 2.47 (m.) (6H); 3.02(m.)(9H•); 6.1 (s.)(5H•); 7.32 (q.)(11H•); 7.84 (t.) (1H.) \( (J_{P,A} = 6) \) and \( (J_{P,B} = 12) \).

(D.). Preparation of n-propylcarbonyltriphenylphosphine-
\( \pi \)-cyclopentadienyliron.

(i.). Reaction of halide with n-propylmagnesium chloride.

Bromocarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron (1·0108g. 2·2 mmole.) was suspended in sodium dried ether (50 ml.) in a purged Schlenk tube, and cooled to 0°C. Addition of a two fold excess of n-propylmagnesium chloride and stirring for two hours gave a white-buff precipitate and a clear dark amber solution. Degassed, cooled distilled water (10 ml.) was added quickly, with very vigorous stirring, to the cooled reaction mixture to give an amber ethereal layer and a dark brown aqueous layer. The latter was indicative of a great deal of decomposition on hydrolysis. The aqueous layer was frozen out with a carbon dioxide - acetone bath and the ethereal layer filtered off and dried (sodium sulphate.) Most of the ether was removed and the
resultant dark brown solution was chromatographed on neutral alumina using hexane as the eluent, to yield three yellow-orange fractions. Finally elution with ether gave a green solution, identified as chlorocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron.

The yield of impure n-propyl derivative from the column was approximately 75\%. This result appeared to be very encouraging until the infra-red spectrum was investigated. This showed that two metal carbonyl containing species were obtained, having carbonyl stretching frequencies at 1939 and 1916 cm\(^{-1}\) (in cyclohexane.) (cf. \(\pi\)-C\(_5\)H\(_5\)Fe(CO)P\(_3\)Br at 1962 cm\(^{-1}\) in cyclohexane.)

The reaction was repeated several times, using identical conditions but the ratio of production of the two complexes varied on every occasion. It was, however, found that if the reaction was carried out at room temperature then on most occasions only one product was isolated. This was the complex showing a carbonyl stretching frequency at 1939 cm\(^{-1}\) (in cyclohexane.)

The conditions of work up were varied by using water, water and triethylamine, chromatography, and aqueous saturated ammonium chloride. None of these altered the observations already recorded. It was, therefore, decided that the two complexes were formed during the reaction, and not during the work up.

(ii.). Reaction of halide with n-propyl lithium.

This reaction proved very complex and unusual and so was studied in great detail. The following facets of the reaction were studied:

(1.). Mixture of reagents.

Best yields were obtained by adding solid bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron to the n-propyl lithium, rather than any other method of addition, such as the addition
of n-propyl lithium to the halide in solid form, or solution, or the addition of a solution of the halide to the n-propyl lithium.

(2.). Rate of addition.

This appeared to be very critical to high yield and the cleanliness of the reaction. Rapid addition of the organometallic halide always resulted in the production of a very dark brown reaction mixture, which on work up gave low yields. Slow addition, for example 2g. over half an hour, to an excess of lithium reagent, gave a much better yield and a lighter amber brown reaction mixture.

(3.). Molar ratio of the reactants.

In the literature it is interesting to note that many reactions involving lithium reagents, or Grignard reagents use conditions in which the organic reagents are in large excess, sometimes as much as twentyfold excess. 160

It was found when investigating this reaction that if a one to one or one to two molar ratio were used the chances of the initial amber reaction product, turning green, with the production of the organometallic halide were very high. However, when the molar ratio was increased to one to four this reversion did not take place so readily and the yields, calculated on the organometallic bromide, were much improved.

(4.). Temperature of the reaction.

This factor was crucial to the product formed. When the bromide was added slowly to the n-propyl lithium at -78°C, a clear amber solution was obtained, which on work up, with degassed distilled water, showed the presence of a metal carbonyl product having a carbonyl stretching frequency at 1939 cm⁻¹ (in cyclohexane.)

If the bromide was added to the n-propyl lithium, at room temperature, a completely different product was isolated, when the initial amber solution was hydrolysed with water. This product /banner.
showed a carbonyl stretching frequency at 1916 cm$^{-1}$ (in cyclohexane.)

At temperatures between room temperature and $-78^\circ$C, a mixture of the two products was obtained. It was impossible to repeat the experiment under identical conditions to obtain the same proportions.

(5.). Isolation.

The method of isolation from the crude reaction mixture was not critical as to which product was formed, but only to the yield. This was proved by doing the reaction at $-78^\circ$C., $0^\circ$C. and room temperature and working up samples of each reaction by different techniques. It was found that the best method was to add triethylamine to the reaction and then filter off the gelatinous adduct formed. Excess triethylamine and lithium salts were washed out with degassed water. This method was found to give much less decomposition than adding the water directly to the reaction mixture without filtering the triethylamine adduct.

Thus the best procedure for preparing the n-propyl derivative from n-propyl lithium was as follows:—

Bromocarbonyltriphenylphosphine-$\pi$-cyclopentadienyl-iron (4.91g. 10 mmole.) was added slowly, under nitrogen, as a solid, to n-propyl lithium at room temperature. Each addition of bromide caused a gradual darkening in the amber colouration, the final mixture being a buff-brown precipitate and a clear amber solution. Triethylamine (5 ml.) was added, dropwise to give a pale brown gelatinous precipitate, which was filtered off to give a clear amber solution. Addition of degassed water (15 ml.) caused very little decomposition. The ethereal layer was dried, after separation from the colourless aqueous layer, and then concentrated to 10 ml. Iso-pentane (10 ml.) was added and the
clear amber solution cooled to -20°C. for several days. This yielded orange chunky crystals or brown chunks of microcrystals. Great care was necessary to obtain the crystals free from triphenylphosphine. This proved very difficult. (0.9 g. 40%) m.p. 129 - 130°C. (under nitrogen). Found: C, 70.36; H, 5.81; P, 7.29; C_{27}H_{27}FeOP requires C, 70.95; H, 5.74; P, 7.05 %. Infra-red (in carbondisulphide): 2948 (m.), 2948 (m.), 2850 (w.), 1905 (vs.), 1256 (w.), 1200 (w.). (in carbon tetrachloride): 2959 (m.), 2959 (m.), 2921 (m.), 1909 (vs.), 1480 (w.), 1459 (w.), 1438 (m.). NMR, (in deuterobenzene) \( \tau \) 2.64 (m.) (6H.); 3.02 (m.) (9H.); 5.89 (s.) (5H.); 8.17 (m.) (2H.); 8.63 (m.) (2H.); 8.84 (t.) (3H.) (J_{CH3,H} = 7.5).

(E.). Preparation of \( \sigma \)-phenylcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron.

(i.) Bromide and phenyl lithium.

Addition of a three-fold excess of phenyl lithium to bromocarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron (0.75 g. 1.57 mmole.) at -60°C. gave an amber reaction mixture. This was treated with cold degassed water, the ethereal layer removed and dried over magnesium sulphate. Removal of the solvent gave an amber oily residue. Chromatography on a neutral alumina column (15 x 1.5 cm.) with pentane gave an orange fraction which yielded red crystals. (0.197 g.) m.p. 168 - 169°C. (literature value 166 - 167°C.) Infra-red (in cyclohexane): 1931 (vs.), 1577 (w.), 1119 (s.). A yellow fraction was also obtained yielding an amber oil shown to be \( \pi \)-C_{5}H_{5}Fe(CO)_{2}C_{6}H_{5}. (0.122 g.) m.p. 22 - 24°C. Infra-red: (in carbondisulphide) 3040 (m.), 2956 (m.), 2924 (w.), 2020 (vs.),
1967(vs.), 1941(m.), 1275(m.), 1010(m.), 828(m.), 734(s.), 699(vs.).

(ii). Bromide and phenylmagnesium bromide.

A two-fold excess of phenylmagnesium bromide was added to bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron (0.709g. 1.45 mmole.) and the mixture stirred for one hour at room temperature. Addition of dioxan, removal of the adduct, and then addition of cold degassed water gave a deep red ethereal layer. This was dried and evaporated to dryness. The residue was recrystallised from ether : n-pentane (1:4). (0.479g. 68%). m.p. 163 - 169°C. (literature value 166 - 167°C.)

Infra-red (in cyclohexane.): 1931(vs.), 1517(w.), 1119(s.).

Reactions of \([\pi-C_5H_5Fe(CO)_2P(C_6H_5)_3]Br\).

(i.). Bromodicarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron (0.2679g.) was refluxed in absolute benzene (25 ml.) under nitrogen. Infra-red spectra of small samples were taken at intervals, throughout twenty four hours. There was no change in the colour of the suspension, the infra-red spectrum, or the NMR. spectrum, thus indicating no production of \(\pi-C_5H_5Fe(CO)P(C_6H_5)_3Br\).

(ii.). The benzene was removed under vacuum, to give back the buff coloured solid, which was suspended in sodium dried toluene (25 ml.) and refluxed under nitrogen. At reflux some complex dissolved to give an amber-gold solution, but no change in the infra-red spectrum was observed.

Both these experiments tend to rule out the possibility of an associative mechanism for the preparation of the complex \(\pi-C_5H_5Fe(CO)P(C_6H_5)_3Br\), from \(\pi-C_5H_5Fe(CO)_2Br\) and triphenylphosphine.

(iii.). To a stirred solution of allylmagnesium chloride
was added bromodicarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyl iron (0.1895 g.) so that there was a slight excess of Grignard reagent. The solution gradually darkened, until after half an hour a dark chocolate solution resulted. Addition of triethylamine (2 drops.) left an amber solution and a dark gelatinous precipitate. Degassed distilled water (8 ml.) was added under nitrogen, and the amber ethereal layer removed. The aqueous was washed with ether (3 x 5 ml.) and the combined extracts dried thoroughly over magnesium sulphate. Removal of the ether gave a dark brown oily material (0.1125 g.). The infra-red spectrum showed a complex pattern of carbonyl stretching frequencies, but these could be sorted out as being from \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(_2\)\(\sigma\)-C\(_3\)H\(_5\), \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(\Pi\)\(\Pi\)Br and finally \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(\Pi\)\(\Pi\)\(\sigma\)-C\(_3\)H\(_5\). Other possible products, that were not observed were, \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(\sigma\)-C\(_3\)H\(_5\) and \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(_2\)Br.

Chromatography of the crude material on a basic alumina column (30 g.) eluting with hexane, and hexane - ether mixtures showed that the major products were \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(\Pi\)\(\Pi\)\(\sigma\)-C\(_3\)H\(_5\) and \(\pi\)-C\(_5\)H\(_5\)Fe(CO)\(\Pi\)\(\Pi\)Br, accounting for 43 and 31 % of the product respectively. These two complexes are the most stable, so it would appear that the controlling factor in product formation is a thermodynamic one.

These observations fit in with the lability of the phosphine discussed later in this thesis.
Protonation of \(\sigma\)-allylcarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron.

As in the dicarbonyl-\(\pi\)-cyclopentadienyliron series a selection of protonating acids were used.

(A.). \(\sigma\)-Allylcarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron (0·4617 g, 1·02 mmole.) was dissolved in dry ether (25 ml.) to give a deep cherry red solution. Protonation with anhydrous hydrogen chloride, prepared from concentrated sulphuric acid and ammonium chloride, gave an immediate pink precipitate. This was washed with ether (5 x 15 ml.), to give a pale pink solid, which on dissolving in acetone, dichloromethane, or methanol gave a clear red solution. On standing, in the case of dichloromethane for only a few minutes, a green solution was obtained.

Recrystallisation of the product, from liquid sulphur dioxide and ether gave red crystals. These showed remarkable instability turning green in an hour, with the expulsion of propene (identified by gas infra-red spectrum.). A sample of the red crystalline product (0·0910 g, 0·19 mmole.) was dissolved in a minimum of water (3 ml.) and treated with an excess of a saturated solution of potassium hexafluorophosphate. A great deal of decomposition was apparent, producing a green product, and no hexafluorophosphate salt was isolated.

(B.). \(\sigma\)-Allylcarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron (0·2715 g, 0·6 mmole.) was dissolved in benzene (10 ml.) under nitrogen to yield a deep cherry red solution. Addition of one molar equivalent of trifluoroacetic acid in benzene solution gave, immediately, a brown oily complex on the sides of the vessel. On shaking for five minutes this oily complex dissolved and the solution became green in colour. The benzene was removed.
to yield a green oily solid, which was recrystallised from a benzene-hexane (3-1.) mixture to yield dark green crystals. (0.14g. 45 %)
m.p. 115 - 117°C. Found: C, 60.4; H, 4.2; P, 6.21;
C_{26}H_{20}F_3FeO_2P requires C, 59.4; H, 3.81; P, 6.09 %. Infra-red
(in carbondisulphide.): 1961(vs.), 1699(s.), 1140(s.)
NMR. (in deuterochloroform.) \( \text{C}^3 \text{H}^4 \text{m.} \text{C}^{15} \text{H}^2 \text{s.} \text{C}^5 \text{H}^3 \text{s.} \text{C}^5 \text{H}^3 \text{s.} \)

This experiment was repeated in an NMR. tube, in order to
try an prove the existence of the protonated species as an unstable
intermediate. Better results were obtained, however, when the
spectrum was obtained using deuterochloroform as a solvent. The
results of this work are discussed in detail in the discussion
chapter of this thesis.

(C.). Following the failure of the previous attempts
at protonation, it was decided to try with an acid that had a less
nucleophilic anion. This suggested two acids, fluoroboric acid and
fluorosulphonic acid.

\( \sigma \)-Allylcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron
(0.1939g. 0.44 mmole.) was dissolved in cyclohexane (25 ml.)
under nitrogen, and the resulting red solution treated dropwise,
with one molar equivalent of fluorosulphonic acid, in cyclohexane
solution. A brown oil was formed together with some white floculent
precipitate. The latter was removed with the supernatant and the
oil washed with cyclohexane (3 x 5 ml.). Finally all the solvent
was removed, under high vacuum, to give a brown oily solid, which
was soluble in acetone, chlorobenzene, and dichloromethane, to
give red brown solutions. On standing for a few minutes all those
solutions became green.

(D.). \( \sigma \)-Allylcarbonyltriphenylphosphine-\( \pi \)-cyclo-
pentadienyliron (0.9781g. 1.92 mmole.) was dissolved in ether
(25 ml.) and treated, dropwise, with a slight excess (1.1 Molar.)
of fluoroaboric acid, in ether solution. This gave a bright pink-red precipitate, and a colourless supernatant. The latter was removed and the precipitate washed with ether (4 x 20 ml.). Removal of the solvent gave a pale pink solid. The infra-red spectrum of this solid showed the presence of a carbonyl stretching frequency at about 1990 cm\(^{-1}\), in dichloromethane, acetone, HCB., and nujol.

The solid was dissolved in liquid sulphur dioxide (15 ml.) and then ether (5 ml.) added. The deep red-brown solution was allowed to stand at - 10°C. under nitrogen, for an hour. During this time the sulphur dioxide slowly evaporated, depositing large red crystals. These showed the same basic infra-red spectrum, as that obtained on the crude sample. (0.84g. 80 %.) Infra-red (in chlorobenzene.): 1992(vs.)

Found: C, 59.67; H, 4.7; P, 6.18; \( C_{27}H_{26}BF_{4}FeOP \) requires C, 59.91; H, 4.81; P, 5.92 %.

NMR: (in sulphur dioxide.)

\[
\begin{align*}
\text{H}_3^3 & \quad \text{H}_2^2 \\
\text{C} & \quad \text{CH}_3
\end{align*}
\]

Isomer A: \( \gamma \) 4.96 (s.) (5H.) 5.95 (d.) (1H.) \( (J_{2,4} = 15.\) 6.72 (m.) (1H.) \( (J_{2,3} = 8) \) 8.2 (d.) (3H.) \( (J_{CH}_3,2 = 7.5) \) .

Isomer B: \( \gamma \) 5.05 (s.) (5H.) 7.16 (m.) (1H.) 7.5 (m.) (1H.) 8.69 (d.) (3H.) \( (J_{CH}_3,2 = 7.5) \) .

Reactions of \( \tau-C_{6}H_{5}Fe(CO)\frac{1}{3}C_{6}H_{5}^+BF_{4}^- \)

(A.). To prove that there was an easily displaceable ligand present in the molecule, the tetrafluoroborate salt (0.0591 g. 0.11 mmole.) was dissolved in acetone (4 ml.) to give a pale pink solution. Addition of a one molar excess of solid potassium iodide with stirring under nitrogen, produced a colour change in the solution from red to green, over a period of ten minutes.
Ether (10 ml.) was added, and the potassium salts removed from the solution, by the addition of distilled water (10 ml.). The green ethereal layer was removed and the aqueous layer was washed with ether (3 x 10 ml.). The combined ethereal extracts were evaporated to dryness, and a green solid resulted.

(B.). Dissolving the cation in chlorobenzene, acetone or nitrobenzene gave a cherry red solution, which turned brown in five minutes. Infra-red of the solution showed a change from 1992 cm.\(^{-1}\) (in chlorobenzene) to 1979 cm.\(^{-1}\) (in chlorobenzene.). A gas infra-red spectrum of the gas evolved showed it to be propene.

Preparation of \(\sigma\)-propenedicarbonyl-\(\pi\)-cyclpentadienyliiron cation (FIG. 22)

(A.). This method was based on that of Fischer, and involved the shaking together of bromodicarbonyl-\(\pi\)-cyclopentadienyliiron, (1.57 g. 10 mmole.), anhydrous aluminium bromide, (8.01 g. 30 mmole.) in absolute benzene (20 ml.) with 10 ml. of liquid propylene for 72 hours in an autoclave. Only trace amounts of the propene cation were isolated, the main products being bromodicarbonyl-\(\pi\)-cyclpentadienyliiron and \(\pi\)-cyclpentadienyliiron dicarbonyl dimer.

(B.). Protonation of \(\sigma\)-allyldicarbonyl-\(\pi\)-cyclpentadienyliiron with anhydrous hydrogen chloride has been shown to give the olefinic cation, as the chloride. This was found to be very hygroscopic and so was converted rapidly, with excess potassium hexafluorophosphate, into the hexafluorophosphate. The latter was air and heat stable and could be stored for long periods of time, as fine yellow crystals.

With hydrogen bromide a less hygroscopic salt was obtained, but yields were low.
Fig. 22.

\[
\begin{align*}
&\text{Fe} \quad \text{OC} \quad \text{CH}_2\text{CH}=\text{CH}_2 \\
&\text{Fe} \quad \text{OC} \quad \text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
&\text{HX} \quad \text{Ph}_3\text{C}^+ \quad \text{BF}_4^- \\
&\left[ \begin{array}{c}
\text{Fe} \\
\text{OC} \\
\text{CHCH}_3 \\
\text{CO} \\
\end{array} \right] + \\
&\left[ \begin{array}{c}
\text{Fe} \\
\text{OC} \\
\text{CH}_2 \\
\text{CO} \\
\end{array} \right] + \\
&\text{AlCl}_3 \\
&\text{CH}_2=\text{CHCH}_3 \\
&\text{CH}_2=\text{CHCH}_3
\end{align*}
\]
Protonation was also carried out with trifluoroacetic or tetrafluoroboric acid.

$\sigma$-allyldicarbonyl-$\pi$-cyclopentadienyliron (1.513g, 6.94 \text{ mmole.}) in distilled dry THF. was cooled, with stirring, usually to - 78°C., but certainly to below 0°C. A THF solution of trifluoroacetic acid (20 ml. of 0.493 N.) was added slowly under nitrogen. The mixture was stirred rapidly for five minutes, to allow complete reaction. Infra-red spot tests, between sodium chloride plates, showed the disappearance of the $\sigma$-allyl derivative (2010 cm$^{-1}$ (vs.), 1948 cm$^{-1}$ (vs.)) and the appearance of two new bands at 2070 cm$^{-1}$ (vs.), 2035 cm$^{-1}$ (vs.), these should be compared with the reported PF$_6$ complex bands at, 2082 cm$^{-1}$ (vs.), and 2053 cm$^{-1}$ (vs.) and the PtCl$_6^{2-}$ bands at 2070 cm$^{-1}$ (vs.) and 2031 cm$^{-1}$ (vs.)

(C.). The hydride abstraction of the $n$-propyl derivative, using triphenylmethylfluoroborate, was performed under literature conditions, except that the reaction was carried out in ether, and not THF.

(D.). Since the above methods, except for (A.), do not start from the free olefin, attempts were made to make cations such as $\left[\pi$-C$_5$H$_5$Fe(CO)$_2\right]^+$ or $\left[\pi$-C$_5$H$_5$Fe(CO)$_2$(solvent)$\right]^+$, which, it was hoped, would coordinate the olefin.

(i.). Silver trifluoroacetate.

Cyclopentadienylirondicarbonyldimer (40 mg, 0.11 mmole.) was dissolved in acetonitrile (5 ml.), under nitrogen and silver trifluoroacetate (30 mg, 0.17 mmole.) (i.e. a 1 : 1.5 molar ratio) added. The initial crimson solution rapidly became dull, giving a brown suspension. The latter was removed by centrifugation, to give an orange supernatant. Excess acetonitrile was removed under high vacuum to give a green-brown solid. Infra-red spectrum (in chloroform.) showed no dimer, but the presence
of two new carbonyl stretching frequencies at 2061 and 2016 cm$^{-1}$

No coordinated acetonitrile was observed in the NMR., or infra-red spectra of the complex. The complex could not be obtained in crystals pure enough for analysis, but since the carbonyl stretching frequencies were close to those of the halides, it seemed to be the $\sigma$-trifluoroacetate, in analogy to $\pi$-C$_5$H$_5$Fe(CO)$_3$OCOCF$_3$.

The reaction was repeated in sodium dried benzene (5 ml.) to see whether the reaction proceeded differently in the presence of a weaker coordinating solvent. It was found, however, that an identical reaction took place, giving a product having carbonyl stretching frequencies at 2017 and 2060 cm$^{-1}$ (in chloroform.)

(ii.). Silver acetate.

Rather than a serious attempt to oxidatively cleave the dimer this experiment was performed to see whether a less nucleophilic group, like acetate, would give the $\sigma$-acetate, in a similar manner to the trifluoroacetate.

Cyclopentadienyliron dicarbonyldimer (20 mg. 0.05 mmole.) and silver acetate (15 mg. 0.09 mmole.) were shaken, under nitrogen, in acetonitrile, (4 ml.). After several hours the crimson solution had not really changed colour, and the infra-red spectrum obtained, on the red solution, after removal of solvent, showed large amounts of starting dimer and a new peak at 2050 cm$^{-1}$. It was impossible, even working on a larger scale to isolate the complex giving this band.

Addition of potassium tetrafluoroborate (20 mg.) to the reaction mixture, outlined above, produced a slow darkening in colour, and the slow production of a brown precipitate. The reaction was followed by infra-red spectroscopy, which showed that, after two hours, all the starting material had disappeared. Four new carbonyl
stretching frequencies were observed. Two of these may be assigned to the acetonitrile coordinated cation, \( \left[ \pi-C_5H_5Fe(CO)_2CH_3CN \right] BF_4^- \), whilst the other two, of weaker intensity, at 2063 and 2010 cm\(^{-1}\) might be due to the production of some acetate, \( \pi-C_5H_5Fe(CO)_2(OCOCH_3) \) (iii.). Silver tetrafluoroborate.

Addition of a two and a half molar excess of anhydrous silver tetrafluoroborate to \( \pi \)-cyclopentadienyliron-dicarbonyldimer, in acetone, acetonitrile, benzene, or pyridine solution gave a rapid reaction. A slight darkening in colour was noted, and this was accompanied by the disappearance of the carbonyl stretching frequencies of the starting dimer. The complexes were not isolated, but were considered to be, by the analogy of those already reported, \(^{162}\) of the form \( \left[ \pi-C_5H_5Fe(CO)_2(solv) \right]^+ \).

Infra-red (in pyridine.): 2021(vs.), 2076(vs.), (in benzene.) 2020(vs.), 2070(vs.), (in acetone.) 2021(vs.), 2069(vs.) (in acetonitrile.) 2036(vs.), 2079(vs.).

Saturation of the red solution with propene did not give the propene cation \( \left[ \pi-C_5H_5Fe(CO)_2C_3H_6 \right]^+ \), by displacement of the solvent molecule.

Nucleophilic attack, by methyl lithium, on \( \pi \)-cyclopentadienyl dicarbonyliron-\( \pi \)-propene cation.

All the methyl lithium, used as a nucleophilic reagent in this section, was prepared from dimethyl mercury. This was to eliminate the possibility of competition between the methyl anion and iodide.

(A.). Reactions of methyl lithium with the \( \pi \)-propene cation as the hexafluorophosphate.

\( \pi \)-propenedicarbonyl-\( \pi \)-cyclopentadienyliron hexa-
fluorophosphate (206 mg, 0.57 mmole.) was suspended in dry ether under nitrogen at -78°C. An equimolar amount of methyl lithium was added dropwise with good stirring. There was an almost immediate darkening in colour, which developed even more on stirring at -78°C. for a further thirty minutes. On allowing the mixture to settle a clear yellow supernatant was obtained. This was removed and the precipitate was washed with more ether (3 x 2 ml.). The combined ether extracts were evaporated to dryness, under high vacuum in a sublimation apparatus, and then sublimed at 0.01 mm. Hg, and 20°C. onto a cold finger at -78°C. A yellow solid was obtained, which by comparison with an authentic sample was shown to be the \( \sigma \)-methyl derivative, \( \pi-C_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3 \). m.p. 76 - 77°C. Infra-red (in carbon tetrachloride.) 2010(vs.), 1959(vs.), 1923(w.). NMR. (in deuterobenzene.) \( \gamma \) 5.9(s.)(5H.), 9.9(s.)(3H.).

(B.). Reaction of methyl lithium with the \( \pi \)-propene cation as the trifluoroacetate.

\( \sigma \)-Allyldicarbonyl-\( \pi \)-cyclopentadienyliron (1.513g. 6.94 mmole.) in dry THF. (30 ml.) was stirred at -78°C. under nitrogen, whilst trifluoroacetic acid, in dry THF. (20 ml. of 0.493N.) was added slowly. On complete addition the stirred solution of the cation was treated directly with an ethereal solution of methyl lithium (100 ml. of 0.203 N.), still at -78°C. After adding just a little of the methyl lithium (2 ml.) a bright yellow precipitate was observed. As more methyl lithium was added the precipitate became darker and darker in colour, and at the end of the addition the reaction mixture had a green tinge to it. The supernatant also gradually darkened from amber to brown. The mixture was taken up in pentane (50 ml.) and washed with water (3 x 25 ml.). The organic layer, after drying over potassium carbonate and removal of solvent, gave a dark brown viscous liquid.
Chromatography on a neutral alumina column, using n-pentane as the eluent, gave a yellow solution, which on slow removal of the solvent gave an amber oil. The infra-red and NMR spectra of this complex showed it to be $\sigma$-methyldicarbonyl-$\pi$-cyclopentadienyliiron.

