LASER INDUCED PYROLYSIS OF TRANSITION METAL ORGANOMETALLIC COMPLEXES

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

by
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Abstract

Pyrolysis mechanisms of a number of transition metal organometallic compounds of iron, manganese, cobalt, and chromium have been studied by employing carbon dioxide infrared laser powered homogeneous pyrolysis (CO$_2$ IR LPHP). This was coupled with a variety of analytical techniques, particularly NMR and IR spectroscopies and gas chromatography, to identify reaction products.

The pyrolysis of butadiene iron tricarbonyl, BdFeTC, produced a wide range of organic reaction products, especially butadiene, cis- and trans- butene-2, ethyne, benzene, and polymers of butadiene. The formation of benzene was thought to be due to trimerisation of ethyne.

The laser pyrolysis of CH$_3$Mn(CO)$_5$ and CH$_3$COMn(CO)$_5$ yielded methane and carbon monoxide as observed pyrolysis products. In the case of CH$_3$COMn(CO)$_5$, the reaction takes place in two steps, beginning with the loss of one CO group to form methyl manganese pentacarbonyl which is found to be a reversible reaction. Both CH$_3$Mn(CO)$_5$ and CH$_3$COMn(CO)$_5$ afforded trimethyl silane manganese pentacarbonyl and methane as reaction products when co-pyrolysed with trimethyl silane.

The pyrolyses of C$_5$H$_7$Mn(CO)$_3$, and CH$_3$C$_5$H$_4$Mn(CO)$_3$ were investigated and were found to begin with the successive loss of CO followed by the homolytic breakage of the C$_5$H$_7$-Mn or CH$_3$C$_5$H$_4$-Mn bond. The observed reaction products of C$_5$H$_7$C$_5$H$_4$Mn(CO)$_3$ were cyclopentadiene, benzene, ethyne and methylcyclopentadiene. The source of benzene was thought to be the isomerisation of the methyl cyclopentadiene radical. In the case of LPHP of C$_5$H$_7$Mn(CO)$_3$, detected organic reaction products were cyclopentadiene and ethyne.

Metalloocene compounds of iron, cobalt and chromium investigated by the same technique yielded cyclopentadiene, ethyne, benzene and naphthalene (except naphthalene was not observed in the pyrolysis of chromocene). The mechanism of formation of ethyne and benzene is similar to cyclopentadiene manganese tricarbonyl compounds but the occurrence of naphthalene is thought to be due to the dimerisation of cyclopentadiene and cyclopentadienyl radical while both are coordinated to the metal atom to yield a dicyclopentadienyl radical, followed by isomerisation to azulene radical then on to form naphthalene radical and finally naphthalene.
Dedicated to Naciye and Neslihan Hazel.
Acknowledgements

My special thanks must go to my supervisors Prof. D. K. Russell and Dr A. M. Ellis, for their help, encouragement, guidance and supervision throughout this work. It is not possible to express in words my gratitude to them who have spent invaluable time for many discussions, reading and giving comments during the course of this work.

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Last but not least, I would also like to thank the Firat Universitesi for giving me this opportunity to come to England and enabling me to complete this work, without which it would not have been possible to undertake such a long course in England.
Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester, between April 1991 and September 1995. The work has not been submitted for any other degree at this or any other university.

Signed: [Signature]

Date: 9.10.1995
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<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcMnPC</td>
<td>Acetyl manganese pentacarbonyl</td>
</tr>
<tr>
<td>BdFeTC</td>
<td>Butadiene iron tricarbonyl</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadiene</td>
</tr>
<tr>
<td>CpMnTC</td>
<td>Cyclopentadienyl manganese tricarbonyl</td>
</tr>
<tr>
<td>DAcMnPC</td>
<td>d$_3$-Acetyl manganese pentacarbonyl</td>
</tr>
<tr>
<td>DMeMnPC</td>
<td>d$_3$-Methyl manganese pentacarbonyl</td>
</tr>
<tr>
<td>FPC</td>
<td>Iron pentacarbonyl</td>
</tr>
<tr>
<td>FT IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FT IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>IR LHPH</td>
<td>Infrared laser powered homogeneous pyrolysis</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MeCpMnTC</td>
<td>Methylcyclopentadienyl manganese tricarbonyl</td>
</tr>
<tr>
<td>MeMnPC</td>
<td>Methyl manganese pentacarbonyl</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapour deposition</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal organic vapour phase epitaxy</td>
</tr>
<tr>
<td>R</td>
<td>Radical</td>
</tr>
<tr>
<td>SFR</td>
<td>Stirred flow reactor</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethyl silane</td>
</tr>
<tr>
<td>TMSMnPC</td>
<td>Trimethyl silane manganese pentacarbonyl</td>
</tr>
</tbody>
</table>

XIV
Chapter 1

Introduction
Chapter 1

The nature of light and materials has always been a subject of interest to human beings. In early stages of science or magic, light was considered as one of the elements of the universe. Newton, in his pioneering work in the 17th century, used a glass prism to separate white light into its coloured components, i.e. its spectrum. Later in 1860, Bunsen and Kirchhoff developed a prism spectroscope which proved to be highly useful for analytical purposes. During the 20th century, the relationships between light and chemistry have been worked out in great detail, and most of the fundamentals of spectroscopic techniques were discovered during this period.¹

One of the key technological developments involving light in this century has been the invention of the laser. The first laser, namely the ammonia maser, was made in the microwave region by Schawlow et al. in 1958². The next major step was the ruby³ laser operating in the visible region of the spectrum, which was demonstrated in 1960 by Maiman. Polanyi⁴ proposed the names iraser and maser for lasers which emit light in the infrared and microwave regions of the electromagnetic spectrum respectively, and laser for those in the visible region of the electromagnetic spectrum. Iraser and maser vanished in time leaving the popular acronym laser referring to Light Amplification by the Stimulated Emission of Radiation. Subsequently, an array of solid, liquid and gas lasers have been developed for operation across the UV, IR, and visible spectral regions. Many applications have resulted from the discovery of lasers in both fundamental scientific research and in technical applications such as cutting and welding, cosmetic surgery, CD player operation, laser printers and so on.

From 1960 onwards, the increasing availability of intense monochromatic laser sources provided a tremendous momentum for a wide range of spectroscopic investigations. The most immediately obvious application of early lasers was to Raman spectroscopy in the gas, liquid, or solid phase.⁵ Laser radiation is very much more intense than that from, for example, a mercury arc which was commonly used as
a Raman source before 1960. As a result of the greater source intensity, much weaker Raman scattering can now be observed.

With the use of lasers as light sources, we can no longer think in terms of generally applicable experimental methods. A wide variety of ingenious techniques have been devised using laser sources and it would be impossible and inappropriate to describe all of them here but, nevertheless a few applications of lasers to chemistry and organometallic compounds is described in brief here.

Lasers are ideal for the controlled initiation of reactions, and allow high sensitivity for detection of transient intermediates and stable products that can be selective in both space and time. Bauer\(^6\) reviewed the potential of laser applications in the chemical industry by considering material costs, levels of throughput and competition from conventional sources of radiation. Use of lasers for chemical processing has been suggested in the following areas:

* For destruction of specific impurities. (COCl\(_2\) in BCl\(_3\); PH\(_3\), AsH\(_3\), B\(_2\)H\(_6\) in SiH\(_4\))
* For initiation of chain reactions. (Synthesis of vinyl chloride; of oximes)
* Where conventional processes are extremely energy intensive. (Separation of \(^{235}\)U/\(^{238}\)U; T or D/H; undesirable isotopes of Zr or Li)
* Photoactivation of pre-catalyst, and augmented absorption/desorption cycles. (Photo isomerisation of alkenes in the presence of transition metal carbonyls)
* To induce isomerisations, to generate thermodynamically less favoured isomers or stereospecific isomers.
* Enhance isotopic labels in bio-organics by destruction of the more common species, to avoid complex synthetic routes.
* In general -where preparative costs are secondary- where there is a requirement for small quantities of a specific products (Stereospecific insertions, synthesis of isotopically labelled chemicals).

The first CO\(_2\) IR laser application to chemistry was to separate isotopes, the first demonstration being made by Mayer et al.\(^7\) In 1974 Letokhov and co-workers reported the separation of \(^{11}\)B and \(^{10}\)B by exposing a mixture of BCl\(_3\) and D\(_2\)S to a
Chapter 1

pulsed CO₂ laser. A large number of halogenated molecules, mostly methanes, have been subjected to isotope-selective infrared multiphoton dissociation. Parthasarathy et al.⁹ have examined ¹³C enrichment by IR laser chemistry of CF₃Br/Cl₂ mixtures and neat CF₂HCl. Pola et al.¹⁰ have demonstrated the successful removal of hydrogen-containing organic impurities from germanium tetrachloride via CW CO₂ laser-powered homogeneous and selective pyrolysis of organic impurities into gaseous compounds that are easily separable from germanium chloride. It has also found use in removing unwanted species from materials. Begley¹¹ demonstrated desulfurisation and gasification of coal by high power CW or pulsed lasers.

Lasers offer the potential for preparation of unique quantities of reactants, with unique spatial and temporal properties. Because reasonably high vapour pressure can be obtained with organometallics, laser pyrolysis can be used to produce large gas phase quantities of highly refractory metals.¹²

The interaction of lasers and gas-phase organometallics have been reviewed by Chaiken.¹³ Lasers offer specific advantages for the synthesis of particle and cluster-based materials, such as fine powders to be used in solar-energy collectors and high surface area powders¹⁴,¹⁵ like carbides, nitrides, oxycarbides, and sulphides. Laser pyrolysis of transition metal (Cr, Mo, W, Mn, Fe, Co) carbonyls and substituted carbonyls have yielded high surface area powders of the metals.¹²

Films of different types are having an increasing impact on technological progress. These films may have various properties, functions and applications. Electrically, they may be superconductors, conductors, semiconductors, insulators, dielectrics or ferroelectrics. The importance of thin films is illustrated by their applications in microelectronics. Depending on the film material and its applications different deposition methods have been employed.
Since the pioneering growth work of Manasevit,\textsuperscript{16,17,18} the manufacture of semiconductors has been widely studied. The most important techniques available for the growth of these materials are \textit{liquid phase epitaxy} (LPE), \textit{molecular beam epitaxy} (MBE), \textit{metal organic vapour phase epitaxy} (MOVPE), \textit{chloride/hydride vapour-phase epitaxy} (CHVPE), \textit{photo-chemical vapour deposition} (Photo-CVD), \textit{metal organic chemical vapour deposition} (MOCVD), and \textit{laser-induced chemical vapour deposition} (LCVD). In-depth descriptions of each of these methods can be found in a number of books, including \textit{Semiconductor Devices; Physics and Technology}, by S. M. Sze.\textsuperscript{19} However the attributes of each one will be briefly discussed in this chapter.

LPE is a technique used for the deposition of epitaxial layers from supersaturated solutions. Only very simple apparatus is required to produce layers of high purity semiconductors, but the thickness uniformity of the layers is often poor in quality and there is difficulty involved in the growth of alloys containing both Al and In.

In the MBE technique, elemental sources are evaporated at a controlled rate onto a heated substrate under ultra-high vacuum conditions. The advantages of this method are that alloys with abrupt interfaces can be produced, and the growth process can be monitored as the crystal is built up one atomic layer at a time. Unfortunately, this technique is not commercially viable; it is expensive in terms of both the initial outlay and the operating costs.

In MOCVD reactors, precursors such as alkylmetals are seeded in a carrier gas (usually hydrogen or helium) and flowed over a heated substrate. Chemical breakdown is observed at high enough temperatures, resulting in metal deposition on the substrate. The principal gaseous products observed in the reactor exhaust are mainly methane and ethane. Previous investigations of MOCVD processes have focused mainly on gas transport, adduct formation, and reactions occurring in the
boundary layer above the substrate, but the actual gas phase and surface mechanisms are in most cases poorly understood.20

By far the most important and versatile technique is MOVPE. It has great advantages over the other epitaxial methods, since high purity and abrupt interfaces can be produced. The MOVPE process is highly suitable for large scale industrial production, but several problems still remain in that the reagents needed are often expensive and hazardous, coupled with the fact that there are a large number of parameters which have to be precisely controlled to ensure the required standards.

Although photo-chemical vapour deposition (Photo-CVD) is capable of producing various kinds of films at low temperatures via photolytic reactions of source gases, the quality of these films is not as good as those produced by high-temperature processes.21 In the case of metals, the electrical resistivity of photodeposited films often becomes much higher than that of the bulk, and as a result it can happen that their applications are severely limited.22 Photodeposited films are often contaminated with carbon impurities, and the electrical conductivity is normally poor; however, good results can be obtained with the use of lasers.22

Laser-induced chemical vapour deposition (LCVD) permits the single-step production of microstructures and fabrication of their extended films. An overview of the various possibilities of this technique, on the different systems investigated, and on the experimental arrangements employed is given by Bauerle.23 The metal precursor molecules most frequently employed in LCVD are halogen compounds, hydrides, alkyls, carbonyls and various organometallic coordination complexes. For the application of LCVD in micro-patterning, the proper selection of precursor molecules is of particular importance. Halides and hydrides require, in general, higher temperatures than organometallic compounds; however, utilisation of organic-based precursors is often linked with the incorporation of large amounts of impurities into
the deposit, in particular carbon. Such impurities alter the physical and chemical properties of the deposited materials and usually have undesirable effects. In LCVD it is assumed that the laser light is exclusively absorbed by molecules on the surface of the substrate or by the already deposited material. The laser-induced temperature rise on this surface also heats the adjacent gas phase. Thus, laser radiation can photothermally activate the reaction.\textsuperscript{12}

There are two kind of laser deposition, i.e. light-induced pyro-deposition and photo-deposition. In the case of light-induced pyro-deposition,\textsuperscript{24,25} the laser beam is focused to heat a local spot on a solid surface up to a high temperature, on which the colliding organic metal molecules are heated to dissociate into metal atoms. Because the high temperature can improve the diffusion of doping atoms into the crystal to form the P-N junction, light-induced pyro-deposition suits localised doping. A number of high energy lasers, e.g. CO\textsubscript{2}, YAG and argon ion lasers, can be used for this purpose. In the case of photo-deposition\textsuperscript{26} a short wavelength laser, e.g. an excimer laser or a frequency doubled argon ion laser can be used. The UV light is focused in front of the solid surface where the precursor molecules are excited into excited electronic states through absorbing one or more UV photons. The molecules then dissociate into metal atoms and other fragments through internal energy transfer, as long as the exciting energy is larger than the appropriate bond energies of the molecules. The metal atoms diffuse to deposit on the solid surface nearby. During the process of photo-deposition there is little heat generated, thus aiding the growth of good quality films with minimal stress.\textsuperscript{27}

Future advances in the semiconductor industry now rest heavily upon precursor molecule design rather than the experimental conditions employed. Recently there has been a shift in emphasis towards achieving a fundamental understanding of the precise mechanisms of the growth process. A wide range of techniques that include mass spectrometry of the reaction products, spectroscopic techniques to detect unstable
Chapter 1

intermediates, radical trapping, isotopic labelling and kinetic studies have been applied in an attempt to clarify the contributions of various components, e.g. homogeneous versus heterogeneous, intramolecular versus radical processes, initiation by metal alkyl or Group V precursor, etc.

The technique of Infrared Laser Powered Homogeneous Pyrolysis (IR LPHP) has been shown by Atiya\textsuperscript{28} to be well-suited for studying the thermal decomposition of organometallic compounds under strictly homogeneous conditions. It has been applied to a number of main group organometallics.\textsuperscript{29,30} Homogeneous chemistry is enforced by using localised laser heating of a gas sample cell. Products from this process are ejected into cold regions of the cell and can therefore be subjected to a variety of standard analytical techniques, such as IR and NMR spectroscopies and gas chromatography. By observing the products formed, a considerable amount of information on the mechanisms of purely gas phase processes can be deduced. In this work, IR LPHP has been applied to transition metal organometallic compounds with the aim of isolating and characterising primary pyrolysis products. Building on the previous studies of main group organometallic compounds, this work extends IR LPHP to the study of homogeneous thermal decomposition of transition metal organometallics. There have been no previous studies of transition metal organometallic compounds by IR LPHP. As will be shown, these studies provide an interesting insight into the mechanistic chemistry of the compounds chosen for investigation. In addition, some of the compounds have uses or potential uses as precursors in transition metal deposition in semiconductor films and other devices.

Chapter 2 provides an outline of the experimental methodology of IR LPHP and the specific techniques used in this work. An LPHP study of butadiene iron tricarbonyl and co-pyrolysis of butadiene with iron pentacarbonyl is then presented in Chapter 3, followed in Chapter 4 by a study of acetyl manganese pentacarbonyl and methyl manganese pentacarbonyl both on their own and with trimethyl silane. Chapter 5 deals
Chapter 1

with cyclopentadiene and methyl cyclopentadiene manganese tricarbonyl pyrolysis reactions, while a similar study is presented in Chapter 6 for the pyrolysis of ferrocene, chromocene and cobaltocene. Overall conclusions drawn from all the above studies are provided in Chapter 7.
REFERENCES

Chapter 1


Chapter 2

Experimental
Chapter 2

2.1 Introduction

In this chapter the chemical reagents, the experimental techniques and the equipment used for all the experiments will be described. The majority of the equipment for the IR LPHP was originally designed by Atiya, with some recent modifications being made, especially to allow synthesis and pre-pyrolysis preparations.

2.2 Chemicals

In Table 2.1 the sources of chemical reagents used are listed while Table 2.2 summarises the organometallic compounds used for the experiments including those which were synthesised in house. Acronyms for the organometallics are also given as the compounds will often be abbreviated in this form in the text.

Table 2.1 List of chemical reagents used.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Formula</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde-d$_3$</td>
<td>CD$_2$CHO</td>
<td>Aldrich</td>
</tr>
<tr>
<td>d$_6$ Toluene</td>
<td>C$_6$H$_5$CD$_6$</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dicyclopentadiene</td>
<td>(C$_5$H$_5$)$_2$</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Calcium Hydride</td>
<td>CaH$_2$</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Acetyl Acrylate</td>
<td>(CH$_3$CHO)$_2$O</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Sulphur Hexafluoride</td>
<td>SF$_6$</td>
<td>BOC Ltd.</td>
</tr>
<tr>
<td>Trimethyl Silane</td>
<td>(CH$_3$)$_3$SiH</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>C$_2$H$_5$OC$_2$H$_5$</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>C$_9$H$_8$O</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CCl$_2$H$_2$</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
### Table 2.2 List of organometallic compounds used.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula</th>
<th>Acronym</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimanganese decacarbonyl</td>
<td>Mn$<em>2$(CO)$</em>{10}$</td>
<td>—</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dicyclopentadiene iron</td>
<td>Fe$_2$(C$_5$H$_5$)$_2$</td>
<td>Ferrocene</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dicyclopentadiene chromium</td>
<td>Cr$_2$(C$_5$H$_5$)$_2$</td>
<td>Chromocene</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dicyclopentadiene cobalt</td>
<td>Co$_2$(C$_5$H$_5$)$_2$</td>
<td>Cobaltocene</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dicobalt octacarbonyl</td>
<td>Co$_2$(CO)$_8$</td>
<td>—</td>
<td>Strem Chemical</td>
</tr>
<tr>
<td>Iron pentacarbonyl</td>
<td>Fe(CO)$_5$</td>
<td>FPC</td>
<td>Strem Chemical</td>
</tr>
<tr>
<td>Acetyl manganese pentacarbonyl</td>
<td>CH$_3$COMn(CO)$_3$</td>
<td>AcMnPC</td>
<td>Synthesised</td>
</tr>
<tr>
<td>Methyl manganese pentacarbonyl</td>
<td>CH$_3$Mn(CO)$_3$</td>
<td>MeMnPC</td>
<td>Synthesised</td>
</tr>
<tr>
<td>D$_5$-Acetyl manganese pentacarbonyl</td>
<td>CD$_5$COMn(CO)$_3$</td>
<td>DAcMnPC</td>
<td>Synthesised</td>
</tr>
<tr>
<td>D$_5$-Methyl manganese pentacarbonyl</td>
<td>CD$_5$Mn(CO)$_3$</td>
<td>DMeMnPC</td>
<td>Synthesised</td>
</tr>
<tr>
<td>n$_5$-Butadiene iron tricarbonyl</td>
<td>C$_4$H$_6$Fe(CO)$_3$</td>
<td>BdFeTC</td>
<td>Strem Chemical</td>
</tr>
<tr>
<td>n$_5$-Cyclopentadienyl manganese tricarbonyl</td>
<td>CD$_5$Mn(CO)$_3$</td>
<td>CpMnTC</td>
<td>Strem Chemical</td>
</tr>
<tr>
<td>n$_5$-Methylcyclopentadienyl manganese tricarbonyl</td>
<td>CH$_3$C$_5$H$_4$Mn(CO)$_3$</td>
<td>MeCpMnTC</td>
<td>Strem Chemical</td>
</tr>
</tbody>
</table>

#### 2.3 Vacuum lines

In general, organometallic compounds used in the experiments are air sensitive, pyrophoric, moisture sensitive and toxic; therefore vacuum line techniques were employed. Two vacuum lines have been used for handling and preparing chemicals.

1. This line which was designed by Grady$^2$ and was built for handling organometallic compounds before and after LPHP reactions is shown in Figure 2.1. The line was constructed from 15 mm diameter, 2 mm thick Pyrex glass. It is fitted with J. Young 'O' ring vacuum taps and PTFE high vacuum screw cap joints and is equipped with six greaseless PTFE high vacuum screw cap joints by which sample tube, NMR tube and reaction cells can be connected to the line.
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From Figure 2.1 it can be seen that the line was specially constructed so that the sections of the line can be isolated in order that reaction cell filling and static distillation can be carried out. A U-tube was added to the line in order to purify SF₆, after transfer from a cylinder, and store it on the line for future use when necessary.

A U-trap, cooled by liquid nitrogen, is included to stop any of the compounds entering into the vacuum pumps. The line was equipped with a Pirani PRL10K gauge (range from 10 to 10⁻⁴ mbar) and MKS-122A baratron (of range 0.-100 torr) for measuring of the pressure of samples introduced into the line. The line was connected to an Edwards EO2 oil diffusion pump (Dow Corning 702 silicone oil) backed by an Edwards E2M5 two-stage rotary pump. The typical vacuum obtained using the rotary pump was around 10⁻² mbar and with the diffusion pump on 10⁻⁵ mbar could be attained.

The second line was designed to allow the separation and purification of samples synthesised in the lab, as well as the handling of organometallic compounds pre and post LPHP experiments. This second line was required for dynamic distillation of organometallic compounds, especially those which are less volatile. Static distillation of less volatile organometallic compound under vacuum, leakage of air through taps causes a build up pressure in the line, as well as causing very slow distillation and subsequently stopping the distillation process. There is also danger of reacting the organometallic compound with air if the distillation process becomes to long. In addition to solving the problem just mentioned, dynamic distillation is also faster than static distillation.

Another advantage of this is that, during a long LPHP reaction, pressure in the cell increases gradually with time. Pressure increase could be either from reaction products or leakage of air through the tap. Transfer of cell contents to an NMR
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tube under static distillation does not allow less volatile reaction products to be transferred into the NMR tube. Use of this line easier for NMR studies for several reasons. Firstly, the cell contents can be transferred to one of the U-tube using liquid nitrogen as a coolant. Then the contents of the U-tube can be transferred to an NMR tube straightforward. If desired, reaction products can also be separated according to their melting points. Another advantage is that dynamic distillation of samples at different temperatures at the same time is possible using three extractable U-tubes. This allowed us to separate compounds with boiling points or more precisely, vapour pressures, close to each other at a given temperature.

The vacuum line was constructed from 2 mm thick and 15 mm diameter Pyrex glass. After a few minor modifications the line has the current shape shown in Figure 2.2 As indicated above, the vacuum line has three U-tubes, which can be isolated and extracted from the line, and six PTFE high vacuum screw cap joints by which experimental accessories can be connected to the line when necessary. As can be seen from Figure 2.2, different parts of the line can be isolated for static distillation and transferring samples to a reaction cell.

The vacuum line was equipped with an Edwards Pirani gauge PR10C (10 to \(10^{-1}\) mbar) and a MKS-122A Baratron (\(10^{-2}\) to \(10^{2}\) torr) for the measurement of samples taken into the line and cell. A U-trap cooled by liquid nitrogen was connected between the vacuum line and an Edwards E2M5 two-stage rotary pump.
Figure 2.1. Vacuum line used for the IR-LHP experiments.
Figure 2.2. Vacuum line used for synthesis and purification of organometallic compounds as well as LHP experiments.
2.4 The Carbon Dioxide Laser

The first molecular laser operating in the IR region of the electromagnetic spectrum was the CO$_2$ laser, discovered by Patel et al. in 1964. The carbon dioxide laser operates on transitions between the (001) and the (100) and (020) vibrational levels of CO$_2$, as illustrated in Figure 2.3. Population inversion is achieved in an electric discharge by collisions of electrons with ground state CO$_2$ molecules. This process, however, can be made more efficient by admixing nitrogen and helium. In the electric discharge, the N$_2$ molecules are vibrationally excited to the v=1 vibrational level, which is 18 cm$^{-1}$ below the (001) level of CO$_2$ and is metastable. Hence upon collisions of N$_2$(v=1) with a ground state CO$_2$ molecule, efficient transfer of energy to the (001) level of CO$_2$ can take place producing a population inversion between the (001) level and the (100) and (020) levels. Depopulation of the lower laser states (100) and (020) occurs by collisions with helium atoms, thus enabling the population to be recycled. Each vibrational level in the CO$_2$ molecule also has associated with it a set of rotational levels (not shown in Figure 2.3). Consequently, laser emission may be realised over a range of vibration-rotation components of these vibrational transitions, with the result that IR laser radiation at about 200 discrete wavelengths ranging from 10.6 μm to 9.6 μm may be obtained.

Two different kinds of laser were used for the IR LPHP experiments, both of which were made by Edinburgh Instruments. One of them was a static gas filled RF excited CO$_2$ laser capable of operating in both continuous and pulsed modes at 10.6 μm, with an output power from 0.1 to 3.0 W in pulsed mode and 3.0 W in continuous mode. This laser was especially useful for those compounds that require low pyrolysis temperatures (100-300 °C).
The second laser used for the experimental work was an Edinburgh Instruments PL4 free-running CO$_2$ laser, operating at 10.6 μm. This laser consists of the following components, which are also illustrated in Figure 2.4: a cooled (C) Pyrex discharge tube (D) sealed at both ends by ZnSe Brewster windows (W), a rear mirror (M) and an output coupling mirror (OC), with reflectivity of 75%, mounted on a piezo-electric transducer (PZT). The discharge tube has an active length of 130 cm and the overall cavity length of the instrument is 180 cm. Fine tuning of the cavity is accomplished by adjustment of the PZT.

**Figure 2.3**  Energy level diagram for CO$_2$ laser.
Figure 2.4 Components of a free running continuous wave CO₂ laser. A water cooled (C) Pyrex discharge tube (D), ZnSe Brewster windows (W), rear mirror (M), output coupling mirror (OC), piezo-electric transducer (PZT), regulated metering valve (MV), vacuum gauge (G).
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The laser operates on a mixture of 9% CO$_2$, 13.5% N$_2$, and 77.5% He, which is flowed through the discharge tube at a pressure regulated by a metering valve (MV) and measured by a vacuum gauge (G). The electric discharge is provided by an Edinburgh Instruments (PS4R) power supply rated at 30 kV, 30 mA. By controlling the current supplied to the laser and the pressure of gas flowing through it, laser powers ranging from 0.5 to 40 W could be obtained. The diameter of the emerging beam is 7.5 mm with a divergence of less than 2 milliradians. The laser power is monitored by a Coherent Power meter, Model 201, calibrated to give a signal of 0.4 mV/W of power absorbed. The rise time of the meter is approximately 1 second.

2.5 CO$_2$ IR Laser Powered Homogeneous Pyrolysis

2.5.1 Introduction

After the discovery of high power IR molecular lasers, it was recognised that they have the potential for the study of chemical reactions, particularly in the gas phase. In early experiments, it was hoped that the narrow band excitation provided by laser sources could be used in the efficient separation of isotopes. It has soon become clear, however, that IR lasers had the potential for considerably wider applications in kinetic and mechanistic investigations. In particular, the need for a chance coincidence between laser output and absorption in the target molecule could be eliminated by use of a chemically inert IR absorber to transfer energy from the laser to a sample. In this method, energy is absorbed in the vibrational mode of the absorber and rapidly converted into heat through efficient relaxation processes. Energy is then transferred to the target molecule via collisions in much the same manner as in conventional pyrolysis. This process is known as Infrared Laser Powered Homogeneous Pyrolysis (IR LPHP).
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Following the pioneering work of Tardieu de Maleissye\textsuperscript{9} \textit{et al.}, this technique was further developed by a number of workers, especially Shaub and Bauer,\textsuperscript{10} Smith\textsuperscript{11} \textit{et al.}, Pola\textsuperscript{12} and Zitter.\textsuperscript{13} The IR LPHP technique has been extensively reviewed in a recent article by Russell\textsuperscript{7} in which more detailed information can be found. In this chapter, only the essential elements of the IR LPHP technique which were used to carry out the pyrolysis experiments presented in this thesis are described.

The major advantage conferred by this technique, in comparison with conventional methods, is that energy is directly given into the gas phase,\textsuperscript{2} generating a static temperature profile in which the centre of the pyrolysis cell may reach as high as 1500 K while the cell walls remain at room temperature, consequently, the initiation of reaction is entirely homogeneous. This can lead to great simplification in disentangling the contributions of homogeneous and heterogeneous processes in complex systems. This is especially important in cases where deposition occurs, as the surface can act as an auto-catalyst for primary or subsequent processes. However, the generation of an inherently non-uniform temperature brings its own problems, especially in the extraction of meaningful kinetic parameters from the observed rates. In spite of this, the IR LPHP process still has significant advantages over conventional 'hot-walled' pyrolysis techniques. This was clearly demonstrated by Ashworth\textsuperscript{14} \textit{et al.} in the oxidation of tetramethyl tin.

2.5.2 Experimental Equipment

In this study, the typical apparatus used for an IR LPHP experiment is illustrated in Figure 2.5. In this arrangement, a few torr of reagent compound and about 10 torr of SF\textsubscript{6} were introduced into the reaction cell. The cell was then exposed to the output of the IR laser and the change in chemical composition was monitored by one or more of a number of techniques, these being IR spectroscopy, NMR spectroscopy, GC-MS.
2.5.3 Reaction Cells

Pyrolysis cells for IR LPHP experiments are constructed from Pyrex and are usually small in size (100-200 cm³). At the pressure used (a few torr), only small quantities of materials are therefore required. For pyrolysis reactions, three different types of reaction cell were used, each one specially designed for a different requirement, while the cell diameter was kept constant in accordance with the ZnSe window diameter.

Although different type (shape and length) of reaction cell were used by Atiya, Grady and Linney, two more were added to the list, these being the joint and the heated cells which will be described in *vide infra*. When a reaction cell was chosen two things were considered. Firstly, how volatile the compound is and the secondly, how intense was the absorption cross-section of the compound to be studied. If the compound is
very volatile, and absorption cross-section very high (metal carbonyl compounds have very strong absorption cross-section at the carbonyl stretching region (~2000 cm\(^{-1}\)) of the infrared spectrum.) the short reaction cell was used, mainly for the purpose of having an IR spectrum as a reference for comparison after LPHP reaction. If the compound has a moderate volatility and the absorption cross-section of the compound or reaction products after LPHP are low, long reaction cells were usually used. In the case of extremely low volatile compound, like ferrocene, the heated cell was used. Although the joint cell designed especially to investigate the deposition products after an LPHP reaction, convenience of using it made it a very popular reaction cell in the LPHP experiments throughout this work.

The main designs of reaction cell which were used for the LPHP experiments are shown in Figures 2.6, 2.7 and 2.8. The simplest cell is made of 2 mm thick, 3.5 cm outer-diameter, 10 cm long (length of the cell could be varied accordingly with the requirements of the experiment which was being performed, as mentioned earlier) Pyrex glass and is fitted with a J. Young high vacuum tap. A schematic drawing of this cell is shown in Figure 2.6. Zinc selenide windows were attached to both ends using quick setting epoxy resin.

The second and most widely used cell was a joint cell shown in Figure 2.7, which consists of two halves that can be attached via an O-ring joint. This cell is 13 cm long, 3.5 cm diameter and once again is composed of 2 mm thick Pyrex glass. This cell was the one used to investigate non-volatile products produced by LPHP. In addition to studying the volatile reaction products, it is often useful to study involatile reaction products which are difficult to detect by IR. Because transfer of involatile reaction products is very difficult or sometimes impossible by vacuum line techniques, opening the cell and rinsing with the solvent to dissolve organic residues is the only option. These products can then be investigated by NMR spectroscopy.
In order to get some deposited material from the standard reaction cell, the ZnSe windows must be separated by dissolving the epoxy resin, by keeping the cell in CH$_2$Cl$_2$ overnight which in turn may cause contamination of deposit (contamination does not come from CH$_2$Cl$_2$ itself, it comes from dissolved epoxy resin in the solvent); in addition, solvent may wash out any organic residue from the cell as well. The problems mentioned above can be eliminated by using the joint cell, as well as saving time, since it is not any more necessary to dissolve the epoxy resin to dismantle the ZnSe windows from the cell body. It takes at least two days to re-use the same reaction cell after an LPHP reaction, while the joint cell can be ready to re-use the same day after cleaning and pumping on the line for a few hours.

If the room temperature vapour pressure of the compound is not sufficient for study by LPHP, increasing the cell temperature is necessary. Electrical heating tape, driven by a variac, around the standard reaction cell can overcome the problem but estimating and controlling the temperature of the cell is difficult. To control the cell temperature and prevent over heating, a new cell was designed and used of the type shown in Figure 2.8. This has the same dimensions as the first one but in addition there is a heating jacket round the cell which was heated by a hot fluid connected to a reservoir. Up to 85 °C could be obtained using water as a heating fluid, and over 100 °C could be obtained with a fluid of higher boiling point, such as diethylmalonate (boiling point 199 °C). At temperatures over 100 °C, however the rubber tubing was less reliable, often resulting in failure of tubing.
Figure 2.6 Schematic diagram of a standard reaction cell.

Figure 2.7 Schematic diagram of a joint reaction cell.
2.5.4 Window Materials

The choice of window material is important for the success of an IR LPHP experiment. The material must be highly transparent to the laser radiation and possess a high degree of mechanical strength. These requirements, coupled with economical considerations, have led to the establishment of NaCl and KCl as the materials used by the majority of workers. However, there are a number of drawbacks associated with their use. The most important of these is the generation of hot spots caused by absorption of laser radiation by solid deposits on the windows, which can easily lead to thermal stresses and subsequent failure of the window. Another problem is that alkali halide materials are hygroscopic and even a trace of absorbed water can drastically alter the course of reaction of moisture sensitive organometallic
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compounds. Fortunately, all these problems are overcome by the use of ZnSe windows, which have lower absorption around 10 μm, lower thermal expansion and higher thermal conductivity than alkali halide windows. ZnSe windows are expensive but their greater durability and non-hygroscopic nature makes them very attractive for use with air and moisture sensitive organometallic compounds.

2.5.5 Photosensitisers

The ideal photosensitiser material must have the following characteristics:

- Very strong absorption of radiation at wavelengths emitted by the laser;
- Very rapid intra-molecular vibration-vibration and vibration-rotation translation energy conversion, and very efficient intermolecular energy transfer;
- High thermal stability and chemical inertness;
- Low thermal conductivity.

The most popular photosensitiser is SF₆. This molecule has an extremely large absorption cross-section for a number of lines in the CO₂ laser spectrum, reaching a maximum of $1.8 \times 10^7$ mol⁻¹cm⁻² (at room temperature) for the 10P(16) line near 948 cm⁻¹. This leads to an absorption of >99.5% of incident laser light over a path of 55 mm, at the working pressure of 10 torr. It is extremely resistant to chemical reaction and thermally stable at temperatures well above 1200 K. SF₆ is also a poor thermal conductor, which results in the generation of static, highly inhomogeneous temperature profiles at modest laser power.

SiF₄ has also found widespread use as a photosensitiser. While it is thermally more stable than SF₆, it is a somewhat poorer IR absorber and fairly reactive towards moisture, and therefore its use is limited. If a reactant absorption bond coincides with the laser output frequency, it alone can be used as a photosensitiser e.g. C₂H₄, NH₃.
2.5.6 Absorption and disposal of laser energy

A number of detailed experimental and theoretical investigations have been carried out to determine the precise mechanisms of the IR LPHP technique. These studies have centred around three main areas: the mechanism of absorption of radiation by the photosensitiser, the transfer of this energy with the subsequent production of heat and the shape of the temperature profile generated. Details of these studies may be found in the IR LPHP review by Russell.7

Table 2.3 lists the infrared active bands of the SF$_6$ molecule, together with their assignments. Figure 2.9 (IR spectrum of SF$_6$) shows an FTIR spectrum recorded of SF$_6$. Nowak and Lyman in 1975 investigated the interaction of the photosensitiser, SF$_6$, with CO$_2$ laser radiation.17 These workers found that the SF$_6$ molecule has an extremely high absorption cross section for a significant number of lines in the CO$_2$ laser spectrum. IR laser radiation is absorbed by SF$_6$ into the $\nu_3$ triply degenerate S-F stretching vibration. If the effects of both bleaching and temperature are disregarded, this results in an absorption of >99.5% of the incident laser light over a path length of 5 cm using 10 torr of SF$_6$.

Most important as far as IR LPHP is concerned is not the precise fate of the absorbed infrared energy, but the rate at which it appears as heat (translational energy) in the system. Recently Sugawara and co-workers reported the vibrational relaxation time of SF$_6$ to be 10 $\mu$s torr.21 This was measured by using a pulsed TEA CO$_2$ laser and infrared diode laser spectroscopy on a mixture of CO$_2$ and SF$_6$. From this work, it can be concluded that infrared radiation absorbed by 10 torr of SF$_6$ will appear as heat in the reaction cell within about 1 $\mu$s.
A crucial feature of IR LPHP is the generation of a highly inhomogeneous temperature profile within the reaction cell. It is this feature that allows detection and isolation of primary reaction products. However, the non-uniform temperature distribution is also the main drawback associated with this technique, since rates of reactions are dependent upon temperature and therefore the amount of kinetic data which can be obtained is limited. There have been numerous investigations of this profile, using a variety of methods: chemical thermometers,\textsuperscript{10} interferometers,\textsuperscript{23} thermocouples\textsuperscript{6,24} and tunable IR diode laser spectroscopy.\textsuperscript{1}
Table 2.3  Band positions and assignments in the FTIR spectrum of SF₆. * s=strong, m=medium, w=weak, v=very. # Assignments are taken from Lagemann and Jones\(^2\) and in this case \(\nu\) represents symmetry labels only. * Transition resonant with CO₂ laser output.