In the description of the protonation of the $\sigma$-allyl it was shown that a series of solvents were used, the others being benzene, and cyclohexane. With the $\pi$-propene cations, derived from these experiments, it was found, even on prolonged stirring, that there was an insignificant amount of reaction in different solvents, when a one to one molar ratio of methyl lithium was used. In both cases it needed a two to one molar ratio to encourage the attack to proceed, this could have been due to the inhomogeneity of the reaction mixture.

(C.). Reaction of methyl lithium with the $\pi$-propene cation as the fluorosulphonate.

A tetrahydrofuran solution of $\pi$-propenedicarbonyl-$\pi$-cyclopentadienyliironfluorosulphonate (169·1g. 0·47 mmole.) was treated with methyl lithium at 0°C. No visible change was noted on addition, but after five minutes stirring the mixture began to darken. It was stirred for half an hour. Addition of cold water (5 ml.) gave a greenish brown mixture, which was extracted with petrol (30 - 40°C. fraction.) (3 x 10 ml.) and the combined extracts dried over potassium carbonate. Removal of solvent gave a yellow oily solid of identical properties to the $\sigma$-methyl derivative, $\pi$-$\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$.

Similar results were obtained with the $\pi$-propene cation made in benzene or cyclohexane solution.

(D.). Reaction of methyl lithium with the $\pi$-propene cation as the chloride.
90 -

\[ \sigma\text{-Allyldicarbonyl-}\pi\text{-cyclopentadienyliron} (272 \text{ mg. 0.75 mmole.}), \]
in dry ether (30 ml.) was treated with dry hydrogen chloride gas, until the solution became colourless and the pale yellow precipitate coagulated, and was immediately reacted with an equimolar amount of methyl lithium, in ether at \(-78^\circ\text{C}\). A dark brown solution resulted. This was hydrolysed with water (2 ml.) and the organic solution dried over potassium carbonate. Chromatography of the brown residue, after removal of solvent, on a neutral alumina column (15 x 1 cm.) with ether gave two bands. The first band was bright yellow, giving pale yellow crystals, shown to be the \(\sigma\)-methyl derivative (65 mg. 45\%). The second band was shown to be the dimeric species \([\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2\).

If all the excess hydrogen chloride was removed after protonation the yield was, consistently, found to be 95\% of \(\sigma\text{-methyldicarbonyl-}\pi\text{-cyclopentadienyliron}.\)

**Nucleophilic attack by phenyl lithium, on \(\pi\text{-cyclopentadienylidicarbonyl-}\)iron-\(\pi\)-propene cation.**

(A.). Reaction of \(\pi\)-propene cation as the chloride with phenyl lithium.

\(\sigma\text{-Allyldicarbonyl-}\pi\text{-cyclopentadienyliron} (281.6 \text{ mg. 0.78 mmole.}), \) in dry ether (20 ml.) was treated with anhydrous hydrogen chloride gas. Removal of half of the ether gave a yellow precipitate, free from any excess hydrogen chloride. Treatment, at \(-78^\circ\text{C.}\) under nitrogen, with an equimolar amount of phenyl lithium caused the solution to slowly darken in colour. The reaction was monitored by infra-red spectroscopy, which showed the reaction to be complete after forty five minutes. It was then treated
with degassed water (10 ml.) and the ethereal layer removed, the aqueous layer being washed with ether (3 x 5 ml.) and the combined ethereal extracts dried over sodium sulphate. Removal of solvent gave a yellow oily residue, which was taken up in petrol (30 - 40°C. fraction.) (1 ml.), and chromatographed on a neutral alumina column (10 x 1 cm.) using a petrol (30 - 40°C. fraction.) : cyclohexane (1 : 1) mixture, as eluent.

The infra-red spectrum of the crude reaction product, showed the presence of four strong carbonyl stretching frequencies. The chromatography separated these into two yellow fractions, each fraction exhibiting two strong carbonyl stretching frequencies. The second yellow fraction obtained was evaporated to an oily residue, which was crystallised from n-pentane at -78°C., to give pale crystals. Spectral and TLC. properties were identical to an authentic sample of o-phenyldicarbonyl-π-cyclopentadienyliron (89 mg. 45%). m.p. 33 - 34°C. Infra-red (in cyclohexane.): 2021(vs.), 1979(vs.), 1454(m.), 1260(w.), 906(w.), 862(w.). NMR. (in cyclohexane.) 7 2.65(m.) (5H.), 5.31(s.) (5H.).

The other complex isolated from the column proved very difficult to isolate, and identify. The amber oily residue obtained, on removal of solvent, was dissolved in a minimum of isopentane and cooled to -78°C. Attempts to isolate crystals from this proved to be impossible. The NMR spectrum showed the presence of no phenyl ring, and on closer study showed the complex to be the o-allyl derivative, π-C₅H₅Fe(CO)₂CH₂CH=CH₂. (68 mg. 40%). Infra-red (film.): 2010(vs.), 1948(vs.), 1608(s.), 1190(s.), 1178(s.). NMR. (in cyclohexane.): 7 7.99(q.) (2H.), J(CH₂) = 8.6, 5.5 (s.) (5H.), 5.3(m.) (2H.), 3.89(m.) (1H.).
(B.). Reaction of the \( \pi \)-propene cation as the trifluoroacetate with phenyl lithium.

\[ \sigma\text{-Allyldicarbonyl-} \pi \text{-cyclopentadienyliiron (109.4 mg, 0.30 mmole.) was dissolved in dry ether (15 ml.) and cooled to -78°C. An equimolar amount of trifluoroacetic acid, as standard ethereal solution was added dropwise. Infra-red spectroscopy showed the reaction to be complete after five minutes. Addition of phenyl lithium, slowly with stirring, gave an almost immediate colour change from the pale amber solution to a deep chocolate brown solution. A sample removed within a minute of mixing showed the presence of olefinic species, the dimer \([\pi \text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2\) and two other carbonyl stretching frequencies. (N.B. not four, as obtained with the \( \pi \)-propene chloride.) Work up of the whole mixture after four minutes, with degassed water (5 ml.) gave, on removal of the solvent, an oily brown residue.\]

Chromatography of the residue, with petrol (30 - 40°C. fraction.), on a neutral alumina column (15 x 1 cm.) gave yellow fractions, from which an amber oil was obtained. Repeat reactions were carried out with identical results. TLC. (run on alumina micro slides, in cyclohexane.) indicated that the product was not \( \sigma \)-phenylidicarbonyl-\( \pi \)-cyclopentadienyliiron, and it ran as one spot. Infra-red, NMR., TLC., and protonation properties of the product were identical with an authentic sample of \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyliiron.
SECTION (iv.)

MOLYBDENUM SERIES.

Molybdenum hexacarbonyl was obtained from Alfa Inorganic and used without further purification, to prepare chlorotricarbonyl-$\pi$-cyclopentadienylmolybdenum, by a route similar to that outlined by Coffey. The major difference being the use of sodium cyclopentadienide in DMF solution, rather than the lithium reagent used by Coffey, as this was easier to prepare, and the reaction was cleaner when adding the water and acetic acid, to convert the sodium salt to the hydride.

Preparation of phosphine substituted halides.

Chlorodicarbonylphosphine-$\pi$-cyclopentadienylmolybdenum complexes were prepared by the reported thermal method, of refluxing in benzene under nitrogen, in the molar ratio of one to one and a quarter of the organometallic halide to the phosphine. The products were recrystallised from benzene hexane mixtures. Reaction conditions are summarised in Table V. below.

TABLE V.

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Reaction time (hrs.)</th>
<th>Yield(%)</th>
<th>$\nu_{C=C}$ (in CCl$_4$)</th>
<th>m.p.(°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylphosphine</td>
<td>1.50</td>
<td>65</td>
<td>1982, 1894</td>
<td>202-3</td>
</tr>
<tr>
<td>Tricyclohexylphosphine</td>
<td>72.</td>
<td>70</td>
<td>1960, 1880</td>
<td>214-5</td>
</tr>
<tr>
<td>Triphenylphosphite</td>
<td>5.</td>
<td>80</td>
<td>1996, 1918</td>
<td>139-41</td>
</tr>
</tbody>
</table>
Preparation of \( \sigma \)-allyltricarbonyl-\( \pi \)-cyclopentadienylmolybdenum.

(i.) Chlorotricarbonyl-\( \pi \)-cyclopentadienylmolybdenum (0.903 g, 2.78 mmole.) was dissolved in dry THF (15 ml.), which had been freshly distilled from lithium aluminium hydride, under nitrogen, to give a dark maroon-red solution. Sodium-potassium alloy was added and the resulting mixture shaken vigorously to give a very fine suspension of the alloy. The red solution rapidly gave a brown suspension, the alloy sinking to the bottom, with the salts produced. The mixture was centrifuged to remove the excess alloy with the "crud". Addition of an excess of allyl tosylate gave a yellow solution, which was treated with methanol, to destroy the excess alloy, and then pentane to extract the excess allyl tosylate. Removal of the solvent gave a yellow oily complex, (415 mg, 34%)

Infra-red (neat film): 3080 (w.), 2970 (w.), 2019 (vs.), 1928 (vs.), 1640 (w.), 1614 (s.), 1427 (s.).

This complex showed similar spectral properties to \( \sigma \)-allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten, and not those reported by Green.

Parallel experiments were run in which the excess sodium-potassium alloy was destroyed with methanol, under nitrogen, before adding the allyl tosylate. Again a yellow oily material was isolated. However, even working in a good dry box, if left for any length of time, the product decomposed to give a deep red complex.

Investigation of this product showed the presence of small quantities of the dimeric species, \( [\pi-C_5H_5Mo(CO)_3]_2 \), together with traces of the oxygen complexes.

This reaction was also performed using the sodium salt, prepared directly from molybdenum hexacarbonyl and sodium cyclopentadienide, in DMF. The sodium salt was purified by removal of the solvent, followed by extraction of all the volatile complexes.
by sublimation at 50°C. and 0.01 mm. Hg. pressure. This method
gave better yields, due to the higher yields of the sodium salt,
but suffered from the disadvantage that it could not be used for
phosphine analogues.

(ii.) Chloride and Grignard.

Whereas, for most of the other σ-allyls prepared in,
this work, this method gave clean, high yield reactions, for this
system it was disappointing.

Slow addition of a saturated solution of chlorotricarbonyl-
π-cyclopentadienylmolybdenum (151.2 mg. 0.46 mmole.) in ether to
a stirred ethereal solution of allylmagnesium bromide, (1 mole.
excess.) under nitrogen at 0°C., produced a clear yellow solution.
Addition of triethylamine, (2 drops.) gave an amber solution, and
a yellow and brown oily precipitate, which on addition of degassed
water (2 ml.) became red. The ethereal layer was separated and the
aqueous layer extracted with ether (3 x 2 ml.). The combined extracts
were dried over potassium carbonate, and on removal of solvent a
mixture of red crystals and an amber oil was obtained. This
proved to be mainly the dimeric species \([\pi-\mathrm{C}_5\mathrm{H}_5\mathrm{Mo}((\mathrm{CO})_3)]_2\) together
with a very small amount of the σ- and π-allyl derivatives.

The reaction was repeated and the yellow reaction product
treated directly with degassed water. This gave a mixture similar
to that just described. Use of ammonium chloride (saturated aqueous.)
also gave the same mixture, together with traces of the chloride
derivative.

The yellow reaction product obtained from chlorotricarbonyl-
π-cyclopentadienylmolybdenum (207.1 mg. 0.64 mmole.) was
chromatographed, using a pentane : benzene mixture, on a basic
alumina column. Only two bands were observed on the column.
These two yellow bands both gave deep yellow oils on removal of solvent. The first was identified as the σ-allyl (69 mg, 34 %.) m.p. approximately 0°C. Infra-red (neat film.) 3080(w.), 2970(w.), 2019(vs.), 1928(vs.), 1640(w.), 1614(s.), 1427(s.).

The second complex was shown to be the π-allyl (31 mg, 19 %.) m.p. 130 - 131°C. (dec.) (literature value 134°C.) Infra-red (in carbon disulphide): 1963(vs.), 1814(vs.). NMR. (in deuterobenzene) \( ^2J \) 9.2 (a.) (2H.); 7.4 (q.) (2H.); 6.75 (m.) (1H.); 5.28 (s.) (5H.).

The yields were improved over other work up techniques, but were still quite low. Since the other work up techniques were so unreliable, it was impossible to work up part of the reaction by the basic alumina column and part by the other method, to show whether the π-allyl was produced on the column, or was present in the reaction mixture. Infra-red spectrum of the crude reaction mixture suggested the former to be the case.

Preparation of σ-methyltricarbonyl-π-cyclopentadienylmolybdenum.

(i.) Chlorotricarbonyl-π-cyclopentadienylmolybdenum (352 mg, 1.10 mmole.) was converted, by treatment with sodium potassium alloy, in freshly distilled THF., into the sodium salt. The reaction mixture was centrifuged, and the clear red solution decentered. Addition of a two molar excess of methyl iodide, and stirring for fifteen minutes produced a light brown-yellow solid residue. Infra-red spectroscopy showed this to contain only one metal carbonyl complex. Extraction of the residue with an ether : isopentane (1 : 4) (3 x 20 ml.) gave yellow extracts and a white solid residue. Concentration of the combined extracts, and then cooling to -20°C.
gave yellow crystals (147 mg, 45 %) m.p. 122 - 124°C. Infra-red (in carbon tetrachloride): 3100(w.), 2916(m.), 2830(m.), 2022(vs.), 1934(vs.), 1435(w.), 1425(m.). NMR. (in deuterobenzene) \( \gamma 5.5 \) (s.) (5H.); 9.8 (s.) (3H.). Ultra-violet. (in cyclohexane.) 
\( \lambda_{\text{max}} 315\text{m} \mu \text{ molar 2000.} \)
The tungsten hexacarbonyl used was donated by the Climax Molybdenum Company, and was purified by sublimation. It was converted, by reaction with sodium cyclopentadienide, into sodium tricarbonyl-π-cyclopentadienyltungstate. This sodium salt was purified, especially of unreacted tungsten hexacarbonyl, by subliming all the volatile material from the reaction product, at 50°C. and high vacuum, and then either used to prepare σ-allyl or σalkyl derivatives, by direct reaction with allyl or alkyl halides, or was converted to chlorotricarbonyl-π-cyclopentadienyltungsten. The latter involved dissolving the sodium salt in degassed water and ether, under nitrogen. Addition of acetic acid caused an immediate yellow precipitation of the hydride, which was rapidly oxidised, with carbon tetrachloride at room temperature.

Chlorotricarbonyl-π-cyclopentadienyltungsten was extracted with ether, decolourised with charcoal in acetone solution, and finally recrystallised from an acetone : water mixture. Yield 65%.


Preparation of Allyl, Alkyl, and Aryltricarbonyl-π-cyclopentadienyltungsten derivatives.


(i.) From sodium tricarbonyl-π-cyclopentadienyltungstate

Sodium tricarbonyl-π-cyclopentadienyltungstate (0.02 mole.) was dissolved in freshly distilled, dry THF (150 ml.)
and added slowly to an excess of allyl chloride (10 ml.). The resulting mixture was stirred for two hours, under nitrogen at room temperature, and then the solvent was removed under high vacuum. The residue was extracted with petrol (30 - 40°C. fraction.) (4 x 50 ml.) the extracts concentrated, and chromatographed on a neutral alumina column (80 g.), in a nitrogen atmosphere, using petrol (30 - 40°C. fraction.) as the eluent. The solvent was removed rapidly and the yellow crystals stored at -20°C., under nitrogen, (3.52 g. 47%). m.p. 23 - 24°C. (literature value 24 - 26°C.)

Slightly better yields were obtained by the use of allyl tosylate, but not allyl bromide.

(ii.). From chlorotricarbonyl-π-cyclopentadienyl-tungsten.

Chlorotricarbonyl-π-cyclopentadienyltungsten (0.2917 g. 0.8 mmole.) in sodium dried ether was added to a twofold excess of allylmagnesium chloride, at 0°C., under nitrogen, and stirred until the initial red colouration gave way to a golden yellow colour.

The following methods of work up were tried.

(a.) The yellow ethereal layer was treated with degassed distilled water, at 0°C., under nitrogen, and the ethereal layer removed and dried over magnesium sulphate. Removal of the solvent gave a deep yellow oil, which from infra-red spectroscopy observations, was seen to be a mixture of the starting halide and σ-allyltricarbonyl-π-cyclopentadienyltungsten.

(b.) The ethereal solution was treated, at 0°C., with a saturated, aqueous solution, of ammonium chloride. The ethereal layer was separated and dried over magnesium sulphate to yield a pinkish yellow solution. Infra-red study of the oily solid produced, on removal of the solvent, showed the presence of a
fifty-fifty mixture of σ-allyl and chlorotricarbonyl-π-cyclopenta-
dienyltungsten.

(c.) The reaction mixture was concentrated and the ether solution was passed, rapidly through a basic alumina column, using hexane as the eluent. This gave a golden yellow fraction, which on removal of the solvent gave a pure sample of σ-allyltricarbonyl-π-cyclopentadienyltungsten as determined by infra-red and NMR spectroscopy. (0.254 g. 85%) m.p. 28°C. Infra-red (in cyclohexane) : 3120(w.), 3080(m.), 2019(vs.), 1935(s, sh.), 1928(vs.), 1612(m.), 1421(w.), 1357(w.), 1295(w.), 1199(m.), 1109(wh.), 1036(w.), 1072(w.), 1001(m.), 985(m.), 876(s.), 818(s.), 745(m.). NMR. (in cyclohexane.) ζ 4.2 (m.) (1H); 4.8 (s.) (5H); 5.5 (m.) (2H); 7.75 (d) (2H) (JCH2H = 8.6 ).

(E.) Preparation of σ-methyltricarbonyl-π-cyclopentadienyln-
tungsten.

Sodium tricarbonyl-π-cyclopentadienylnitstgtate (1.7 g. 5mmole.) was treated in dry THF solution with an excess of methyl iodide (6 ml.). The resulting yellow-brown suspension was evaporated to dryness, under high vacuum, and the brown residue extracted with ether (5 x 15 ml.). The deep amber solution was placed in a sublimation apparatus and the solvent removed. The residue was sublimed at room temperature/10⁻³ mm. to yield very pale yellow crystals. (1.231 g. 70%) m.p. 143–144°C. (Literature value 144.7 – 145.3°C.) Infra-red (in carbon tetrachloride): 2960(m.), 2874(m.), 2816(w.), 2020(vs.), 1931(vs.), 1427(m.), 1189(m.), 1027(m.), 1007(s.). NMR. (in carbon tetrachloride.) ζ 5.3 (s.) (5H); 9.8 (s.) (3H). Ultra-violet. (in cyclohexane.) λmax 315 μm, molar 2500.
Photolysis of \( \sigma \)-allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten.

(i.) Alone.

\( \sigma \)-Allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten (213 mg, 0.57 mmole.) was dissolved in degassed sodium dried ether (20 ml.) to give a pale yellow solution, which was irradiated, under nitrogen, with a 125 Watt ultra-violet lamp, at 10 cm. The photolysis was followed by infra-red spectroscopy, which showed the disappearance of the \( \sigma \)-allyl derivative after three hours. The now light brown solution was concentrated and chromatographed on a neutral alumina column (30 g.) using petrol (30 - 40°C, fraction): ether (2 : 3) mixture as the eluent. The first band eluted gave a pale yellow solid, which was shown to be the \( \pi \)-allyldicarbonyl-\( \pi \)-cyclopentadienyltungsten. (128 mg., 65 %.) Infra-red (in carbondisulphide): 2995 (m.), 2925 (m.), 1960 (vs.), 1880 (vs.), 1863 (vs.), 1427 (m.), 1188 (m.), 1007 (s.). NMR. (in deuterobenzene) \( \gamma \) 5.4 (s) (5H.); 6.7 (m.) (1H.); 7.54 (d.) (2H.) (J\textsubscript{H,H} = 7.0); 8.9 (d.) (2H.).

(ii.) with triphenylphosphine.

\( \sigma \)-Allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten (97 mg, 0.26 mmole.) in sodium dried ether (20 ml.). The yellow solution was irradiated, under nitrogen, with a 125 Watt ultra-violet lamp, at 10 cm. A darkening of the solution was noticed after one hour, and infra-red spectroscopy showed the presence of some \( \pi \)-allyldicarbonyl-\( \pi \)-cyclopentadienyltungsten. This was confirmed by comparison of the thin layer chromatograms, run on silica/Kieselguhr in benzene : cyclohexane (1 : 3) of \( \sigma \)-allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten, \( \pi \)-allyldicarbonyl-\( \pi \)-cyclopentadienyltungsten, and the reaction mixture.

Photolysis was carried out for a total of eight hours, and the light brown suspension obtained chromatographed on a neutral
alumina column (15 g.), using a petrol (30 - 40°C.) : ether (2 : 3) mixture as eluent, and this gave pure \(\pi\)-allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten. The only other product isolated was free triphenylphosphine (54 mg., 60%).

This experiment showed that triphenylphosphine did not react with the \(\sigma\)-allyl or the \(\pi\)-allyl derivative, under the conditions used for the photolysis.

Reactions of \(\pi\)-allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten.

(A.) Thermal reaction with triphenylphosphine.

\(\pi\)-Allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten (114 mg. 0.33 mmole.) was refluxed with an equimolar amount of triphenylphosphine (86.8 mg., 0.33 mmole.) in anhydrous ether, under nitrogen. The reaction was followed by infra-red spectroscopy, which showed that after fifteen and a half hours no reaction had occurred, other than some decomposition of the \(\pi\)-allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten.

A repeat experiment was carried out in refluxing benzene, and this also proved unsuccessful.

(B.) Thermal reaction with tricyclohexylphosphine.

\(\pi\)-Allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten (91 mg. 0.26 mmole.) and tricyclohexylphosphine (75.9 mg. 0.27 mmole.) were refluxed under nitrogen in sodium dried benzene. Infra-red studies showed that there was no new carbonyl complex formed. The only result was some thermal degradation of both the tricyclohexylphosphine and the \(\pi\)-allyldicarbonyl-\(\pi\)-cyclopentadienyltungsten.
Production and reaction of \( \pi \)-propenetricarbonyl-\( \pi \)-cyclopentadienyl-tungsten cation.

Protonation of \( \sigma \)-allyl derivatives.

\( \sigma \)-Allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten was taken up in sodium dried ether and treated with dry hydrogen chloride gas, yielding immediately a yellow precipitate and a colourless supernatant.

Removal of half of the solvent, to ensure that there was no excess of hydrogen chloride present, followed by the addition of degassed water, and then excess potassium hexafluorophosphate gave another yellow solid, which slowly decomposed when exposed to air. The hexafluorophosphate was slightly soluble in water, but there was some decomposition, evolving propene gas.

It was found that the amount of hydrogen chloride used was critical, even a slight excess brought about a rapid evolution of propene, to give chlorotricarbonyl-\( \pi \)-cyclopentadienyltungsten, the process being catalysed by any traces of moisture in the gas. The chloride was identified by infra-red spectroscopy, melting point and by comparison of the \( R_f \) on thin layer chromatography, run on silica gel plates, using cyclohexane as the eluent. Infra-red (in HCB.) of \( \pi \)-propenetricarbonyl-\( \pi \)-cyclopentadienyltungsten-hexafluorophosphate : 2111(s.), 2056(vs.), 2003(vs.), 1439(m.), 1420(m.). Infra-red (in cyclohexane.) of chlorotricarbonyl-\( \pi \)-cyclopentadienyltungsten : 2049 (vs.), 1973(vvs.), 1953(vs.).

Nucleophilic attack on \( \pi \)-propenetricarbonyl-\( \pi \)-cyclopentadienyl-tungsten cation.

(i.) Reaction with methyl lithium.

\( \sigma \)-Allyltricarbonyl-\( \pi \)-cyclopentadienyltungsten (241 mg.)
0.65 mmole.) was dissolved in dry ether (20 ml.) and protonated at 
-78°C. with hydrogen chloride to give the olefinic species. All the 
volatile matter was removed under high vacuum, thus removing any 
excess acid present. The yellow residue was resuspended in dry 
ether (10 ml.) and cooled to -78°C. One molar equivalent of methyl 
lithium was added dropwise to the yellow solution, causing a very 
slight darkening of colour. The mixture was allowed to warm slowly 
with stirring to 0°C. and then degassed water (2 ml.) was added to 
destroy any excess methyl lithium and remove the lithium chloride.
The dried yellow ethereal solution was pumped to dryness to give 
an impure yellow solid. This was chromatographed on a small neutral 
alumina column (25g.) to give a yellow solution, which on slow 
evaporation of solvent gave pale yellow crystals. (136 mg. 60 %.) 
m.p. 142 - 143°C. (literature value 140°C., and 144.7 - 145.3°C.) 
NMR. (in carbon tetrachloride.) ω 5.3 (s.)(5H.); 9.8 (s.)(3H.)

(ii.) Reaction with phenyl lithium.

The π-proponetricarbonyl-π-cyclopentadienyltungsten 
cation was prepared as indicated above. Addition of an equimolar 
amount of phenyl lithium at -78°C. caused no reaction, the infra-red 
spectrum showing the presence of starting material. The mixture was 
allowed to warm slowly to room temperature, and then it was stirred 
for six hours. After work up, with degassed water, the major product 
was the π-allyl, πC₅H₅W(CO)₃CH₂CH=CH₂ m.p. 26 - 28°C. Infra-red 
(in cyclohexane.): 2019(vs.), 1935(s,sh.), 1928(vs.).

Preparation of phosphine substituted chlorides.

The preparation of these halides was carried out in refluxing 
benzene, under nitrogen, using a one to one and a half molar ratio 
of the organometallic halide to phosphine, for fifteen hours.
The products were chromatographed on a small neutral alumina column (10 cm. x 1.5 cm.) before recrystallisation, either from a benzene : hexane mixture, or ether.

\[
\pi-C_{5}H_{5}W(CO)_{2}[P(C_{6}H_{5})_{3}]Cl \text{ (yield 70\%.) m.p. 191 - 192°C.}
\]
Infra-red (in carbon disulphide): 1962(vs.), 1874(vs.).

\[
\pi-C_{5}H_{5}W(CO)_{2}[P(C_{6}H_{11})_{3}]Cl \text{ (yield 65\%.) m.p. 207 - 208°C.}
\]
Infra-red (in cyclohexane): 1956(vs.), 1871(vs.). Found C, 48.0; H, 5.9; P, 5.6; \text{C}_{25}H_{38}ClO_{2}FW requires C, 48.2; H, 6.1; P, 5.4%.

Preparation of \(\sigma\)-allyl, alkyl, and aryl phosphine substituted derivatives.

(A.). Preparation of \(\sigma\)-allyldicarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyltungsten.

(i.) The attempted photolysis of \(\sigma\)-allyl and \(\pi\)-allyl derivatives with triphenylphosphine. (already reviewed.) This proved completely unsuccessful.

(ii.) The reaction of chlorodicarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyltungsten with allylmagnesium chloride.

An ethereal solution of chlorodicarbonyl-triphenylphosphine-\(\pi\)-cyclopentadienyltungsten was added, at room temperature, under nitrogen, to a threefold excess of allylmagnesium chloride. On stirring for an hour the initial pink solution became orange. Chromatography of the orange reaction product, on basic and neutral alumina, using hexane and ether mixtures as eluents, gave only the starting chloro complex back again. There was considerable decomposition on the column. Other methods of work-up, that were tried, also proved unsuccessful.
CHAPTER V.