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Assignment #</th>
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<tbody>
<tr>
<td>1718 cm(^{-1})</td>
<td>(\nu_1 + \nu_3)</td>
</tr>
<tr>
<td>1587 cm(^{-1})</td>
<td>(\nu_1 + \nu_2)</td>
</tr>
<tr>
<td>1387 cm(^{-1})</td>
<td>(\nu_1 + \nu_4)</td>
</tr>
<tr>
<td>1282 cm(^{-1})</td>
<td>(2 \nu_2)</td>
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<td>1255 cm(^{-1})</td>
<td>(\nu_2 + \nu_4)</td>
</tr>
<tr>
<td>1137 cm(^{-1})</td>
<td>(\nu_4 + \nu_5)</td>
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<td>985 cm(^{-1})</td>
<td>(\nu_2 + \nu_6)</td>
</tr>
<tr>
<td>948 cm(^{-1})</td>
<td>(\nu_3)</td>
</tr>
<tr>
<td>885 cm(^{-1})</td>
<td>(\nu_5 + \nu_6) (R)</td>
</tr>
<tr>
<td>869 cm(^{-1})</td>
<td>(\nu_5 + \nu_6) (Q)</td>
</tr>
<tr>
<td>856 cm(^{-1})</td>
<td>(\nu_5 + \nu_6) (P)</td>
</tr>
<tr>
<td>625 cm(^{-1})</td>
<td>(\nu_4) (R)</td>
</tr>
<tr>
<td>615 cm(^{-1})</td>
<td>(\nu_4) (Q)</td>
</tr>
<tr>
<td>604 cm(^{-1})</td>
<td>(\nu_4) (P)</td>
</tr>
</tbody>
</table>

Determining the temperature distribution is a complex problem because of the number of variables that have to be taken into account. These include the extent of laser radiation absorption by SF₆, which is dependent on the laser power, temperature and density, together with the effects of conduction, convection and heat released during chemical reactions. Therefore an accurate measurement of the temperature profile is severely hampered by its extreme sensitivity to the experimental conditions employed. However, the recent use of pulsed excitation has helped to overcome some of the difficulties experienced. The experimental details of this technique are to be found in several articles by McMillen \(et \ al.\)\(^{25,26}\). In our own laboratory, Atiya investigated the temperature distribution produced using a CO₂ laser and SF₆ as photosensitiser.\(^1\)

Three different methods were used:
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• A visual determination of the reaction area was made by photographing the emission of iodine atoms produced in a chemiluminescent reaction.

• Tunable IR diode laser spectroscopy was used to record the vibrational-rotation components of a CO (<0.5 torr) and SF$_6$ mixture, during CO$_2$ laser irradiation. Figure 2.10 shows the isotherm obtained and Figure 2.11 illustrates the plot of mean temperature along the probe beam path through the axis of the cell versus laser power for two positions along the cell.

• Ethyl ethanoate was used as a chemical thermometer, since its kinetic parameters are well known. The results obtained when 10 torr of ethyl ethanoate and 10 torr of SF$_6$ were pyrolysed are also presented in Figure 2.11. This mixture was irradiated at a number of different laser powers and the reaction was monitored by FTIR spectroscopy. The initial rate of this first order reaction was recorded at a variety of laser powers.

Atiya drew the following conclusions based on the results of all three experimental methods: the temperature produced by the CO$_2$ laser radiation is clearly non-uniform throughout the reaction cell, while the hottest part of the cell is to be found some 1 cm from the entrance window, and the temperature distribution is cylindrically symmetrical.

Figure 2.10 Isotherm of the laser-heated gas mixture.
Figure 2.11 Temperature as a function of laser power in IR LPHP measured by tuneable IR diode laser spectroscopy at the cell entrance window *, and 3.8 cm from the window Δ. For comparison, temperatures estimated using CH$_3$COOC$_2$H$_5$ as a chemical thermometer also presented ◊.

2.6 Sample Preparation

Liquid and volatile solid organometallic compounds were distilled and stored under vacuum in standard Pyrex sample tubes of the type shown in Figure 2.12. The photosensitiser gas, SF$_6$, was stored either in the U-tube on the vacuum line (Figure 2.1) or in a 250 ml Pyrex flask fitted with a greaseless high vacuum tap. It was filled directly from the cylinder via the port shown in Figure 2.1. Before each experiment SF$_6$ was pumped at 77 K, in order to remove any oxygen present. This was followed by removal of residual water at 197 K. NMR samples were prepared using a 5 mm
wide J. Young NMR tube fitted with high vacuum tap. Transfer of sample and solvents were made on the line under vacuum. $d_8$-toluene was used as an NMR solvent, dried on CaH$_2$ and degassed on the vacuum line by liquid nitrogen and transferred into a Pyrex sample tube over CaH$_2$.

Figure 2.12 Sample tube used for storing the organometallic compounds.

Before each experiment all the samples and solvents were subjected to several freeze-pump-thaw cycles at 77 K and 196 K depending upon the sample melting point. The purpose of this was to remove any traces of decomposition products from the sample, a precaution particularly important for organometallic compounds as leakage of air through the vacuum tap causes the production of hydrocarbons from subsequent
hydrolysis and/or oxidation. In addition, some organometallic compounds decompose slowly in the absence of air even at low temperatures producing hydrocarbons.

Before starting an LPHP experiment, the reaction cell, was conditioned with the organometallic compounds to be studied followed by running of FT IR spectrum of the compound on its own. After that both reaction cell and the vacuum line were evacuated and then the reaction cell was filled with the required pressure of the reactant gas or gases and about 10 torr of SF₆. Before pyrolysis, an FT IR spectrum of the cell contents was taken and used as a reference for any pyrolysis reaction that might take place during laser irradiation.

On completion of an LPHP reaction, the cell contents were transferred to one of the U-tubes cooled by liquid nitrogen under dynamic distillation on the line, then transferred to an NMR tube following addition of solvent.

2.7 Monitoring of Reactions

The composition of the cell contents may be monitored by any conventional method. The majority of the LPHP workers have favoured the non-invasive spectroscopic technique of IR spectroscopy, but some workers have used mass spectrometry and gas chromatography. In this study, mostly FT-IR (Digilab FTS40), NMR (300 MHz Bruker AM300 FT-NMR) and GC-MS (Hewlett Packard HP5995C) were used to monitor the reaction course in the cell.

2.8 Advantages and disadvantages of IR LPHP

The advantages of LPHP can be listed as follows. First, very small amounts of sample are required (a few μg) and therefore expensive compounds can be studied. The relatively simple experimental set up makes control of the system easy, and very high temperatures can be obtained in a very short time (μs scale). Because reaction takes
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place in the centre of the cell and the surface effects are negligible, reaction can be considered as a pure homogeneous reaction. The non-uniform temperature profile in the reaction cell means that reaction products ejected away from the centre of the cell are cooled and therefore undergo no secondary chemistry.

As for disadvantages, the non-uniform temperature profile brings its own problem for kinetic studies as mentioned earlier. During the course of reaction, reaction products alter the composition of cell contents which in turn effect the heat capacity and thermal conductivity of the system. This makes it impossible to keep the temperature constant in the reaction cell through out the reaction. In addition, because reaction takes place in the gas phase, the sample has to have enough vapour pressure so that LPHP reaction can take place. This limitation makes the technique inapplicable for many compounds.
2.9 REFERENCES

5. Manufacturer handbook, Edinburgh Instruments Ltd.
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Chapter 3

Pyrolysis of Butadiene Iron Tricarbonyl and Co-pyrolysis of Iron Pentacarbonyl with Butadiene
3.1 Introduction

Organo-iron compounds have an important place in organotransition metal chemistry, both historically and in respect of their variety and utility. Historically, iron featured in many 'firsts' in the organometallic field. The first organometallic compound synthesised was Fe(CN)$_2$(CNEt)$_4$ in 1881.1 Mond who had described his first metal carbonyl Ni(CO)$_4$, in the same year, prepared his second, Fe(CO)$_5$, in 1891 along with the di and trinuclear iron carbonyls Fe$_2$(CO)$_9$ and Fe$_3$(CO)$_{12}$, respectively.2 When Reihlen3 added butadiene to Fe$_2$(CO)$_9$ the first hydrocarbon-iron complex butadiene iron tricarbonyl was obtained. However, the structure of this product remained unknown until re-investigated in the late 1950's. Indeed Fe$_2$(CO)$_9$, obtained by photolysis of Fe(CO)$_5$, was the first metal carbonyl to have its structure determined by X-ray crystallography.4 Improvements in structure determination and a much enhanced understanding of chemical bonding, notably the concept of \( \pi \)-bonding, permitted rapid growth of the subject following the discovery of ferrocene in 1951.5 Moreover, ferrocene was not only the first of the now vast range of cyclopentadienyl metal complexes, but also the first organometallic compound with typical aromatic character. It owes much of its rich chemistry to the ease of electrophilic substitution.6

Ligands capable of accepting an appreciable amount of \( \pi \)-electron density, from the metal atoms into empty \( \pi \) or \( \pi^* \) orbitals of their own are referred to as \( \pi \)-acceptor or \( \pi \)-acid ligands. Of these, carbon monoxide is the most important and the most extensively studied. The way in which CO engages in bonding to a metal atom is illustrated in Figure 3.1 and may be stated as follows:

1. Overlap of a filled carbon s orbital with a s-type orbital on the metal atom as in Figure 3.1. Electron flow C \( \rightarrow \) M in such a dative overlap would lead to an unacceptable concentration of electron density on the metal atom. The metal therefore attempts to reduce this charge (Pauling's electroneutrality principle) by pushing electrons back to the ligands.
2. A second dative overlap of a filled dπ or hybrid dpπ metal orbital with the empty pσ orbital on carbon monoxide, which can act as a receptor of electron density.

![Diagram showing dative overlap and backdonation in metal carbonyls](image)

**Figure 3.1** The s and π bonding in metal carbonyls; only the M-C bonding orbitals are included; shaded orbitals are filled and unshaded orbitals are nominally vacant.

This bonding mechanism is synergetic. The drift of metal electrons, referred to as "back-bonding" into CO orbitals, tends to make the CO as a whole negative, hence to increase its basicity via the σ orbital of carbon; at the same time the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. Thus up to a point the effects of σ-bond formation strengthen the π bonding, and vice versa.⁷

Many carbonyl complexes are of considerable structural interest as well as being important in industrial chemistry. Carbonyl derivatives of at least one type are known for all of the transition metals. The simplest carbonyls are of the type M(CO)ₓ, e.g. Ni(CO)₄, Fe(CO)₅, Cr(CO)₆. These compounds are all hydrophobic, volatile and soluble to varying degrees in non-polar solvents. Of the d-block metals, the ones that form stable mononuclear carbonyls are principally those that require an integral number of carbonyl ligands to attain the number of valence electrons in the succeeding noble gas atom which is known as the eighteen electron rule. The only important
exception is V(CO)₆ molecule (3d³ 4s²). Although there are exceptions, for the majority of simpler transition metal organometallics, and especially for the mononuclear and binuclear metal carbonyls and their derivatives, the 18 electron rule is a useful model. Electron donated by various ligand to a transition metal in an organometallic compound is given in Table 3.1.

The structure of butadiene iron tricarbonyl has been determined by X-ray diffraction and is shown in Figure 3.2. In this structure, the carbon atoms of the butadiene adopt a cis configuration and are planar. The plane of the four carbons is not quite parallel to that formed by the three carbons of the CO groups. The iron atom lies below the plane of the butadiene and is approximately equidistant from the four carbons.

Figure 3.2 Crystal structure of η⁴-1,3 butadiene iron tricarbonyl.
Table 3.1 Some selected types of metal-carbon bonding and number of electrons (e) donated to a transition metal by some typical ligands found in organometallic compounds.

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Number of Electrons (e)</th>
</tr>
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<tbody>
<tr>
<td>M—CO</td>
<td>2 e from CO</td>
</tr>
<tr>
<td>M—R</td>
<td>2 e from R</td>
</tr>
<tr>
<td>M—X</td>
<td>2 e from X</td>
</tr>
<tr>
<td>M—(\overline{CR_2})</td>
<td>2 e from alkene</td>
</tr>
<tr>
<td>R_2C(\overset{\sigma}{\text{M}})CR_2</td>
<td>4 e from allyl anion</td>
</tr>
<tr>
<td>R_2C(\overset{\bigtriangleup}{\text{M}}) CR_2</td>
<td>4 e from diene</td>
</tr>
<tr>
<td>(\overset{\circ}{\text{M}})</td>
<td>6 e from cyclopentadienyl (Cp')</td>
</tr>
<tr>
<td>(\overset{\boxdot}{\text{M}})</td>
<td>6 e from arene</td>
</tr>
</tbody>
</table>

Transition metal complexes have been used extensively in industrial and laboratory processes to catalyse a variety of chemical reactions. The Fe(CO)_3 moiety in particular is prone to bind \(\eta^4\) and its alkene complexes have been much used in organic synthesis.\(^1\) The main features of transition metal complexes as catalysts are selectivity and catalytic activity under mild conditions. Selectivity of homogeneous catalysts can be varied by the use of different metal centre and altering the ligand coordinated to the metal atom.\(^1\) Of these, Ziegler-Natta catalysts, which catalyse alkene to polyalkene are the most studied and one of industrial importance.
There has not been much study of the pyrolysis of the organoiron compounds; however, there has been one reported study of pyrolysis reactions of butadiene iron carbonyl concerning the thermodynamic data in respect to bond homolysis.\textsuperscript{12} It was reported that the reaction products were butadiene, carbon monoxide, and atomic iron, together with some oligomers and polymers of butadiene.

The main objective of this chapter was to investigate the CO\textsubscript{2} IR LPHP of butadiene iron tricarbonyl under homogeneous conditions. There is overwhelming evidence\textsuperscript{13,14} that the extreme sensitivity of the majority of organometallic species to surface catalysed reactions may obscure the homogeneous decomposition process and it would be of considerable interest to investigate butadiene iron tricarbonyl under homogeneous conditions. Pyrolysis of BdFeTC has been performed using two techniques: i. CO\textsubscript{2} IR LPHP and ii. conventional hot walled SFR. As will be described later, results from the two methods were compared and found to be different in respect to reaction products. While reaction from LPHP of BdFeTC yields unexpected products such as benzene, pyrolysis of BdFeTC by conventional hot walled SFR technique yielded only the butadiene as an organic reaction product. One of the aims of this chapter is to try and understand how these intriguing observations arise by suggesting a pyrolysis mechanism for BdFeTC.

3.2 Experimental

3.2.1 Chemicals

The purification and handling of the samples used for the IR LPHP study of BdFeTC and related compounds have been described in chapter 2. The purity of BdFeTC, butadiene, and FPC were checked by FT IR and \textsuperscript{1}H NMR spectroscopy. Figures 3.3 and 3.4 report the IR and NMR spectra of BdFeTC, respectively and the band positions in the corresponding spectra are given in Tables 3.2 and 3.3.
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Table 3.2 Gas phase FT IR spectral data of BdFeTC in 12 cm long cell at room temperature, assignments are taken from Davidson\textsuperscript{15} liquid phase spectral data of BdFeTC (ν:stretching, δ:bending, ρ:wagging).

<table>
<thead>
<tr>
<th>BdFeTC</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>670.7</td>
<td>ρ(CH)</td>
</tr>
<tr>
<td>789.4</td>
<td>ρ(CH)</td>
</tr>
<tr>
<td>1049.0</td>
<td>δ(CH\textsubscript{2})</td>
</tr>
<tr>
<td>1202.0</td>
<td>δ(CH) or ν(C-C)</td>
</tr>
<tr>
<td>1475.4</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1481.7</td>
<td></td>
</tr>
<tr>
<td>1960.0</td>
<td>ν(CO)</td>
</tr>
</tbody>
</table>

Table 3.3 Assignment of \textsuperscript{1}H NMR spectrum of BdFeTC.

<table>
<thead>
<tr>
<th>Chemical shift ppm</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.12 Doublet</td>
<td>H\textsubscript{a}</td>
</tr>
<tr>
<td>-0.15 Doublet</td>
<td>H\textsubscript{b}</td>
</tr>
<tr>
<td>1.35 Multiplets</td>
<td>H\textsubscript{b}</td>
</tr>
<tr>
<td>4.7 Multiplets</td>
<td>H\textsubscript{c}</td>
</tr>
</tbody>
</table>

![Diagram of BdFeTC molecule]
3.2.2 Apparatus

The apparatus used has been described in detail in Chapter 2. Briefly, the low power CO\textsubscript{2} laser and the standard reaction cell shown in Figure 2.6 were used for initial pyrolysis studies. Later the joint cell shown in Figure 2.7 and the more powerful free running CO\textsubscript{2} laser were generally used for the LPHP of BdFeTC and the other related compounds. To compare the outcome of LPHP with conventional pyrolysis, the SFR technique was also used in some experiments. The pyrolysis reaction course was monitored by using two different techniques, FT IR, \textsuperscript{1}H NMR spectroscopy and GC-MS used for laser pyrolysis, and GC-MS for conventional hot walled pyrolysis of BdFeTC.

The vapour pressure of BdFeTC is relatively low (1.3 torr at room temperature) and the reaction products have very weak IR absorbance bands. If more reactant could be drawn into the reaction cell, the chance of observing weak bands in the IR spectrum would obviously be increased. To do this, part of the cell was cooled to 77 K and a small amount of BdFeTC was condensed into the cell. After warming the cell up to room temperature, followed by introducing 10 torr of SF\textsubscript{6} into the reaction cell, the cell is saturated by the vapour of BdFeTC to enable us to see the less intense IR band in the spectrum. Another benefit of doing this is that, during laser pyrolysis, consumed reactant can also be replaced from the liquid in the cell. As a result, more starting material can react and more reaction products can be accumulated in the cell permitting better IR, NMR and GC-MS results.

Conventional pyrolysis of BdFeTC was performed in a Stirred Flow Reactor (SFR) of the type shown in Figure 3.5. This consists of a spherical quartz vessel of volume 10 cm\textsuperscript{3}, at the centre of which is a simple jet inlet, which provides rapid mixing and thermal equilibration of the reagents. The reactor is placed in an electrically heated conventional furnace capable of providing temperatures up to the softening
temperature of quartz (over 850 K). Reactant diluted in a carrier gas (He, 25 ml/min) is introduced to the reactor. Pyrolysis temperatures employed were in the range of 330 to 653 K and furnace temperature was increased 10 K after each successful experiment. The reaction in the vessel competes with the sweeping out of reagents and products, so that a controllable proportion of conversion may be achieved. The reaction vessel effluent was monitored by computerised GC-MS.

A typical experiment proceeds as follows. One torr of BdFeTC was introduced to the vacuum line from a freshly degassed sample tube. Then a small portion of the sample was injected through SFR at a certain temperature by means of a carrier gas and then into the liquid nitrogen cooled trap. After three minutes of acquisition in the trap, liquid nitrogen was replaced with hot water bath at 373 K, and the composition of the trapped mixture were analysed by GC-MS.

![Schematic diagram of SFR reactor.](image-url)
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3.3 Pyrolysis of Butadiene Iron Tricarbonyl

3.3.1 IR LPHP of BdFeTC

Laser pyrolysis of BdFeTC/SF₆ mixtures (1.3/10 torr) as carried out at laser powers ranging from 0.5 to 1.5 W, the mixture appearing to be thermally stable below 0.5 W. Because of the non-uniform temperature profile in the cell, the precise pyrolysis temperature cannot be defined. However, on comparison with the work of Atiya,¹⁶ a rough estimate is that the laser power range employed spans a temperature range of 450-550 K. The pyrolysis products of BdFeTC were analysed by FT IR, elemental analysis and GC-MS with results as follows.

i. FT IR Spectrum

The decay of BdFeTC was monitored by using the decaying peaks of BdFeTC and emerging new peaks like the free CO vibration between 2100-2250 cm⁻¹, a mysterious sharp band at 673 cm⁻¹ in IR, and a butadiene band at 908 cm⁻¹, as well as visually monitoring the black deposit on the walls and window. These IR bands were the only clearly identifiable features associated with the starting material or reaction products. Others were either overlapped by stronger SF₆ peaks or too weak to be seen in the spectrum initially. Carbonyl peaks of BdFeTC are very strong, but since its absorbance is off scale under these conditions, the changes that take place during the pyrolysis were nearly indistinguishable by monitoring the carbonyl peaks. For that reason carbonyl peaks were not used to monitor pyrolysis reaction course, instead emerging new peaks were favoured for this purpose.