DISCUSSION AND RESULTS.
Discussion of the preparation of \( \sigma \)-bonded derivatives.

Survey of the preparation of \( \sigma \)-bonded organometallic derivatives.

The \( \sigma \)-bonded derivatives of organometallic systems may be prepared by a variety of routes \(^{164,114}\) and in general they tend to be sublimable solids, of low melting points, or liquids which, especially in solution, are very sensitive to moisture, oxygen, and light.

The following general methods of preparation have been used:

1). Insertion Reactions.

These important reactions involve the insertion of an organic moiety normally into a metal-hydrogen bond. Its importance lies in the fact that it is involved in the Ziegler-Natta polymerisation, hydrogenation, carbonylation etc.

The reaction of diazomethane with metal hydride or halides gives \( \sigma \)-alkyl complexes, for example:

\[
\pi-C_5H_5Mo(CO)_3H + CH_2N_2 \rightarrow \pi-C_5H_5Mo(CO)_3CH_3 + N_2 \quad (\text{ref. 114})
\]

\[
ClIr(CO)[P(C_6H_5)_3]_2 + CH_2N_2 \rightarrow ClCH_2Ir(CO)[P(C_6H_5)_3]_2 \quad (\text{ref. 165})
\]

Olefins and acetylenes insert into metal-hydrogen bonds to give alkyl and alkenyl complexes, for example:

\[
\pi-C_5H_5Fe(CO)_2H + CH_2=CHCH=CH_2 \rightarrow CH_3CH=CHCH_2Fe(CO)_2(\pi-C_5H_5) \quad \text{(ref. 115)}
\]

\[
HMn(CO)_5 + CF_2=CF_2 \rightarrow HCFCF_2Mn(CO)_5 \quad (\text{ref. 166.})
\]

2). Reaction of Grignard reagents with halides.

\[
\pi-C_5H_5Fe(CO)_2Cl + CH_3MgI \rightarrow \pi-C_5H_5Fe(CO)_2CH_3 + MgCl_2 \quad 114
\]
This method is unpredictable in that, for certain reactions, very high yields are obtained, but for others low yields, together with dimerisation, are obtained, for example:

\[ 3 \pi-C_5H_5Fe(CO)_2Cl + 3C_6H_5MgBr \rightarrow \pi-C_5H_5Fe(CO)_2C_6H_5 (5\%) + C_{12}H_{10} \]

\[ + [\pi-C_5H_5Fe(CO)_2]_2 + 3MgClBr \]

3). Reaction of alkali metal reagents with halides, for example:

\[ \pi-C_5H_5Fe(CO)_2Br + NaC_5H_5 \rightarrow \pi-C_5H_5Fe(CO)_2\sigma-C_5H_5 + NaBr \]

The higher nucleophilicity of sodium or lithium alkyls over Grignard reagents enables the reaction to be carried out at lower temperatures, giving much cleaner reactions, for example, phenyl lithium reacts with \( \pi \)-cyclopentadienylirondicarbonylbromide at \(-78^\circ C\), to give high yields of the \( \sigma \)-phenyl derivative, and no dicyclopentadienyldiirontetracarbonyl.

4). Reaction of organic halides with transition metal anions.

\[ \pi-C_5H_5Fe(CO)_2Na + C_2H_5I \rightarrow \pi-C_5H_5Fe(CO)_2C_2H_5 + NaI \]

This method is most versatile, of those quoted, because it can be adapted for preparing acyl, allyl, alkyl, and aryl derivatives, as well as for other ligands, with little dimerisation, for example:

\[ \pi-C_5H_5Fe(CO)_2Na + ClSi(CH_3)_3 \rightarrow \pi-C_5H_5Fe(CO)_2Si(CH_3)_3 \]

The preparation and properties of transition metal carbonyl anions has been reviewed by R.B. King.

It has been possible, by measuring the rates of reaction of organic halides with various metal anions to arrive at a semi-quantitative estimation of the relative nucleophilicities of the
The observed nucleophilicities decrease in the order
\[ \pi-C_5H_5Fe(CO)_2^- > \pi-C_5H_5Ru(CO)_2^- > \pi-C_5H_5W(CO)_3^- > \pi-C_5H_5Mo(CO)_3^- > \pi-C_5H_5Cr(CO)_3^- \]

The reactivity of halogen atoms also affects the rate and the yield of the reaction, as does the size and the reactivity of the organo-group. For instance, phenyl and vinyl halides give low yields, whereas other alkyl, allyl, and benzyl halides give good yields. Thus \( \pi-C_5H_5Fe(CO)_2^- \) reacts slowly with iodobenzene, to give a 2% yield of the \( \sigma \)-phenyl complex, whereas methyl iodide gives 70% yield of the methyl complex.\(^{114}\)

A more specific arylating agent has been found with cumin compounds, for example, \( (C_6H_5)_3SBF_4 \) reacts with sodiumcyclopentadienyldicarbonylferrate, to give the \( \sigma \)-phenyl in 40% yield.\(^{171}\)

Elimination reactions.

Thermal elimination reactions of acyl complexes usually occur under mild conditions below 150°C.

\[ CH_3COMn(CO)_5 \xrightarrow{\text{heat}} CH_3Mn(CO)_5 + CO \quad \text{(ref. 172.)} \]

For resistant compounds photolysis is sometimes employed.

\[ \pi-C_5H_5Fe(CO)_2COCH_3 \xrightarrow{\text{hv}} \pi-C_5H_5Fe(CO)_2CH_3 \quad \text{(ref. 173.)} \]

Of the methods enlisted in the survey, methods 2, 3, and 4 were used in this work. Method 4, the reaction of organic halides and the transition metal anions, was in most cases the cleanest and the best method of preparing the non-phosphine containing \( \sigma \)-alkyl derivatives, especially if the anion was prepared in high yield directly from the pure metal carbonyl, and sodiumcyclopentadienide. The method, however, was not very successful for the phosphine
substituted complexes, since in making the anion much decomposition took place, with the formation of free triphenylphosphine.

Methods 2 and 3 were found to be acceptable in all other cases, with the exception of the carbonyltriphenylphosphine-\(\kappa\)-cyclopentadienyliron system.

Decomposition of excess Grignard reagents.

This normally simple manipulation caused a great deal of trouble in this work. As will be seen from the experimental details all the standard methods of chromatography on alumina, addition of water, or ethyl acetate, and evaporation to dryness, followed by extraction with iso-pentane, were tried. In some cases these proved to be successful, but mainly their use was limited to those complexes that had no coordinated phosphines.

The use of a different approach in the precipitation of excess Grignard and magnesium halide with triethylamine or dioxan proved more successful. Triethylamine was, in general, the less efficient of the two, being harder to remove afterwards, and there was always the possibility of the triethylamine reacting with the organometallic.

The best procedure was, therefore, found to be the addition of dioxan, in excess. This gave an immediate white, gelatinous precipitate, which was removed by filtration. The filtrate was then treated with degassed cold distilled water, in all cases with very little decomposition. Addition of water, before the removal of the dioxan gave as much, if not more, decomposition than on straight addition of water. Most of the excess dioxan washed out with the water, but that which remained was pumped off under high vacuum, before recrystallisation of the product.
Reactions of Bromocarbonyltriphenylphosphine-π-cyclopentadienyliron.

Treatment of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron with n-propylmagnesium chloride, in molar ratios varying from one to one, to one to four, at -78°C., gave two products, with carbonyl stretching frequencies at 1939 cm\(^{-1}\) and 1916 cm\(^{-1}\). A similar result was observed when the reaction was performed at 0°C., but at room temperature only one product was obtained, that showing a carbonyl stretching frequency at 1939 cm\(^{-1}\).

Reaction of the bromide with n-propyl lithium, at -78°C., gave the "1939 cm\(^{-1}\) complex", at room temperature the "1916 cm\(^{-1}\) complex", and at intermediate temperatures a mixture of the two. In addition a very small amount of the n-propylcarbonyl-π-cyclopentadienyliron was produced.

The complex having a carbonyl stretching frequency at 1916 cm\(^{-1}\) was isolated as deep red-brown crystals. The NMR. spectrum of this complex showed it to be the n-propyl derivative, the carbonyl stretching frequency is also within a few wave numbers of the σ-methyl, allyl, and phenyl derivatives. Attempts to isolate the other yellow complex as a crystalline complex failed, due to its high instability. It was very susceptible to the presence of traces of Lewis acids and reacted a factor of ten times faster with chloroform than the σ-methyl or σ-propyl derivatives, to give chlorocarbonyltriphenylphosphine-π-cyclopentadienyliron. These observations suggested that the complex might be the hydride, \( \pi-C_5H_5Fe(CO)P(\sigma)\sigma_3H \). However this could not be proved, since the complex could not be isolated from the reaction mixture. It has been claimed that this hydride has been obtained as a yellow crystalline solid.

Treatment of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron with methyl, phenyl, or benzylmagnesium chloride gave
a very high yield of the \( \sigma \)-alkyl/aryl derivative, with few side products. However the reaction of methyl or phenyl lithium always gave a mixture of two products, identified as \( \sigma \)-alkylcarbonyl-triphenylphosphine-\( \pi \)-cyclopentadienyliron and \( \sigma \)-alkyldicarbonyl-\( \pi \)-cyclopentadienyliron. Some free triphenylphosphine was also isolated. At first the purity of the starting bromide was suspected, but this was shown to be absolutely free from any impurity. Additional support was given to this by the observation that the ratio of the products varied with temperature.

A detailed examination of the reaction showed that a sixfold excess of phenyl lithium at room temperature gave a ratio of products that was approximately 60 : 40, \( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)Ph : \( \pi \)-C\(_5\)H\(_5\)Fe(CO)P\(_3\)Ph based on the extinction coefficient of the carbonyl stretching frequency. If the reaction was carried out at -60°C, the ratio changed to 40 : 60, \( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)Ph : \( \pi \)-C\(_5\)H\(_5\)Fe(CO)P\(_3\)Ph. However when using methyl lithium the ratio appeared to be independent of the temperature, there only being about 1 or 2% of the \( \sigma \)-methyl-dicarbonyl-\( \pi \)-cyclopentadienyliron formed.

The experiments were then carefully studied using a 1 : 1 and 1 : 2 mixture of the organometallic bromide and phenyl lithium respectively. The reaction was considerably slower, taking about sixty hours, rather than about half an hour with the larger excess phenyl lithium. However, the results showed that this did not effect the reaction significantly, other than to slightly increase the amount of the dicarbonyl system present. Mass balance experiments showed that the amount of \( \sigma \)-phenyldicarbonyl-\( \pi \)-cyclopentadienyliron accounted for just over half the carbon monoxide present in the initial bromide.

These experiments, together with those involving the use of \( n \)-propyl lithium, which gave about 5 - 10% of the dicarbonyl
derivative, would seem to indicate that the disproportionation is due to some steric factor as well as a Lewis acid catalysed "carbonyl swap" in the initial bromide. If the latter happened exclusively one would expect roughly similar ratios for all the lithium reagents. Bromocarbonyltriphosphine-\(\pi\)-cyclopentadienyliron was shown to react with magnesium bromide trietherate, prepared from magnesium and dibromomethane in ether, to give some bromodicarbonyl-\(\pi\)-cyclopentadienyliron. This rearrangement took, however, four or five hours. Also instability of the \(\sigma\)-alkyl derivative, in the presence of Lewis acid is not uncommon, for example, similar Lewis acid labilisation has been observed in the preparation of tetrabenzyl titanium, from titanium tetrachloride, and benzylmagnesium chloride. Better yields, and greater stability were obtained using \(\text{TiCl}_4\cdot 2\text{L}\) (where \(\text{L}\) is pyridine or piperidine.) since the Lewis acid was complexed to the pyridine or piperidine, with the formation of complexes such as \(\text{MgCl}_2\cdot 2\text{L}, \text{MgBr}_2\cdot 4\text{L},\) and \(\text{MgI}_2\cdot 4\text{L}\).

As a test to see whether steric factors were crucial, bromocarbonyltriphosphine-\(\pi\)-cyclopentadienyliron was treated with a twofold excess of anthracene lithium, in the hope of isolating dicyclopentadienyldiiron tetracarbonyl, \([\pi-C_5\text{H}_5\text{Fe(CO)}_2]_2\) as the only carbonyl containing complex. Unfortunately this proved unsuccessful. A small quantity of the dimer was observed, together with some starting bromide, but much was lost through decomposition. Parallel experiments using bromodicarbonyl-\(\pi\)-cyclopentadienyliron gave high yields of the dimer, \([\pi-C_5\text{H}_5\text{Fe(CO)}_2]_2\).

\(\sigma\)-Phenylcarbonyltriphosphine-\(\pi\)-cyclopentadienyliron was prepared from the bromide by treatment with the Grignard reagent to give stable red crystals. Treatment of an ethereal solution of this complex with excess phenyl lithium caused a slight amount of decomposition, but no production of a dicarbonyl system. This would
indicate that the "carbonyl swop" is not taking place via attack of excess phenyl lithium, for example on the phosphine, followed by disproportionation.

Infra-red spectroscopy indicates that treatment of the bromocarbonyltriphenylphosphite-π-cyclopentadienyliron, with phenyl lithium gives the σ-phenylcarbonyltriphenylphosphite-π-cyclopentadienyliron, with none of the σ-phenyllicarbonyl-π-cyclopentadienyliron. The σ-phenyl has not been fully characterised, deduction being from carbonyl stretching frequency correlation (in cyclohexane - 1935 cm⁻¹). This result, however, fits in with the hypothesis of steric factors influencing the disproportionation, since insertion of the oxygen atom removes the phenyl rings further away from the metal atom. This then reduces the steric crowding at the metal centre.

From all these observations it is clear, that in this sequence of reactions, there are two competing reactions. The first is the attack, by the lithium or magnesium reagent, on the metal to give the σ-alkyl metal complex; the other is the Lewis acid induced rearrangement. The latter is dealt with thoroughly later.

For the smaller nucleophiles, methyl and propyl, the rate of direct attack is faster, due to the lower steric hindrance encountered, but for the larger nucleophiles, like phenyl, the approach is more hindered, and therefore the reaction is slower. This allows the slower Lewis acid induced rearrangement to take place as a competitive reaction.

If the Lewis acid induced disproportionation does take place in analogy to the reaction on page 154 it would be expected that one intermediate might be \( \text{[π-C}_5\text{H}_5\text{Fe(CO)}_2\text{P}^\Phi_3]⁺ \). It has been shown that this salt reacts with phenyl lithium to give \( \text{π-C}_5\text{H}_5\text{Fe(CO)}_2\text{C}_6\text{H}_5 \).
and exo-\((C_6H_5)C_5H_5Fe(CO)_2Ph\) as the only products. However, treatment of this salt with allylmagnesium chloride was shown, in this work to give three of the six possible covalent products. The three complexes isolated were \(\pi-C_5H_5Fe(CO)C_3H_5\), \(\pi-C_5H_5Fe(CO)Br\), and \(\pi-C_5H_5Fe(CO)PhC_3H_5\). The dominant species were the latter two, being isolated, after chromatography, in 31 and 43% yield respectively. The other expected complexes not observed were \(\pi-C_5H_5Fe(CO)C_3H_5\), \(\pi-C_5H_5Fe(CO)Br\), and exo-\((C_3H_5)C_5H_5Fe(CO)_2Ph\).

The reaction would appear to be controlled by the production of the more thermodynamically stable system, and shows that it is possible for both the carbonyl and the triphenylphosphine to be ejected. This would fit in with all the observations recorded above.
Preparation of π-propene cations.

Three methods of preparation have been reported in the literature, for the π-propene cations of iron, molybdenum and tungsten carbonyl-π-cyclopentadienyl systems.

The first involves the direct combination of the olefin with the metal. This method necessitates the in situ formation of the unsaturated cation, for example, \([\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^+\text{AlBr}_4^-\) by reacting the Lewis acid and the halide together, in the presence of large pressures of the olefin. Although good yields are claimed for this reaction, it is very time consuming, and very dependent on absolutely moisture free conditions. The major products isolated from this reaction, when performed in this work, were the bromide \(\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}\) and the dimer \([\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^2_2\).

The second standard method is the protonation of a metal \(\sigma\)-allyl derivative. This method is again reported to give high yields, but as will be seen in the following discussion is not as specific as it might have been hoped.

The final method is the hydride abstraction of a metal \(\sigma\)-propyl derivative, with a hydride abstractor such as triphenylmethyl cation, \((\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-\).

The following discussion describes some of the results obtained using these methods, together with some attempted new ones.

Discussion of Protonation.

The treatment of organometallic complexes with acids is one of those reactions which it seems are tried on all new organometallic complexes, to see what happens. The results can be very varied, as well as very interesting. Wilkinson, and his research workers treated many complexes with strong acids, in attempts to "protonate"
them. Detailed spectral studies of these systems showed evidence for metal-hydrogen bonds. Whilst metal-hydrogen bonds can be useful synthetically, for example, in preparing halides, by reacting with halogenated solvents, or preparing 6-allyl derivatives, by the insertion of olefins into the metal-hydrogen bond, in Wilkinson's work the metal-hydrogen bonds were produced in charged complexes, which rather limited their usefulness.

More interesting results were obtained when protonation actually took place on a ligand attached to the metal, as a direct result of the metal participation. An example of this type of reaction of acids is with metal acyl complexes. The ketonic carbonyl stretching frequency of an organic ketone is approximately 1720 cm⁻¹, but for a metal acyl complex it is about 1650 cm⁻¹. Whether this shift is due to some interaction of the metal with the carbonyl, or whether it is due to the partial double bond formation of the metal, with the π-orbitals of the carbonyl group, is not certain. The carbonyl group would be expected to become very susceptible to electrophilic attack, for instance protonation.

Thus the acyl π-C₅H₅Fe(CO)P(C₆H₅)₃(COCH₃) is readily protonated with anhydrous hydrogen chloride. (FIG. 23.)

![Fig. 23.](image-url)
Closely linked with this mode of protonation is that of the metal-ether complexes, which readily cleave, yielding the substituted methyl derivatives. \textsuperscript{181, 182} (FIG. 24.)

It is proposed that the intermediate in these acid cleavage reactions is the carbene species, $M=\text{CH}_2^+$, which being a very reactive species would explain the fast reaction times.

A related acid cleavage is observed in the reaction of perchloric acid with 1-hydroxy-2,4-pentadieneirontricarbonyl, to give the pentadienyl cation. \textsuperscript{183} (FIG. 25.)

Fig. 24.

Fig. 25.
Protonation of a ligand without cleavage of any part of it is typified by the protonation of metal σ-allyl complexes. In most of these protonations the protonating system has been anhydrous hydrogen chloride, in light petrol. This method of protonation was used on σ-allyldicarbonyl-π-cyclopentadienyliron, yielding the π-propene species, \( \left[ \pi-C_5H_5Fe(CO)_2C_3H_6 \right]^+Cl^- \), which proved to be extremely hygroscopic, giving rapidly, diamagnetic red-brown aqueous solutions, which slowly evolved a gas, found to be propene, forming the aquo complex \( \left[ \pi-C_5H_5Fe(CO)_2H_2O \right]^+ \). By treatment of the π-propene cation, generated by hydrogen chloride, with a strong aqueous solution of either ammonium hexafluorophosphate or tetrafluoroborate, it was possible to isolate a salt, which was air stable for several days. Thus it was possible to overcome the hygroscopic nature of the initial system. There still remained, however, a big disadvantage to this particular method of generating the π-propene cation, in that it was necessary to use a gaseous acid in the protonation, and this made it difficult to titrate the acid. In normal circumstances the excess acid would not be significant, but in these systems the excess acid resulted in the evolution of propene, and the formation of the covalent chloride, for example, \( \pi-C_5H_5Fe(CO)_2Cl \). (FIG. 26.)

Modifications of this procedure involved, firstly, an attempted preparation of the corresponding bromide salt, by the protonating of the σ-allyl in light petrol (30 - 40°C. fraction.) with dry hydrogen bromide. Unfortunately, however, although the bromide salt produced was much less hygroscopic than the corresponding chloride, it suffered from the disadvantage, like the chloride, as regards excess acid. In fact, as might have been expected, the tendency to form covalent bromide seemed considerably worse.
It was impossible to use any aqueous acids in this system, because of the ready expulsion of propene, with the formation of the aquo cation, $\left[\pi-C_5H_5Fe(CO)_2H_2O\right]^+$. In an attempt to overcome this subsequent reaction several different acids were used. The acids were chosen with certain aims in view.

The first obvious criterion was that the acid should either be a liquid, or a solid, so that a standard solution could be prepared. This could then be titrated, against the $\sigma$-allyl derivative, so that no excess acid was used. The second criterion was to find an acid that would give a salt that was non-hygroscopic thus eliminating the necessity to convert the initial cation into the hexafluorophosphate, or the tetrafluoroborate salt. Whilst bearing in mind these two points, particularly the second, it was required that the $\pi$-propene cation formed should be soluble in a common organic solvent; one of the major disadvantages of converting the $\pi$-propene chloride into the more stable hexafluorophosphate, or the tetrafluoroborate, is both these salts are insoluble in all the common organic solvents. The need for this solubility
was that reactions that were to be carried out on the π-propene cation, for example, nucleophilic attack, would proceed much faster, and probably more specifically in a homogeneous mixture, rather than under heterogeneous conditions.

Two acids seemed, possibly, to fill all these three criteria, these were fluorosulphonic acid and trifluoroacetic acid, but the second and third criteria could only be tested under experimental conditions.

Standard solutions of the two above named acids were made up in three different solvents, THF, benzene, and cyclohexane. However, due to the nature of the acids, these solutions could not be stored for very long, even at low temperatures, since they polymerised the solvents. When an ethereal solution of σ-allyldicarbonyl-π-cyclopentadienyliiron was protonated with a THF, solution of trifluoroacetic acid (molar ratio 1 : 1) at temperatures ranging from -78°C. to room temperature, there was a slight darkening of the initial yellow solution, but no other signs of reaction, such as precipitation. The infra-red spectrum of this solution showed that all the σ-allyl derivative, (carbonyl stretching frequency at 2010(vs.) and 1948 (vs.) cm\(^{-1}\)) had disappeared, and two new carbonyl bands at 2070 and 2035 cm\(^{-1}\) had appeared. This shift in the carbonyl stretching frequency was consistent with the formation of the cationic species.

Protonation in benzene proceeded after a two minute induction period to give a brown oil and a colourless supernatant.

In cyclohexane a similar reaction was observed but with the formation of a mauve supernatant. The brown oil produced in both cases was soluble in THF, giving an amber solution.

Parallel studies using fluorosulphonic acid as the protonating agent again gave the best results when performed in THF. However
the standard solutions of fluorosulphonic acid were very difficult
to store, due to the polymerisation of the solvent.

It was therefore found that the three criteria required of
a protonating acid were best fulfilled by trifluoroacetic acid in
THF solution.

Table VI shows the carbonyl stretching frequencies of the
products of these protonation studies.

<table>
<thead>
<tr>
<th>Protonating Acid</th>
<th>Solvent</th>
<th>$\nu_{C=O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroacetic</td>
<td>Benzene</td>
<td>2074, 2040.</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>2080, 2045.</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>2070, 2036.</td>
</tr>
<tr>
<td>Fluorosulphonic</td>
<td>Benzene</td>
<td>2070, 2025.</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>2070, 2022.</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>2067, 2019.</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>Petrol (30-40°)</td>
<td>2079, 2043.</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>Petrol (30-40°)</td>
<td>2031, 2046.</td>
</tr>
</tbody>
</table>

The different values are due to the fact that they were
obtained as neat films between sodium chloride plates where oily
products were obtained. Thus the presence of small amounts of
the solvent used could cause the observed shifts. It is however,
noticeable that the general shift, on treatment with acid, is
between 60 and 80 wavenumbers, and are in the same region as the
reported hexafluorophosphate or hexachloroplatinate derivatives.
One of the side reactions tried, as a direct result of the ability to protonate \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyliiron, with fluorosulphonic acid, was the methylation of the \( \sigma \)-allyl derivative with methyl fluorosulphonate. This reaction could give, not only a \( \pi \)-olefin cation, but also form one new carbon-carbon bond at the same time. Addition of a very slight excess of methyl sulphonate, to the \( \sigma \)-allyl derivative in dry THF, caused the initial yellow solution to lose its colour, and produce a yellow precipitate, that had carbonyl stretching frequencies at 2075 and 2035 cm\(^{-1}\) (in nujol). When the same experiment was performed in an NMR. tube, using deuterochloroform as the solvent, the reaction appeared to be very much slower, and accompanied by a large amount of decomposition. The latter, despite repeated centrifugation, prevented any good NMR. spectral data from being recorded. However the shift in carbonyl stretching frequencies is indicative of some form of cation being present, and shows that the product is not the \( \sigma \)-methyl derivative, \( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)CH\(_3\), since this has carbonyl stretching frequencies at 2010(vs.), and 1965(vs.), and 1935(w.) cm\(^{-1}\) (in cyclohexane.) The last being due to the carbon\(^{13}\) oxygen stretching frequency.

Unfortunately this experiment was not repeated, due to the lack of time, the protonation at that time, being the more important experiment. It is indicative, however, that this type of reaction may be useful in organic synthesis, since it has been shown, by NMR. studies, that deuterium chloride protonates \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyliiron always on the \( \gamma \)-carbon.\(^{115}\) NMR. studies should, if decomposition can be avoided, show which position the methyl attacks, but there is no real evidence to suggest that
this electrophilic attack should be any different in its point of attack. Thus, this process would give a method of forming new, specific carbon-carbon bonds. If nucleophilic attack, by carbon nucleophiles, were possible on the resulting π-olefin cation, then a second carbon-carbon bond could be formed, again it would be hoped, in a specific manner.

The course of the reaction could therefore be that shown in FIG. 27.

\[
\begin{align*}
\text{Fe} & \quad \text{CH}_2\text{SO}_3\text{F} \\
\text{OC} & \quad \text{CH}_2\text{CH} = \text{CH}_2 \\
\text{CO} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Fe} & \quad \text{CH}_2 \\
\text{OC} & \quad \text{CHCH}_2\text{CH}_3 \\
\text{CO} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Fe} & \quad \text{CH}_2 \text{BR} \\
\text{OC} & \quad \text{CH}_{2}\text{CHR} \\
\text{CO} & \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{Fe} & \quad \text{CH}_2 \text{R} \\
\text{OC} & \quad \text{CHCH}_2\text{R} \\
\text{CO} & \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

**Fig. 27.**

The protonation of σ-allyltricarbonyl-π-cyclopentadienyl-molybdenum \(^{118}\) and tungsten \(^{117}\) has also been carried out by Green, using anhydrous hydrogen chloride. Repeat of this work gave a pale yellow precipitate, from ethereal solution, as reported.

It also, as reported
"Decomposes slowly when exposed to air, and even when kept under nitrogen it darkens in the light."