Further exposure to laser radiation led to the gradual disappearance of BdFeTC and generation of free CO, as well as producing a black deposit (presumably iron with hydrocarbons) on the window and cell walls.
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Figure 3.6 IR spectra of PAnTC before (A) and after (B) IR-LHHP reaction with liquid sample in the cell.
Deposits on the front window during pyrolysis, where the laser beam was introduced, caused a dramatic loss of intensity inside the cell which presumably stopped pyrolysis, as well as causing poor IR signal during FT IR scans. When this point was reached, LPHP reactions were stopped. To try and prevent free iron from depositing on the window, magnetic bars were used but with little effect.

In order to clarify the changes that took place after laser pyrolysis, the pre-pyrolysis spectrum of BdFeTC shown in Figure 3.6 A was computer subtracted from the spectrum of BdFeTC after pyrolysis (Figure 3.6 B). This yielded the spectrum shown in Figure 3.7 (the imperfect subtraction of the intense SF$_6$ peak around 940 cm$^{-1}$ is due to its considerable intensity). In the subtracted spectrum there are a few strong peaks which could not be identified.

From the subtracted FT IR spectrum of BdFeTC, the major observable pyrolysis products were free butadiene, which has characteristic bands at 908, 1013, 1380, and 1596 cm$^{-1}$, and free carbon monoxide which has P and R rotational structure between 2100-2250 cm$^{-1}$. The spectrum also contains a considerable amount of benzene, which has a characteristically strong peak at 673 cm$^{-1}$, with other weak bands at 1037, and 1483 cm$^{-1}$. Some ethene, which has peaks at 911 cm$^{-1}$, was also seen, as with trans-2-butene with its peak buried under SF$_6$, cis-2-butene which has a peak at 1653 cm$^{-1}$. A very weak ethyne peak at 729 cm$^{-1}$ could also be assigned.

**II. $^1$H NMR Spectrum**

Following laser irradiation of the sample, the cell contents were transferred to an NMR tube on a vacuum line. The solvent, d$_9$-toluene, was degassed at 77 K following distillation into the NMR tube at 77 K. The NMR tube was sealed off and a spectrum was recorded at room temperature. Table 3.4 reports the $^1$H NMR spectral data recorded and Figure 3.8 shows the NMR spectrum of pyrolysis products and
Figure 3.8 Proton NMR spectra of BdFeTC after IR LPHP reaction.

Δ: Benzene
*: Ethyne
ϕ: cis-2-Butene
ϕ: Butadiene
♀: trans-2-Butene
Θ: Ethene
Table 3.4 \(^1\text{H} \text{NMR chemical shift of reaction products of IR LPHP of BdFeTC.} \)

<table>
<thead>
<tr>
<th>Chemical Shift/ppm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.12 Doublet</td>
<td>BdFeTC, 8CH(_3)</td>
</tr>
<tr>
<td>-0.15 Doublet</td>
<td>BdFeTC, 8CH</td>
</tr>
<tr>
<td>1.35 Multiplets</td>
<td>BdFeTC, 8CH(_2)</td>
</tr>
<tr>
<td>4.70 Multiplets</td>
<td>BdFeTC, 8CH-</td>
</tr>
<tr>
<td>7.13 Singlet</td>
<td>Benzene, 8CH</td>
</tr>
<tr>
<td>6.20 Multiplets</td>
<td>Butadiene, 8CH-</td>
</tr>
<tr>
<td>5.0 Multiplets</td>
<td>Butadiene</td>
</tr>
<tr>
<td>5.50 Singlet</td>
<td>Ethene</td>
</tr>
<tr>
<td>1.56 Doublet</td>
<td>Cis-2-Butene</td>
</tr>
<tr>
<td>1.51 Doublet</td>
<td>Trans-2-Butene</td>
</tr>
</tbody>
</table>

unreacted starting material. A sharp singlet resonance at 7.13 ppm was observed and identified as benzene,\(^{17}\) while a second singlet at 5.50 ppm represents ethene (C\(_2\)H\(_4\)).

One of the main pyrolysis products of BdFeTC is free butadiene, which can clearly be identified from the two multiplets at 6.20 and 5.0 ppm. Other features are the cis/trans butene doublet at 1.56 and 1.51 ppm respectively, and unreacted BdFeTC resonances at -0.12 (doublet), -0.15 (doublet), 1.35 (multiplets) and 4.70 ppm (multiplets).\(^{18}\) The peak at 0.4 ppm is an impurity from the solvent.

iii. GC-MS data

After same IR LPHP reactions, the cell contents were transferred to a sample tube and GC-MS data was recorded for a small proportion of the sample. After a few runs, the gas chromatogram showed four main peaks, as can be seen in Figure 3.9. From the mass spectra of each peak they were assigned to free butadiene, benzene, 1-butene, 2-butene and toluene.
iv. Elemental analysis

Organometallic compounds of iron have been known to have a catalytic effect on the polymerisation of alkene compounds. To see if any of the butadiene products was involved in reactions it was decided to look at the composition of the deposit on the cell window. If there was a polymerisation reaction, we would not expect to observe polybutene in the IR and NMR spectra, due to its high molecular weight and therefore less volatile nature. Consequently C, H, Fe elemental analysis of the deposit from the reaction cell were made after removal of the windows from the cell in order to learn more about its composition. This gave its empirical formula very close to Fe(C\textsubscript{2}H\textsubscript{3}), indicating that possible polymerisation reaction had taken place during the IR LPHP reaction catalysed by iron. If iron is eliminated from the formula, empirically C\textsubscript{2}H\textsubscript{3} is left. Could this be the sign of a polymer? Examination of the starting material, butadiene iron tricarbonyl, suggested that when it decomposes, the reaction products are likely to be butadiene, iron and carbon monoxide. Butadiene is a highly volatile gas, and for that reason cannot condense into the deposited iron at the atmospheric pressure. It must be very unvolatile and contains hydrogen for that reason it can not be carbon black or graphite as well. It must therefore be some sort of organic compound with a high molecular weight, originating from butadiene, since it is a well known fact that dienes are specially prone to polymerisation reaction by the catalysis of organometallic compounds. From these facts, it can be concluded that LPHP of BdFeTC results in polymerisation of butadiene after or when it is still on the iron atom.

3.3.2 Pyrolysis of BdFeTC in SFR

From GC-MS data, it was observed that butadiene iron tricarbonyl is thermally stable below 463 K. Pyrolysis reactions began at about 463 K yielding the reaction products
free butadiene, carbon monoxide with a very small amount of vinylcyclohexene. GC-MS data from SFR pyrolysis of butadiene iron tricarbonyl at 463 K is given in Figure 3.10.

![GC-MS spectrum of BdFeTC after IR LPHP reaction.](image)

**Figure 3.9** GC-MS spectrum of BdFeTC after IR LPHP reaction.

![GC-MS spectrum of BdFeTC after pyrolysis by SFR.](image)

**Figure 3.10** GC-MS spectrum of BdFeTC after pyrolysis by SFR.
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3.4 Co-pyrolysis of Butadiene with FFC

Although the conventional pyrolysis products of BdFeTC were mainly butadiene, vinyl cyclohexene, octadiene with oligomers and polymers of butadiene, reported^19^

\[
\text{Fe(CO)}_3 \xrightleftharpoons{\Delta} \text{Fe - 3 CO} + \text{butadiene} + \left(\text{oligomers and polymers of butadiene}\right)_n \quad (3.1)
\]

the picture that emerges from the studies of BdFeTC by IR LPHP described in the previous section is rather different. The most surprising observation was detection of benzene. Although there have been some studies reporting the occurrence of benzene from the pyrolysis of butadiene at high temperatures (over 1000 K), there has been given no reaction mechanism proposed to explain how it is formed. The evidence obtained from the LPHP of BdFeTC was not sufficient to construct a reasonable pyrolysis mechanism.

In order to get more information on the mechanism of IR LPHP of BdFeTC, more experiments were required. For example, laser pyrolysis of labelled butadiene iron tricarbonyl or substituted butadiene iron tricarbonyl would be informative. The commercial unavailability of these iron compounds meant that substituted butadiene iron tricarbonyl and labelled butadiene iron tricarbonyl, namely 2,3 dimethyl butadiene iron tricarbonyl (DMB) and 1,1,4,4 tetra D-butadiene iron tricarbonyl (LBdFeTC), were synthesised in our laboratory. Synthetic routes for diene iron tricarbonyl have been reported in the literature,^{20,21,22} (commonly photolysis by UV light, reflux in a solvent etc.). In an attempt to synthesise these organometallic compounds the laser was used but was not a great success. Instead, substituted butadienes and iron pentacarbonyl were pyrolysed together with SF\(_6\), operating with the laser just below
decomposition threshold power of the starting materials. Before the co-pyrolysis reaction was performed butadiene and iron pentacarbonyl were pyrolysed individually to obtain the laser power at which the pyrolysis reaction take place and to observe the products found.

3.4.1 IR LPHP of FPC

CO$_2$ IR LPHP of iron pentacarbonyl was carried out in a standard reaction cell, with the irradiation laser power ranging from 0.5 to 2.0 W. Pyrolysis began at about 1 W laser power, eventually yielding a black deposit on the cell wall and windows. From Figure 3.11, it can be easily seen that the carbonyl peak of iron pentacarbonyl at 1900-2100 cm$^{-1}$ decreased and free carbon monoxide peaks emerged next to the carbonyl peak at about 2100-2250 cm$^{-1}$ following pyrolysis.

Increasing the iron pentacarbonyl concentration in the cell and introducing about 1.5 W laser power to the reaction cell gave an unusual black iron deposit inside the cell shaped rather like a spider’s web. After the volatile contents of the reaction cell were pumped away on the vacuum line, exposure of the remaining cell contents to air produced an immediate red flash in the cell, which was presumably caused by the rapid oxidation of small particles of iron to iron oxide.$^{23}$

3.4.2 IR LPHP of Butadiene

2.4 torr of butadiene and 10 torr of SF$_6$ were introduced into the reaction cell followed by laser irradiation. The laser power ranged from 0.4 to 3.0 W and the reaction course was monitored by FT IR spectroscopy. From the FT IR spectrum of the reaction cell, there was no change in the spectrum, suggesting that butadiene does not undergo any homogeneous pyrolysis reaction in this temperature range, which was about 600 K maximum.$^{24}$
3.4.3 Co-pyrolysis of Butadiene with FPC

Co-pyrolysis of butadiene with iron pentacarbonyl was carried out using 5 torr of butadiene, 5 torr of iron pentacarbonyl and about 10 torr of SF$_6$ in the joint cell. The laser power range from 1.6 to 6.0 W was used for the co-pyrolysis reaction. Iron pentacarbonyl started to decompose at 2.5 W giving free carbon monoxide and a black iron deposit on the window. Exposing the reaction cell to laser radiation at the same power for four minutes led to the appearance of a peak at 673 cm$^{-1}$, due to benzene, which is the strongest peak in the IR spectrum of laser pyrolysis of BdFeTC shown in Figure 3.12; irradiation was stopped when both windows were covered with black film.
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$\phi$: Carbon monoxide

Figure 3.1.1 IR spectra of pyrolysis of iron pentacarbonyl before (A) and after (B) IR LPHP reaction.
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Figure 3.12 IR spectra of co-pyrolysis of butadine with iron pentacarbonyl before (A) and after (B) IR LPH reaction.
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3.5 Discussion

Although numerous iron olefin compound have been prepared and characterised, very few experiments have been performed on their pyrolysis. There has been one reported study of conventional pyrolysis of BdFeTC in which the pyrolysis products were free butadiene, carbon monoxide, iron together with some oligomers and polymers. Laser pyrolysis of BdFeTC gave a rather different result from the conventional pyrolysis in which the reaction products were mainly butadiene, mixture of butenes and a considerable amount of benzene. On the other hand, SFR pyrolysis of BdFeTC gave only free butadiene as a volatile organic reaction product together carbon monoxide and some unvolatile organic residue, probably polymers of butadiene. However, the SFR reactor was not examined after pyrolysis for any organic residue which might have been produced during pyrolysis.

Although experiments on pyrolysis of butadiene iron carbonyl compounds are lacking, there have been some studies on the pyrolysis of butadiene itself by the application of different methods. Reaction mechanisms of pyrolysis and photolysis of butadiene have been worked out fairly well, and it was thought that this may help to understand the pyrolysis mechanism of BdFeTC.

First, we look at the reaction of butadiene on heating, then briefly mention interaction of butadiene with light. Pyrolysis of butadiene can take two different routes in accordance with the pyrolysis temperature: the first one, at low temperature (below 1000 K) results in a Diels-Alders cyclisation reaction yielding 4-vinyl cyclohexene and 1,4 octadiene (3.12). The second one, at higher temperature (above 1000 K) results in a wide variety of reaction products such as, ethene, methane, butene, benzene, toluene, propene as a result of decomposition (3.13).
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\[ \text{C}_4\text{H}_6 + \text{C}_2\text{H}_4 \xrightarrow{T<1000 \text{ K}} \text{C}_8\text{H}_{16} + \text{C}_2\text{H}_4 \]  
(3.2)

\[ \text{C}_4\text{H}_6 \xrightarrow{T>1000 \text{ K}} \text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 \]  
(3.3)

High temperature pyrolysis studies of butadiene (1500-2000 K) using a shock-tube and time of flight mass spectrometry combined with a comprehensive single-pulse product analysis, showed that butadiene dissociates mainly through

\[ \text{C}_4\text{H}_6 \rightarrow 2 \text{C}_2\text{H}_3^* \]  
(3.4)

and vinyl dissociation:

\[ \text{C}_2\text{H}_3^* + \text{M} \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{M} \]  
(3.5)

In similar conditions Kiefer et al. proposed another pathway to dissociation of 1,3-butadiene, that of molecular dissociation:

\[ \text{C}_4\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \]  
(3.6)

\[ \text{C}_4\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{C} = \text{CH}_2 \]  
(3.7)

\[ \text{C}_4\text{H}_6 \rightarrow \text{C} = \text{CH} = \text{CH} = \text{CH}_2 \]  
(3.8)
and it was observed that below 1400 K nearly equal amounts of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} were generated during pyrolysis of 1,3-butadiene and the next most abundant product is vinyl ethyne. At higher temperatures both C\textsubscript{2}H\textsubscript{4} and C\textsubscript{4}H\textsubscript{4} decrease and C\textsubscript{2}H\textsubscript{2} becomes the major product."}\textsuperscript{31}

Pyrolysis of 1,3-butadiene has been studied on several occasions below 1000 K.\textsuperscript{32,33,34,35} At 700 K the principle product is 4-vinyl cyclohexene produced by Diels-Alder cycloaddition,\textsuperscript{36} but at higher temperatures radical chain processes take place.\textsuperscript{37,38} 14C labelled 1,3 butadiene was pyrolysed at temperature from 1010 to 1050 K and various hydrocarbon compounds from methane to cyclopentadiene, methyl cyclopentadiene, benzene, cyclohexadiene and toluene were detected.\textsuperscript{39}

There have been some studies on the photochemistry of cyclobutene and its derivatives to investigate the reaction mechanisms involved.\textsuperscript{40,41,42,43} Photochemical reaction of cyclobutenes at 185 nm has been studied in n-heptane solution,\textsuperscript{44} and it was found that the photolysis products butadiene, ethene, methane, cyclopropane, and ethyne as illustrated in equation 3.9.

\begin{equation}
\begin{array}{c}
\text{hv} \\
185 \text{ nm} \\
\end{array}
\begin{array}{c}
\circlearrowright \\
+ \\
\rightarrow \\
\text{+} \\
\text{+} \\
\end{array}
\end{equation}

The photolysis and IR LPHP reactions are such as butene, ethene, ethyne. Although similar reaction products can be observed by conventional pyrolysis of butadiene at high temperatures\textsuperscript{45} the difference is that butadiene does not undergo any pyrolysis reaction at the temperatures at which laser pyrolysis takes place, whereas photolysis reactions of cyclobutene take place at room temperature. It is evident that iron catalyses the laser pyrolysis reaction of butadiene. We believe that the reaction mechanism for
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the pyrolysis of BdFeTC is similar to photolysis of cyclobutene, rather than the high temperature pyrolysis of butadiene which gives a wide range of hydrocarbon fragments.

It was reported that pyrolysis of butadiene over 1500 K showed that it dissociates mainly through a vinyl radical followed by loss one hydrogen atom to yield ethyne.\(^4\)\(^6\) Another dissociation mechanism suggested was that the molecular one, in which the reaction products were ethene and ethyne.\(^4\)\(^7\) However both works did not mention the occurrence of benzene as a pyrolysis product. Pyrolysis of butadiene by CO\(_2\) IR laser over 1500 K resulted in a variety of organic molecules from methane to benzene and toluene.\(^4\)\(^8\)

Like the pyrolysis of butadiene over 1000 K, laser pyrolysis of BdFeTC gave similar reaction products, ethyne, ethene, and benzene. There have been some reaction mechanisms suggested for the reaction mechanism of butadiene, involving radical\(^4\)\(^9\) and molecular\(^5\)\(^0\) dissociation. In the case of BdFeTC, the pyrolysis products are wide ranging, including ethyne, ethene, butene, butadiene and interestingly toluene and benzene, which is of interest to us, even though the pyrolysis temperature is considerable lower in comparison with the pyrolysis of butadiene itself, which is over 1000 K. This shows that pyrolysis of butadiene iron tricarbonyl by the laser is homogeneous, and iron has the role of lowering the activation energy needed to yield pyrolysis of the butadiene. This conclusion is drawn from the fact that butadiene itself does not react at the same conditions as BdFeTC does, and co-pyrolysis of butadiene with FPC giving similar reaction products at the same conditions.

The interesting thing about the laser pyrolysis of BdFeTC is the production of benzene, which is of interest to us. There has been quite a lot of work done to understand the reaction mechanism of benzene, though most of them was unsuccessful, however they were useful in other ways as well. For example, co-
Chapter 3

Pyrolysis of substituted butadiene with iron pentacarbonyl did not give much evidence if not any to explain what is going on in the pyrolysis cell, but it did show the possibility of synthesis of butadiene iron carbonyl compounds by CO$_2$ IR laser pyrolysis in the gas phase.

The reaction mechanism for the CO$_2$ IR LPHP of BdFeTC proposed is the radical mechanism. Because of the butene is produced as a reaction product, during the pyrolysis hydrogen transfer to butadiene must take place. Cleavage of butadiene occurs while it is still attached to the iron atom, possibly via a cyclobutene iron intermediate, this then cleavages to cyclobutene, which is unstable at that temperature and it proceeds further to form vinyl radical, which is not stable, it either breaks up to ethyne and hydrogen radical or react with one of the molecule to abstract a hydrogen to form ethene. Production of benzene occurs when three ethyne molecules trimerise, presumable by the catalysis of the iron present in the cell.

Laser pyrolysis of BdFeTC gave a similar kind of reaction products like the conventional pyrolysis of butadiene at higher temperatures. It was certainly obvious that the iron moiety in the molecule plays a crucial role in this reaction, and secondly, that pyrolysis reaction was completely free from catalytic effect of reactor. It was evident from the conventional pyrolysis of BdFeTC in SFR that the reaction products were only free butadiene, carbon monoxide and iron, whereas in IR LPHP the reaction products were isomers of butene, butadiene, free carbon monoxide, considerable amount of benzene and small amount of toluene, polybutene and iron.

In the first step of the pyrolysis reaction, BdFeTC loses its first carbon monoxide molecule, then the second and subsequently the third one. After that, butadiene cyclisation takes place while still on the iron atom. Then it could break into two different ways. The first one is a molecular mechanism in which ethyne and ethene is formed as a result of cleavages of cyclobutene while still is coordinated to iron atom.
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In this mechanism explanation of 2-butene is like this; if the butadiene iron moiety coordinates to second butadiene to form dibutadiene iron carbonyl, with the intramolecular hydrogen transfer from one butadiene to other one cis-2-butene is formed, this leads to predominance of cis-2-butene to trans-2-butene.

\[
\begin{align*}
\text{Fe(CO)}_3 & \rightarrow \text{Fe(CO)}_2 + \text{CO} \\
\text{Fe(CO)}_2 & \rightarrow \text{Fe CO} + \text{CO} \\
\text{Fe CO} & \rightarrow \text{Fe} + \text{CO} \\
\text{Fe} & \rightarrow \square \text{Fe} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + \text{Fe} \\
\text{Fe CO} + \quad & \rightarrow \quad \text{Fe} + \text{CO} \\
\text{Fe} + \square \text{Fe} + \text{CO} & \rightarrow \quad \square \text{Fe} + \text{CO} \\
\square \text{Fe} & \rightarrow \quad 2\text{C}_2\text{H}_2 + \text{Fe}
\end{align*}
\]

(3.10) (3.11) (3.12) (3.13) (3.14) (3.15) (3.16)

The second one is a radicalic way in which the cyclobutene is breaks into two forming two vinyl radical. After the formation of vinyl radical, it may lose one of its H with
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one electron on it forming ethyne and hydrogen radical, or it may react with one of the free butadiene transferring one hydrogen radical to it giving ethyne and butene radical. This radical may rearrange itself and may react with unreacted butadiene or vinyl ethyne radical or even hydrogen radical to produce isomers of butene. If the two vinyl radicals react with each other they may produce ethyne and ethene.

\[ \text{C}_2\text{H}_2 + \text{H}^\circ \rightarrow \text{C}_2\text{H}_2 + \text{H}^\circ \]  \hspace{1cm} (3.17)

\[ \text{C}_2\text{H}_3^* \rightarrow \text{C}_2\text{H}_2 + \text{H}^\circ \]  \hspace{1cm} (3.18)

\[ 3 \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2 \]  \hspace{1cm} (3.19)

\[ \text{C}_2\text{H}_3^* + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \]  \hspace{1cm} (3.20)

\[ \text{C}_2\text{H}_2 + \text{H}^\circ \rightarrow \text{C}_2\text{H}_2 \]  \hspace{1cm} (3.21)

\[ \text{C}_2\text{H}_3^* \rightarrow \text{C}_2\text{H}_2 + \text{H}^\circ \]  \hspace{1cm} (3.22)

\[ 2 \text{C}_2\text{H}_3^* \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \]  \hspace{1cm} (3.23)

\[ \text{Fe} \rightarrow \text{C}_2\text{H}_2 + \text{Fe} \]  \hspace{1cm} (3.24)

The significance of this reaction over the other methods is that the pyrolysis reaction takes place at much lower temperature in comparison with earlier work. For that reason it is believed that pyrolysis products do not undergo further reaction. In the
case of high temperature pyrolysis, further reaction can occur, thus breaking up the reaction products to its fragments, destroying all the valuable data for reaction.

3.6 Conclusion

From the laser and conventional pyrolysis of BdFeTC and the other co-pyrolysis reactions it can be concluded that conventional pyrolysis and LPHP of BdFeTC are different, and they produce different reaction products. The main point of the LPHP results is that it closer to the photolysis of butadiene than its pyrolysis reaction. This is because the butadiene is in a configuration on the iron atom which forces it into an excited electronic state. It is believed that LPHP reaction is homogeneous and free from the catalytic effects of reaction cell wall.

Pyrolysis of FPC with LPHP resulted an active deposit in the reaction cell, and also co-pyrolysis with butadiene and substituted butadiene gave iron carbonyl adducts of these olefins, showing that it also can be used for synthetic purpose. Reaction mechanisms for the laser pyrolysis of BdFeTC and production of benzene is proposed.
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3.7 REFERENCES

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IR LPHP of Acetyl Manganese and Methyl Manganese Pentacarbonyl, Co-pyrolysis with Trimethyl Silane
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4.1 Introduction

Metal Organic Chemical Vapour Deposition (MOCVD) of transition metal carbonyls in the presence of silane or disilane is known to produce metal-silicide films. Transition metal doped silicon films are of particular interest because of their use in microelectronics and their potential for providing transition from semi- to metallic-type conductors depends on the manganese:silicon relative stoichiometry. Methylmanganese pentacarbonyl (MeMnPC) has recently been reported as a new organometallic feed stock in the growth of manganese containing alloys.

Methyl and acyl complexes of manganese pentacarbonyl play a vital role in numerous catalytic processes. Acetyl manganese pentacarbonyl (AcMnPC) and methyl manganese pentacarbonyl (MeMnPC), have been widely studied for their stereochemistry and especially CO insertion into MeMnPC and decarbonylation of AcMnPC.

While most organometallic compounds of the main group elements are unreactive towards carbon monoxide, many transition metal alkyls are known to undergo insertion with CO to give transition metal acyls. Insertion of an unsaturated compound into an M-C or M-H bond is a very important elementary reaction in many catalytic and stoichiometric reactions. In many cases this reaction is reversible. The reverse process is called decarbonylation, CO deinsertion or extrusion reaction. The forward and reverse reactions probably proceed in a concerted manner through a three-centered transition state.

\[
\begin{align*}
\text{Catalysts:} & \quad \text{Ln} & \quad \text{M} & \quad \text{R} \\
\text{LnM} & \quad \text{CO} & \quad \text{LnM} & \quad \text{R} \\
\text{N} & \quad \text{M} & \quad \text{C} & \quad \text{R} \\
\end{align*}
\]

(4.1)
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An obvious requirement for the reaction to proceed is that the R and CO groups are situated in mutually cis positions; if they are not, an isomerisation to bring them to the cis positions must take place first.

It has been established that CO insertion proceeds by alkyl migration to the coordinated CO ligand in most cases. For this reason the term migratory insertion is preferred by some authors. The alkyl migration mechanism has been confirmed for the reaction of methyl manganese pentacarbonyl with CO labelled with $^{13}$C and $^{14}$C, ($^\text{CO} = ^{13}\text{CO}$ or $^{14}\text{CO}$).

The added labeled CO was found to occupy the position cis to the unlabelled acetyl group in the product acetyl manganese complex. Furthermore, in the decarbonylation of $\text{CH}_3^\ast\text{COMn(CO)}_5$ the methyl manganese complex formed was found to have the $^\ast\text{CO}$ ligand only at positions cis to the methyl group.
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The rate of reaction is enhanced in polar solvents. Detailed studies of these systems show that the stereochemistry at the metal depends on various factors, including solvent effects,\textsuperscript{13} the nature of the ligand, and presence or absence of a catalyst.\textsuperscript{11}

Many different CO insertion reaction mechanisms have been suggested.\textsuperscript{14} Calderazzo et al.\textsuperscript{5} suggested that CO insertion in MeMnPC is solvent assisted; there is a linear relationship between \((D-1)/(2D+1)\) (D: dielectric constant of solvent) and the rate constant \(k\). A mechanism for the CO insertion into MeMnPC via an activated structure is shown below.

![CO insertion mechanism to MeMnPC](image)

This occurs by direct combination of CO with CH\(_3\)Mn(CO)\(_5\). Two main mechanisms have been proposed by Noack\textsuperscript{6} for the carbonylation of MeMnPC (Figure 4.1), (a) carbonyl insertion, and (b) methyl migration:

![Mechanisms](image)

**Figure 4.1** CO insertion mechanism to MeMnPC a) CO insertion, b) methyl migration.
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$^{13}$CO insertion to MeMnPC was studied by Thomas et al., and it was shown that methyl migration occurs through a square-based pyramid with a basal acetyl group. Bent and Cotton suggested solvent effects on CO insertion reaction to MeMnPC that in the first step, which is a solvent dependent route, solvent molecules act as the inducing nucleophile and a solvent coordinated acyl complex is formed. The second step is displacement of the solvent by the nucleophile. In a number of investigations, the rate constant $k_1$ has been found to increase with polarity of solvent, and this stage has been described as being solvent assisted.

Reaction of acetyl complexes of manganese pentacarbonyl with HMR$_3$ (M= Si, Sn) has been investigated by Wegman, who reported that the reaction products were acetaldehyde and R$_3$MMn(CO)$_5$ in solution. Trimethylsilyl manganese pentacarbonyl and a series of germyl pentacarbonyl manganese complexes were synthesised, and their physical properties probed using IR, Raman, NMR and mass spectra. It was found that TMSMnPC is an effective catalyst for hydrosilating Fp(COR) compounds (Fp=Fe(CO)$_2$(Tl-C$_5$H$_5$)) with mono, di and trihydrosilanes. The synthesis and properties of TMSMnPC have been studied by Berry and MacDiarmid and different synthesis mechanisms have been suggested in solution.

In this chapter pyrolysis reactions of AcMnPC and MeMnPC, both with and without trimethyl silane (TMS), were investigated using LPHP, followed by spectroscopic analysis of the products. On the basis of these data, reaction mechanisms are proposed. Although laser pyrolysis of both AcMnPC and MeMnPC have not been previously carried out, they were pyrolysed by conventional methods and, in the present investigation, the results obtained are different from those of earlier workers.
4.3 4.2.1 Chemicals

The chemicals studied in this chapter, acetylmanganese pentacarbonyl (AcMnPC), methylmanganese pentacarbonyl (MeMnPC), d3-acetylmanganese pentacarbonyl (DAcMnPC) were synthesised in our laboratory as described below. The following chemical reagents, dimanganesedecacarbonyl, acetylchloride, d3-acetylchloride, tetrahydrofuran (THF), hexane, trimethylsilane (TMS), mercury, and metallic sodium were purchased from Aldrich Ltd. and used without further purification (except THF, which was freshly distilled before use). The processes used for purification and handling of the AcMnPC, MeMnPC, DAcMnPC, and TMS employed in this study have been described in Chapter 2.

AcMnPC was synthesised from acetyl chloride and dimanganesedecacarbonyl by the following procedure.22 A 500 ml two-necked flask was removed from a drying oven and flushed well with prepurified nitrogen; a gas inlet was attached to the side neck. The flask was charged with 4.0 ml of Hg and stirred under nitrogen gas; then 0.5 g of sodium metal was added to the stirred mercury puddle in small pieces, one at a time, under continuous nitrogen flush. After the sodium amalgam was cooled to room temperature, 50 ml of freshly distilled tetrahydrofuran was introduced followed by addition of 3.0 g of decacarbonyl dimanganese. The yellow solution was stirred at 25 °C under nitrogen for 75 minutes. After that, the mercury residue was taken out, the solution was cooled to -78 °C in dry ice-acetone slush bath, and 1.2 ml of acetylchloride was added with a syringe from a freshly opened bottle. The solution was stirred at -78 °C for an hour, and the bath was then removed and stirring carried out for another hour. The solvent was removed at reduced pressure with a water aspirator (5 torr, 25 °C), and the solid residue was stirred with 100 ml of hexane for 30 minutes at 25 °C. The hexane solution was then filtered and the filtrate was cooled to -20 °C for 20 hours. The crystallized solid was collected on a glass frit in air, and...
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dried briefly, using a water aspirator. It was then put into a sample vessel and purified by trap-to-trap distillation on a vacuum line, at -78 °C in dry ice acetone slush bath. Off-white crystals were collected, in 48% yield. These were characterised by melting point23 54-56 °C, IR34.24 and 1H NMR24 spectroscopy.

DAcMnPC was synthesised by the procedure explained above, using CD3COCl. MeMnPC and DMeMnPC were synthesised by Dr. M. Pennington, and were used without any further purification, except for degassing before use every time.

Because of difficulties of obtaining spectral data of organometallic compounds, it is intended to give these data where it is relevant. This does not show, whether a compound is 100 % or 99 % pure. In all the experiments which have been performed, the purity of the chemical compounds was satisfactory for the purpose of our work. Spectral data of the compounds which have been subjected to laser pyrolysis is summarised below briefly, either as spectral data, as a spectrum, or both where it is appropriate.

1H NMR spectra of AcMnPC gave a singlet at 2.197-δ(CH3CO) ppm at room temperature, while MeMnPC was gave a singlet at 0.218-δ(CH3) ppm. Two singlets arose from the 1H NMR spectrum of TMS, one at 0.028-δ(CH3) ppm and the second one at 0.022-δ(SiH) ppm. A list of the bands of the compounds mentioned are in Table 4.1 and FT IR spectra of the compounds are given in Figures 4.2, 4.3, 4.4.
Figure 4.2 FT-IR spectrum of (A) AlN/C.
Figure 4.3 'HNMR spectrum of AcMnPC
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Table 4.1 1H NMR spectral data of the starting materials, AcMnPC, MeMnPC and TMS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift /ppm</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcMnPC</td>
<td>2.197 singlet</td>
<td>δ(CH₃COMn)</td>
</tr>
<tr>
<td>MeMnPC</td>
<td>0.218 singlet</td>
<td>δ(CH₂Mn)</td>
</tr>
<tr>
<td>TMSH</td>
<td>0.028 singlet</td>
<td>δ((CH₃)₂Si)</td>
</tr>
<tr>
<td></td>
<td>0.022 singlet</td>
<td>δ(SiH)</td>
</tr>
</tbody>
</table>

Table 4.2 FT IR spectral data of AcMnPC.

<table>
<thead>
<tr>
<th>Wave number /cm⁻¹</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>654.5</td>
<td>μ(CH₂)</td>
</tr>
<tr>
<td>912.4</td>
<td>μ(CH₂)</td>
</tr>
<tr>
<td>1064.5</td>
<td>δ(CH₃)</td>
</tr>
<tr>
<td>1671.5</td>
<td>ν(CH₂CO)</td>
</tr>
<tr>
<td>2019.1</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2056.5</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2120.0</td>
<td>ν(CO)</td>
</tr>
</tbody>
</table>

Table 4.3 FT IR spectral data of MeMnPC.

<table>
<thead>
<tr>
<th>Wave number /cm⁻¹</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>654.7</td>
<td>μ(CH₃)² or (Mn-CO)</td>
</tr>
<tr>
<td>1190.9</td>
<td>μ(CH₂)</td>
</tr>
<tr>
<td>1961.3</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2003.0</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2023.7</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2116.1</td>
<td>ν(CO)</td>
</tr>
<tr>
<td>2917.0</td>
<td>ν(C-H)</td>
</tr>
</tbody>
</table>
Table 4.4 FT IR spectral data of TMS.

<table>
<thead>
<tr>
<th>Wave number /cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>709.2</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>717.6</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>841.0</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>855.2</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>869.0</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>903.6</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>911.7</td>
<td>(\rho(CH_3))</td>
</tr>
<tr>
<td>1256.5</td>
<td>(\delta(CH_3))</td>
</tr>
<tr>
<td>1268.2</td>
<td>(\delta(CH_3))</td>
</tr>
<tr>
<td>2114.2</td>
<td>(v(Si-H)) P</td>
</tr>
<tr>
<td>2127.5</td>
<td>(v(Si-H)) Q</td>
</tr>
<tr>
<td>2141.2</td>
<td>(v(Si-H)) R</td>
</tr>
<tr>
<td>2964.5</td>
<td>(v(C-H))</td>
</tr>
<tr>
<td>2978.6</td>
<td>(v(C-H))</td>
</tr>
</tbody>
</table>

4.2.2 Apparatus

The equipment used has also been described in Chapter 2. All the experiments were carried out using the cell illustrated in Figure 2.10.

4.3 Results and Discussion

4.3.1 LPHP of MeMnPC

2 torr of MeMnPC and 10 torr of SF\(_6\) were introduced into the cell, followed by exposure to laser radiation, with powers varying from 0.2 to 0.5 W. No reaction was observed up to 0.5 W; above that, the MeMnPC started to decompose giving a black deposit on the front window of the cell. Figure 4.5 shows the IR spectrum of MeMnPC before and after pyrolysis.
Figure 4.5 FTIR spectrum of IR LPHP of MeMnPC before (A) and after (B) pyrolysis.
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Two peaks at 1305 and 3016 cm⁻¹ which correspond to CH₄ bending and stretching vibrations and a band between 2100-2250 cm⁻¹ confirm that the visible pyrolysis products are CH₄ and free CO. Our findings are in agreement with studies of the pyrolysis kinetics of MeMnPC by SFR in combination with gas chromatography. In these other studies, it was found that the principal reaction products were CH₄ and dimanganese decacarbonyl, and that the reaction was a first order process. However in our work, dimanganese decacarbonyl is unlikely to be seen, presumably it decomposes further to CO and Mn. A reaction mechanism for LPHP of MeMnPC is illustrated on page 89.

4.3.2 LPHP of AcMnPC

i. Laser Pyrolysis at Low Concentration

In this experiment, 0.24 torr AcMnPC (the vapour pressure of AcMnPC at room temperature) and 10 torr SF₆ were subjected to IR LPHP. The laser power was varied over the range from 0.2 to 1.5 W.

Monitoring of the reaction cell by FT IR spectroscopy during laser irradiation showed that AcMnPC was being pyrolysed, and that pyrolysis took place in two steps. The first step, at low laser power (at about 0.3 W), was indicated by decay of the acetyl carbonyl peak at 1671 cm⁻¹, which eventually disappeared; at the same time a very weak CO signal appeared in the region 2050-2200 cm⁻¹. The Mn(CO)₅ region of the spectrum changed considerably; two peaks at 2058 cm⁻¹ and at 1650 cm⁻¹, corresponding to the acetyl and manganese pentacarbonyl decreased in intensity. It was observed that MeMnPC was formed (IR spectrum identical with MeMnPC, Figure 4.4) according to the reaction:
Formation of MeMnPC was also observed, as evidenced by IR features at 2058 cm\(^{-1}\) and at 1650 cm\(^{-1}\). MeMnPC is presumably formed by the reaction when the laser power was increased to 0.4-0.5 W, the free CO signal increased, and the Mn(CO)\(_5\) region of the spectrum started to decrease. At the same time, peaks at 1305 and 3016 cm\(^{-1}\), corresponding to CH\(_4\) bending and stretching vibrations, were observed (Figure 4.6), and a black film was deposited on the front window. One possible process responsible for these observations is summarised in the chemical reaction below:

\[
\text{CH}_3\text{Mn(CO)}_5 \rightarrow \text{CH}_3\text{Mn(CO)}_2 + \text{CO}
\]  

(4.5)

It can be concluded from the LPHP of AcMnPC that the pyrolysis reaction takes place in two steps. In the first step at low laser power, which is a decarbonylation of AcMnPC to yield MeMnPC, carbon monoxide is released from AcMnPC to give MeMnPC via acetyl manganese tetracarbonyl (AcMnTC) then followed by methyl migration to the empty site on the manganese to give MeMnPC as shown below.

\[
\text{CH}_3\text{Mn(CO)}_5 \rightarrow \text{CH}_4 + \text{CO} + \text{Mn} + \text{MnC}
\]  

(4.6)

(4.7)
In the second step, LPHP of MeMnPC takes place with higher laser power at about 0.5 W to yield CH$_4$, CO, Mn, and MnC, as reaction products as a result of decomposition of MeMnPC. The likely reaction mechanism is as follows:

$$\text{CH}_3\text{Mn(CO)}_5 \rightarrow \text{CH}_3 + \text{Mn(CO)}_5$$  \hspace{1cm} (4.8)

$$\text{CH}_3 + \text{CH}_2\text{Mn(CO)}_5 \rightarrow \text{CH}_4 + \text{CH}_2\text{Mn(CO)}_5$$  \hspace{1cm} (4.9)

$$\text{CH}_3 + \text{CH}_2\text{Mn(CO)}_5 \rightarrow \text{CH}_4 + \text{CHMn(CO)}_5$$  \hspace{1cm} (4.10)

$$\text{CH}_3 + \text{CHMn(CO)}_5 \rightarrow \text{CH}_4 + \text{MnC(CO)}_5$$  \hspace{1cm} (4.11)

$$\text{MnC(CO)}_5 \rightarrow \text{MnC} + 5 \text{CO}$$  \hspace{1cm} (4.12)

$$\text{Mn(CO)}_5 \rightarrow \text{Mn} + 5 \text{CO}$$  \hspace{1cm} (4.13)

$$2 \text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_{10}$$  \hspace{1cm} (4.14)

Although there have been proposed different reaction mechanism for decarbonylation of AcMnPC, which is described earlier in the introduction section, our proposal is not new. At first decarbonylation of AcMnPC takes place, which is a loss of one of the carbonyl groups bonded to the manganese atom in the cis- position to acetyl group, followed by migration of methyl group to an empty valence orbital of manganese. As a result of this methylmanganese pentacarbonyl is formed. Increased laser power causes further reaction to methane, carbon monoxide, metallic manganese and manganese carbide.
Figure 4.6 FTIR spectrum of IR LPHP of AcmAaPC after laser pyrolysis (first step).
Figure 4.7 FTIR spectrum of IR LPHP of AcMnPC after laser pyrolysis (second step).
Chapter 4

II. Laser Pyrolysis with excess of AcMnPC

The vapour pressure of AcMnPC is quite low and so in order to obtain a replenishable supply in the reaction cell AcMnPC was sublimed into the cell, followed by the addition of 10 torr of SF₆. The cell was then isolated from the vacuum line and exposed to laser radiation. Pyrolysis reaction took place at about 0.4 W of laser power and the pyrolysis reaction was characterised by the decay of the acetyl band at 1671 cm⁻¹ in the FTIR spectrum.