No real explanation of this observation was presented, and one is left to assume the complete decomposition of the solid. When the reaction of anhydrous hydrogen chloride with $\sigma$-allyltricarbonyl-$\pi$-cyclopentadienyltungsten was studied carefully, the reason for this darkening became obvious.

A clear yellow ethereal solution of $\sigma$-allyltricarbonyl-$\pi$-cyclopentadienyltungsten was treated, at room temperature under nitrogen, with a deficiency of hydrogen chloride. The infra-red spectrum of a sample of the reaction mixture showed the presence of five new carbonyl bands. Three of these bands were identical to those of the chloride, $\pi$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-$\eta$-
tungsten was treated with one molar equivalent of trifluoroacetic acid in THF solution at \(-78^\circ\text{C.}\), under nitrogen, and after thirty minutes a slight darkening of the solution was observed. However the infra-red spectrum of a sample of the mixture showed only the presence of the \(\sigma\)-allyl derivative. The mixture was allowed to warm slowly, with stirring, to room temperature. This, although causing even more darkening in the colour of the solution, still brought no change in the infra-red spectrum. The mixture was cooled again and the acid content doubled, with still no change, and so the acid was doubled again, and still this produced no change in the infra-red spectrum. This was a surprising result, even though trifluoroacetic acid is weaker than hydrogen chloride.

It appears therefore, that the possibility must be considered in the reaction of hydrogen chloride with \(\sigma\)-allyltricarbonyl-\(\pi\)-cyclopentadienyltungsten, that the \(\sigma\)-allyl is very difficult to protonate, and this is the rate determining step in the formation of the \(\pi\)-propene cation, and not the fast rate at which the \(\pi\)-propene cation decomposes.

The reason why the \(\sigma\)-allyltricarbonyl-\(\pi\)-cyclopentadienyltungsten should be difficult to protonate is hard to see, but one possible reason is that with the larger metal atom, in the case of tungsten, the \(\sigma\)-allyl grouping can orientate itself in such a way as to optimise the amount of bonding in the \(\beta\)-position. Thus using the \(\beta\)-effect to stabilise the \(\sigma\)-allyl derivative, as shown in FIG. 28.

This would then remove much of the electron density from the double bond making protonation, that is electrophilic attack, much less easy. This possibility, however, seems unlikely when the carbon–carbon double bond stretch of the uncoordinated double bond is considered.
In the tungsten and molybdenum σ-allyl derivatives the stretching frequency is at 1609 and 1612 cm\(^{-1}\) (neat film) respectively, whilst in σ-allyldicarboxyl-π-cyclopentadienyliron it is at 1608 cm\(^{-1}\) (neat film.) Thus there is no evidence for any extra coordination to the metal, in the case of the molybdenum or tungsten, over the iron σ-allyl derivative.

In protonation attempts in the related phosphine substituted derivatives, \(\pi-C_5H_5M(CO)_2[P(C_6H_5)_3]CH_2CH=CH_2\) (where \(M\) is tungsten or molybdenum) with hydrogen chloride no evidence for a protonated species was acquired. The only product isolated was the chloride, \(\pi-C_5H_5M(CO)_2P(C_6H_5)_3Cl\).

Wilkinson 177 showed that the treatment of σ-methyltricarbonyl-π-cyclopentadienyltungsten or molybdenum with trifluoroacetic acid liberated methane and formed the covalent trifluoroacetate derivative, \(\pi-C_5H_5M(CO)_3OCOCF_3\). By analogy to the protonation of the hydride, \(\pi-C_5H_5W(CO)_3H\) with \(BF_3\cdot H_2O\cdot CF_3COOH\), to give \([\pi-C_5H_5W(CO)_3H]^+\), which on standing, for several hours, became red, due to the formation of \(\pi-C_5H_5W(CO)_3O\cdot COCF_3\), it was suggested that initial protonation of the σ-methyl took place at the metal. An intramolecular hydrogen transfer would then eliminate methane, and give the covalent trifluoroacetate, as
shown in FIG. 29.

The analogous reaction with the \( \sigma \)-allyl derivative would of course imply the transient formation of the \( \pi \)-propene cation on the proton transfer. (See FIG. 30.(i.)

Fig. 29.

Fig. 30.(i).
This mechanism thus incorporates the idea of an unstable π-propene cation undergoing an intramolecular nucleophilic attack. It seems reasonable to suggest that this type of mechanism is operational in the protonation of σ-allyltricarbonyl-π-cyclopentadienyl tungsten, with hydrogen chloride. The reason why it is not observed for trifluoroacetic acid protonation is not clear—the slightly increased steric hindrance between a σ-methyl and σ-allyl would not appear to be sufficient to prevent protonation. In the case of the phosphine substituted complexes, however, steric factors probably do play a part in preventing protonation.

Tests on various other σ-alkyl and aryl derivatives showed that the σ-alkyl metal bond could be broken by strong acids, such as hydrogen chloride, and this, as will be seen later, was used as a means of identifying certain σ-alkyl derivatives; the organic products being passed through a gas-liquid chromatography column, and thus identified.

In the protonation studies on σ-allyltriphenylphosphine-π-cyclopentadienyliron the first acid tried was hydrogen chloride, and from the transient band obtained in the infra-red (FIG. 30(ii)) it seemed possible that the initial product formed was the π-propene species, \([\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{P(C}_6\text{H}_5)_3\text{C}_3\text{H}_6]\) _Cl_. A solution infrared spectrum of the pure cation could not be obtained, because whenever the cation was dissolved it rapidly decomposed. Spectra in acetone and dichloromethane both showed the presence of a carbonyl stretching frequency at 1995 cm\(^{-1}\), which within minutes disappeared with the production of a new carbonyl band at 1960 cm\(^{-1}\). This change was accompanied by a colour change from red to green. There are several possible reasons for this reaction. The change in dichloromethane could be due to the reaction of the cation with the solvent to give the covalent chloride. This,
IR spectra of \( \pi-C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH=CH_2 \)

(a). in carbon disulphide

(b). on addition of \( CF_3CO_2H \) or HCl.

(c). ten minutes later than (b).

Fig. 30(ii).
however, would not explain the parallel results obtained when using acetone. The one feature common to both experiments was that the spectra were obtained using sodium chloride cells. A reaction with the cell was therefore possible. This possibility was eliminated by dissolving a small amount of the cation in the two different solvents in glass vessels, and observation over a period of fifteen minutes showed that both solutions changed from red to green. The final proof was obtained by the isolation of the green product and its identification as the chloride, \( \pi \text{C}_5 \text{H}_5 \text{Fe(CO)} \text{Py}_3 \text{Cl} \), which could have only been formed by the intramolecular nucleophilic attack of the chloride ion on the cation, in the case of acetone, either before or after the expulsion of propene.

\[
[\pi \text{C}_5 \text{H}_5 \text{Fe(CO)} \text{Py}_3 \text{C}_3 \text{H}_6]^+ \text{Cl}^- \rightarrow \pi \text{C}_5 \text{H}_5 \text{Fe(CO)} \text{Py}_3 \text{Cl} + \text{C}_3 \text{H}_6
\]

Proof of this theory was thought to have been found by the observation that the treatment of the \( \alpha \)-allyl derivative with a one molar equivalent of trifluoroacetic acid in benzene or THF, produced an initial brown oily material, which on stirring gave, within five minutes a green solution. The experiment was carried out in an NMR. tube in an attempt to prove that the brown oil was the protonated species. This unfortunately was not easy to do, but the transient appearance of a signal at 4.47 was thought to be due to the \( \pi \)-cyclopentadienyl ring protons in the cation, since the positive charge on the metal would be expected to shift the \( \delta \) value of the signal to a lower \( \delta \) value. The green complex obtained from the protonation was purified and shown to have bonds characteristic of the trifluoroacetate group (trifluoroacetate carbonyl stretching frequency is at 1699 cm\(^{-1}\), and \( \nu(CF_3) \) at 1140 cm\(^{-1}\).
The production of this trifluoroacetate derivative can be explained by the same process of intramolecular nucleophilic attack postulated for the chloride, since, although there is a factor of several powers of ten difference in the relative nucleophilicities of the chloride and the trifluoroacetate ions, the trifluoroacetate is quite nucleophilic, especially in the presence of a strongly electron attracting species. However, when the same sequence of colour changes were observed for the reaction of the σ-allyl with fluorosulphonic acid, this hypothesis seemed a little suspect, since the fluorosulphonate ion is not generally considered to be very nucleophilic.

The hypothesis forwarded so far has regarded the main criterion, for the rearrangement, to be the nucleophilic nature of the counterion. Since the fluorosulphonate ion also undergoes this rearrangement there may be a more, or at least, equally important criterion. This could quite possibly be a thermodynamic effect, in which the stability of the product is the determining factor. The stability would be influenced by the amount of backbonding possible between the metal and the attacking anion, which would be less for the chloride, but the higher nucleophilicity would compensate for this, whereas for the less nucleophilic trifluoroacetate and fluorosulphonate anions there is much more chance of back bonding into the carbon, or sulphur, oxygen double bond taking place.

In a further attempt to identify the propene cation which was assumed to be the red-brown intermediate complex, a low temperature NMR study of the protonation was carried out in deuterochloroform. Chloroform is normally, like all other chlorinated solvents, expected to attack σ-allyl and alkyl complexes to give the chloride, but it was found that σ-allylcarbonyltri-
phenylphosphine-\(\pi\)-cyclopentadienyliron was stable under nitrogen in chloroform solution for several hours at room temperature. If the solution, however, was heated to 30 - 35°C, the red solution rapidly darkened and within two or three minutes became dark green, with the formation of the chloride, \(\pi-C_5H_5Fe(CO)P\sigma_3Cl\).

The NMR. spectrum of \(\sigma\)-allylcarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron was obtained in deuterochloroform and deuterobenzene at 20°C. (FIG. 31 (i.), and FIG. 31 (ii.).) In all the spectra of \(\sigma\)-allyl derivatives in the literature the methylene group adjacent to the metal atom appears as a broad doublet or quadruplet. For example:

\[
\begin{align*}
\pi-C_5H_5Mo(CO)_3CH_2CH=CH_2 & \quad 118 \quad \text{Doublet } (J(CH_2,H) = 8) \\
\pi-C_5H_5Fe(CO)_2CH_2CH=CH_2 & \quad 7.93 \quad \text{Quartet } (J(CH_2,H) = 8.4) \\
Mn(CO)_5CH_2CH=CH_2 & \quad 184 \quad 8.19 \quad \text{Doublet}
\end{align*}
\]

However in this \(\sigma\)-allyl complex there are two diastereotopic protons giving rise to clearly separated signals (multiplets at 7.98 and 8.7°C). The multiplicity is presumably brought about by the complexing with the phosphorus, through the metal (cf. \(J_{CH_3,P} = 7.5\) for \(\pi-C_5H_5Fe(CO)P\sigma_3CH_3\)).

A spectrum of the same \(\sigma\)-allyl derivative in deuterobenzene shows the same diastereotopic protons, with a coupling to phosphorus of approximately 7 c/s. The major significance, however, of this spectrum was that the signals had been shifted down field, considerably, with respect to the chloroform spectrum. Table VII shows these shifts when the protons are assigned as follows:—
Fig. 31.

\[
\eta^1\text{C}_5\text{H}_5\text{Fe(CO)}\text{P(C}_6\text{H}_5\text{)}_2\text{CH}_2\text{CH=CH}_2
\]

(i.) in \text{CDCl}_3.

(ii.) in \text{C}_6\text{D}_6.
TABLE VII

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Position CHCl₃</th>
<th>Position C₆H₆</th>
<th>Downfield Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>7·98, 8·7</td>
<td>7·7, 8·2</td>
<td>0·28, 0·5</td>
</tr>
<tr>
<td>H³ and H⁴</td>
<td>5·5, 5·65</td>
<td>5·11, 5·26</td>
<td>0·39, 0·39</td>
</tr>
<tr>
<td>H²</td>
<td>3·9</td>
<td>3·52</td>
<td>0·33</td>
</tr>
<tr>
<td>π-C₅H₅</td>
<td>5·84</td>
<td>5·96</td>
<td>-0·12</td>
</tr>
</tbody>
</table>

It would appear that there are similar shifts in the non-equivalent methylene protons of the σ-benzyl derivative. (Table VIII.)

TABLE VIII

<table>
<thead>
<tr>
<th>Position CHCl₃</th>
<th>Position C₆H₆</th>
<th>Downfield Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>8·15</td>
<td>7·84</td>
<td>0·31</td>
</tr>
<tr>
<td>7·46</td>
<td>7·32</td>
<td>0·14</td>
</tr>
</tbody>
</table>

These shifts show remarkable differences from those in the dicarbonyl-π-cyclopentadienyliron system. Table IX shows the shifts for σ-allyldicarbonyl-π-cyclopentadienyliron in benzene, deuterochloroform and cyclohexane. It will be seen that there are remarkable similarities between the shifts in cyclohexane and chloroform. Addition of twelve successive 25μl aliquots of benzene to a solution of σ-allyldicarbonyl-π-cyclopentadienyliron (80 mg.) in cyclohexane (0·6 ml.) shifted the signal due to the π-cyclopentadienyl ring to a higher field.
The shifts of the protons shown above are detailed in Table IX.

**TABLE IX.**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Position CHCl₃</th>
<th>Position C₆H₆</th>
<th>Position C₆H₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>7.95</td>
<td>7.90</td>
<td>7.92</td>
</tr>
<tr>
<td>π-C₅H₅</td>
<td>5.41</td>
<td>5.99</td>
<td>5.49</td>
</tr>
<tr>
<td>H₃ and H⁴</td>
<td>5.63</td>
<td>5.42</td>
<td>5.6</td>
</tr>
<tr>
<td>5.4*</td>
<td></td>
<td>5.26</td>
<td>5.4*</td>
</tr>
<tr>
<td>H₂</td>
<td>4.06</td>
<td>3.92</td>
<td>4.09</td>
</tr>
</tbody>
</table>

* Estimated value - signal masked by π-C₅H₅ ring.

These shifts are to be investigated further, but they would appear to be due to the presence of specifically orientated benzene molecules solvating the complex. The abnormal shifts, in the case of σ-alkylcarbonyltriphénylphosphine-π-cyclopentadienyliron may be due to the bulky phosphine disrupting the benzene stacking.

To the deuterochloroform solution of σ-alkylcarbonyltriphénylphosphine-π-cyclopentadienyliron, at -40°C, was added a one molar equivalent of trifluoroacetic acid, and the spectrum redetermined. Unfortunately, due to the difficulties in obtaining the spectrum, no clear spectral details were obtained until the reaction was allowed to warm to -15°C. This was probably due to some precipitation of the salt from the solution at the lower temperature. At -15°C, the singlet, due to the π-cyclopentadienyl ring of the σ-allyl derivative was at 5.74. This signal disappeared on protonation, with the production of a new signal at 4.94. This shift would be
expected if the metal atom became more positively charged. The
signal was, however, very broad, and the spectrum showed the presence
of two methyl signals at 8.21 and 8.72. These were later (page 136.)
shown, for the salt, \( \left[ \pi C_5H_5Fe(CO)P(C_3H_6) \right] BF_4 \), to be due to the
presence of two isomers. This also explained the broadness of the
\( \pi \)-cyclopentadienyl ring signal - two different signals merging into
one broad one. The isomers, however, appeared to be in about a
one to one ratio, as compared to a three to one ratio as in the
tetrafluoroborate salt. (Page 136.)

On allowing the reaction mixture to warm to room temperature
there was a fall in the intensity of the \( \pi \)-cyclopentadienyl ring
singlet at 4.94 and an increase in a sharp singlet at 5.3. After
being at 20°C for twenty minutes there was one \( \pi \)-cyclopentadienyl
peak at 5.3 and another small peak at 5.4. The only other product
that could be identified from the NMR. spectrum was free propene.

Attempts to identify an iron-hydrogen bond, on protonation, in
the NMR. failed - the field being scanned from 10 up to 30 -
the most likely region for this type of signal. The infra-red
studies showed no band due to an iron-hydrogen bond in the region
1900 - 2100 cm\(^{-1}\), although, due to the broadness of the parent
carbonyl band, and the speed with which it is converted to the covalent
complex, much of this region was effectively blanked out. It is
pertinent that in both the infra-red and NMR. spectra, the spectra
obtained, on initial protonation, changed directly to the final spectra -
no intermediate being observed. This would seem to rule out the
possibility of there being initial attack of the proton at the metal,
followed by an intramolecular proton shift; unless this process is
so fast that it proceeds rapidly, even at low temperatures.

From this study it would appear that the protonation of
\( \sigma \)-allylcarbonyltriphenylphosphine-\( \pi \)-cyclopentadienyliron proceeds
by the same route as proposed by Green\textsuperscript{115} for the protonation of ω-allylcarbonyl-cyclopentadienyliron, except that the π-propene cation produced is much more unstable, decomposing at room temperature to the thermodynamically stable products, propene and trifluoroacetocarbonyltriphenylphosphine-cyclopentadienyliron. From one set of variable temperature NMR spectra, it was possible to see the production of two new signals due to the π-cyclopentadienyl rings. These two signals were identified as being the chloride, ω-C\textsubscript{5}H\textsubscript{5}Fe(CO)P\textsubscript{3}Cl and the trifluoroacetate, ω-C\textsubscript{5}H\textsubscript{5}Fe(CO)P\textsubscript{3}OCOCF\textsubscript{3}, thus indicating that the π-propene cation can decompose by two different routes at room temperature. Firstly, it can decompose by the same intramolecular nucleophilic attack as has been seen in the non-chlorinated solvents, such as acetone and benzene, to give the trifluoroacetate, or secondly, it can react with the solvent, for example when chlorinated solvents are used, to give the chloride.

In an attempt to isolate the π-propene cation as a stable salt the protonating acid was changed to fluoroboric acid. Treatment of an ethereal solution of ω-allylcarbonyltriphenylphosphine-cyclopentadienyliron with an ethereal solution of fluoroboric acid at room temperature gave an immediate red precipitate. This was washed well, with ether, and then recrystallised from a sulphur dioxide-ether 4:1 mixture, to yield bright red crystals. On dissolving these crystals in common solvents, such as acetone, nitrobenzene, and chlorobenzene, there was always a change from a red solution to brown, and finally to green. The colour changes were accompanied by corresponding changes in the infra-red characteristics. The initial red solution had a carbonyl stretching frequency at 1992 cm\textsuperscript{-1}, which within five minutes disappeared, with the simultaneous appearance of a band at 1979 cm\textsuperscript{-1}. This complex changed over a period of forty minutes to the green complex, having a carbonyl stretching frequency at
(i.)

\[ [m-\text{C}_5\text{H}_5\text{Fe(CO)}\{\text{P(C}_6\text{H}_5\text{)}_3\}] \text{C}_3\text{H}_6 \] \( \text{BF}_4 \)

in \( \text{SO}_2 \) at \(-10^\circ\text{C}\).

(ii.)

\[ [\pi-\text{C}_5\text{H}_5\text{Fe(CO)}\{\text{P(C}_6\text{H}_5\text{)}_3\}] \] \( \text{BF}_4 \)

in \( \text{SO}_2 \) at \(0^\circ\text{C}\).
1966 cm\(^{-1}\). In chlorobenzene this latter step proceeded much more rapidly.

In an attempt to prove that the red crystalline complex isolated was the \(\pi\)-propene cation, \(\left[\pi-C_6H_5Fe(CO)P(C_3H_6)\right]^+\), the NMR. spectrum was obtained in liquid sulphur dioxide, the only solvent from which the complex could be reclaimed. (FIG. 32 (i))

The NMR. spectrum at -10\(^\circ\)C showed two singlets, due to the \(\pi\)-cyclopentadienyl rings, at 4.96 and 5.05 in the ratio of approximately three to one respectively. Initial thoughts were that the samples were impure, but this proved to be incorrect. The explanation being the presence of two isomers. Supporting evidence for this was the corresponding ratio of the signals due to coordinated propylene and the \(\pi\)-cyclopentadienyl rings.

The isomers appeared to have been produced by the orientation of the propene moiety in the cation. The methyl group of the propene taking up a site pointing away, or towards the phosphine group, as shown in FIG. 33

![Minor isomer](image1)

![Major isomer](image2)

**Fig. 33**
The NMR. spectral analysis of \([\pi-C_5H_5Fe(CO)_2C_3H_6]ClO_4\) has been reported by Green, 115 (FIG. 34.)

By comparison of the spectrum obtained for \([\pi-C_5H_5Fe(CO)CPh_3C_3H_6]^+\) it can be seen that only one methyl group is very close to that reported by Green 115 (8.2 \(\tau\) as compared to 8.14 \(\tau\)). Consideration of the steric positions that the propene can occupy make it plausible that this signal is due to the isomer that has the methyl group of the propyl pointing towards the carbonyl carbon. The minor isomer, with the methyl signal at 8.69 \(\tau\) would then be that with the methyl pointing towards the triphenylphosphine moiety. This would be expected to be the less stable of the two isomers, purely on steric grounds.

It is interesting to note that the signal due to the proton on the same carbon as the methyl group has moved to a higher field in the phosphine substituted complex - from 5.00 \(\tau\) to 5.72 \(\tau\).

On warming this solution to 0\(^\circ\)C. there was a slow change in the spectrum, (FIG. 32(ii.) ). A new \(\pi\)-cyclopentadienyl signal was observed at 4.49 \(\tau\). This was accompanied by the disappearance of all the signals due to the coordinated propene, and the appearance of signals due to free propene. This was verified by the comparison with a standard spectrum in which the methyl signal of the propene was seen as a double triplet, in which long range coupling could be seen. This coupling disappeared on coordination to the metal.

These results show, conclusively, that the protonation of \(\pi\)-allyl carbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron, with fluoroboric acid, gives the \(\pi\)-propene salt, \([\pi-C_5H_5Fe(CO)CPh_3C_3H_6]^+BF_4^-\), which is stable when in the solid state. However, in solution the propene becomes uncoordinated to give the unsaturated cation, \([\pi-C_5H_5Fe(CO)CPh_3]^+BF_4^-\), or the solvent coordinated cation,
NMR spectrum of $[\text{H}^1 \cdot \text{C}_5 \text{H}_5 \cdot \text{Fe} \cdot \text{CO}_2 \cdot \text{C}_3 \text{H}_3]^+$ in liq. SO$_2$. 
\[
\left[\pi-C_5H_5Fe(\text{CO})PF_3(S)\right]BF_4. \text{ Proof of this was obtained by the comparison of the NMR and infra-red spectra of the cation obtained from the reaction of the bromide, } \pi-C_5H_5Fe(\text{CO})PF_3\text{Br, and silver tetrafluoroborate, in liquid sulphur dioxide, with that obtained on the loss of propene from the } \pi\text{-propene cation.}
\]

In view of these results a general mechanism, for the reactions discussed in this section on protonation, may be suggested. This is that the protonation with an acid (HX.) occurs to give, initially, the \( \pi\text{-propene cation, either by initial attack at the metal followed by intramolecular rearrangement, or by direct attack at the ligand. The } \pi\text{-propene cation then dissociates into the unsaturated cation, } \left[\pi-C_5H_5M(\text{CO})_n\right]^+ \text{ or } \left[\pi-C_5H_5M(\text{CO})_mPF_3\right]^+ \text{ and propene, this step being the rate determining step. The system, therefore undergoes intramolecular nucleophilic attack, to give the covalent product, } \pi-C_5H_5M(\text{CO})_nX \text{ or } \pi-C_5H_5M(\text{CO})_mPF_3X, \text{ or solvation to give the solvated cation, } \left[\pi-C_5H_5M(\text{CO})_n(S)\right]^+ \text{ or } \left[\pi-C_5H_5M(\text{CO})_mPF_3(S)\right]^+.\]

\[
\pi-C_5H_5M(\text{CO})_nCH_2CH=CH_2 \xrightarrow{\text{HX}} \left[\pi-C_5H_5M(\text{CO})_nC_3H_6\right]^+ \\
\pi-C_5H_5M(\text{CO})_nX \leftarrow \left[\pi-C_5H_5M(\text{CO})_n\right]^+ \\
\text{ or } \left[\pi-C_5H_5M(\text{CO})_n(S)\right]^+
\]
Hydride Abstraction

Green and his coworkers\textsuperscript{153} have proposed that in the hydride abstraction of a metal $\sigma$-alkyl derivative with triphenylmethyltetrafluoroborate, there is a bimolecular mechanism; since the complexes do not react readily with mineral acids to evolve hydrogen; thus eliminating any mechanism involving the equilibrium:

\[
M\text{-CH}_2\text{CH}_2\text{CH}_3 \rightarrow M^+\text{CH}_2=\text{CHCH}_3 + \text{H}^-
\]

The proposed mechanism is that the removal of the hydride ion is assisted by the iron atom. The resulting carbonium ion intermediate is then stabilized by the formation of a bond with the metal. (See FIG. 35.)

Fig. 35.

The process is reversed by the treatment of the $\pi$-propene cation with an ethereal suspension of sodium borohydride.

Hydride abstraction of $\sigma$-propyldicarbonyl-$\pi$-cyclopentadienyliron with triphenylmethyltetrafluoroborate was shown to give the $\pi$-propene salt, $[\pi$-C$_5$H$_5$Fe(CO)$_2$C$_3$H$_6$]BF$_4$, in high yields. However when the phosphine substituted system was used the results were most surprising.

On treatment of $\sigma$-propylcarbonyltriphenylphosphine-$\pi$-cyclopentadienyliron, in ethereal solution, with a suspension of one molar equivalent of triphenylmethyltetrafluoroborate the solution gradually lost its colour and the precipitate changed from the deep orange of the trityl cation to a pale yellow. When this process was
complete — about six hours — the supernatant was decanted and the precipitate was washed several times with ether. Removal of the final traces of ether gave a pale lemon yellow solid, which showed the presence of two strong carbonyl stretching frequencies in the infra-red spectrum, neither of which was due to the \( \sigma \)-propyl.

From the protonation studies on the corresponding \( \sigma \)-allyl the \( \pi \)-propene cation was expected to show one strong carbonyl stretching frequency at 1990 – 2000 cm\(^{-1}\). This new complex showed carbonyl stretching frequencies at 2057 and 2011 cm\(^{-1}\) (in dichloromethane). Repetition of this experiment always gave the same result, as did an experiment in which the amount of trityl cation was slightly reduced.

The new complex was found, after much work, to be the salt \( \left[ \pi-C_5H_5Fe(CO)_2\Phi_3 \right]BF_4 \). An authentic sample of this salt was prepared from \( \left[ \pi-C_5H_5Fe(CO)_2\Phi_3 \right]Br \), a by-product from the preparation of the covalent bromide, by an anion exchange with silver tetrafluoro-borate. The formation of this particular cation in this reaction was completely unexpected. The first reaction must have been the removal of a hydride ion from the \( \sigma \)-propyl derivative, to give the required salt, \( \left[ \pi-C_5H_5Fe(CO)\Phi_3C_3H_6 \right]BF_4 \). This particular cation has also been prepared by the protonation of the \( \sigma \)-allyl derivative, with fluoroboric acid and shown to be quite stable, at room temperature as a solid, but not in solution. If, however, it is assumed that either the cation is attacked by ether, over a period of six hours, or that the cation is decomposed by some by-product of the actual reaction, then the first step in the decomposition must be the loss of propene. This will result in the formation of the unsaturated cation, \( \left[ \pi-C_5H_5Fe(CO)\Phi_3 \right]BF_4 \), a step that has been shown to occur at \( 0^\circ C \) in liquid sulphur dioxide. (see discussion of protonation.) This cation is the same initial product postulated as occurring
in the reaction of bromocarbonyltriphosphine-π-cyclopentadienyl-
iron with Lewis acids (Page 147.), in which the cations 
\[ \pi-C_5H_5Fe(CO)_3P\beta_3^+ \] and \[ \pi-C_5H_5Fe(CO)_2Br(CO)Fe(C_5H_5) \] are 
produced. The latter cannot be formed in the hydride abstraction 
due to the bridging species. A further discussion of this will 
occurs later (page 154.)

Two possible factors that might influence this disproportion-
ation are the crowded steric conditions forced upon the molecule, 
by the presence of the phosphine, which will have an anchimeric 
effect on the leaving of the propene, and secondly the possible 
coordination of ether. It is normally recognised that THF, coordinates 
quite strongly in metal complexes, but it is not generally realised 
that ether can, in certain circumstances do the same, although a 
few ether complexes have been reported. 185

The ether could in fact be coordinated with the formation 
of the saturated cation, \[ \pi-C_5H_5Fe(CO)P\beta_3(S)BF_4. \]

In an attempt to try and understand this reaction two more 
experiments were carried out. \( \sigma \)-Propylcarbonyltriphosphine-
π-cyclopentadienyliron was dissolved in dichloromethane and its 
infra-red spectrum obtained. This was shown not to change over a 
period of about an hour, and so an equimolar amount of triphenyl-
methyltetrafluoroborate, in dichloromethane, was added. Within two 
minutes the reaction had proceeded to completion. The carbonyl 
stretching frequency at 1900 cm\(^{-1}\) faded completely and was replaced 
directly by two new bands at 2010 and 2055 cm\(^{-1}\). Thus the ether in 
the original reaction had no effect on the reaction, other than to 
slow it down, probably because of the heterogeneous conditions. 
Furthermore it is unlikely that a cation is formed in which the 
solvent is coordinated, as this cannot happen in the dichloromethane 
example, thus eliminating that interesting, but unlikely possibility
that the second carbonyl originated from the ether coordinated to the cation. The second experiment was to treat, under both the dichloromethane and the ether conditions, small quantities of the \( \sigma \)-methyl and the \( \sigma \)-allyl derivatives with the triphenylmethyltetrafluoroborate. In both cases it should not be possible to hydride abstract, and so no reaction should occur. In fact for the \( \sigma \)-methyl derivative a reaction does occur, but not to give the cation obtained from the \( \sigma \)-propyl. The carbonyl stretching frequency of the \( \sigma \)-methyl at 1903 cm\(^{-1} \) (in dichloromethane) gradually decreases over a period of fifteen minutes to two thirds of its original intensity, with the production of two new 'humps' at 2000 and 1960 cm\(^{-1} \). However, after this time the original carbonyl band increases in intensity to almost its original position, after one hour. This would suggest some sort of reversible reaction, perhaps to give a carbene type intermediate complex, which then reconverts to the original complex, but this is unlikely as the intermediate would be very reactive.

These two reactions do not, therefore, tell us much more than that this particular reaction is specific for the \( \sigma \)-propyl. At the present this reaction is not fully understood, but it is thought that the salt, \([\pi-C_5H_5Fe(CO)PF_3]BF_4\) converts, in an analogous way, to that in the Lewis acid induced rearrangement (page 154.). Thus some sort of unstable dimeric, or cluster complex is formed, for example the dimer \([\pi-C_5H_5Fe(CO)PF_3]_2\). This may then convert to the more thermodynamically stable species \([\pi-C_5H_5Fe(CO)_{2}PF_3]BF_4\).
Attempted new methods of preparation of \( \pi \)-butene cation

It will have been noticed that only the first of the three methods described so far starts from the free olefin. It would be useful, especially to industry, if a method of preparation could be developed in which the free olefin was coordinated onto the metal system by a simple reaction, carried out under mild conditions, especially of pressure. Initial ideas involved the preparation of an unsaturated cationic species which, in solution, would absorb the olefin, to give the saturated cation, thus paralleling the work of Fischer, but looking for new Lewis acids which would be more effective, and less susceptible to the presence of moisture.

These ideas were given more encouragement by the reported oxidative cleavage of dicyclopentadienyltetracarbonyldiiron with ferric perchlorate in acetone or acetonitrile, to give cationic complexes of the type, \( [\pi-C_5H_5Fe(CO)_2L]^+ \) where \( L \) was a coordinated solvent molecule. The use of perchlorates however, was adjudged to make this particular procedure explosive, and hence, while bearing these results in mind, alternative methods of cleavage, and hence production of the unsaturated cationic species were investigated.

A). Use of silver salts.

It was decided to attempt a preparation of 'unsaturated' cations using silver salts. Very little chemistry has been reported on the reactions of silver salts with this type of system, although it has been reported that silver nitrate with chlorodicarbonyl-\( \pi \)-cyclopentadienyliron gives an ionic species. Repeat of these experiments showed that when chloro- and bromo-dicarbonyl-\( \pi \)-cyclopentadienyliron were treated with an ethereal solution of silver
nitrate there was a ten and two minute induction period respectively. This was followed by the slow production of a brown precipitate, which was shown to contain no carbonyl frequencies, and looked very much like typical oxidation material in this series. The infra-red spectrum of the red supernatant showed the same stretching frequencies as those exhibited by the starting material, except that the bands were very slightly broadened at their bases. Attempts to improve the spectra, by expansion and other techniques, however, failed to show the presence of a clear shoulder. It must be remembered that, in this work, the shifts in the carbonyl stretching frequencies may be very small, as shown in Table X.

<table>
<thead>
<tr>
<th>Complex.</th>
<th>Solvent.</th>
<th>( \nu \text{C=O (cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\pi-C_5H_5Fe(CO)_2CH_3CN]^-)</td>
<td>CH(_2)Cl(_2)</td>
<td>2080, 2035.</td>
</tr>
<tr>
<td>(\pi-C_5H_5Fe(CO)_2Cl)</td>
<td>CHCl(_3)</td>
<td>2055, 2010.</td>
</tr>
<tr>
<td>([\pi-C_5H_5Fe(CO)_2]^+)</td>
<td>CH(_2)Cl(_2)</td>
<td>2040, 1985.</td>
</tr>
</tbody>
</table>

These results, although not conclusive, would tend to disagree with the reported observations. Similar results were obtained with the chloro derivative, when the silver salt was changed to the perchlorate. However, when using the bromide a white precipitation was produced, on shaking for several minutes, as well as a red oily solid. The infra-red spectrum of this complex showed strong carbonyl bands at 2090 and 2045 cm\(^{-1}\) (in dichloromethane). These were not due to the bromide nor, on comparison of spectra, to the bromide bridged cation, \(\left[\pi-C_5H_5Fe(CO)_2Br-(CO)_2Fe(C_5H_5)\right]^+\).

The first two silver salts reacted with the dimer were tried for completeness, rather than with any expectation of isolating the
cation. When dicyclopentadienyltetracarbonyldiiron was treated with silver trifluoroacetate in acetonitrile or acetone solution, the initial crimson solution rapidly became very dull, mainly due to the formation of a very fine suspension of brown oxidation material. Removal of the latter gave a bright orange supernatant yielding, on removal of excess acetonitrile under high vacuum, a very deep brown—red solid. The infra-red spectrum of this solid showed the presence of no starting dimer, but of two new carbonyl bands at 2016 and 2061 cm\(^{-1}\) (in chloroform). Comparison with the \(\sigma\)-trifluoroacetate, also prepared during this work, showed them to be identical. This is not altogether an unexpected result, for if the cation is formed transiently, as was indicated by the presence of the orange solution, trifluoroacetate is sufficiently nucleophilic to attack the metal.

For interest's sake only, the next silver complex used was the acetate. The reason for this was simply to see whether the acetate would be able to undergo the same reactions as the trifluoroacetate. When the organometallic dimer was shaken with silver acetate in acetonitrile or acetone solution there was no obvious reaction. After six hours the infra-red spectrum of the reaction mixture still showed no new carbonyl containing complexes. Addition of a small amount of potassium tetrafluoroborate to this reaction mixture produced a very slow darkening in the colour of the mixture, together with the slow production of a brown precipitate. Monitoring the reaction by infra-red spectroscopy showed that this process was complete after two hours; the reaction mixture then showing four new carbonyl stretching frequencies. Two of these were very intense and could, by comparison with the perchlorate complexes described above, and authentic samples prepared afterwards, be assigned to the acetonitrile coordinated cation, \([\eta^1-C_5H_5Fe(CO)_2CH_3CN]^+\), whilst the other two bands, of much weaker intensity, at 2068 and
2010 cm\(^{-1}\), were present in such small quantities, that it was not possible to isolate them. Various possibilities can be suggested for a complex exhibiting such carbonyl bonds. It would be nice to think that this complex was the \(\sigma\)-acetate, \(\pi-C_{6}H_{5}Fe(\text{CO})_{2}OCOC\text{H}_{3}\). Comparison with the values for the trifluoroacetate derivative (2016 and 2061 cm\(^{-1}\) in chloroform) show the closeness of the two sets of stretching frequencies. A slightly more unlikely possibility is that the complex is dimeric in nature, in analogy to the bromide bridged cation, \(\left[\pi-C_{6}H_{5}Fe(\text{CO})_{2-Br-}(\text{CO})_{2}Fe(C_{5}H_{5})\right]^{+}\).

In order to shed more light on this problem the obvious reaction was to treat the organometallic dimer with silver tetrafluoroborate, presumably the species formed in situ in the previous experiment. An acetonitrile or acetone solution of dicyclopentadienyltetracarbonyldiiron was treated with silver tetrafluoroborate. New carbonyl stretching frequencies were observed at 2079 and 2036 cm\(^{-1}\). This was the solvent coordinated cation, \(\left[\pi-C_{6}H_{5}Fe(\text{CO})_{2}(S)\right]^{+}\). The spectral properties agreed with those reported by Meyer and his coworkers. \(^{186}\) Similar cations were formed by treatment of bromodicarbonylcyclopentadienyliron with a molar equivalent of silver tetrafluoroborate in acetonitrile. There was however no displacement of the solvent molecule when propene was bubbled through the acetonitrile solution, under various conditions. Attempts were also made to displace the solvent molecule with propene, using acetone solutions, as acetone is a weaker coordinating ligand, than acetonitrile, but this failed as well.

Treatment of bromocarbonyltriphosphene-\(\pi\)-cyclopentadienyliron with a molar equivalent of silver tetrafluoroborate in chlorobenzene gave a slow production of a new carbonyl species, with stretching frequencies at 1979 cm\(^{-1}\) (in chlorobenzene). There was however considerable decomposition and the reaction was quite slow.
When the reaction was carried out in liquid sulphur dioxide, at -10°C, a rapid clean reaction was obtained. This yielded a red-brown solution from which was obtained a red-brown solid, having a carbonyl stretching frequency at 1979 cm\(^{-1}\). This product was shown to be identical, in spectral details, with that obtained after evolution of propene from \([\pi-C_5H_5Fe(CO)P\equivC_3H_6]BF_4\). There was no tendency to form the bromide bridged species, \([\pi-C_5H_5Fe(CO)\equivBr-(CO)\equivFe(\pi-C_5H_5)]^+\), even when the reactants were mixed in a two to one molar ratio. The cation, \([\pi-C_5H_5Fe(CO)P\equivC_3H_6]^+\), formed was treated at -10°C with propene. Stirring for several hours at propene reflux temperature gradually gave an orange colouration. Removal of the sulphur dioxide gave a yellow-orange solid, which was then recrystallised from sulphur dioxide: ether mixture, to give an orange-red crystalline complex, which was shown, by spectral properties, to be identical with the salt, \([\pi-C_5H_5Fe(CO)P\equivC_3H_6]^+BF_4^-\).

(B.) Action of Lewis acids.

Lewis acids are used throughout all branches of chemistry as very effective electron acceptors in many systems. In this role they appear to be needed in only catalytic amounts to obtain good yields. An example of this is the preparation of the diarenemetal complexes by the reducing Friedel Crafts reaction, in which aluminium is the reducing agent and aluminium chloride the catalyst.

\[3CrCl_3 + 6C_6H_6 + 2Al \rightarrow AlCl_3 \rightarrow 3[(C_6H_6)_2Cr]AlCl_4\]

The mechanism of Lewis acid reactions are varied, and not always fully understood. In some cases, for example, the nickel acetoacetate, diene and aluminium trialkyls the Lewis acid is
present as a reducing agent.

In other systems, however, such as the dicarbonyl-π-cyclopentadienyliron system, there are several possible reaction pathways and mechanisms. Attack of the Lewis acid on a carbonyl group, in organic chemistry, is well known, for example in the Friedal-Crafts acylation process, the reaction of acyl chloride and aluminium chloride, in carbondisulphide, form stable crystalline complexes. The organometallic analogue to this reaction, is the reaction of triethylaluminium with dicyclopentadienyldiiron tetracarbonyl in which attack on the bridging carbonyl gives, \[ \left[ \pi-C_5H_5Fe(CO)\right]_2(COAl(C_2H_5)_3) \] and \( (\pi-C_5H_5)Fe_4[COAl(C_2H_5)_3]_4 \). This is not a very surprising result, since the bridging carbonyls approach, more closely than any other metal carbonyl, to the normal organic carbonyl. This is illustrated by the infra-red carbonyl stretching frequencies. The normal range of organic carbonyls is between 1600 and 1750 cm\(^{-1}\), whilst that of a terminal metal carbonyl is in the region 1900 to 2100 cm\(^{-1}\). The bridging carbonyl shows a stretching frequency at approximately 1800 cm\(^{-1}\), and hence is intermediate.

This type of attack is not the only course of reaction available for such a system. The reaction of halodicarbonyl-π-cyclopentadienyliron with aluminium halides has been shown to form, initially, an unsaturated salt, \[ \left[ \pi-C_5H_5Fe(CO)\right]_2AlX_4 \]. If the reaction was carried out in liquid sulphur dioxide at \(-10^\circ C\), the unsaturated cation either coordinates one molecule of sulphur dioxide, to give the saturated salt, \[ \left[ \pi-C_5H_5Fe(CO)\right]_2(SO_2)AlBr_4 \], or reacts with a further molecule of the starting material, to give the halogen bridged salt, \[ \left[ \pi-C_5H_5Fe(CO)\right]_2Br-(CO)Fe(\pi-C_5H_5)AlBr_4 \]. Dimerisation of the sulphur dioxide complex would give, on expulsion of sulphur dioxide, the same bridged species. The cation was isolated as the thermally stable hexafluorophosphate salt;
The synthetic usefulness of this reaction is the formation of the unsaturated cationic species, for this may react with a variety of ligands to give the saturated cation. The example quoted above was the insertion of sulphur dioxide, but the reaction is of more synthetic use when preparing olefin and arene complexes.

$$\pi-C_5H_5Fe(CO)_2Br + CH_3CH=CH_2 \xrightarrow{AlBr_3/C_6H_6} \left[\pi-C_5H_5Fe(CO)_2C_3H_6\right]AlBr_4$$

$$\pi=C_5H_5Mo(CO)_3Cl + C_6H_6 \xrightarrow{80^\circ/AlBr_3} \left[\pi-C_5H_5Mo(CO)_3C_3H_6\right]AlBr_4$$
In an attempt to extend these reactions to the phosphine containing system, bromocarbonyltriphenylphosphine-π-cyclopentadienyliron was treated with aluminium halides. The introduction of the phosphine increases the possible sites of attack, by the Lewis acid, to three, the bromine atom, the carbonyl group or the phosphine. The initial experiment was performed under the conditions used by Fischer 191 for the dicarbonyl system. A benzene solution of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron was treated with a twofold excess of aluminium bromide. The colour of the mixture rapidly changed, on shaking, from green to red-brown, with the production of a deep red oil, showing carbonyl stretching frequencies at 2070, 2060, 2038, and 2020 cm⁻¹ (in benzene). Pure complexes could not be isolated from this mixture, but the mixture did undergo a surprising reaction with chloroform. Addition of chloroform caused an immediate evolution of gas and the production of chlorodicarbonyl-π-cyclopentadienyliron. The gas was identified by infra-red spectroscopy as an approximate 3:1 mixture of hydrogen chloride to hydrogen bromide. This could not be induced by heating, or any other treatment, and the ratio was not varied on using ethanol containing chloroform, ethanol free chloroform, or even deuterochloroform (no deuterochloride or bromide was detected). The reaction of chloroform with aluminium bromide in benzene did not produce any hydrogen chloride. This observation has not yet been explained.

On shaking together equimolar amounts of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron and anhydrous aluminium bromide, in chlorobenzene, under nitrogen, a brown-red solution was produced. The reaction was found to have proceeded about 20% after half an hour, and after leaving for several days had only gone 25%. Two carbonyl stretching frequencies were observed in the infra-red spectrum, at 2050 and 2008 cm⁻¹ (in chlorobenzene), and
by comparison with standard spectra, indicated the possible presence of bromodicarbonyl-π-cyclopentadienyliron. This was confirmed by the isolation of the complex. In following the reaction carefully by infra-red spectroscopy, no other carbonyl stretching frequency was observed. Therefore if any other intermediate unsaturated cationic species, such as \([\pi-\text{C}_5\text{H}_5\text{Fe(CO)P}^3]^{+}\text{AlBr}_4^-\) or bridged cation is formed, it is formed in such small amounts, or decomposes rapidly to bromodicarbonyl-π-cyclopentadienyliron, that its carbonyl stretching frequency could not be observed. A similar observation to this was observed when the bromide was treated with an equimolar amount of magnesium chloride trieth- erate.

When one and a half moles of aluminium bromide was added to one mole of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron in chlorobenzene, at room temperature, there was a very rapid colour change from deep green to dark chocolate brown. The infra-red spectrum of the reaction product showed a carbonyl stretching frequency at 1986 cm\(^{-1}\) (in chlorobenzene). The intensity of this band was seen to decay quite rapidly sometimes, but on other occasions, even when the conditions of preparation were the same, quite slowly. This decay in intensity was, however, always accompanied by the production of four new carbonyl stretching frequencies, all in the region 2000 to 2100 cm\(^{-1}\). Both the sharpness of the bands, and their position suggested that they possibly contained no coordinated phosphine group. A possible explanation of these observations is that the initial attack of the Lewis acid is to give the uncoordinated cationic species, \([\pi-\text{C}_5\text{H}_5\text{Fe(CO)P}^3]^{+}\text{AlBr}_4^-\), or a fully saturated cation, \([\pi-\text{C}_5\text{H}_5\text{Fe(CO)P}^3(S)]^{+}\text{AlBr}_4^-\), in which chlorobenzene is coordinated to the metal. Since the complex, in the conditions under which it is made, proved very unstable, which of these two possibilities was actually correct was hard to ascertain, however, it is possible to
make correlations in this particular system.

One particular experiment that clarified the subject somewhat was the conductimetric titration of various organometallic halides with aluminium halides. It has already been stated that the synthetic use of the unsaturated cationic species is their usefulness as synthetic intermediates in the production of arene and olefin complexes. The object of the conductimetric titrations was to determine, if possible, what ionic species were produced, and whether certain ratios of organometallic bromide to Lewis acid would give a solution which would readily adsorb an olefin at normal pressures and temperatures. In these experiments it was possible to see, from the conductimetric graphs produced, certain plateaus. (FIG. 37.). For systems such as aluminium bromide and bromodicarbonyl-\(\pi\)-cyclopentadienyliiron it was possible to identify both the unsaturated and the bridged cationic species. The significant difference between this system and the carbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliiron system is that in THF., with no Lewis acid, no ionic species could be detected, even on prolonged standing in the dicarbonyl system, but in the phosphine substituted complex, on standing in THF. solution, with no Lewis acid present, there was a steady increase in conductivity. This increase was associated with a colour change from green to green-brown. These changes were supported by an infra-red study of the two systems. In THF. solution it was shown that the spectrum of bromodicarbonyl-\(\pi\)-cyclopentadienyliiron did not change, even over forty eight hours, but for bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliiron it was found that the intensity of absorption at 1962 cm\(^{-1}\) (in THF.) slowly diminished. At the same time new peaks developed, the major product being that giving a carbonyl stretching frequency at
Conductimetric titration of \( \text{H}_{5}\text{C}_5\text{Fe(CO)}_2\text{Cl} \) vs \( \text{AlCl}_3 \)

Vol. of \( \text{AlCl}_3 \) solution added (ml.)
1986 cm\(^{-1}\) (in THF.) Although it was impossible to isolate the complex, it would seem that the THF was coordinating to the metal, with the formation of a fully coordinated cation, \(\left[\pi-C_5H_5Fe(CO)PPh_3(THF)\right]^+\). The possibility of the unsaturated cation, \(\left[\pi-C_5H_5Fe(CO)PPh_3\right]^+\) being formed could not be eliminated, due to the inability to isolate and analyse the complex, but its presence was unlikely, because only in strong coordinating solvents, such as THF, DMF, or DMSO was the conducting species formed.

These observations were supported by the NMR. spectrum of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron in deuterated dimethyl sulphoxide. A change in the position of the π-cyclopentadienyl singlet was observed from 5.41 \(\tau\) to 4.42 \(\tau\). This shift is similar to that obtained for \(\left[\pi-C_5H_5Fe(CO)PPh_3\right]BF_4\) in liquid sulphur dioxide (4.49 \(\tau\)), obtained from the bromide and silver tetrafluoroborate in liquid sulphur dioxide.

Treatment of bromocarbonyltriphenylphosphine-π-cyclopentadienyliron with a fourfold excess of aluminium bromide gave an immediate colour change from green to red-brown. The infra-red spectrum of the mixture, at this time showed five new carbonyl stretching frequencies at 2074, 2059, 2036, 2018, and 1986 cm\(^{-1}\). The latter disappeared within fifteen minutes, with an increase in the intensity of the four other bands, which were identical to those obtained in the previous experiment. Attempts to isolate the complexes proved unsuccessful - in most cases the only crystalline complexes isolated were bromodicarbonyl-π-cyclopentadienyliron or bromocarbonyltriphenylphosphine-π-cyclopentadienyliron, - everything else being an oil.

Identification of the complexes had, therefore to be asserted from the comparison with the spectra of these and known complexes.
As bromodicarbonyl-\(\pi\)-cyclopentadienyliron was produced on decomposition of these complexes, for instance by heating to 100 °C., and from the sharpness of the carbonyl stretching frequencies, it would appear that at least one of the complexes must have no phosphine. A possible complex could, therefore, be the bromo-bridged complex, 
\[ \left[ \pi-C_5H_5Fe(CO)_2Br-(CO)_2Fe(\pi-C_5H_5) \right] AlBr_4. \]
This was therefore prepared. The preparation was carried out in liquid sulphur dioxide, using a two to one molar ratio, of organometallic bromide to aluminium bromide. The complex, however, had to be isolated as the tetrafluoroborate, which was undesirable, as the counter ion was certain to effect the carbonyl stretching frequencies. It was found that the reaction proceeded just as well in chlorobenzene, with aluminium bromide, to give a complex showing carbonyl stretching frequencies at 2015 and 2036 cm\(^{-1}\) (in chlorobenzene) — identical to one pair of carbonyl stretching frequencies in the mixture.

The other complex was originally thought to be the corresponding phosphine containing bridged species, 
\[ \left[ \pi-C_5H_5Fe(CO)P(C_3)Br-(CO)P(C_3)Fe(\pi-C_5H_5) \right] AlBr_4. \]
However attempts to prepare this complex, by analogous routes to the dicarbonyl system failed. In sulphur dioxide the only product isolated was 
\[ \left[ \pi-C_5H_5Fe(CO)P(C_3) \right] AlBr_4, \]
with a carbonyl stretching frequency at 1986 cm\(^{-1}\) (in chlorobenzene.) Similar results were obtained using two moles of bromide to one of silver tetrafluoroborate. No reaction was observed in chlorobenzene, even after forty eight hours.

Following this failure it was observed that the complex, 
\[ \left[ \pi-C_5H_5Fe(CO)_2P(C_3) \right] Br \] had very similar carbonyl stretching frequencies to those obtained in the reaction mixture. The bromide was, therefore suspended in chlorobenzene and a one molar equivalent of aluminium bromide added. The original yellow suspension rapidly changed to a bright red solution, showing carbonyl stretching frequencies at
2059 and 2018 cm\(^{-1}\) (in chlorobenzene.) Attempts to isolate and analyse these salts are still being made, but they are extremely sensitive to moisture.

In trying to elucidate the complete mechanism of this reaction it is very difficult to see how the salt, \([\pi-C_5H_5Fe(CO)_2P(C_6H_5)_3]X\), converts to \([\pi-C_5H_5Fe(CO)_2P(C_6H_5)_3]X\). This process seems to occur directly in the hydride abstraction of the \(\sigma\)-propyl derivative, but in the Lewis acid reaction the presence of the bromide bridged species indicates that this might be an intermediate. It was shown by treatment of a chlorobenzene solution of the salt, \([\pi-C_5H_5Fe(CO)_2Br-(CO)_2Fe(\pi-C_5H_5)]AlBr_4\) with triphenylphosphine, that conversion took place to the salt, \([\pi-C_5H_5Fe(CO)_2P(C_6H_5)_3]AlBr_4\), readily at room temperature. There was no conversion, however, of \([\pi-C_5H_5Fe(CO)_2P(C_6H_5)_3]AlBr_4\) to the bromide-bridged species.

In the Lewis acid induced rearrangement the following (FIG. 38.)

\[
\begin{align*}
\text{[intermediate]} & \rightarrow \text{[reactant]} \\
\text{[intermediate]} & \rightarrow \text{[product]}
\end{align*}
\]

pathway can, therefore, be suggested.

Fig. 38.
The nature of the intermediate, at this stage, is unknown. Two possibilities are however available. Either the cation, \([\pi-C_5H_5Fe(CO)\text{P} \text{Pr}_3]^{+}\) forms an unstable cluster complex, \([\pi-C_5H_5Fe(CO)\text{Pr}_3]_n\), where \(n\) is probably 2, 3, or 4, or the original complex loses carbon monoxide, which is then trapped by another molecule of the cation. Work on this aspect is continuing.

Comparison of these results with the mechanism of the iodination of dicyclopentadienyldiiron(tetracarbonyl)\(^ {193}\) and the monosubstituted phosphine complexes, \((\pi-C_5H_5)\text{Fe}_2(CO)_3(\text{Pr}_3)\) show close similarities. These results showed evidence for two mechanistic pathways. (FIG. 39.)