After a certain period of laser irradiation of the cell at the same power, the decarbonylation reaction of AcMnPC ceased even though the cell was subjected to further laser radiation which did not effect the acetyl band intensity at 1671 cm⁻¹ and free CO band intensities in the region of 2150-2250 cm⁻¹ (Figure 4.8). From this it was concluded that once this situation had been reached, the decarbonylation of AcMnPC had reached an equilibrium. To reduce the CO concentration in the cell, all cell contents were frozen by liquid nitrogen and the CO and other volatile gas products were pumped away on the vacuum line. After that SF₆ was added, then the cell was warmed to room temperature, followed by further exposure to laser irradiation. Pyrolysis reaction took place (Figure 4.9) until a second equilibrium was obtained. When full laser power was applied to the cell, all the AcMnPC peaks disappeared, forming CH₄, Mn, MnC, CO.

\[
\text{CH}_3\text{COMn(CO)}_5 \rightleftharpoons \text{CH}_2\text{Mn(CO)}_5 + \text{CO} \quad (4.15)
\]

This reaction has been studied by several workers in the past, who found solvent-assisted CO insertion into MeMnPC or decarbonylation of AcMnPC.²⁶,⁶,¹⁵,¹⁶
However, this is the first time that the equilibrium reaction of the decarbonylation of AcMnPC has been observed in the gas phase by the novel technique of IR LPHP.

4.3.3 Co-Pyrolysis with TMS

1. LPHP of TMS

1.5 torr of TMS and 10 torr of SF₆ were introduced into a pyrolysis cell which was subjected to LPHP at various powers ranging from 0.2 to 3.0 W, while monitoring the reaction by IR spectroscopy. There was no change even with long laser exposure times (~6 minutes); this shows that TMS alone does not undergo pyrolysis reaction under these conditions (see Figure 4.10).

2. LPHP of AcMnPC with TMS

To obtain sufficient AcMnPC in the reaction cell, AcMnPC was sublimed into the cell (cooled by liquid nitrogen), and then about 2 torr of TMS and 14 torr of SF₆ were added. Subsequently this mixture was exposed to the laser beam at various laser powers in the range from 0.1 to 0.5 W in steps of 0.1 W, and reaction was monitored by IR spectroscopy. No reaction was observed until the power was raised above 0.4 W at which point a white deposit was obtained on the front window of the reaction cell, and free CO and CH₄ were also detected from the IR spectrum (Figure 4.11). On completing the laser pyrolysis, the contents of the reaction cell were analysed by ¹H NMR spectroscopy using d₅-toluene as the solvent (Figure 4.12).

The IR data for the co-pyrolysis of AcMnPC with TMS showed that while the CH₃CO peak has disappeared at 1671 cm⁻¹, new peaks have grown in at 1305 and 3016 cm⁻¹ which correspond to methane. The band at about 2100 cm⁻¹ (corresponding to the TMS Si-H stretching vibration peak) reduced in intensity at the same time as the Mn(CO)₅ peak was shifting. The ¹H NMR spectrum of the cell contents are consistent with this result, showing a singlet at 0.12 ppm corresponding to the CH₄.
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Figure 4.3 FTIR spectrum of LRHPE of AxMPC after 6 minutes laser radiation (equilibrated).
Figure 4.9 FTIR spectrum of IR LPHP of AchHeC after removal of CO subsequent LPHP irradiation (equilibrium).
Figure 4.11 FT-IR spectrum of 1PPP of AchNPc with TMS before (A) and after (B) pyrolysis.
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and a singlet at 0.42 ppm due to (CH$_3$)$_3$SiMn(CO)$_5$. This result led us to infer that co-pyrolysis of AcMnPC with TMS yields TMSMnPC, CH$_4$, CO, and not acetaldehyde as was observed by Wegman.$^{17}$ A possible reaction mechanism is as follows.

\[
\begin{align*}
\text{CH}_3\text{CO} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{I} \quad \text{C} \quad \text{O} \\
\text{Mn} \quad \text{oo} \quad \text{c} \quad \text{r} \quad \text{I} \quad \text{c} \quad \text{O} \\
\text{CO} \quad \text{CO} \\
\text{CH}_3
\end{align*}
\]

(4.16)

III. LIPR of MeMnPC and TMS

1.5 torr of MeMnPC, 1.5 torr of TMS and 10 torr of SF$_6$ were placed in the pyrolysis cell and subjected to laser irradiation in the power range 0.1 to 0.5 W. When the laser power reached 0.5 W, MeMnPC reacted with TMS, and CH$_4$ peaks were seen at 1305 and 3016 cm$^{-1}$, along with the carbonyl region of MeMnPC and an appreciable decrease in the Si-H stretching band at about 2150 cm$^{-1}$ (Figure 4.13). The NMR
spectrum of the cell contents (Figure 4.14) showed singlets at 0.12 ppm and at 0.42 ppm corresponding to CH$_4$ and TMSMnPC respectively.

The results of co-pyrolysis of TMS with MeMnPC showed similar results from the IR spectrum with bands at 1304 and 3016 cm$^{-1}$ corresponding to CH$_4$ and a band at 2094 cm$^{-1}$ attributable to TMSMnPC.

To show that the fourth hydrogen of methane comes from TMS rather than the methyl group of the acetyl ligand, d$_3$-AcMnPC (DAcMnPC) was co-pyrolysed with TMS using the same conditions as with AcMnPC + TMS. The pyrolysis reaction started at the same laser power (0.3 W) and an IR spectrum of the cell contents showed two peaks at 2993 and 1036 cm$^{-1}$, corresponding to CD$_3$H. However there was no sign of CH$_4$, CH$_3$D and CD$_2$H$_2$ in the IR spectrum (Figure 4.15). The TMSMnPC IR band was observed at 2094 cm$^{-1}$, at the same position as observed with AcMnPC and TMS co-pyrolysis. After completing the pyrolysis, an NMR spectrum was recorded and a singlet at 0.10 ppm corresponding to CD$_3$H and a singlet at 0.42 ppm corresponding to TMSMnPC (Figure 4.16) were observed.

It is clear from the IR and NMR spectra of the co-pyrolysis that the methyl group in AcMnPC reacts with TMS to form CH$_4$, (CD$_3$H in the case of DAcMnPC), CO and TMSMnPC.

A possible reaction mechanism for co-pyrolysis of MeMnPC with TMS is proposed as follows. First, the methyl group migrates to one of the neighbouring CO groups to form CH$_3$COMn(CO)$_4$; then TMS approaches the unsaturated Mn, and binds to the metal centre. The methyl group from AcMnTC and hydrogen from TMS then form CH$_4$ in a process summarised in the following schematic diagram.
Figure 4.33 FTIR spectrum for L-HFB of MeAlPC with TMS before (A) and after (B) pyrolysis.
Figure 4.14 1H NMR spectrum of LPPP of 4mAnMoC with TMOS after laser pyrolysis.
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Figure 4.15 FTIR spectrum of co-pyrolysis of DADMAC and TMS after laser pyrolysis.
Figure 4.16 $^1$H NMR spectrum of co-pyrolysis of DAcMaPC with TMS after laser pyrolysis.

# : CD$_3$H
Θ : TMSMPC
4.4 Conclusions

From the results of this LPHP study of MeMnPC, it can be concluded that MeMnPC decomposes to CH₄, CO, Mn, MnC, and the decomposition reaction is initiated by the homolysis of CH₃-Mn bond. Although esr studies of MeMnPC by Mills²⁸ could not trap the methyl radical it is believed that the pyrolysis reaction takes radical route, since Mn(CO)₅ radicals were observed.

In the case of AcMnPC, pyrolysis takes place at two slightly different laser powers, one of which is the relatively low laser power of about 0.4 W. In this stage, decarbonylation of AcMnPC takes place for which different reaction mechanisms have been proposed; it is more likely that in this stage decarbonylation occurs not from the acyl group, but that manganese pentacarbonyl loses one of its carbonyl ligands giving
acetyl manganesetetracarbonyl sub-species, followed by migration of the methyl of acyl group to an empty valence of manganese atom to give MeMnPC as a reaction product. Then MeMnPC pyrolyses, at the slightly higher power of about 0.5 W, to methane, free carbon monoxide, manganese and manganese carbide. Pyrolysis of MeMnPC is initiated with the cleavage of methyl manganese bond. The fourth hydrogen comes from unreacted MeMnPC or a molecule that has already lost one or more of its hydrogen.

Pyrolysis of AcMnPC revealed that the decarbonylation reaction is not a one way reaction to MeMnPC and CO, but that it is an equilibrium reaction. When the concentration of CO reached a certain vapour pressure in the cell, the rate of the decarbonylation reaction of AcMnPC becomes equal to that of insertion of CO to MeMnPC; at this point, the reaction is in equilibrium. It was observed that when the partial pressure of CO was reduced more AcMnPC reacts to give MeMnPC at the same laser power. This is the first observation of decarbonylation and CO insertion reactions of AcMnPC and MeMnPC respectively in the gas phase. Earlier studies suggested that the CO insertion reaction was solvent assisted and polarity of solvent is effects the reaction.5

Co-pyrolysis of TMS with AcMnPC and MeMnPC produced methane and TMSMnPC; in the case of AcMnPC carbon monoxide is generated in addition. The fourth hydrogen of the methane produced comes not from unreacted AcMnPC or MeMnPC as in the case of pyrolysis of individual compounds, but from TMS; this was demonstrated by co-pyrolysing TMS with DAcMnPC, which produced CD$_3$H, CO, and TMSMnPC. There was not observed any of the other deuterated isomers of methane, CD$_2$H$_2$, CH$_4$, CD$_4$, indicating that there was not any other side reaction. There was no sign of the acetaldehyde or any other species in the LPHP reaction, as was reported by Wegman,17 but methane was formed instead.
4.5 REFERENCES


Chapter 4


Chapter 5

Laser Pyrolysis of Cyclopentadienyl Manganese Tricarbonyl and Methylcyclopentadienyl Manganese Tricarbonyl
Chapter 5

5.1 Introduction

Cyclopentadienyl manganese tricarbonyl (CpMnTC) and its methyl derivative methylcyclopentadienyl manganese tricarbonyl (MeCpMnTC) serve as typical \( \eta^5 \)-bonded compounds, with CpMnTC being one of the earliest known and best characterised \( \eta \)-bonded systems.\(^1\) They are both thermally stable and relatively volatile, with CpMnTC being volatile, yellow crystalline solid, while MeCpMnTC is a less volatile orange liquid.\(^2\)

The physical properties and chemistry of CpMnTC and its derivatives have been extensively investigated\(^3\) with major emphasis on the bonding and reactions of the cyclopentadienyl ring system.

Recently, there has been some interest in the pyrolytic behaviour of MeCpMnTC and CpMnTC. MeCpMnTC in particular has found applications as an antiknock agent in gasoline\(^5,3\) and has been proposed as a source of Mn in processes such as Molecular Organic Chemical Vapour Deposition (MOCVD), Molecular Organic Vapour Phase Epitaxy (MOVPE), and Molecular Beam Epitaxy (MBE).\(^4\) For example, MeCpMnTC has been used as a source of manganese in the preparation of metal films of C\(_{d_{1-x}}\)Mn\(_x\)Te, where 0\(\leq x \leq 0.7\),\(^5\) and to grow MnHgTe films by MOVPE.\(^6\)

In the last few years there has been a resurgence of interest in the broader chemistry of cyclopentadienyl compounds of manganese. For example, UV photolysis of MeCpMnTC in supercritical fluid solvents generates dinitrogen compounds\(^7\) by substitution of CO group by N\(_2\). The same kind of reaction was achieved by electro-catalytic substitution of CO from MeCpMnTC.\(^8\) The coordination chemistry of perhalogenated cyclopentadienyl manganese carbonyl\(^9\) and electron transfer properties of Cp and substituted CpMnTC\(^10\) have been also studied along with oxidative addition of CpMn to silanes.\(^11\)
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The pyrolysis of MeCpMnTC has been investigated by coupling a quadrupole mass spectrometer to an MOVPE reactor by a capillary.\textsuperscript{12} It was reported that pyrolysis took place by successive loss of carbonyl groups followed by breaking of the $\eta^5$-C$_5$H$_5$-Mn ring bond. The cleavage of the $\eta^5$-C$_5$H$_5$-Mn bond was found to be the rate limiting step. Although the pyrolysis of MeCpMnTC has been studied previously and a reaction mechanism has been proposed, the fate of the Cp ring after the $\eta^5$-C$_5$H$_5$-Mn fission is unknown and is one of the topics of investigation in the present study.

It is well known from work performed on both main-group\textsuperscript{13} and transition metal complexes\textsuperscript{14} that the investigation of the pyrolysis of organometallic compounds is full of difficulties arising largely from the competition between homogeneous and surface reactions. As already mentioned elsewhere in this thesis, Infrared Laser Powered Homogeneous Pyrolysis (IR LPHP) can disentangle these effects by focusing purely on the gas phase chemistry.\textsuperscript{15} In this chapter, the pyrolysis of MeCpMnTC and CpMnTC have been investigated using IR LPHP to provide the reaction mechanism under homogeneous conditions. As will be discussed, the results obtained reveal surprising hydrocarbon reaction products including benzene and ethyne, compounds not detected in earlier studies. To obtain insight into the reaction mechanisms, CpMnTC and MeCpMnTC have been subjected to co-pyrolysis with perdeuterio methyl manganese pentacarbonyl (DMeMnPC). The pyrolysis of DMeMnPC takes place at lower temperatures than CpMnTC and MeCpMnTC, and results in the generation of methyl radicals. These in turn provide a useful 'tracer' which reveals certain aspects of the reaction mechanism. In the light of these experiments, reaction mechanisms were proposed for the LPHP of both CpMnTC and MeCpMnTC.
5.2 Experimental

Because of their low vapour pressures cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl were condensed into the reaction cell from a vacuum line by cooling part of the cell with liquid nitrogen. After warming up the cell to room temperature, about 10 torr of SF₆ was introduced into the cell. The cell was then subjected to CO₂ IR laser powers ranging from 0.2 to 1.5 W. For the co-pyrolysis of CpMnTC and MeCpMnTC with DMeMnPC, approximately equal amounts of the two reagents (estimated partial pressures of 0.25 to 2.4 torr, respectively) and about 10 torr of photosensitiser were employed. The reaction course was monitored using FT IR spectroscopy. On completion, the contents of the reaction cell were transferred to an NMR tube on a vacuum line and a ¹H NMR spectrum was recorded.

5.2.1 Chemicals

CpMnTC and MeCpMnTC were purchased from Aldrich and Johnson Matthey Chemical Co., respectively. DMeMnPC was synthesised by the modification of the literature method for preparing methyl manganese pentacarbonyl¹⁶ (described in Chapter 4). All compounds were purified by repeated trap-to-trap distillation before use and their purities were checked by FT IR and ¹H NMR spectroscopies. Figures 5.1 and 5.2 show FT IR spectra of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, respectively. The ¹H NMR spectrum of CpMnTC shows a singlet at 4.1 ppm while that of MeCpMnTC shows a singlet at 1.45 δ(-CH₃) and a doublet at 3.9 ppm δ(-C₅H₄). The FT IR and NMR data reveal that the compounds which have been studied in this work were relatively free from impurities and therefore satisfy the requirements for meaningful IR LPHP studies.
Figure 5.1 Gas-phase FT IR spectrum of C₆MnTC.
Figure 5.2 Gas-phase FTIR spectrum of Me$_2$PoloTc
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Table 5.1 IR vibrational data for cyclopentadienyl manganese tricarbonyl.17

<table>
<thead>
<tr>
<th>Wavenumber / cm⁻¹</th>
<th>Assignment</th>
<th>Wavenumber / cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
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<td>3129 m</td>
<td>v(CH)</td>
<td>1029 sh</td>
<td></td>
</tr>
<tr>
<td>3113 sh</td>
<td>v(CH)</td>
<td>1012 s</td>
<td>δ(CH)</td>
</tr>
<tr>
<td>3087 w</td>
<td>v(CH)</td>
<td>920 m</td>
<td>δ(CC)</td>
</tr>
<tr>
<td>2040 vs</td>
<td>v(CO)</td>
<td>866 s</td>
<td>p(CH)</td>
</tr>
<tr>
<td>1952 vs</td>
<td>v(CO)</td>
<td>853 s</td>
<td>p(CH)</td>
</tr>
<tr>
<td>1411 m</td>
<td>v(CC)</td>
<td>670 s</td>
<td>v(CC)</td>
</tr>
<tr>
<td>1360 m</td>
<td>v(CC)</td>
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<td>δ(MnCO)</td>
</tr>
<tr>
<td>1265 sh</td>
<td></td>
<td>546 sh</td>
<td></td>
</tr>
<tr>
<td>1193 m</td>
<td>δ(CH)</td>
<td>535 s</td>
<td>δ(MnCO)</td>
</tr>
<tr>
<td>1117 w</td>
<td>v(Ring)</td>
<td>492 w</td>
<td>v(Mn-CO)</td>
</tr>
<tr>
<td>1078 m</td>
<td>p(CH)</td>
<td>384 w</td>
<td>v(MnC)</td>
</tr>
<tr>
<td>1070 m</td>
<td></td>
<td>375 m</td>
<td></td>
</tr>
<tr>
<td>1050 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

v:stretching, δ:bending, p:wagging, w:weak, m:medium, s:strong, vs:very strong, sh:shoulder.
Table 5.2 IR vibrational data for methylcyclopentadienyl manganese tricarbonyl.\(^{18}\)

<table>
<thead>
<tr>
<th>Wavenumber / cm(^{-1})</th>
<th>Assignment</th>
<th>Wavenumber / cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3113 w(m)</td>
<td>(\nu(CH))</td>
<td>1358 v(w)</td>
<td></td>
</tr>
<tr>
<td>2969 m</td>
<td>(\nu(CH))</td>
<td>1264 w</td>
<td></td>
</tr>
<tr>
<td>2938 ms</td>
<td>(\nu(CH))</td>
<td>1238 w</td>
<td>(\delta(CH) + \nu(CH-Me))</td>
</tr>
<tr>
<td>2910 m, sh</td>
<td>(\nu(CH))</td>
<td>1205 w</td>
<td></td>
</tr>
<tr>
<td>2041 s, sh</td>
<td></td>
<td>1156 w</td>
<td></td>
</tr>
<tr>
<td>2037 vs</td>
<td>(\nu(CO))</td>
<td>1125 v(w)</td>
<td>(\delta(CH))</td>
</tr>
<tr>
<td>2032.7 s, sh</td>
<td></td>
<td>1065 m</td>
<td>(\nu ring + \delta(CH))</td>
</tr>
<tr>
<td>1965.7 s, sh</td>
<td></td>
<td>1044 m, sh</td>
<td>(\delta(CH) + p(CH_3))</td>
</tr>
<tr>
<td>1963 vs</td>
<td></td>
<td>1031 s</td>
<td>(\delta(CH))</td>
</tr>
<tr>
<td>1959 vs</td>
<td>(\nu(CO))</td>
<td>982 w</td>
<td>(\nu ring distortion))</td>
</tr>
<tr>
<td>1956.4 s, sh</td>
<td></td>
<td>928 m</td>
<td>(\delta(CH))</td>
</tr>
<tr>
<td>1484 s</td>
<td>(\nu(CC))</td>
<td>906 w, br</td>
<td>(\delta(CH))</td>
</tr>
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<td>(\delta(CH))</td>
<td>843 v, sh</td>
<td>(\nu ring distortion))</td>
</tr>
<tr>
<td>1455 m, sh</td>
<td>(\delta(CH))</td>
<td>833 v</td>
<td>(\delta(CH))</td>
</tr>
<tr>
<td>1389 w, sh</td>
<td>(\nu(CC) + \delta(CH))</td>
<td>667 v</td>
<td>(\delta(Mn-C-O))</td>
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<tr>
<td>1379 m-s</td>
<td>(\nu(CC))</td>
<td>636 v</td>
<td>(\delta(Mn-C-O))</td>
</tr>
</tbody>
</table>

\(v:\)stretching, \(\delta:\)bending, \(p:\)wagging, \(w:\)weak, \(m:\)medium, \(s:\)strong, \(vs:\)very strong, \(sh:\)shoulder.
5.2.2 Apparatus

The experimental apparatus for the LPHP of CpMnTC and MeCpMnTC was described in detail in chapter 2.

5.3 Results

5.3.1 IR LPHP of CpMnTC

Pyrolysis started at a laser power of 1.8 W, quite close to the minimum pyrolysis power for methylcyclopentadienyl manganese tricarbonyl (1.5 W; see next section). The start of pyrolysis was indicated visually with the deposition of a yellow film on the front window of the reaction cell. After partial pyrolysis, the cell was removed and an FT IR spectrum was recorded. This spectrum is shown in Figure 5(B) and can be compared with the spectrum of the starting material (Figure 5(A)). New bands in the IR spectrum can be seen at 663, 729, 673, 807, 895 cm⁻¹. These bands are assigned to cyclopentadiene (663, 807, and 895 cm⁻¹), and ethyne (729 cm⁻¹), with some additional unidentified peaks in the range 1200-1400 cm⁻¹. Assignment was made by comparing these bands with IR tables and running pure benzene and cyclopentadiene FT IR spectra. After laser irradiation the cell contents were transferred to an NMR tube on the vacuum line and an ¹H NMR spectrum was then taken at room temperature. The NMR data showed the presence of ethyne (1.6 ppm), cyclopentadiene (a quintet at 2.65, two complexes at 6.27 and 6.48 ppm), and benzene (a singlet at 7.13 ppm).
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5.3.2 IR LPHP of MeCpMnTC

In the case of MeCpMnTC pyrolysis began at 1.5 W and was accompanied by the appearance of a yellow film on the front window of the cell. In the FT IR spectrum, run before (A) and after (B) pyrolysis (see in Figure 5.4, new peaks were observed following pyrolysis and can be assigned to methylcyclopentadiene, which has characteristic bands at 734, 746, 756, 900, 1330, 1354, 1376, 1448, and several bands between 2800 - 3100 cm\(^{-1}\), cyclopentadiene, which has bands at 663, 807, and 901 cm\(^{-1}\), and benzene which has a characteristic sharp Q branch at 673 cm\(^{-1}\).
Figure 5.5 FTIR spectra obtained before (A) and after (B) IR LRPEP of Cyhal/TC.
Figure 5.4 FTIR spectra obtained before (A) and after (B) LPHP of MeCpMnTC.
5.3.3 IR LPHP of CpMnTC with DMeMnPC

Approximately equal amounts of CpMnTC and DMeMnPC in the presence of 10 torr of photosensitiser were exposed to CO$_2$ IR laser powers ranging from 0.5 to 1.2 W. Pyrolysis began at 0.7 W, as indicated from FT IR data (see Figure 5.5). New peaks in the FT IR spectrum appeared at 730 cm$^{-1}$, which is assigned as ethyne, and at 1036 and 2999 cm$^{-1}$, corresponding to CDH$_3$. As the pyrolysis proceeded a small peak appeared at 807 cm$^{-1}$ due to free cyclopentadiene, which presumable arose from the pyrolysis of CpMnTC by a sudden increase in the laser power during the experiments. Free CO peaks can also be seen between 2050 and 2250 cm$^{-1}$.

5.3.4 IR LPHP of MeCpMnTC with DMeMnPC

Co-pyrolysis of MeCpMnTC with DMeMnPC began at the same laser power (0.7 W) as for CpMnTC/DMeMnPC. The FT IR data (see Figure 5.6) showed new IR bands, corresponding to CDH$_3$ (1036 and 1036 cm$^{-1}$), and CD$_4$ (a peak at 2170 cm$^{-1}$). The appearance of CD$_4$ is due to the high concentration of DMeMnPC in the cell, which is difficult to add in a controlled amount when introduced into the cell. Methylcyclopentadiene peaks appeared at 807, 1136, 1257 cm$^{-1}$, along with free CO bands between 2050-2250 cm$^{-1}$. Because of the low concentration of the reaction products in the cell, only the strongest bands can be clearly identified.
Figure 5.5 FTIR spectra obtained before (A) and after (B) IR LPHP of CpMnTC with DMoMnPC.
Figure 5.6 FTIR spectra obtained before (A) and after (B) IR-LPP of MeCyanATC with DMSO/MeCN.
The temperature of the cell during laser irradiation is not well defined, as discussed in more detail in chapter 2. Comparisons with independent measurements of the rate of decomposition of CH$_3$CO$_2$CH$_3$ indicate that the pyrolysis laser powers employed for CpMnTC and MeCpMnTC, which are 1.5 and 1.8 W respectively, generate maximum temperatures of 520 and 620 K. These temperatures are consistent with the findings of a kinetic study of the above mentioned compounds using the SFR technique.$^{19,21}$ From the kinetic study it was shown that the Cp-Mn bond is stronger than the Mn-CO bond and as a result of this, pyrolysis starts with successive loss of CO followed by homolytic cleavage of the Cp-Mn (or MeCp-Mn) bond.

The pyrolysis of CpMnTC and MeCpMnTC has also been investigated by quadrupole mass spectrometry$^{20}$ where it was observed that the most intense peak was CpMn$^+$, this agrees with the SFR data in that it indicates that the Cp-Mn bond is stronger than the Mn-CO bond. However, neither the mass spectrometry nor the SFR kinetic study have addressed the ultimate fate of Cp or MeCp once detached from the metal. Our work on CpMnTC and MeCpMnTC by IR LPHP has revealed substantial amounts of ethyne and benzene, in addition to the expected gas-phase pyrolysis products of CO, Cp and MeCp. This suggests that during the laser pyrolysis further reaction takes place. In what follows, we try to propose a more complete mechanism to explain the observations made in this and other experimental work, including a discussion of how species such as ethyne and benzene could be formed.
5.4.1 CpMnTC

Dealing first with CpMnTC, the pyrolysis of this compound is believed to begin with the sequential loss of CO from CpMnTC, as mentioned above.

\[ \text{Mn(CO)}_3 \rightarrow \text{Mn(CO)}_2 + \text{CO} \text{, etc.} \]  

(5.1)

This ultimately leaves the CpMn entity, which could decompose in a number of ways but the simplest is of course breakage of the Cp-Mn bond. This is supported by the observation of cyclopentadiene in the FT IR and NMR spectra of the pyrolysis products. In addition, the free cyclopentadienyl radical has been observed in a matrix isolation / ESR experiment by Mills\textsuperscript{21} following pyrolysis of CpMnTC. Note that conversion of the Cp radical to cyclopentadiene is likely to occur by abstraction of a hydrogen atom from unreacted starting material, i.e.

\[ \text{Mn(CO)}_3 + \cdot \text{H} \rightarrow \text{Cp} + \text{Mn(CO)}_3 \]  

(5.2)

At the pyrolysis temperatures used, cyclopentadiene does not undergo significant further reaction. Evidence for this comes from two sources. First, on complete decomposition of the starting material, further laser pyrolysis produced no change in the concentration of
cyclopentadiene. Second, control laser pyrolysis experiments on cyclopentadiene dimer produced no reaction, apart from dissociation of the dimer to the monomer.

Consequently, the formation of ethyne must come from reaction of the \( \text{CpMnTC} \) radical. Further evidence for this comes from the co-pyrolysis of \( \text{CpMnTC} \) with \( \text{DMeMnPC} \). This experiment was performed to identify reactions of the \( \text{CpMnTC} \) radical at temperatures below the pyrolysis onset of the \( \text{CpMnTC} \) starting material. \( \text{DMeMnPC} \) decomposes to produce methyl radicals as described in Chapter 4, and these can then abstract a hydrogen atom from \( \text{CpMnTC} \) yielding the \( \text{CpMnTC} \) radical. As mentioned in section 5.3.3, this co-pyrolysis produced mainly ethyne and free CO. From this data, we can see that the \( \text{CpMnTC} \) radical undergoes decomposition forming ethyne and CO. The fate of the manganese is not clear, but it is possible that manganese carbide is formed, i.e. the overall process (non-stoichiometric) is:

\[
\text{Mn (CO)}_3 \xrightarrow{\text{C}} \text{C}_2\text{H}_2 + \text{MnC} + \text{CO} \quad (5.3)
\]

The formation of ethyne presumably occurs from the decomposition of the \( \text{CpMn} \) radical after complete CO loss from \( \text{CpMnTC} \). Specifically, we have

\[
\begin{align*}
\text{CpMn(CO)}_3 &\rightarrow \text{CpMn(CO)}_2 + \text{CO}, \text{etc} \\
\text{CpMn} &\rightarrow 2\text{C}_2\text{H}_2 + \text{MnC}
\end{align*}
\]

(5.4) (5.5)
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Some supporting evidence for this suggestion comes from the observation of a 1:2 ratio of cyclopentadiene versus ethyne from the proton NMR data. This is precisely the ratio which would be expected if the fate of \( \text{Cp} \) radicals was hydrogen abstraction from the starting material (reaction 5.2) followed by decomposition of \( \text{CpMnTC} \) by reactions (5.4) and (5.5). This assumes loss of \( \text{CpMnTC} \) only by the fragmentation route (5.5) i.e. no other steps such as radical recombination occur. The latter is unlikely given the expected low radical concentrations under our conditions.

Note that no benzene was formed in both the pyrolysis reaction of \( \text{CpMnTC} \) alone and in its co-pyrolysis with \( \text{DMeMnPC} \). The reason probably is that, while cyclisation of ethyne to benzene occurs under some certain conditions, for example high temperature, catalysis by metal or organometallic compounds is essential. In our case, it does not seem to satisfy the requirements of cyclisation reaction. Therefore, benzene has not been observed in the cases of the pyrolysis of \( \text{CpMnTC} \) alone and co-pyrolysis with \( \text{DMeMnPC} \).

5.4.2 \( \text{MeCpMnTC} \)

In the pyrolysis of \( \text{MeCpMnTC} \), it is believed that much of the pyrolysis mechanism parallels that of \( \text{CpMnTC} \). Thus the first stage involves sequential loss of CO from \( \text{MeCpMnTC} \), i.e.

\[
\text{Me(CO)₃ Mn} \xrightarrow{\text{LHP}} \text{Me(CO)₂ Mn} + \text{CO}, \text{etc.}
\]  

(5.6)
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The remaining MeCpMn moiety, could decompose in a number of different ways but the simplest and most likely is cleavage of the MeCp-Mn bond.

\[ \text{MeCpMn} \rightarrow \text{MeCp} + \text{Mn} \]  \hspace{1cm} (5.7)

This is in agreement with the observation of methylcyclopentadiene in the FT IR and proton NMR spectra of the pyrolysis products. On the other hand, Mills in his work on the pyrolysis behaviour of MeCpMnTC probed by matrix isolation / ESR, failed to observe MeCp or MeCpMn radicals in the matrix. However, a vinyl type radical was observed instead. The reason for this could be the nature of the pyrolysis, i.e. it is likely that pyrolysis is extremely sensitive to catalytic effects of the surfaces. In the matrix isolation / ESR study, the pyrolysis takes place in a hot wall environment, rather than under guaranteed homogeneous conditions as in the present study. Thus a comparison between the LPHP and hot wall pyrolysis matrix isolation /ESR studies may be of limited value.

\[ \text{MeCp} \rightarrow \text{MeCpH} \]  \hspace{1cm} (5.8)

Note that, unpaired electron shown as a dot on MeCp in the reaction (5.7) should not be taken to imply that the unpaired electron is localised at the C\textsubscript{2} carbon, i.e. it is merely convenient notation.
Assuming the MeCp radical is formed, it is likely to rearrange to the more stable isomer, \( \text{CH}_2\text{C}_5\text{H}_4 \). This is a well-known character of aromatic ring systems.\(^{22}\) The dissociation energies of R-H bonds provide a measure of the relative stability of free radicals, i.e. the phenyl radical has a lowest C-H bond dissociation energy of 464 kJ/mol, while for \( \text{PhCH}_2 \) the dissociation energy is 368 kJ/mol.\(^{23}\) Therefore, the \( \text{PhCH}_2 \) radical is energetically more stable than the Ph radical. Although the equivalent C-H bond dissociation energy data is unavailable for five-membered rings, it seems likely that the same qualitative arguments will apply.

The \( \text{CH}_2\text{C}_5\text{H}_4 \) radical may potentially undergo a number of different reactions. One possibility is conversion to methylcyclopentadiene, via abstraction of a hydrogen atom from unreacted starting material or from some intermediate:

\[
\text{Mn (CO)}_3 + \text{CH}_2\text{C}_5\text{H}_4 \rightarrow \text{CH}_2\text{C}_5\text{H}_3 + \text{Mn (CO)}_3
\] (5.9)

As alluded to earlier, the occurrence of this or some similar reaction is supported by the observation of methylcyclopentadiene in the FT IR and NMR spectra of the pyrolysis products.

Another possibility is the rearrangement of the \( \text{CH}_2\text{C}_5\text{H}_4 \) radical to form benzene. Previous studies by Slaugh\(^{24}\) and by Sustmann and Lubble\(^{25}\) have revealed the transformation of a 5-membered system, the \( \text{CH}_2\text{C}_5\text{H}_5 \) radical, to form a 6-membered ring, in the gas phase at temperatures exceeding 373 K. If such a process is taking place
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under our conditions, and the temperatures we produced would seem to sufficiently high to make this possible, then this route would explain the observation of benzene in the FT IR and NMR spectra.

![Chemical structure](image)

(5.10)

One possibility that must also be considered is the formation of cyclopentadiene and manganese carbide, as a result of decomposition of the MnCpMn radical:

![Chemical structure](image)

(5.11)

This would of course be consistent with the observation of cyclopentadiene in the FT IR and NMR spectra. In addition, the ESR study of the pyrolysis of MeCpMnTC and CpMnTC, by Mills revealed some anisotropic ESR features which have been tentatively assigned to some manganese carbide, possibly MnC. It is also worthwhile noting that MnC formation has been suggested as source of contamination of Mn films grown by molecular beam epitaxy using CpMnTC precursor. However, the precise nature of the species labelled "MnC cannot be determined from the observation of gas phase studies.
Additional information about the decomposition mechanism comes from the co-pyrolysis of MeCpMnTC with DMeMnPC. As mentioned earlier, DMeMnPC decomposes to yield methyl radicals at lower temperatures than required for the pyrolysis of MeCpMnTC alone. Methyl radicals are then able to abstract hydrogen atoms from MeCpMnTC to form CD$_3$H, leaving behind the +CH$_2$C$_3$H$_4$ radical. As mentioned in section 5.3.4, this co-pyrolysis affords mainly CD$_3$H, cyclopentadiene, carbon monoxide, and a small amount of CD$_4$. The fate of the manganese is unclear, but is more likely to form manganese carbide. Evidence for this is the appearance of cyclopentadiene from this co-pyrolysis instead of methylcyclopentadiene. In the co-pyrolysis no benzene is observed, presumably because the pyrolysis temperature is not high enough for the rearrangement (reaction 5.10) (the co-pyrolysis temperature is estimated to be about 370 K). The overall co-pyrolysis reaction of MeCpMnTC with DMeMnPC (non-stochiometric) is given below:

\[
\begin{align*}
\text{Mn(CO)}_3 + \text{CD}_3 & \quad \rightarrow \quad \left[ \text{CD}_3\text{H} + \text{CH}_2\text{C}_3\text{H}_4 + \text{C}_5\text{H}_6 + \text{CH}_5\text{C}_5\text{H}_5 + \text{CO} + \text{CD}_4 \right] \\
\text{(5.12)}
\end{align*}
\]

### 5.4.3 Overall reaction mechanisms

In this section, the discussion given above is summarised by providing complete pyrolysis reaction mechanisms for both CpMnTC and MeCpMnTC. In these mechanisms, species observed spectroscopically are highlighted. For CpMnTC we have:

\[
\begin{align*}
\text{C}_5\text{H}_3\text{Mn(CO)}_3 & \quad \leftrightarrow \quad \text{C}_5\text{H}_2\text{Mn(CO)}_2 + \text{CO} \\
\text{(5.13)}
\end{align*}
\]
The mechanism proposed for homogeneous thermal decomposition of MeCpMnTC is as follows:

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.14)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + \text{CO} \]  
(5.15)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.16)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + 2\text{CO} \]  
(5.17)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.18)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + \text{CO} \]  
(5.19)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + \text{CO} \]  
(5.20)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + \text{CO} \]  
(5.21)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.22)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.23)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{CO} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} + \text{CO} \]  
(5.24)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.25)

\[ \text{CH}_3\text{C}_5\text{H}_4\text{Mn} \rightarrow \text{CH}_3\text{C}_5\text{H}_4\text{Mn} + \text{H}_2 \text{Mn} \]  
(5.26)
5.5 Conclusions and future work

CpMnTC and MeCpMnTC have been pyrolysed using IR LPHP and new pyrolysis products were found in addition to those found in earlier pyrolysis studies. The fundamental difference between this and earlier work is that pyrolysis in the present study takes place under homogeneous conditions, while the other techniques inevitably face the prospect of heterogeneous conditions.