![Fig. 39.](image)
The monosubstituted derivatives, \((\pi-C_5H_5)_2Fe_2(CO)_3PR_3\), (where R is Et, n-Pr, n-Bu, CMe, OEt, 0Pr-i, OBu-n, and OPh.) were shown to react with iodine in dichloromethane, to form \(\left[\pi-C_5H_5Fe(CO)_2PR_3\right]I\), as well as \(\pi-C_5H_5Fe(CO)_2I\) and \(\pi-C_5H_5Fe(CO)PR_3I\). In benzene the major product was the ionic species, with only traces of the two neutral products. This shows that the reaction can still proceed by the two mechanistic pathways, however, workers were unable to isolate the bromo-bridged cation, \(\left[\pi-C_5H_5Fe(CO)_2Br-(CO)(PR_3)Fe(\pi-C_5H_5)\right]^+\).

These results show that monosubstituted complexes give unstable intermediates, so that in the system studied in the Lewis acid reactions, where disubstituted complexes are expected as intermediates, these would be expected to be even more unstable, due to steric conditions. In view of this it would appear that the unknown intermediate might be the unstable, \(\left[\pi-C_5H_5Fe(CO)P\Phi_3\right]_2\), or the bromo-bridged cation, \(\left[\pi-C_5H_5Fe(CO)P\Phi_3-Br-(P\Phi_3)(CO)Fe(\pi-C_5H_5)\right]^+\).

If these complexes were formed, one would expect them to be in equilibrium with the cation, \(\left[\pi-C_5H_5Fe(CO)P\Phi_3\right]^+\), with the equilibrium very much in favour of the latter cation. It must also, however, be able to convert to the fully saturated cation, \(\left[\pi-C_5H_5Fe(CO)_2P\Phi_3\right]^+\), see FIG. 40.

Attempts to prepare the dimer, \(\left[\pi-C_5H_5Fe(CO)P\Phi_3\right]_2\), have proved unsuccessful. Many methods of preparation have been tried, including attempts to prepare the hydride, \(\pi-C_5H_5Fe(CO)P\Phi_3H\), and then, in analogy to the dicarbonyl hydride, \(\pi-C_5H_5Fe(CO)_2H\), induce it to dimerise. It was, however, observed that in certain of the phenyl lithium reactions, and on treatment with THF, bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron gave a transient infra-red band, at 1735 cm\(^{-1}\). Whenever this band appeared the product always contained some of the dicarbonyl species. It was postulated that
This complex might be the dimer, \( [\pi-C_5H_5Fe(CO)P\{3}_2]^2 \), in which the bridging carbonyl frequency was at 1735 cm\(^{-1}\). This would not seem unreasonable as the dimer, \( [\pi-C_5H_5Fe(CO)]_2 \), has bridging carbonyl frequencies at 1790 - 1800 cm\(^{-1}\). However no complex was ever isolated.

![Diagram]

If path B. is used the obvious question is where does the rest of the molecule go. Attempts to isolate non-carbonyl containing complexes from the reaction mixtures have proved unsuccessful. If salts of the type \( [\pi-C_5H_5FeP\{3}]^+ \) or \( [\pi-C_5H_5Fe(P\{3}]_2^+ \) were formed, these may be expected to be quite unstable. One possible reason why no complexes of this type have been isolated is that the phosphine may form adducts with excess Lewis acid, of the form \( P\{3\cdot AlBr_3 \). An alternative product could be the salt \( P\{3\cdot AlBr_4 \). In support of this Haines and du Preez \( \text{193} \) assumed that the covalent halide, \( \pi-C_5H_5Fe(CO)_2X \) was formed from the halogen bridged species, and not
from the tricarbonyl cation, \([\pi-C_5H_5Fe(CO)_3]^+\). To see whether this held for the more sterically crowded mono-phosphine substituted cation, the salt was heated. For the tetrafluoroborate, or bromide, refluxing in benzene or toluene produced no change over many hours. This not only shows the thermal stability of the salt, but also that the preparation of bromocarbonyltriphenylphosphine-\(\pi\)-cyclopentadienyliron from bromodicarbonyl-\(\pi\)-cyclopentadienyliron and triphenylphosphine is unlikely to proceed through an associative mechanism, to form the over coordinated species, which could then lose carbon monoxide or triphenylphosphine.

One can conclude that the Lewis acid assisted formation of unsaturated cations, which can react with olefins, must be approached with great care, for this system. Preliminary experiments with other systems of this type, for example, \(\pi-C_5H_5Mo(CO)_2PH_3Cl\), suggest that similar reactions may be occurring.
Reactions of \( \pi \)-Propene cations.

In previous sections it has been shown that \( \pi \)-propene cations can be formed by several different routes, the most convenient of these being the protonation of the \( \sigma \)-allyl derivatives with an acid in standard THF. or ether solution. Besides the convenience of being able to titrate the correct amount of acid needed, this method has the added advantage of, when using trifluoroacetic acid, giving a THF. solution of the \( \pi \)-propene cation. Unfortunately the only system in which the trifluoroacetate could be formed, and kept for several days, even at 0°C. was the dicarbonyl-\( \pi \)-cyclopentadienyliiron system. By the other routes, the cation formed was, or was converted to, the hexafluorophosphate or tetrafluoroborate derivative, because of the thermal and oxidative stability of these salts. However both of these salts proved very difficult to dissolve in any organic solvents, which meant that any reactions, involving nucleophilic attack, performed on them were done under heterogeneous, rather than homogeneous conditions.

Two different classes of nucleophilic attack involving the carbon nucleophiles were investigated. Firstly there were those in which the same nucleophile was used, but the anions of the metal complex varied, and secondly the reverse, in which the complex was kept the same, and the size and nucleophilicity of the nucleophile varied.

These two sets of experiments were designed to show the influence of the size, and nature of the nucleophile, and of the size of the metal complex, on the direction of the reaction. This, it was hoped, would help elucidate the mechanism of nucleophilic attack. Two main possibilities, as with the electrophilic attack on the \( \sigma \)-allyl, are available. The first involves attack directly on the ligand, whilst the other requires initial attack at the metal, followed by an
intramolecular rearrangement. Most reported nucleophilic attacks, on metal systems, appear to go via the former mechanism, for example, the nucleophilic attack, by phenyl lithium, on cobalticenium ions has been shown, by an X-ray study, to give the exo-configuration. If the metal were attacked first, and the adduct then rearranged, the endo-configuration would be anticipated. (See Fig. 41.)

\[
\text{M} \quad \text{PhLi} \quad \text{M}
\]

Fig. 41.

The investigation of the first type of attack, that is where the nucleophile is kept the same and the counter ion varied, was undertaken first. The nucleophile first used was the simplest carbon nucleophile, the methyl anion.

The \( \pi \)-propene cation, \([\pi-C_5H_5Fe(CO)_2C_2H_6]^+\) as the chloride, the hexafluorophosphate, the trifluoroacetate and the fluorosulphonate, was treated, under varying conditions with methyl lithium. The temperature was varied from \(-78^\circ\text{C.}\) to \(0^\circ\text{C.}\), and the concentration by a factor of four. The amount of methyl lithium was always kept at one molar equivalent. In all cases a yellow-amber oily solid was produced, and this was shown, by the comparison with authentic samples, to be the \( \sigma \)-methyl, \( \pi-C_5H_5Fe(CO)_2CH_3 \). These experiments show, that in the case of the methyl group, attack at the metal is preferred and
that if, at the time of nucleophilic attack at the metal, the propene is still attached, then there is no intramolecular rearrangement, with the methyl shifting to the coordinated propene moiety. This may be due to steric over crowding around the metal on the introduction of the methyl, and this being eased by the production of the most thermodynamically stable product, that is the \( \sigma \)-methyl,\( \pi \)-C\(_5\)H\(_5\)Fe(CO)\(_2\)Me.

These experiments show, moreover, that the anion present seems to make very little difference to the position of attack, even though the size of the counterion varies considerably in the four cases investigated. This is rather surprising, for if a model is made of the \( \pi \)-propene cation, it can be seen that the anion has two main sites available to it. It can either position itself trans to the propene molecule, or to the \( \pi \)-cyclopentadienyl ring. (See, FIG. 42.)

![Fig. 42.](image)

If attack of the nucleophile is to be at the \( \pi \)-propene site, it would be expected that the size of the anion would make little difference. There is a slight possibility of repulsion between the nucleophile and the counterion, when the latter is at the base of the molecule, but this is unlikely to be very much. However, if the nucleophile attacks the metal, either with expulsion of propene, or
followed by intramolecular rearrangement, then the size of the counterion might be expected to influence the speed, or the direction of the attack. In the experiments performed the chloride ion was the smallest counterion used. This \( \pi \)-propene salt was found to give a 95% yield of \( \sigma \)-methyldicarbonyl-\( \pi \)-cyclopentadienyliron, consistently, provided that, after the protonation with hydrogen chloride, the volume of ether was reduced to half. This process removed all the excess acid, which had a detrimental effect on the yield. Without this ploy the yield varied between 45 and 95%. This would indicate that the size has the effect of only lowering the yield of the \( \sigma \)-methyl derivative, since the hexafluorophosphate salt gave only a 70% yield. No other product was isolated in either case.

Since there appeared to be a steric factor controlling the yields of the previous reactions, the size of the nucleophile was increased, to see whether the yield would be lowered even further, or even attack at the metal prevented completely. The size was increased by the use of the phenyl anion as phenyl lithium.

The \( \pi \)-propene, as the chloride was obtained by protonation with hydrogen chloride, and all the excess acid removed. The salt was then treated with an equimolar amount of phenyl lithium at \(-78^\circ\text{C.}\), under nitrogen, causing the mixture to slowly darken in colour. Monitoring of the reaction by infra-red spectroscopy showed that the \( \pi \)-propene cation had disappeared after forty five minutes. The mixture was washed well with degassed distilled water and then the ether then removed from the dried ethereal layer, to yield a yellow oily mixture, which showed the presence of four new carbonyl stretching frequencies at 2020, 2003, 1916, and 1958 cm\(^{-1}\) (in cyclohexane.) The oily material was chromatographed on a neutral alumina column, using a petrol (30 - 40°C. fraction): cyclohexane (1:1)
mixture as eluent. This separated the mixture, as expected, into two yellow fractions. Each fraction exhibited two strong carbonyl stretching frequencies.

The second yellow fraction obtained was evaporated to an oily residue, which was crystallised from an iso-pentane solution, at \(-78^\circ C\), to give pale yellow crystals in 45% yield. These were low melting, \((33 - 34^\circ C)\) and in spectral, and TLC. properties were identical to an authentic sample of \(\sigma\)-phenyldicarbonyl-\(\pi\)-cyclopentadienyliron. Thus nucleophilic attack had still been possible at the iron atom, even though a larger nucleophile had been used.

The other complex, from the first yellow fraction obtained from the column, proved to be more difficult to isolate, purify and identify. The amber oily residue obtained, on removal of the solvent was dissolved in a minimum of iso-pentane and cooled to \(-78^\circ C\).

Attempts to isolate the crystals from this solution proved impossible. Hopes that the complex was the \(\sigma\)-propylbenzene or cumene derivatives, which one would expect to be difficult to isolate were lowered by the fact that the NMR. spectrum of the crude material showed no phenyl ring protons. The rechromatographed product was sublimed in a molecular distillation unit, with a very short path length, to yield approximately a 40% yield of \(\sigma\)-allyldicarbonyl-\(\pi\)-cyclopentadienyliron.

To prove conclusively that the reaction mixture contained no \(\sigma\)-propylbenzene or \(\sigma\)-cumene derivatives, the instability of the iron-carbon bond was used to advantage, rather than the usual disadvantage! It was shown that the \(\sigma\)-bond was sufficiently unstable to be cleaved by excess hydrogen chloride gas to give the alkane and chlorodicarbonyl-\(\pi\)-cyclopentadienyliron. This presumably occurred by an identical mechanism to that already discussed in the section on the protonation of \(\sigma\)-allyl derivatives.
The crude reaction product, before chromatography, was dissolved in dry ether, and a slow rate (one bubble through the concentrated sulphuric acid used for drying, every two seconds.) of hydrogen chloride was passed through the solution. After thirty minutes the initial golden yellow solution had become colourless, with the production of a red-brown oily precipitate. A yellow crystalline solid was observed around the sides of the flask, just above the solvent level. Chromatography of the concentrated supernatant showed the presence of some organic compounds and traces of the chloride, \( \pi-C\text{\textsubscript{5}H\textsubscript{5}}Fe(CO)\text{\textsubscript{2}}Cl \). The red-brown oily precipitate was shown to be the chloride, together with non-carbonyl containing oxidation products. The yellow solid, from the sides of the flask, was shown, from the infra-red and NMR. spectra to be the \( \pi \)-propene cation, \( \left[ \pi-C\text{\textsubscript{5}H\textsubscript{5}}Fe(CO)\text{\textsubscript{2}}C\text{\textsubscript{3}H\textsubscript{6}} \right]^+ \), and not, as was first thought, the chloro-bridged derivative, \( \left[ \pi-C\text{\textsubscript{5}H\textsubscript{5}}Fe(CO)\text{\textsubscript{2}}Cl-(CO)\text{\textsubscript{2}}Fe(CO)\text{\textsubscript{2}}(\pi-C\text{\textsubscript{5}H\textsubscript{5}}) \right]Cl_2 \).

The fractions obtained from the column were passed through a six foot gas-liquid chromatography column of 20%(w/w) LAC-2-R-446 on chromosorb. Comparison with a pure sample of propylbenzene and cumene, showed that neither of these compounds were formed during the reaction. Benzene was identified as being present, thus proving that the \( \sigma \)-phenyl derivative was formed in the original reaction mixture.

To ensure that the chromatography on the neutral alumina column had not affected the reaction products, the crude reaction mixture, after treatment with hydrogen chloride, was distilled to dryness. The distillate was then carefully concentrated, using a Vigreux column. The resulting pale yellow solution was shown, by infra-red spectroscopy, to have no organometallic carbonyl complex present, and so was passed through the gas-liquid chromatography column, under the same conditions as used above. This again showed that no cumene, or
propylbenzene to be present.

Piecing together the evidence from these experiments it was possible to show that the nucleophilic attack of phenyl lithium, on the π-propene cation gave the σ-phenylidicarbonyl-π-cyclopentadienyl-iron and the σ-allylidicarbonyl-π-cyclopentadienyliron. The latter was confirmed by the presence of some of the π-propene cation, after the cleavage reaction with hydrogen chloride, and by the NMR. spectrum of the sublimation fraction from the neutral alumina chromatography. The gas-liquid chromatography did not show the presence of any propene, either because it came off with the solvent, or it was lost during the distillation of the crude material.

Thus nucleophilic attack, by the phenyl anion on the π-propene cation as the chloride, has been shown not to proceed with attack at the π-cyclopentadienyl ring, or at the coordinated propene. The only attack being observed at the metal, to give the σ-phenyl derivative. The production of the σ-allyl derivative was at first very puzzling, and the experiment was repeated several times, great care being taken to ensure that the reaction went to completion, and that the resulting π-propene cation was pure. Having ensured this the σ-allyl derivative could only be assumed to occur by proton abstraction from the π-propene cation, by the phenyl lithium.

The hydride abstraction from the σ-propyl derivative, to give the π-propene cation ¹⁵⁸ has been shown to be a reversible process; the reduction of the π-propene cation occurring in ether with sodium borohydride. However, the reverse process to the σ-allyl protonation has not previously reported in this system. The nearest process to this is the deprotonation of the π-ketimine complex, formed on protonation of σ-cyanomethyl complex. ¹⁹⁵ (FIG. 43.)
In this case the reversal being produced when the \( \pi \)-ketimine complex was heated to 100°C.

The production of the \( \sigma \)-phenyl derivative was not too surprising after the results obtained with the attack of methyl lithium. However, the production of the \( \sigma \)-allyl derivative was not expected, in preference to the \( \sigma \)-cumene or \( \sigma \)-propylbenzene derivative, or the complexes in which the nucleophilic attack had taken place at the \( \pi \)-cyclopentadienyl ring. This contrasts with the reported nucleophilic attack by phenyl and pentafluorophenyl lithium on the salts of the type, \( [\pi-C_5H_5Fe(CO)_2P\phi_3]I \). 142, 196 In this system attack took place mainly at the \( \pi \)-cyclopentadienyl ring, for example, treatment of \( [\pi-C_5H_5Fe(CO)_2P\phi_3]I \), with pentafluorophenyl lithium for two hours, at 0°C. in ether, gave a 56% yield, after chromatography and recrystallisation, of exo-\( C_6F_5C_5H_5Fe(CO)_2P\phi_3 \). These results were further support for the type of reaction observed earlier, in the reduction of the cation with sodium borohydride, to give \( \pi-C_5H_5Fe(CO)_2P\phi_3 \). 71

The path that these reactions take appears to be determined by the presence of the triphenylphosphine moiety. The product which would have been expected on purely thermodynamic grounds, would be
the pentafluorobenzoyl derivative, \( \pi-C_5H_5Fe(CO)PF_3COC_6F_5 \). Reasons for this not being the major product are probably due to both the steric and electronic effects of the phosphine, and the replacement of a carbonyl by triphenylphosphine would result in the remaining terminal carbonyls becoming more electron rich, and thus less amenable to nucleophilic attack. The steric effect would not be expected to play such an important part in the reduction of this phosphine substituted cation with sodium borohydride, but here again the major product is that derived from attack at the \( \pi \)-cyclopentadienyl ring. Again the exo-configuration was obtained, thus making the possibility of prior attack at the metal unlikely. In the same experiment on the non-phosphine substituted salt, \( [\pi-C_5H_5Fe(CO)_3]PF_6 \), the major product is the hydride, \( \pi-C_5H_5Fe(CO)_2H \), which rapidly dimerises, with the expulsion of hydrogen, to give \( [\pi-C_5H_5Fe(CO)_2]_2 \). It is possible that this reaction may go through the formylderivative, \( \pi-C_5H_5Fe(CO)_2CHO \), by direct attack on the carbonyl, followed by rapid decarbonylation. This has never been established.

Further support for these observations, on the effect of triphenylphosphine, is obtained in the reaction of pentafluorophenyl lithium with \( [\pi-C_5H_5Fe(CO)_3]PF_6 \). This gave three different products. These were the o-phenyl, \( \pi-C_5H_5Fe(CO)_2C_6F_5 \), in 12.7% yield, the benzoyl derivative, \( \pi-C_5H_5Fe(CO)_2COC_6F_5 \), in 17.6% yield, and a small amount of the product derived from attack at the \( \pi \)-cyclopentadienyl ring. This system, therefore, proceeds to some extent by all three possible routes of nucleophilic attack, that is by displacement of a carbonyl group by direct attack at the metal, attack on the carbonyl group, or attack at the \( \pi \)-cyclopentadienyl ring.

The one significant feature in this work, is the low yields that were obtained, compared to the higher ones observed during the
research reported in this thesis. The low yields were probably due to the reaction of the products with excess of the lithium reagents. It is very unfortunate as it means that mechanisms cannot be eliminated, or others proved conclusively.

Nucleophilic attack of phenyl lithium on the \( \pi \)-propene-dicarbonyl-\( \pi \)-cyclopentadienyliron trifluoroacetate proceeded by almost the same route as that observed in the chloride salt.

Addition of a one molar equivalent of phenyl lithium, at \(-78^\circ C\), to a stirred solution of the trifluoroacetate resulted in an almost immediate colour change from pale amber to deep chocolate brown. A sample, taken within one minute of mixing, showed, in the infra-red spectrum, the presence of the olefinic cation, and also the dimer, \( \left[ \pi-C_5H_5Fe(CO)_2 \right]_2 \) and four other new carbonyl stretching frequencies. This contrasts to the chloride salt, where four new carbonyl stretching frequencies were seen, but no dimer. Work up of the whole sample, after forty minutes, gave, on removal of solvent, an oily brown residue. Chromatography of this residue, with petrol (30 - 40°C. fraction.) on a neutral alumina column proved to be not very successful, since of the fifteen 3 ml. fractions obtained, only the second and third contained any metal carbonyl complexes - about half of the product having decomposed on the column.

Repeat reactions were carried out with identical results. Thin layer chromatography on alumina, with cyclohexane, indicated that part of the product was \( \sigma \)-phenyldicarbonyl-\( \pi \)-cyclopentadienyliron. This was confirmed by the NMR. spectrum, which also suggested the presence of \( \sigma \)-allyldicarbonyl-\( \pi \)-cyclopentadienyliron. This was confirmed by infra-red spectroscopy, and then its protonation properties. The yields of isolated complexes were 29 \% for the \( \sigma \)-phenyl derivative, and 41 \% for the \( \sigma \)-allyl derivative. Since the
σ-phenyl derivative is more stable any decomposition on the column would be expected to only lower the yield of the σ-allyl derivative.

Thus when the π-propene cation, as the trifluoroacetate salt, is used there is no attack at the π-cyclopentadienyl ring, and less direct attack at the metal with expulsion of the propene molecule. This shows that the counterion of the π-propene complex can have an effect in the direction the reaction will take. It would appear that the deprotonation process is more favourable in the π-Propene-trifluoroacetate salt, than the nucleophilic attack at the metal. It is hard to see what difference there is between the chloride, and the trifluoroacetate ion, other than size, that could effect the reaction. The larger size of the trifluoroacetate ion may sufficiently slow direct attack at the metal to allow deprotonation.

All the reactions discussed so far have proceeded with no attack on the π-propene moiety or the π-cyclopentadienyl ring. As has already been discussed triphenylphosphine may provide the correct geometry and electronic conditions in a molecule, to enable this type of nucleophilic attack to take place. Thus the reactions, in which the nucleophile was kept the same, and the counterion varied were temporally halted, until such time as the π-propene cation, 

$$\left[\pi-C_5H_5Fe(CO)P\left(\text{OP}_{3}C_3H_6\right)\right]^+$$

could be made.

The experiments using different nucleophiles on the same cation were however tried on the non-phosphine containing system. We have already seen that the size of the nucleophile has the effect of opening another route, in that methyl lithium reacts with the π-propene trifluoroacetate salt to give exclusively the σ-methyl derivative, whereas the phenyl lithium attacks to give the σ-phenyl and the σ-allyl derivatives. Attempts were made to react anthracene lithium with the trifluoroacetate salt. With this reagent it would be impossible to form the σ-aryl derivative by direct attack at the metal.
Unfortunately the reaction gave very low yields, the only two products isolated were the dimer, $\left[\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\right]_2$, and, in very small yield the $\sigma$-allyldicarbonyl-$\pi$-cyclopentadienyliron.

The nucleophilicity of the attacking nucleophile was lowered by reacting the $\pi$-propene cation, as the trifluoroacetate, with phenylmagnesium bromide. When an ethereal solution of the Grignard reagent was added to a THF solution of the $\pi$-propene salt there was an immediate precipitation. This was found to be the $\pi$-propene cation. Stirring the resultant suspension, at $-78^\circ\text{C}$, for several hours, produced no change in the infra-red spectrum. Allowing the mixture to warm to $0^\circ\text{C}$, still produced no reaction. Treatment of a small sample of the reaction mixture with phenyl lithium gave the normal mixture of $\sigma$-phenyl and $\sigma$-allyl derivatives. Stirring of the Grignard reaction mixture, at room temperature for two hours, gave two new carbonyl stretching frequencies, but these were shown to be due to the bromide, $\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$.

Thus the change in the nucleophilicity has meant a complete change in the reaction pathway. Phenylmagnesium bromide is not, it appears nucleophilic enough to attack the cation, before attack by the bromide can take place. The mechanism for the bromide attack may be the replacement of the trifluoroacetate by $\text{MgBr}_3$, produced by decomposition of the Grignard reagent, followed by an intramolecular rearrangement, or just attack by the bromide anion. An alternative mechanism is the loss of propene, to give the unsaturated cation, $\left[\pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\right]^+$, which then undergoes a series of reactions with the Lewis acid, $\text{MgBr}_2$, similar to those described in the section on Lewis acids.

Attempts to perform these reactions, using cadmium salts, were abandoned at this stage, as they are even less nucleophilic in character.
The nucleophilic attack of methyl and phenyl lithium, on the \( \pi \)-propenetricarbonyl-\( \pi \)-cyclopentadienyltungsten and molybdenum hexafluorophosphate was investigated. The hexafluorophosphate was prepared, in low yield, from the protonation of the \( \sigma \)-allyl derivative with hydrogen chloride, followed by treatment with aqueous potassium hexafluorophosphate. In all cases direct attack at the metal took place, with the expulsion of propene, to give the \( \sigma \)-methyl and the \( \sigma \)-phenyl derivatives.

General survey of the properties of \( \pi \)-propene complexes.

Olefin complexes of the transition metals have been reviewed in many massive tomes, \(^{197}\) but they are generally concerned with the documentation of reactions, rather than the correlation of trends within groups of complexes. Many anomalies are still unexplained, for instance the bonding theories prevalent at the present time do not really explain the bonding of silver olefin complexes. On the Dewar model the properties of the olefin should change but, for example, the double bond distances in the bullvalene complex, "140
\[ (C_8H_{10})_3AgBF_4 \] are still 1.34 Å.

In the systems studied in this work, and their \( \pi \)-propene analogues, it has been possible to show that there is a relationship between the \( \nu_{C=6} \) and the \( \tau \) values for the coordinated propene. Since higher \( \tau \) values indicate a higher magnetic shielding of the olefin, it must mean that in forming the stronger \( \pi \)-bond, by stronger back donation, there is a corresponding increase in the shielding.

Table XI shows that parallel trends can also be seen in the value for the \( \pi \)-cyclopentadienyl ring.
TABLE XI.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{CH_3}$</th>
<th>$\nu_{C_5H_5}$</th>
<th>$\nu_{C=C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\pi-C_5H_5Mo(CO)_3C_3H_6]^{+}$</td>
<td>7.99</td>
<td>4.05</td>
<td>1507</td>
</tr>
<tr>
<td>$[\pi-C_5H_5Fe(CO)_3C_3H_6]^{+}$</td>
<td>7.78</td>
<td>4.01</td>
<td>1459</td>
</tr>
<tr>
<td>$[\pi-C_5H_5Fe(CO)_2C_3H_6]^{+}$</td>
<td>8.14</td>
<td>4.63</td>
<td>1533</td>
</tr>
<tr>
<td>$[\pi-C_5H_5Fe(CO)_2P_3C_3H_6]^{+}$</td>
<td>8.2</td>
<td>4.94</td>
<td>1541</td>
</tr>
<tr>
<td>$(C_3H_6)_2Rhacac$</td>
<td>8.69</td>
<td>5.05</td>
<td>1560</td>
</tr>
</tbody>
</table>

As King has already shown, for many $\pi$-cyclopentadienyl metal carbonyl complexes, it is possible to relate the $\nu$ value of the $\pi$-cyclopentadienyl ring signal to the force constants of the carbonyls, it should be possible to correlate changes in $\nu_{C=O}$, $\nu_{C=C}$, and the $\nu$ values. This would enable one to study, more carefully, the subtle electronic changes, brought about by changing one ligand in a fixed system. For example, it would be possible to study the effect of one of the carbonyls on the complex, $[\pi-C_5H_5Fe(CO)_2C_3H_6]^{+}$, by a whole range of phosphines, of similar and different steric requirements. This could give much more detailed knowledge of the complexes than is known at present, hence enabling a better understanding of the bonding in these systems.

Changing the ligands at the metal should effect the $\nu$ value and $\nu_{C=C}$ as it will control the d-electron donor properties of the metal. In the $\pi$-ethylene complexes of rhodium a $\pi$-cyclopentadienyl ring vastly improves the donor properties, over the acetyl-acetonate ligand. (See Table XII.)
### TABLE XII

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mean ( \tau ) (ppm.)</th>
<th>( \nu_{C=C} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((C_2H_4)_2Rh(C_5H_5))</td>
<td>8.1</td>
<td>1493</td>
</tr>
<tr>
<td>((C_2H_4)_2Rh,acac.)</td>
<td>6.9</td>
<td>1525</td>
</tr>
</tbody>
</table>

This effect is reversed by placing electron releasing substituents on the olefin, as these will have the effect of making the olefin a poorer acceptor ligand. This is illustrated in Ziese's salt, where stability is in the order ethylene > propylene > cis 2-butene.
Thermolysis of o-allylcarbonyltriphenylphosphine-π-cyclopentadienyliron.

Whilst attempting to prepare a pure sample of this o-allyl derivative, a sublimation was tried at $10^{-3}$ mmHg. No sublimation took place over several hours at $19.5^\circ C$, but on slowly raising the temperature to $25^\circ C$, the cold finger became slightly yellow.

The "sublimation" proceeded quite rapidly at $30^\circ C$. The initial amber oil was found to give a mixture of brown and white solid, as the non-volatile residue, and pale yellow crystals, as the sublimed material. The latter, however, became very oily at room temperature.

NMR and infra-red spectra showed the sublimate to be almost pure π-allylcarbonyl-π-cyclopentadienyliron. The only impurity present was a very small trace of triphenylphosphine, which had also sublimed.

In general the exchange of one carbonyl group for a triphenylphosphine tends to make the o-alkyl and aryl derivatives more stable. The o-propyl derivative, $\pi$-C$_5$H$_5$Fe(CO)P(cyclohexane)$_2$CH$_3$, for example melts at 129 - 130°C, whilst the corresponding dicarbonyl complex, $\pi$-C$_5$H$_5$Fe(CO)$_2$CH$_2$CH$_2$CH$_3$, is an oil, which is thermally unstable above 40 - 50°C. In o-alkylcarbonyltriphenylphosphine-π-cyclopentadienyliron, although the phosphine adds considerable thermal stability (m.p. 104 - 105°C. with decomposition) an obvious driving force for this thermal rearrangement is the thermodynamic stability of the two products (FIG. 44.)

In order to see whether this rearrangement was enhanced by certain solvents, and to obtain kinetic data on the reaction, standard solutions were monitored carefully by infra-red spectroscopy. (FIG. 45)
Infra-red kinetic study of the thermolysis of
\( \eta^1-C_5H_5Fe(CO)[P(C_6H_{13})_3]CH_2CH=CH_2 \) in cyclohexane
at 67.5°C.

Fig. 45.
The infra-red spectrometer (Perkin Elmer 621.) was programmed to read linearly in Absorbance. The absorbance of the carbonyl stretching frequency of \( \pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}\left(\text{C}_6\text{H}_{12}\right)_3\text{CH}_2\text{CH} = \text{CH}_2 \), designated \( A_{1918} \) (in cyclohexane.) and \( A_{1903} \) (in THF.), and that of the product, \( \pi-\text{C}_5\text{H}_5\text{Fe}(\text{CO})\pi-\text{C}_3\text{H}_5 \), designated \( A_{1952} \) (in cyclohexane.) and \( A_{1940} \) (in THF.) were then read directly from the spectra. As the bands, especially in cyclohexane, were very sharp, the peak height was recorded, rather than the area under the peak.

Tables XIII, XIV, XV, XVI, XVII, and XVIII show typical results. The initial \( A_{1918} \) or \( A_{1903} \) was taken as being zero \% reaction, in the calculation of \( \log(100 - \% \text{ reaction}) \). At each temperature the experiment was repeated several times, to ensure reproducibility of results. The lower temperature experiments were not taken to completion, due to the slow decomposition of the product and the reactant, over the duration of the experiment.
### TABLE XIII.

Reaction in cyclohexane, at 47.4°C, and a concentration of 4.5 mg/ml.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Temp. (°C.)</th>
<th>A1918</th>
<th>A1952</th>
<th>Log. (100 - % reaction.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.6</td>
<td>38.3</td>
<td>2.6</td>
<td>2.0000</td>
</tr>
<tr>
<td>22</td>
<td>47.4</td>
<td>36.8</td>
<td>3.5</td>
<td>1.9826</td>
</tr>
<tr>
<td>70</td>
<td>47.5</td>
<td>33.9</td>
<td>5.5</td>
<td>1.9470</td>
</tr>
<tr>
<td>102</td>
<td>47.4</td>
<td>33.1</td>
<td>7.0</td>
<td>1.9366</td>
</tr>
<tr>
<td>131</td>
<td>47.4</td>
<td>32.2</td>
<td>8.4</td>
<td>1.9247</td>
</tr>
<tr>
<td>147</td>
<td>47.3</td>
<td>31.0</td>
<td>9.5</td>
<td>1.9182</td>
</tr>
<tr>
<td>205</td>
<td>47.4</td>
<td>29.9</td>
<td>11.3</td>
<td>1.8945</td>
</tr>
<tr>
<td>293</td>
<td>47.5</td>
<td>26.2</td>
<td>15.0</td>
<td>1.8851</td>
</tr>
<tr>
<td>340</td>
<td>47.3</td>
<td>25.1</td>
<td>16.9</td>
<td>1.8165</td>
</tr>
<tr>
<td>370</td>
<td>47.2</td>
<td>23.1</td>
<td>16.9</td>
<td>1.7804</td>
</tr>
<tr>
<td>419</td>
<td>47.4</td>
<td>22.0</td>
<td>19.8</td>
<td>1.7592</td>
</tr>
<tr>
<td>496</td>
<td>47.3</td>
<td>18.5</td>
<td>25.2</td>
<td>1.6340</td>
</tr>
<tr>
<td>630</td>
<td>47.4</td>
<td>15.0</td>
<td>27.6</td>
<td>1.5929</td>
</tr>
</tbody>
</table>

### TABLE XIV.

Reaction in cyclohexane, at 60.9°C, and a concentration of 4.2 mg/ml.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Temp. (°C.)</th>
<th>A1918</th>
<th>A1952</th>
<th>Log. (100 - % reaction.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.1</td>
<td>29.5</td>
<td>-</td>
<td>2.0000</td>
</tr>
<tr>
<td>11</td>
<td>60.9</td>
<td>26.2</td>
<td>4</td>
<td>1.9485</td>
</tr>
<tr>
<td>19</td>
<td>61.0</td>
<td>25.1</td>
<td>5.1</td>
<td>1.9299</td>
</tr>
<tr>
<td>47</td>
<td>60.8</td>
<td>19.6</td>
<td>11.0</td>
<td>1.8225</td>
</tr>
<tr>
<td>68</td>
<td>60.8</td>
<td>16.0</td>
<td>15.2</td>
<td>1.7343</td>
</tr>
<tr>
<td>80</td>
<td>60.9</td>
<td>14.5</td>
<td>16.7</td>
<td>1.6916</td>
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<td>94</td>
<td>60.8</td>
<td>12.1</td>
<td>19.1</td>
<td>1.6130</td>
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<tr>
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<td>60.9</td>
<td>11.0</td>
<td>21.2</td>
<td>1.5716</td>
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<td>120</td>
<td>60.8</td>
<td>10.0</td>
<td>22.2</td>
<td>1.5392</td>
</tr>
<tr>
<td>125</td>
<td>60.8</td>
<td>9.5</td>
<td>22.5</td>
<td>1.5079</td>
</tr>
<tr>
<td>135</td>
<td>60.9</td>
<td>8.5</td>
<td>23.3</td>
<td>1.4596</td>
</tr>
<tr>
<td>184</td>
<td>60.8</td>
<td>5.2</td>
<td>27.6</td>
<td>1.2462</td>
</tr>
</tbody>
</table>
### TABLE XV.

Reaction in cyclohexane, at 67.4°C. and a concentration of 4.3 mg./ml.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp (°C.)</th>
<th>$A_{1918}$</th>
<th>$A_{1952}$</th>
<th>$\log_{10}(100 - %\text{reaction})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67.5</td>
<td>32.1</td>
<td>-</td>
<td>2.0000</td>
</tr>
<tr>
<td>10</td>
<td>67.5</td>
<td>28.2</td>
<td>7.1</td>
<td>1.9437</td>
</tr>
<tr>
<td>16</td>
<td>67.4</td>
<td>25.0</td>
<td>12.6</td>
<td>1.8914</td>
</tr>
<tr>
<td>22</td>
<td>67.5</td>
<td>22.2</td>
<td>16.9</td>
<td>1.8399</td>
</tr>
<tr>
<td>26</td>
<td>67.5</td>
<td>21.1</td>
<td>20.0</td>
<td>1.8178</td>
</tr>
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<td>31</td>
<td>67.45</td>
<td>18.7</td>
<td>22.9</td>
<td>1.7653</td>
</tr>
<tr>
<td>36</td>
<td>67.4</td>
<td>17.9</td>
<td>26.1</td>
<td>1.7464</td>
</tr>
<tr>
<td>41</td>
<td>67.4</td>
<td>15.9</td>
<td>23.1</td>
<td>1.6949</td>
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<tr>
<td>47</td>
<td>67.35</td>
<td>14.2</td>
<td>30.9</td>
<td>1.6453</td>
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<tr>
<td>52</td>
<td>67.35</td>
<td>12.8</td>
<td>33.2</td>
<td>1.6007</td>
</tr>
<tr>
<td>56</td>
<td>67.35</td>
<td>11.4</td>
<td>35.1</td>
<td>1.5504</td>
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<tr>
<td>63</td>
<td>67.4</td>
<td>10.1</td>
<td>38.3</td>
<td>1.4978</td>
</tr>
<tr>
<td>80</td>
<td>67.45</td>
<td>7.0</td>
<td>44.1</td>
<td>1.3386</td>
</tr>
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<td>67.5</td>
<td>5.0</td>
<td>49.4</td>
<td>1.1925</td>
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<tr>
<td>173</td>
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<td>55.5</td>
<td>-</td>
</tr>
<tr>
<td>209</td>
<td>67.5</td>
<td>-</td>
<td>57.8</td>
<td>-</td>
</tr>
</tbody>
</table>

### TABLE XVI.

Reaction in THF., at 46.7°C. and a concentration of 5.1 mg./ml.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp (°C.)</th>
<th>$A_{1903}$</th>
<th>$A_{1940}$</th>
<th>$\log_{10}(100 - %\text{reaction})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>46.8</td>
<td>39</td>
<td>-</td>
<td>2.0000</td>
</tr>
<tr>
<td>8</td>
<td>46.8</td>
<td>37.3</td>
<td>-</td>
<td>1.9806</td>
</tr>
<tr>
<td>45</td>
<td>46.7</td>
<td>36.0</td>
<td>-</td>
<td>1.9652</td>
</tr>
<tr>
<td>64</td>
<td>46.7</td>
<td>28.5</td>
<td>-</td>
<td>1.8637</td>
</tr>
<tr>
<td>103</td>
<td>46.7</td>
<td>32.6</td>
<td>5.0</td>
<td>1.9221</td>
</tr>
<tr>
<td>201</td>
<td>46.6</td>
<td>28.6</td>
<td>6.7</td>
<td>1.8653</td>
</tr>
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<td>245</td>
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<td>1.8370</td>
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<td>46.6</td>
<td>23.1</td>
<td>9.8</td>
<td>1.7725</td>
</tr>
<tr>
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<td>46.7</td>
<td>22.5</td>
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<td>403</td>
<td>46.7</td>
<td>21.6</td>
<td>11.6</td>
<td>1.7434</td>
</tr>
<tr>
<td>568</td>
<td>46.7</td>
<td>18.1</td>
<td>14.6</td>
<td>1.6666</td>
</tr>
</tbody>
</table>
### TABLE XVII

Reaction in THF, at 60·6°C, and a concentration of 5·0mg./ml.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp (°C.)</th>
<th>$A_{1923}$</th>
<th>$A_{1940}$</th>
<th>$Log_{10}(100 - %reaction)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60·3</td>
<td>38·2</td>
<td>-</td>
<td>2·3000</td>
</tr>
<tr>
<td>6</td>
<td>60·2</td>
<td>34·5</td>
<td>-</td>
<td>1·9557</td>
</tr>
<tr>
<td>19</td>
<td>60·5</td>
<td>32·2</td>
<td>5·5</td>
<td>1·9253</td>
</tr>
<tr>
<td>37</td>
<td>60·6</td>
<td>29·0</td>
<td>9·0</td>
<td>1·8323</td>
</tr>
<tr>
<td>60</td>
<td>60·6</td>
<td>24·9</td>
<td>12·0</td>
<td>1·8141</td>
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<tr>
<td>105</td>
<td>60·6</td>
<td>19·6</td>
<td>15·7</td>
<td>1·7102</td>
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<td>157</td>
<td>60·6</td>
<td>13·8</td>
<td>20·6</td>
<td>1·5578</td>
</tr>
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<tr>
<td>198</td>
<td>60·6</td>
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<td>1·4221</td>
</tr>
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<td>216</td>
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<td>26·1</td>
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<td>28·6</td>
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<td>-</td>
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</tr>
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<td>523</td>
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<td>-</td>
<td>32·8</td>
<td>-</td>
</tr>
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</table>

### TABLE XVIII

Reaction in THF, at 67·0°C., and a concentration of 5·2mg./ml.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp (°C.)</th>
<th>$A_{1203}$</th>
<th>$A_{1242}$</th>
<th>$Log_{10}(100 - %reaction)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67·0</td>
<td>44·5</td>
<td>-</td>
<td>2·3000</td>
</tr>
<tr>
<td>14</td>
<td>67·0</td>
<td>39·0</td>
<td>6·5</td>
<td>1·9427</td>
</tr>
<tr>
<td>19</td>
<td>66·9</td>
<td>37·1</td>
<td>9·1</td>
<td>1·9210</td>
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<tr>
<td>25</td>
<td>67·0</td>
<td>34·0</td>
<td>10·9</td>
<td>1·8831</td>
</tr>
<tr>
<td>31</td>
<td>67·0</td>
<td>31·3</td>
<td>13·2</td>
<td>1·8471</td>
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<td>67·1</td>
<td>29·0</td>
<td>15·0</td>
<td>1·8140</td>
</tr>
<tr>
<td>44</td>
<td>67·2</td>
<td>26·0</td>
<td>17·6</td>
<td>1·7666</td>
</tr>
<tr>
<td>60</td>
<td>67·0</td>
<td>19·1</td>
<td>22·5</td>
<td>1·6326</td>
</tr>
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<td>67·1</td>
<td>15·1</td>
<td>24·6</td>
<td>1·5306</td>
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<td>11·8</td>
<td>28·6</td>
<td>1·4235</td>
</tr>
<tr>
<td>110</td>
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<td>8·9</td>
<td>26·1</td>
<td>1·3010</td>
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<tr>
<td>226</td>
<td>67·0</td>
<td>-</td>
<td>38·9</td>
<td>-</td>
</tr>
</tbody>
</table>
Summary of Reactions in Cyclohexane.

<table>
<thead>
<tr>
<th>Temp (^\circ K)</th>
<th>(1/T \times 10^3)</th>
<th>Gradient (\times 10^4)</th>
<th>(t_\frac{1}{2}) (min)</th>
<th>(k)</th>
<th>(\log k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340.4</td>
<td>2.938</td>
<td>-6.8</td>
<td>37</td>
<td>3.132 (\times 10^{-4})</td>
<td>4.4944</td>
</tr>
<tr>
<td>333.9</td>
<td>2.995</td>
<td>-40.7</td>
<td>68</td>
<td>1.698 (\times 10^{-4})</td>
<td>4.2301</td>
</tr>
<tr>
<td>320.4</td>
<td>3.121</td>
<td>-83.8</td>
<td>475</td>
<td>2.432 (\times 10^{-5})</td>
<td>5.3859</td>
</tr>
</tbody>
</table>

Summary of reactions in THF.

<table>
<thead>
<tr>
<th>Temp (^\circ K)</th>
<th>(1/T \times 10^3)</th>
<th>Gradient (\times 10^4)</th>
<th>(t_\frac{1}{2}) (min)</th>
<th>(k)</th>
<th>(\log k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>2.941</td>
<td>-6.0</td>
<td>49</td>
<td>2.357 (\times 10^{-4})</td>
<td>7.3724</td>
</tr>
<tr>
<td>333.6</td>
<td>2.998</td>
<td>-23.6</td>
<td>105</td>
<td>1.100 (\times 10^{-4})</td>
<td>4.0414</td>
</tr>
<tr>
<td>319.7</td>
<td>3.123</td>
<td>-66.6</td>
<td>470</td>
<td>2.458 (\times 10^{-5})</td>
<td>5.3905</td>
</tr>
</tbody>
</table>

Plots were made of time (in minutes) against \(\log(100 - \% \text{ reaction})\) (FIG. 46 and 47.) for all results. The best fit straight line was obtained by computing, using a "least squares" and plotter programme. This also printed out accurate values for the gradient (Table XIX and XX.)

FIG. 46 and 47 show that for the reaction in THF. and cyclohexane, at 47\(^\circ\)C. there is virtually no difference in the rate. Slight differences, however, are observed for the two higher
Fig. 46.
The kinetics of the thermolysis of
\[ \text{C}_5\text{H}_5\text{Fe(CO)\left[P\text{(C}_6\text{H}_5\text{)}_{3}\right]CH}_2\text{CH=CH}_2 \] in THF.
Fig. 47.

Kinetics of the thermolysis of 

\[ \pi-C_5H_5Fe(CO)\left[P\left(C_6H_{53}\right)\right]\text{CH}_2\text{CH}=\text{CH}_2 \] in cyclohexane.
temperatures, although they are not sufficiently different to suggest that the solvent has had any influence on the mechanism of the reaction. Parallel experiments were carried out, using dimethylsulphoxide and acetonitrile as solvents. These two solvents, although not studied in such great detail as the cyclohexane and THF systems, showed similar reaction rates. There was, however, a second reaction in both of these solvents giving a broad hump around 2000 cm\(^{-1}\), in the infra-red spectrum, thus limiting the accuracy of the experiment. This was made even worse by the broadness of the carbonyl stretching frequencies in these solvents, causing the merging of the product and reactant bands.

As a comparison, the thermal decomposition of the complex \(\pi-C_5H_5Mo(CO)_2P\(\overset{\mathrm{3}}{\phi}\)CH\(_2\)CH=CH\) was tried at 47\(^\circ\)C., in cyclohexane. The infra-red spectrum of this complex was more complicated, but it was possible to show that the reaction had a half life of approximately 450 minutes, (cf. \(\pi-C_5H_5Fe(CO)\(\overset{\mathrm{3}}{\phi}\)CH\(_2\)CH=CH\) at 475 minutes at the same temperature.)

From the reaction rates, obtained from the first order reaction equation:

\[
t_{0.5} = \frac{2.303}{k} \log 2 = \frac{0.6932}{k}
\]

Arrhenius plots were obtained for the thermal decomposition, in the two solvents, using the Arrhenius equation: (See FIG. 48.)

\[
k = Ae^{-E/RT}
\]

But from Collision Theory:

\[
k = \frac{\Delta S^+ R}{Nh} e^{-\Delta H^+ /RT}
\]

Linking these two equations together, by using \(\Delta H^+ = E - nRT\), in
Fig. 48. Arrhenius plot for thermal decomposition of

\[ \text{r-C}_5\text{H}_5\text{Fe(CO)}\left[\text{P(C}_6\text{H}_{5})_3\right] \text{CH}_2=\text{CH}_2 \]

in C\text{H}_2\text{CN}, in THF.
which \( n \) becomes unity, for reactions in solution, then:

\[
A = e^{\frac{\Delta S^*}{R}}
\]

Hence, on rearrangement, and sublimination:

\[
\Delta S^* = 4.576 \left(10 \log_{10} A - 13.23\right)
\]

Using this expression it was shown that the Entropy of Activation (\( \Delta S^* \)), for the reaction in cyclohexane was +12 eu (\( \ddagger \)), and in THF was +2 eu (\( \ddagger \)). More points on the Arrhenius plots would have been better, as \( \Delta S^* \) is very dependent on the gradient of the Arrhenius plot. The error in \( \Delta S^* \) is an accumulation of errors throughout the experiment, the worst points seeming to be those at lower temperatures. This is not unexpected, due to the instability of both the reactant, and the product, over long periods of time, in solution. The solutions were kept under nitrogen as much as possible, but the constant sampling made it difficult to keep a good atmosphere.

The high positive value of \( \Delta S^* \) for the reaction in cyclohexane, would indicate that a dissociative mechanism is taking place, thus the solvent has no effect on the reaction:

\[
\pi-C_5H_5Fe(CO)PF_3CH_2CH=CH_2 \longrightarrow \pi-C_5H_5Fe(CO)C_3H_5
\]

This is expected, since cyclohexane is not a very strongly coordinating solvent. The lower value of \( \Delta S^* \) for the THF reactions would still indicate that the dissociative mechanism (a.) was operating, but it indicates that a competitive associative mechanism (b.) might also be operational.

\[
(a.) \quad \pi-C_5H_5Fe(CO)PF_3CH_2CH=CH_2 \longrightarrow \pi-C_5H_5Fe(CO)C_3H_5
\]
The kinetics of the nucleophilic substitution, in nickel tetracarbonyl has been shown to proceed by a dissociative ($S_N^1$) mechanism. In these investigations $\Delta S^+$ was shown to be $+7$ to $+14$ e.u., again indicating less order in the transition state, than in the original material.

It would be useful to study the reactions in dimethylsulphoxide and acetonitrile more carefully, to see whether the stronger coordinating solvents give a negative value for $\Delta S^+.$

**General points.**

The maximisation of the energy ($\Delta E$) of the transition from the highest filled d-orbitals into the lowest anti-bonding orbitals is the essential criterion for the stability of σ-complexes on the Chatt-Shaw bonding hypothesis. The loss of a ligand in the σ- to π-rearrangement occurs with the reduction of $\Delta E$, but this is compensated for by the back bonding of the π-system. In the system studied here, there is a possibility of the loss of either carbon monoxide or triphenylphosphine. The former ligand being a very good π-donor. But, as the triphenylphosphine is expelled in preference to the carbonyl, the acceptor properties of the carbonyl are obviously important. In an analogous nickel complex, $\pi$-$\text{C}_5\text{H}_5\text{Ni}($phen)$\text{CH}_2\text{CH}=$CH$_2$, the phosphine is also very labile, readily giving the π-allyl, $\pi$-$\text{C}_5\text{H}_5\text{NiC}_3\text{H}_5$.

The kinetics of this reaction were studied, after the unsuccessful attempt to form $\pi$-$\text{C}_5\text{H}_5\text{Ni}($phen)$\text{CH}_2\text{CH}=$CH$_2$ from $\pi$-$\text{C}_5\text{H}_5\text{W}($CO)$_2\text{PH}_3\text{CH}=$CH$_2$ and the phosphine. In the light of these results, it can be concluded that, if there is any equilibrium in these
reactions, it lies far to the side of the π-allyl, and that carbon monoxide is a much more preferred ligand to triphenylphosphine. As different phosphine substituted complexes are made in the series \( \pi-C_5H_5Fe(CO)PR_3X \) it will be interesting to investigate the effect of the phosphine on the course and the rate of the reaction.
General discussion of infra-red spectroscopy.

In the past few years many papers have appeared dealing specifically with the infra-red spectra of metal carbonyl and cyclopentadienyl metal carbonyl complexes. Most of the interest has been in the identification, and the assignment, of the absorption bands due to the $\nu(MC.\alpha)$, $d(MCO.)$ and the $\pi$-cyclopentadienyl ring vibrations.

In general the carbonyl stretching frequency may be ascribed to the extent of $d-\pi^*$ overlap, between the metal and the carbonyl carbon atom, an increase in the overlap resulting in a decrease in $\nu_{C=O}$. The relationship, however, depends on the geometry, and the substitution of the molecule. Thus substitution of the carbonyl groups by the $\pi$-cyclopentadienyl ring tends to decrease $\nu_{C=O}$, but this will also depend on the magnitude of the $d-\pi^*$ overlap between the metal and the $\pi$-cyclopentadienyl ring; for example, $V(CO)_6$ (in hydrocarbons) $1975 \text{ cm}^{-1}$, but $\pi-C_5H_5V(CO)_4$ (in carbon-disulphide) $2019, 1912 \text{ cm}^{-1}$.

R.B. King has shown that for 78 different complexes of the first row transition metals, the relationship between the $\pi$-cyclopentadienyl proton magnetic resonance chemical shifts, and the carbon-oxygen force constants can be approximated by a straight line, by direct plotting. (See FIG. 49.)

This indicates that the increase in the value of $\tau(C_5H_5)$ may, like the decrease in the value of the $\nu_{C=O}$ frequency, be used as an indicator of increased negative charge on the metal atom, provided that it is realised that this is only approximate.
The first, rather naive approach was made by comparing the symmetrical and the asymmetrical carbonyl stretching frequencies with the electronegativity of the substituent X. (FIG. 50.) The reason for this was that the electronegativity of X determines the amount of electron density which is available on the metal for back donation into the vacant orbitals of the carbonyl and the cyclopentadienyl ring. This approach suffered from several serious disadvantages, for example, electronegativity is itself an uncertain quantity, since there are three different values, determined by Pauling, Allred-Rockow, and Mullikan. Further this method does not allow plotting of alkyl and allyl complexes. Extrapolation of the plot of Pauling's electronegativity value, against the carbonyl stretching frequencies, indicates that the unknown fluoride complex
Fig. 50.

Electronegativity.

- Carbonyl stretching frequencies.

- Cl, Br, I: Pauling's values.
- Δ: Mulliken's values.
\[ \pi-C_5H_5Fe(CO)_2F \] should have carbonyl stretching frequencies at 2100 (\(\pm\) 10.\) and 2050 (\(\pm\) 10.\) cm\(^{-1}\).

The second attempt to obtain a correlation was to plot the stretching frequencies against the Hammet inductive substituent constants, \(\sigma_I\). (FIG. 51.) A previous report \(^{201}\) claimed that a good correlation was obtained for this plot. However, when this relationship was plotted it was found that the equations

\[ V_{\text{asym}} = 94.8I + 1951 \quad \text{and} \quad V_{\text{sym}} = 76.2I + 2007 \]

obtained by Nesmeyanov did not give the correlation co-efficient of unity which was claimed. The critical factor in obtaining the correlation appears to be the solvent used for obtaining the spectra. Nesmeyanov obtained all his spectra in THF. (\(c = 5 \times 10^{-3}\) mole/litre.) whereas the values plotted, in this plot, were obtained in carbon tetrachloride and chloroform. It was found that these values gave better correlation by plotting against the Taft \(\sigma^{*}\) values. This had the added advantage that the values for many more alkyl and aryl complexes have been obtained.

From the plot of the inductive parameter \(\sigma_I\) the carbonyl stretching frequencies of the unknown fluoride, \(\pi-C_5H_5Fe(CO)_2F\) are predicted to be 2053 (\(\pm\) 5.) and 1999 (\(\pm\) 5.) cm\(^{-1}\), whereas from the plot of the Taft's \(\sigma^{*}\) function (FIG. 52\(^{2}\)) the frequencies are predicted as 2053 (\(\pm\) 5.) and 2012 (\(\pm\) 5.) cm\(^{-1}\).

A similar study was made for the carbonyl triphenylphosphine-\(\pi\)-cyclopentadienyliron system, in chloroform solution. (FIG. 53.) From this plot one can predict that the hydride, \(\pi-C_5H_5Fe(CO)P\_3H\_3\), should have a carbonyl stretching at 1920 cm\(^{-1}\). The unidentified complex, isolated in the n-propyl preparations, which was assumed to be the hydride, had this stretching frequency. The complex
Fig. 51.

Carbonyl stretching frequencies.

Taft $\sigma^T$

$\gamma_{\text{sym.}}$

$\gamma_{\text{asym.}}$

$\text{CN}$

$\text{Cl}$

$\text{Br}$

$I$

$\text{CH}_3$

$-0.4$

$0.4$

$0.8$
Carbonyl stretching frequencies.

Taft $\sigma^*$ values.
however, reacted rapidly with the solvent.

Studies of this kind, linked with NMR and other physical techniques, for a series of complexes, will enable quite accurate prediction of the properties of unknown complexes.
Fig. 53.

The graph shows a linear relationship between $\nu_{C=O}$ (frequency of $C=O$ bond) and the Taft $\sigma^*$ values. The data points for various substituents are indicated as follows:

- $\text{Br}$
- $\text{Cl}$
- $\text{CH}_3$
- $\text{C}_6\text{H}_5$

The graph plots $\nu_{C=O}$ on the vertical axis and Taft $\sigma^*$ on the horizontal axis, with the data points落在 a straight line, indicating a strong linear correlation.


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APPENDIX.
Organometallic chemistry of the Rare Earth Metals.

It has been shown how the interest in transition metal organometallic chemistry was stimulated in the 1950's, by the preparation of ferrocene by Pauson and Millar. Similar progress in the rare earth and actinide metal chemistry has only just started, although many bis, tris, or even tetra cyclopentadienyl metal complexes have been known for a few years.

The reaction of uranium tetrachloride with sodium cyclopentadienide, when mixed in the molar ratio of 1:2.8 was shown to give a complex which analysed for $\text{U(C}_5\text{H}_5)_3\text{Cl}$. The complex was found to be thermally stable up to $300^\circ \text{C.}$, melting at $260 - 265^\circ \text{C.}$ in vacuo; but very sensitive to oxidation, to the extent of enflaming. Unlike many other metal cyclopentadienyl complexes, tris(cyclopentadienyl)uraniumchloride, does not react with ferrous chloride to give ferrocene, which would tend to indicate some additional stabilising effect.

The reaction of potassium cyclopentadienide with uranium tetrachloride, at $40^\circ \text{C.}$ for twenty four hours, gave a low yield of $\text{U(C}_5\text{H}_5)_4$. A similar reaction was observed when thorium tetrachloride was allowed to react with sodium cyclopentadienide, at room temperature for two days. The yield was 41 % of the tetra(cyclopentadienyl)thorium. Both complexes are very thermally stable, the thorium complex being sublimable at $250 - 290^\circ \text{C.}$, or $170 - 190^\circ \text{C.}$ under high vacuum.

Analogous complexes are known for the lanthanides, for example, the reaction of anhydrous ytterbium(III) chloride with sodium cyclopentadienide, in THF., was shown to give the tetrahydrofuranate, $\text{Yb(C}_5\text{H}_5)_3\text{C}_4\text{H}_8\text{O}$. This was easily converted
to the ammoniate, Yb(C₅H₅)₃·NH₃, and with anhydrous hydrogen chloride, to Yb(C₅H₅)₃Cl, which was reduced by sodium to bis-(cyclopentadienyl)ytterbium, Yb(C₅H₅)₂. Further studies showed that similar complexes could be obtained by treating a solution of ytterbium, in liquid ammonia, with cyclopentadiene. Bis(cyclopentadienyl)ytterbium is decomposed rapidly, on exposure to air, but is thermally quite stable, for instance, the emerald green product, Yb(C₅H₅)₂, obtained from the yellow tetrahydrofuranate, on pumping at high vacuum, can be sublimed at 360°C, under 10⁻³ mm. Hg. The violet-red THF solution of the bis-(cyclopentadienyl)ytterbium shows only one sharp peak, in the NMR. spectrum, due to the cyclopentadienyl ring, at 5.64 Ζ. This could indicate that the bonding between ytterbium and the cyclopentadienyl rings might be ionic.

In a free cyclopentadienyl group the five molecular π-orbitals are constructed from five 2px atomic orbitals, and are usually portrayed as shown in FIG. (i.)

\[ \Psi_0 \]
\[ \Psi_{+1} \]
\[ \Psi_{-1} \]
\[ \Psi_{-2} \]
\[ \Psi_{+2} \]

Fig. (i.)
Molecular Orbital diagram for Ferrocene.

Fig. (ii).
Calculation of the energy level diagram for ferrocene, showed that the molecular orbitals with symmetry $E_{1g}$ and $E_{1u}$ are all bonding, and hence the chief source of bonding in ferrocene, and other bis-cyclopentadienyl complexes. The $E_{1g}$ and $E_{1u}$ orbitals will bond with the $3d_{xz}$ and the $3d_{yz}$ orbitals, and the $4p_x$ and $4p_y$ orbitals of the iron atom respectively. (See FIG. (ii.))

An important feature of $E_{1g}$ and $E_{1u}$ orbitals is that they contain one nodal plane. The introduction of another nodal plane means that the only metal orbitals that could possibly have the correct symmetry are $f$ orbitals, and a possible ligand cyclo-octatetraene. This was first pointed out by Fischer. (See FIG. (iii.))

If a complex bis-π-cyclo-octatetraene-metal can be prepared it is necessary to share the 20 π-electrons, from the two cyclo-octatetraene dianion rings, and the two from the metal, with the vacant metal orbitals, in symmetry permitted combinations. In order of increasing energy the following (FIG.(iv.)(a.) and (b.)) orbital combinations can be envisaged.

If these combinations are populated in the normal way, that
Fig. (iv). (a).

Metal orbitals.

- 7s
- 7p_z
- 6d_{xz} or 6d_{yz}
- 5f_{xy} and 7p_x

Ligand orbitals.

- A_{1g}
- A_{2u}
- E_{1g}
- E_{1u}
Fig. (iv), (b).

Metal orbitals.

- $d_{x^2-y^2}$ or $d_{xy}$
- $f_{xyz}$
- $f_{z(x^2-y^2)}$
- $f_{x(x^2-3y^2)}$
- $f_{y(3z^2-y^2)}$

Ligand orbitals.

- $E_{2g}$
- $E_{2u}$
- $E_3$
is $A_{1g}(2)$, $A_{2u}(2)$, $E_{1g}(4)$, $E_{1u}(4)$, $E_{2g}(4)$, and $E_{2u}(4)$, there are two electrons still to be placed. These electrons could be placed in the alternative combinations of $A_{1g}$ or in combinations $E_3$. Use of the two $f$ orbitals of $E_3$ by putting one electron into each would give a paramagnetic complex.

Streitwieser \textsuperscript{210} prepared the first complex in this type of metalloocene, using $f$ orbitals. Treatment of uranium tetrachloride in THF, at $0^\circ$C, with a yellow solution of potassium cyclo-octatetraenide, prepared from cyclooctatetraene and potassium in dry oxygen-free THF at $-30^\circ$C, gave, after work up, with degassed water, green crystals of bis(cyclo-octatetraenyl)uranium, now called Uranocene. Interesting properties of uranocene are, it is quite stable to water, acetic acid, and sodium hydroxide; is sparingly soluble in organic solvents, for example, it can be recrystallised from benzene, and, provided that air is excluded, in which it enflames, it can then be sublimed at 180$^\circ$C. and at $3 \times 10^{-3}$mm. Hg. Its inflammability in air is similar to other uranium complexes, which rapidly give the oxides.

If uranocene is a true metalloocene sandwich complex then the symmetry should be $D_{8h}$ or $D_{8d}$, in analogy to ferrocene, which is $D_{5h}$. An X-ray crystallographic study proved this to be true.\textsuperscript{211}

Following the successful preparation of uranocene Streitwieser then prepared an analogous lanthanide complex \textsuperscript{212} from thorium tetrachloride. Thoracene proved to be air sensitive, its yellow crystals going rapidly brown on exposure to air, but not so explosively as uranocene. In other properties thoracene was shown to be the less stable of the two, decomposing on exposure to water, an on heating above 190$^\circ$C., although it was sublimable at 160$^\circ$C., and $10^{-2}$mm. Hg.

The NMR. spectra of the two metalloconenes was interesting.
Uranocene, as a green deuterochloroform solution, showed a small broad hump, at the position of free cyclo-octatetraene, indicating the possibility of paramagnetic species being present; this would fit with the orbital assignments, already discussed. However, on exposing the solution to air a rapid decolouration took place; the NMR spectrum then showed only one sharp signal, due to free cyclo-octatetraene, explainable by assuming that the oxygen had destroyed the paramagnetic species, which adds further support to the concept of f orbitals, as a paramagnetic species is obtained by placing one electron in each of the orbitals, $f_x(x^2-3y^2)$ and $f_y(3x^2-y^2)$. The spectrum of thoracene in dimethylsulphoxide showed a complex multiplet at 6.2 ppm., instead of the sharp singlet, expected for a D$_{8h}$ structure. On exposure to air a singlet appeared at 5.75 ppm., due to cyclooctatetraene, which, it is proposed, showed that the dimethylsulphoxide had destroyed the D$_{8h}$ symmetry of the complex.

Two other types of rare earth and lanthanide cyclooctatetraene complexes, have been reported since the preparation of uranocene. The synthesis of cyclooctatetraenyleuropium and cyclooctatetraenyl- ytterbium was carried out by the dropwise addition of cyclooctatetraene to europium or ytterbium metal, dissolved in liquid ammonia. Both complexes gave good analysis for a 1:1 complex, which was to be expected, from the stable +2 oxidation state of both the metals. Both of the complexes formed, were very sensitive to moisture, and especially to air, in which they both decomposed, with almost explosive violence.

The other class of complex reported was the monocyclooctatetraene lanthanide chlorides, which were formed, as an unexpected product, from the reaction of anhydrous lanthanide
trichlorides, with cyclooctatetraenyldianion and cyclonona-
tetraenyl anion, in dry tetrahydrofuran solution, at -20°C. The
other major product of the reaction was bis-\( \pi \)-cyclooctatetraene
lanthanide potassium salt. The chloride complexes were isolated
as the tetrahydrofuranates, \( \text{Ln(COT)\text{Cl}}_{2}\text{.THF} \), which rapidly
desolvated if heated above 60°C., to give complexes which would
not sublime. An X-Ray diffraction analysis showed the structure
of the cerium complex to be dimeric, with a planar cyclooctatetraene
ring associated with each cerium atom; the latter being
asymmetrically bridged by two chloride atoms.
Aims of this research.

Following the successful preparation of uranocene, it was thought that the lanthanides could provide an opportunity for similar complexes. The only feature of the lanthanide elements that was against this was the depth of the f orbitals, in the general core of the metal. To overcome this it was decided to attempt the preparation of bis-\(\pi\)-cyclooctatetraenylterbium, since if this complex were formed the niobium electron distribution would be obtained about the metal, and this rare gas configuration might cancel out any unfavourable interaction with the f orbitals.

The reasons for trying to make this complex were manifold. Firstly the complex would be the first lanthanide complex in which f orbitals participated in the bonding. This could impart interesting properties, for example, it might prove useful as a catalyst for olefin isomerisations, dimerisations, or epimerisations. Secondly the prospect of being able to prepare sandwich complexes of the lanthanides would enable a study to be made of the reactions of various ring systems, when they are involved in bonding to a rare earth or lanthanide metal. Comparison of these properties with cyclooctatetraene complexes of transition metals, would, perhaps, give interesting insights into the effect of f orbital bonding on the ligands. Following from this there opens up the possibility of performing simple organic chemistry on coordinated ligands, and then removing the substituted ligand by oxidation with oxygen or ceric ion.
Experimental.

Reaction of cyclooctatetraene with ytterbium, in liquid ammonia.

2 : 1 Molar ratio.

All the liquid ammonia was freshly distilled from sodium metal before use.

To freshly distilled liquid ammonia (20 ml.) was added cyclooctatetraene (416 mg. 4 mmole.) in anhydrous ether (1 ml.). To this stirred suspension, at \(-35^\circ C\), was added ytterbium metal (346 mg. 2 mmole.), giving a vigorous exothermic reaction, which was allowed to subside, and return to \(-35^\circ C\), the ammonia just gently refluxing in a carbon dioxide - acetone condenser. A blue material was deposited on the sides of the vessel, just above the solvent level. Anhydrous ether (20 ml.) was added to the reaction mixture, and the ammonia allowed to evaporate. This left a blue suspension, which was washed with more anhydrous ether, (3 x 20 ml.) to remove any excess cyclooctatetraene.

The blue complex was very unstable to air, giving a mixture of white, yellow and brown decomposition products, which presumably were ytterbium oxides, and ammonia complexes. It was completely insoluble in ether and benzene, slightly soluble in pyridine and ammonia, and very soluble in hexamethylphosphoramide. Infra-red (nujol): 1590(w.), 1299(m.), 900(s.), 742(s.), 720(w.), 693(s.), 613(w.). Ultraviolet (in EMFA.) \(\lambda\) 648 m\(\mu\) \(\epsilon\) 500; 624 m\(\mu\) \(\epsilon\) 500; 612 m\(\mu\) \(\epsilon\) 500; 588 m\(\mu\) \(\epsilon\) 600.

All attempts to sublime the material failed, even at 10\(^{-3}\) mm.Hg, and 30\(^{\circ}\)C., a waxy white solid sublimed, leaving a white inorganic residue.

When the experiment was carried out with the reverse addition, that is when cyclooctatetraene was added to a solution of ytterbium in liquid ammonia, the initial blue solution gave immediately
a greenish brown precipitate, which on addition of ether, and removal of ammonia, gave a light royal blue solid. There were no signs of either the "orange" complex, in ammonia, or the pinkish mauve solid obtained in the 1 : 1 reaction, on addition of ether.

1 : 1 Molar ratio.

Ytterbium metal (0.060 g, 0.35 mmole.) was dissolved in distilled ammonia (10 ml.) under nitrogen, to give a weak royal blue solution. To this was added cyclooctatetraene (0.0359 g, 0.35 mmole.) in ether (0.5 ml.). There was an immediate colour change from blue to yellow-brown. After a few minutes traces of blue material, similar to that seen in the 2 : 1 molar ratio experiments, were observed on the sides of the flask, just above the solvent level. The main bulk of the mixture, however, stayed yellow, and gradually turned to an orange suspension, over the period of one hour. Addition of anhydrous ether (15 ml.) and the removal of the ammonia, by evaporation, gave a pink-mauve solid, which was washed with more ether (3 x 20 ml.) to remove any excess cyclooctatetraene. Finally the ether was removed, giving a pale pink solid, which slowly turned to a cream solid, over a period of forty five minutes.

The complex was insoluble in ether and benzene, but readily soluble in dry degassed dimethylformamide, to give a deep blue solution which, although under a good atmosphere of nitrogen, decomposed in five minutes to a green solution. With pyridine a similar green solution was obtained, together with a black and a white solid. The black solid had a definite crystalline form, as seen under the microscope, unlike the white solid. Both these results may be due to minute traces of air, although all the manipulations were carried out in a good dry box, using degassed solvents.

This experiment was also performed by adding ytterbium to cyclooctatetraene in liquid ammonia.
Cyclooctatetraene (0.0694g. 0.68 mmole.) in dry ether (0.5 ml.) was added to freshly distilled liquid ammonia (20 ml.) to give a yellow suspension of cyclooctatetraene. Addition of ytterbium (0.1159g. 0.68 mmole.) to the stirred suspension, at -35°C, gave an immediate yellow-brown suspension. This changed over a period of an hour and a half to a bright orange suspension. Only a very little blue complex was observed. Addition of anhydrous ether (20 ml.) gave a bright pink solid.

Analysis Procedures 215, 216

Analysis of the blue complex from the 2 : 1 Molar experiments.

The blue complex was washed with anhydrous ether (3 x 20 ml.) to remove any organic impurities. Final traces of the ether were removed slowly by passing a very slow jet of nitrogen over the complex, in the dry box. A very pale blue solid was obtained, which was accurately weighed and then hydrolysed by the addition of distilled water (1 ml.) to give a clear supernatant and a grey precipitate, which was then oxidised with 72 % perchloric acid (1 ml.) yielding a slightly yellow viscous liquid. This was shaken for five minutes and then heated in a bath at 80°C, for a further five minutes. An almost saturated solution of oxalic acid was also heated to 80°C, and 1 ml. of this solution added to the oxidised ytterbium complex, giving an immediate white intense precipitate. This was allowed to settle, tested for completeness of precipitation, and then left over night. The ytterbium oxalate was removed to a weighed preheated boat and fired at 900°C, in a muffled furnace, to give the oxide, Yb2O3. The oxide was allowed to cool and then weighed.

By this procedure it was shown that the percentage of ytterbium in the blue complex was 45.3 %.
Analysis Results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Percentage of Ytterbium</th>
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<tbody>
<tr>
<td>Blue crystals from Yb + COT in liquid ammonia.</td>
<td>45.3 (± 2.) %</td>
</tr>
<tr>
<td>Blue crystals from YbI₃ and lithium cyclooctatetraenide</td>
<td>45.7 (± 2.) %</td>
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<tr>
<td>Pink crystals from Yb + COT in liquid ammonia.</td>
<td>63.1 (± 2.) %</td>
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Analysis of the blue complex for ammonia.

The blue ytterbium complex (0.142 g.) was placed in a tared Kjeldahl flask, fitted with a micro splash head, which was attached to a small Liebig condenser. The complex was hydrolysed with distilled water (15 ml.) to give a yellow solid, and slightly yellow supernatant. A solution of caustic soda was prepared by dissolving sodium hydroxide (6 g.) in water (15 ml.). The solution was cooled to room temperature and added via a syringe and septum cap to the hydrolysed ytterbium complex. The gases evolved were passed through standard hydrochloric acid (20 ml. of 0.1 N.) solution. The Kjeldahl flask was warmed, slowly at first, and then more vigorously, to keep a steady stream of bubbles passing through the acid until the volume in the Kjeldahl flask was reduced to one third of its original volume.

The contents of the receiving flask were rapidly titrated against standard sodium hydroxide solution (0.1 N.) using a few drops of bromocresol green as indicator. This indicator was used as
it had an acid transition interval. Indicators with neutral or basic end points not being suitable, because of the presence of ammonium salts.

This procedure was repeated several times, but there was never any evidence for the presence of ammonia.

Preparation of Lithium Cyclooctatetraenide.

Lithium (2.0 g, 0.285 g. atom.) was added, in small pieces, to THF., (200 ml.), which had been freshly distilled from lithium aluminium hydride. Cyclooctatetraene (14 g, 0.135 mmole.) was added, under nitrogen, at -78°C., and the mixture stirred vigorously for four hours. The cherry red mixture was allowed to reach 0°C., very slowly, and then stirred at this temperature for twenty four hours, and then finally stirred at room temperature, for twenty four hours. The dark green solution obtained was stored at -20°C.

Reaction of Lithium cyclooctatetraenide, with ytterbium iodide.

A.) Ytterbium metal (76 mg, 0.44 mmole.) and iodine (248 mg, 0.98 mmole.) were mixed under nitrogen in dry THF. (0.5 ml.). The mixture was warmed slightly at first, and then, on shaking, a dark chocolate coloured suspension was formed, this slowly changed to a pale brown-buff colour. Lithium cyclooctatetraenide was titrated into the suspension under nitrogen, until a permanent blue colour was obtained. The now clear blue solution deposited pink crystals, on standing.

Addition of cyclooctatetraene (60 μl. 0.8 mmole.) to the mixture resulted in the pink crystals turning slowly blue. The transformation could be studied under the microscope, where it was possible to see the two different crystal shapes, and their
interconversion.

E. Ytterbium metal (31 mg. 0·18 mmole.) and iodine (63 mg. 0·25 mmole.) were shaken together in freshly distilled THF, (0·5 ml.) to give the same pale brown-buff coloured suspension as reported above. Cyclooctatetraene (30 μl. 0·4 mmole.) was added. No visible colour change, or other reaction, was noted. However, addition of lithium cyclooctatetraenide (2 ml. 0·4 mole.) produced a blue solution. Cooling to – 10°C. produced blue crystals, similar in form to those observed in experiment (A.). Analysis, by the same techniques as detailed above, showed the percentage of ytterbium to be 45·7(±2.)%.

Reactions of Ytterbium Complexes.

(A.) Reaction of the blue Yb(COT)ₙ with butadiene.

A stirred solution of the blue bis(cyclooctatetraenyl)-ytterbium (107·1 mg.), in freshly distilled dry ether, was kept under nitrogen, whilst butadiene was blown slowly through the suspension. For the first three or four minutes there was no visible change, even in the royal blue solid. However after about seven minutes there was a darkening of the royal blue solid, to a very dark sea-green. The ether never became coloured. On standing, under nitrogen, for fifteen minutes the solid turned slowly yellow, and the supernatant also became yellow. The ethereal layer was removed, and the buff solid washed with anhydrous ether (3 x 2 ml.). The ether fractions were combined, and concentrated to a yellow oil. This mixture was investigated by gas-liquid chromatography, on a 6 foot 20 % LAC. column.

These chromatograms showed the presence of six "peaks", one of which accounted for more than 95 % of the product. This peak was reinforced by adding cyclooctatetraene, to the reaction mixture.
However, the NMR. and ultra-violet spectra of the reaction product showed the presence of only traces of cyclooctatetraene. Ultra-violet (in ether) for cyclooctatetraene $\lambda$ 285 $\mu \varepsilon$ 3000. Ultra-violet (in ether.) for "Unknown" $\lambda$ 215 $\mu \varepsilon$ 1000; $\lambda$ 262 $\mu \varepsilon$ 3900. From these figures, and the NMR. data (4.29 (s.)(6H.) and 7.58(m.) (4H.), the presence of cyclooctatriene was shown. The other five "peaks" were present in very small amounts, and were not identified.

The buff solid obtained in the reaction was washed with ether (3 x 2 ml.) and then treated with an ethereal solution of anhydrous ferric chloride. On shaking, a dark yellow-brown precipitate was obtained. The supernatant ether was shown, by gas-liquid chromatography, to contain no organic material. Acidification of the precipitate, with 1N hydrochloric acid, gave two layers - the lower aqueous layer was a burnt orange colour, and slightly oily in appearance, whilst the ethereal layer was pale yellow. The latter was separated from the aqueous layer, which was washed with ether (2 x 1 ml.). The combined ether extracts were dried over magnesium sulphate. Careful removal of the ether yielded a yellow oily material. Gas-liquid chromatography, and the ultra-violet spectrum, showed the only compound present to be cyclooctatetraene. Ultra-violet (in cyclohexane) $\lambda$ 283 $\mu \varepsilon$ 3000

(B.) Reaction of Yb(COT)$_2$ with triphenylphosphine.

Triphenylphosphine (100 mg.) was dissolved in anhydrous ether (3 ml.) and the blue Yb(COT)$_2$ (50 mg.) added. On shaking the mixture for a few minutes the blue colour gave way to a deep greenish-blue colour, which on standing slowly turned orange. The supernatant ether was decanted, evaporated to dryness, and this yielded a white solid - triphenylphosphine - and an oily yellow material. The mixture was extracted with n-pentane (2 x 1 ml.) to remove the oil. Gas-liquid
chromatography, and the ultra-violet spectrum (in cyclohexane.) $263\, \mu\varepsilon = 3800$; $220\, \mu\varepsilon = 1000$, showed this to be cyclooctatriene.

**Discussion of Results.**

The blue complex formed, on mixing two molecules of cyclo-
octatetraene with one of ytterbium, in ammonia, has been shown to be
different, in properties, from the mono complex, Yb(COT), prepared
by Hayes. Furthermore the analysis agrees approximately with the
formulation of a complex Yb(COT)$_2$. The analysis, however, is not accurate
enough to rule out the possibility of the presence of a molecule of
coordinated solvent, such as ammonia, ether or THF. Analysis for
ammonia, in the blue sample, proved negative, but this was not
conclusive, due to the small amount of ammonia that would have been
expected, in the very small samples used.

Analysis for carbon and hydrogen could not be obtained, due to
the very unstable nature of the complex. Attempts to sublime the blue
complex gave decomposition. In fact pumping the blue complex, under
high vacuum, for a short time gave a rapid colour change, from blue to
white. At present work is being undertaken to obtain the X-Ray
structure of the complex, this is proving very difficult, as the blue
crystals go white very rapidly, on exposure to slightly oxygen-
contaminated nitrogen. Preliminary studies tend to indicate that, on
the colour change, from blue to white, the material becomes less
crystalline in nature. The white material has yet to be investigated,
to see whether any information can be obtained, that can be
extrapolated back, to give further information on the blue complex.

Due to the very unstable nature of the blue complex, obtaining
physical data proved very difficult, and generally unsuccessful. A
paramagnetic solution was obtained in hexamethylformamide, so that
no NMR. spectrum could be obtained. In the ultra-violet spectrum it was possible to follow the decay of some signals, at 590 m\(\mu\) and 640 m\(\mu\) as the decomposition took place. (FIG.(v.)).

Since not much useful information could be obtained from physical techniques, reactions were carried out on the complex, in the hope of understanding the complex more, by revealing some of its chemistry.

The reaction of butadiene with the blue complex, assumed to be Yb(COT)\(_2\), was shown, by gas-liquid chromatography, to form a C\(_8\) compound, shown by its ultra-violet spectrum, to be cyclooctatriene. This was completely unexpected. Cyclooctatetraene, from the ytterbium complex, or 1,5-cyclooctadiene, 4-vinylcyclohexene, or divinylcyclobutane, from the dimerisation of butadiene could have been expected. The reaction was repeated several times, always ensuring that no ammonia, or other impurity was present, but the same result was always achieved. The buff coloured solid, obtained from the same reaction, was shown to yield only cyclooctatetraene, on treatment with ferric chloride and acid.

These results, taken with the observation that the attempted removal of the ligands, from the blue ytterbium complex, with triphenylphosphine, gave cyclooctatriene, made one wonder whether cyclooctatetraene was in fact attached to the ytterbium! In the ammonia preparation route, it could be envisaged that reduction by the ammonia could take place.

Work at this point was suspended, until such time as a good X-Ray crystallographic study could be made. Decomposition, however, continues to make this very difficult.
Fig (v.) Changes in the Ultraviolet spectrum of Yb(COT)$_n$ (blue) in HMPA.