Pyrolysis of both CpMnTC and MeCpMnTC is initiated by the loss of carbon monoxide followed by homolytic cleavage of $\eta^5$-Cp-Mn and $\eta^5$-MeCp-Mn bonds. Identified reaction products for laser pyrolysis of CpMnTC included cyclopentadiene, ethyne, and carbon monoxide, while observed reaction products for pyrolysis of MeCpMnTC were carbon monoxide, methylcyclopentadiene, cyclopentadiene, and benzene. The source of benzene in the pyrolysis of MeCpMnTC was thought to be the isomerisation of $\sigma$CH$_2$C$_2$H$_4$ radical. It was also suggested that rearrangement of $\sigma$CH$_2$C$_2$H$_4$Mn could be responsible of cyclopentadiene formation and the production of manganese carbide. Evidence for this came from studies of hydrogen abstraction from both CpMnTC and MeCpMnTC, using deuterated methyl radicals.

Because of carbon incorporation in films deposited during pyrolysis of both CpMnTC and MeCpMnTC (as discovered in an ESR study by Mills$^2$), it would appear that these are not ideal precursors for the preparation of manganese-containing semiconductor films. The reason for this is that, on cleavages of the $\eta^5$-Cp-Mn bond yields the Cp radical is
formed and the radical chain process set in motion can ultimately lead to MnC formation. For clean manganese film deposition, a possible candidate as a precursor could be a $\eta^6$-ring system, such as benzene, for the simple reason that $\eta^6$-rings will not form radicals as a result of thermal decomposition.

The decomposition of chemistry substituted CpMnTC, such as the halogenated analogues, would provide an interesting complement to the present work and may strengthen our understanding of the mechanistic process. More generally, since the IR LPHP of CpMnTC and MeCpMnTC gave rather interesting results it would be interesting to apply the same technique to other half sandwich organotransition metal compounds. Equally interesting would be to look at the laser pyrolysis of substituted CpMnTC from the mechanistic point of view and the reaction products. Another aspect of future IR LPHP studies related to the present work could be co-pyrolysis of cyclopentadienyl transition metal compounds with organo silicon compounds to probe the reaction mechanisms, as well as investigating the composition of deposited films during laser pyrolysis.
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5.7 REFERENCES


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19. I. Povey, and I. M. T. Davidson, unpublished work.


27. G. P. Mills, personal communication.
Chapter 6

6.1 Introduction

The discovery of ferrocene in 1951 added a new dimension to the chemistry of organometallic compounds. Ferrocene was first prepared independently by two groups. Miller et al. obtained it by heating iron powder with dicyclopentadiene while Pauson and Kealy produced ferrocene during their efforts to synthesise fulvalene by the reaction of cyclopentadienyl magnesium bromide with ferric chloride. Pauson and Kealy proposed a structure having an Fe-Cp σ bond with the formula and structure indicated in Figure 6.1. Immediately after the publication of the papers reporting the unusually thermally stable orange complex of iron, Wilkinson and Fischer realised the problem of representing the structure of this complex as depicted above. They proposed instead a structure consisting of an iron sandwiched between two planar cyclopentadienyl ligands that symmetrically bind the central iron atom. This was the advent of a new era, the discovery of ferrocene together with the invention of the Ziegler process triggering the explosive growth of organotransition metal chemistry.

This discovery coincided with the period when modern analytical instruments were becoming increasingly available in many laboratories. The structure of ferrocene was quickly and firmly established with the aid of physicochemical methods such as IR and NMR spectroscopy and later by X-ray crystallographic analysis. The IR spectrum of ferrocene exhibits only one C-H stretching frequency (3085 cm⁻¹) and the ¹H NMR spectrum shows only one proton resonance at 4.04 ppm. This evidence demonstrates that ferrocene has only one kind of hydrogen and that all of the hydrogens are magnetically equivalent. The iron atom is symmetrically sandwiched between the two cyclopentadienyl rings, with all C-C and C-H bond lengths being equal, and the iron is bonded to the cyclopentadienyl rings rather than to one carbon of each ring. This structure has been confirmed by X-ray diffraction studies that showed
that the distance between the rings is 3.22 Å, the C-C bond lengths are equal to 1.40 Å, and the Fe-C distances are all 2.04 Å.

Two limiting conformations describe the ferrocene molecule, staggered and eclipsed (see in Figure 6.1 (a) and (b) respectively). Crystalline ferrocene exists in the staggered conformation, but in the vapour state the eclipsed conformation is preferred. The barrier to internal rotation of the two rings is, however, rather small.

Figure 6.1 Structural representation of ferrocene 1) Pauson's proposal, 2) staggered (a) and eclipsed (b) views of ferrocene, respectively.

Ferrocene is the first organometallic compound to be identified having an aromatic character. After it was discovered that ferrocene has a catalytic effect in the synthesis of certain organic and organometallic compounds, its study received considerable attention from the scientific community. Some of the most studied catalytic reactions
are; catalyst for the pyrolysis of petroleum pitch\textsuperscript{7} which showed the accelerating effect of iron on the pyrolysis; carbonisation of poly(vinylidene chloride), by which iron containing graphite (0.4-8.9 wt % Fe) were prepared by pyrolysis at 673 K of poly(vinylidene chloride) after mixing with ferrocene\textsuperscript{8}; agent for char suppression during the thermal decomposition of poly(vinyl chloride).\textsuperscript{9} In addition ferrocene has been used as a flame enhancer catalyst.\textsuperscript{10} It has been found that it shortens the time for soot to first appear in flames arising from isooctane/air, causing the formation of solid iron oxide particulate and enhancing the soot burnout.\textsuperscript{10}

Recently, ferrocene has found use as a catalyst for the synthesis of vapour-grown carbon fibers\textsuperscript{11,12} and in the whiskerization of allene on carbon-fibers using a continuous wave CO\textsubscript{2} laser.\textsuperscript{13} Spinel-type iron oxide films (Fe\textsubscript{3}O\textsubscript{4}) have been prepared on sodalime glass substrates by MOCVD using ferrocene\textsuperscript{14} and acetylacetonate barium\textsuperscript{15} as precursor; it was reported that highly crystalline and carbon-free Fe\textsubscript{3}O\textsubscript{4} films were obtained at a temperature of 423 K.

Chromocene (Cr(C\textsubscript{5}H\textsubscript{5})\textsubscript{2}) is known to be an effective catalyst for the formation of high density polyethylene.\textsuperscript{16} Interaction of metallocene (Fe, Mg, Cr) vapour with highly dehydroxylated silica has been reported to give SiOMCp and C\textsubscript{6}H\textsubscript{6} while reaction with CO at room temperature gave well defined neutral and negatively charged polycarbonylic compounds.\textsuperscript{17}

Metallocenes have not been widely used in MOCVD as a precursor to deposition of films, generally because of their low volatilities and because pyrolysis requires rather high temperatures. However, the mode of decomposition of ferrocene is of interest as a non-carbonyl compound, and as a paradigm for other cyclopentadienyl compounds. Naively, one might expect a relatively simple process in which cyclopentadiene is the major organic product. Cyclopentadiene was indeed a major product but as will be seen, a number of other unusual products were observed including ethyne, benzene...
and naphthalene. In this chapter, IR LPHP studies of ferrocene, cobaltocene and chromocene are reported. In this chapter, a reaction mechanism is proposed for the laser pyrolysis of the metallocenes in the light of the evidence obtained from our spectroscopic analysis.

6.2 Experimental

6.2.1 Chemicals

All the metallocenes were purchased from Aldrich Co. and were used without any further purification. To check the purities and to characterise their IR spectra prior to LPHP, FT IR spectra of the metallocenes in the vapour phase at 358 K were recorded. The IR data obtained is summarised in table 6.1 below.

Table 6.1 Gas-phase FT IR data obtained for ferrocene, chromocene, and cobaltocene. Due to the low sample vapour pressures in the cell not all bands could be firmly characterised.

<table>
<thead>
<tr>
<th>Ferrocene Wavenumber cm(^{-1})</th>
<th>Chromocene Wavenumber cm(^{-1})</th>
<th>Cobaltocene Wavenumber cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3105.5 m</td>
<td>1385 m</td>
<td>1410 w</td>
<td>v(CH)</td>
</tr>
<tr>
<td>1105.6 m</td>
<td>901 m</td>
<td></td>
<td>v(Ring)</td>
</tr>
<tr>
<td>1003.6 m</td>
<td></td>
<td></td>
<td>δ(CH)</td>
</tr>
<tr>
<td>838.0 sh</td>
<td>886 m</td>
<td></td>
<td>ρ(CH)</td>
</tr>
<tr>
<td>813.4 vs</td>
<td></td>
<td>800 m</td>
<td>ρ(CH)</td>
</tr>
<tr>
<td>768.9 w</td>
<td></td>
<td></td>
<td>ρ(CH)</td>
</tr>
</tbody>
</table>
6.2.2 Apparatus

Due to their air-sensitivity, all the compounds were introduced into the reaction cell under an inert atmosphere (N₂) in a glove-box. The experimental apparatus and procedure used for the pyrolysis of the metallocenes was largely the same as that already described in chapter 2. The only significant difference was the use of heat to provide usable vapour pressures of the desired compound in the reaction cell. The cell was either heated externally with hot fluid (see Figure 6.2) or with an electric heating tape round the reaction cell. Although the heating tape method was quick and easy to use, temperature fluctuations were a problem. However, temperature over 373 K can be achieved easily with the use of heating tape. On the other hand, heating the cell with a hot fluid had the advantage of allowing rather precise control of the temperature. However, the rubber tubing connecting the reaction cell exterior to the thermostatted bath could not withstand temperature above 373 K. In addition, the heat loss between the cell and thermostatted bath increases at higher temperatures. For this reason the hot fluid method was only used for the experiments performed below 373 K; where higher temperature were required the heating tape method was employed.

In the usual manner described in previous chapters, reaction course was monitored by FT IR spectroscopy and further analysis of the pyrolysis products was derived from proton NMR spectroscopy and GC/MS.
Figure 6.2 Experimental set up for the pyrolysis of metalloccenes by externally heated cell. Connections between the cell and thermostated bath were made using rubber tubing, so that the cell can be moved while being heated.
6.3 Results

6.3.1 IR LPHP of ferrocene

After loading the cell with ferrocene and photosensitiser, \((SF_6)\), as described in earlier chapters, the cell was then heated to about 80 °C (358 K) prior to laser irradiation to generate a sufficiently high vapour pressure of ferrocene in the pyrolysis cell. When the cell temperature stabilised, the mixture was subjected to laser irradiation. Pyrolysis began at about 16 W of laser power, giving new IR bands which are summarised in Table 6.2. Subsequently, the laser power was gradually increased to 20 W, beyond which there were no further changes observed; at this point the laser irradiation was halted. Figure 6.4 shows pre- and post- pyrolysis FT IR spectra of the reaction cell at 358 K.

<table>
<thead>
<tr>
<th>3099</th>
<th>3065</th>
<th>3014</th>
<th>1338</th>
<th>1024</th>
<th>891</th>
</tr>
</thead>
<tbody>
<tr>
<td>807</td>
<td>780</td>
<td>762</td>
<td>729</td>
<td>673</td>
<td>662</td>
</tr>
</tbody>
</table>

After the LPHP reaction was over, the proton NMR spectrum shown in Figure 6.5 was obtained. The observed peaks are; two multiplets at 7.25 and 7.60 ppm, a singlet at 7.13 ppm, two complex bands at 6.28 and 6.47 ppm, a quintet at 2.68 ppm, two singlets at 1.57 ppm and 0.82 ppm and a singlet at 3.98 ppm due to unreacted starting material. Some of these peaks can be assigned quite easily, having already been observed and identified in the work described in chapters 3 and 5. Thus the peaks at 6.28 \(\delta\)CH\(_2\), 6.47 \(\delta\)CH\(_2\), and 2.68 ppm \(\delta\)CH\(_3\) are due to cyclopentadiene (notation of the protons is given in Figure 6.3), while the characteristic resonance at 7.13 ppm is due to benzene. In addition, the singlet at 1.57 ppm can be assigned to ethyne. The
assignment of the remaining NMR peaks has been made from the combination of FT IR, NMR and GC-MS data. Strong IR bands at 780, 1338 and 3065 cm⁻¹ in the FT IR spectrum and the multiplets in the NMR spectrum at 7.25 ppm δCH₄ and 7.60 ppm δCH₂ were assigned to naphthalene. Further evidence in support of naphthalene came from GC-MS analysis. As can be seen from Figure 6.6, the gas chromatogram showed two major peaks corresponding to masses of 128 g/mol and 186 g/mol, which were assigned to naphthalene and unreacted ferrocene, together with less intense peaks which have been assigned to cyclopentadiene and benzene.

Figure 6.3 Labelling of hydrogen environments in naphthalene and cyclopentadiene employed in the text.

Overall reaction products of LPHP of ferrocene are summarised below:

\[
\text{LPHP} \rightarrow \left[ \text{C₅H₆} + \text{C₈H₈} + \text{FeC} + \text{Fe} + \text{C₂H₂} \right] \quad (6.1)
\]
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Figure 6.4: FTIR spectra before (A) and after (B) IR-LHPF of fenoxacene.
\[ q \text{, } t \text{, o} \]

\[ \Delta : \text{Benzene} \]
\[ \text{II} : \text{Naphthalene} \]
\[ \ast : \text{Ethyne} \]
\[ @ : \text{Ferrocene} \]

Figure 6.5 \(^1\)H NMR spectra of the cell contents, after IR LHP reaction of ferrocene was halted.
Figure 6.6 Gas chromatogram of the cell contents of ferrocene after IR LPFP section was over.
6.3.2 IR LPHP of acetyl ferrocene

To assist in the elucidation of the reaction mechanism, pyrolysis studies of acetyl ferrocene and methanol ferrocene (see next section) were performed. It was hoped that these substituted ferrocenes would provide useful information, particularly about the route to naphthalene. However, it turned out that no substituted naphthalenes were observed on pyrolysis of these compounds. Nevertheless, results are provided here for the sake of completeness.

For acetyl ferrocene, pyrolysis started at 12 W of laser power, as evidenced by the formation of a slightly black film deposited on the front window of the cell and by the observation of FT IR features due to methane, benzene, and CO$_2$. FT IR spectra obtained before and after IR LPHP are shown in Figure 6.7. A $^1$H NMR spectrum recorded after the LPHP reaction showed peaks similar to the NMR spectrum following LPHP of ferrocene. A singlet at 7.13 ppm can be assigned to benzene, while cyclopentadiene peak appeared at 6.28 and 6.47 ppm (both multiplets) and at 2.68 ppm (a quintet). Singlets at 5.25 and 1.57 ppm were due to ethene and ethyne respectively, and an unidentified peak was seen at 2.05 ppm. Observed pyrolysis products are given in the reaction below (non-stochiometric)

\[
\text{CH}_2\text{COOH} \rightarrow \overset{\text{LPHP}}{\text{Fe}} + \overset{\text{LPHP}}{\overset{\text{CH}_4 + \text{FeC} + \text{Fe} + \text{CO}_2}{\overset{\text{CH}_2\text{COOH}}{\text{Fe}}}}
\] (6.2)
6.3.3 IR LPHP of methanol ferrocene

After the temperature settled to 358 K in the cell, the sample was irradiated at laser powers ranging from 2 to 16 W. New IR bands started to appear at 12 W as can be seen in Figure 6.8. New bands were observed at 663, 673, 807, 895 cm\(^{-1}\), together with water bands between 1400 and 1700 cm\(^{-1}\). These can be assigned to cyclopentadiene (663, 807 cm\(^{-1}\)), benzene (673 cm\(^{-1}\)), naphthalene (780 cm\(^{-1}\)), and ethyne (729 cm\(^{-1}\)). The overall reaction products of the laser pyrolysis of methanol ferrocene are given below.

\[
\begin{align*}
\text{Fe} & \quad \text{LPHP} \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

\[\text{LPHP} + +
\]

6.3.5 IR LPHP of chromocene

Laser pyrolysis of chromocene was carried out at laser powers ranging from 2 to 7 W with actual pyrolysis beginning at 6 W. FT IR spectra obtained before and after IR LPHP are shown in Figure 6.9; new IR bands appear at 1426, 1375, 1013, 893, 663 cm\(^{-1}\) following pyrolysis. After the pyrolysis was ceased, the cell contents were then pumped away and an FT IR spectrum of the empty cell was recorded to see if there were any involatile reaction products in the cell. Bands at 814, 1013, 1366 and 1429 were found for the remaining contents the cell. These involatile products are possibly due to one or more polymeric species remaining in the cell; however, no further investigations on these residues were carried out. A post-pyrolysis \(^1\)H NMR spectrum
showed the following resonances: two quartets at 7.25 and 7.58 ppm, a singlet at 7.13 ppm, two multiplets at 6.27, and 6.48 ppm, a quintet at 2.68 ppm, and two singlets at 1.57 and 1.05 ppm.

The volatile products in the reaction cell included naphthalene as shown by the strong band at 780 cm\(^{-1}\) in the spectrum IR and the two multiplets at 7.25 and 7.58 ppm in the NMR spectrum. Cyclopentadiene can account for a number of spectral features (see section 6.3.1). The singlet at 1.57 ppm in the NMR spectrum and a band at 729 cm\(^{-1}\) in the IR spectrum represent ethyne while an NMR singlet at 7.13 ppm and an IR band at 673 cm\(^{-1}\) is the proof of benzene formation. However there are some IR and \(^{1}\)H NMR peaks which we have been unable to identify. Overall, the identified reaction products for the laser pyrolysis of chromocene are as follows:

\[
\text{LPHP} \quad \text{CrC} + \text{Cr} \quad (6.4)
\]

### 6.3.6 IR LPHP of cobaltocene

Cobaltocene was heated to 410 K by using heating tape wrapped around the reaction cell. It was then irradiated in the laser power range 2 to 12 W. Pyrolysis took place at 8 W, with a black deposit forming on the front window of the cell, along with new IR bands appearing in the FT IR spectrum of the cell. Figure 6.10 shows FT IR spectra before and after IR LPHP reactions. Observed new IR bands after laser pyrolysis are at 1415, 1261, 1255, 1110 cm\(^{-1}\) and later on new peaks emerged at 859, 1005, 3065, 751, 806, 1034, 1326, 1197 cm\(^{-1}\). A proton NMR spectrum of cobaltocene recorded after the laser pyrolysis was halted showed two multiplets at 6.27 and 6.48 ppm and a
quintet at 2.68 ppm due to cyclopentadiene, and two singlets at 1.57 and 7.13 ppm corresponding to ethyne and benzene, respectively. From both FT IR and proton NMR spectra of the cell after IR LPHP, no naphthalene was formed, unlike the ferrocene and chromocene cases. Observed reaction products of the laser pyrolysis of cobaltocene are summarised below.

\[
\text{Co} \xrightarrow{\text{LPHP}} \quad \text{C}_{2}H_{2} \quad + \quad \text{Co} + \text{CoC}
\]

(6.5)
Figure 6.7 FTIR spectra before (A) and after (B) LPHP of acetylferrrocene.
Figure 6.8 FTIR spectra of the reaction cell before (A) and after (B) the laser pyrolysis of methanol ferrocene.
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Figure 6.9 FTIR spectra of the reaction cell before (A) and after (B) the laser pyrolysis of chromencore.
Because metallocene compounds consist of two cyclopentadienyl rings and one metal atom sandwiched between them, pyrolysis reaction is most likely to start with the loss of one of the cyclopentadiene ligands:

\[
M^+ \quad \Leftrightarrow \quad \text{Cp}^* + \text{MCp}
\]  

(6.6)

The formation of the cyclopentadienyl radical may then begin a radical chain reaction process leading to the formation of a number of reaction products. Of course, there is a second possibility, dimerisation, but this has low probability for reasonably low radical concentrations; this is confirmed by the lack of evidence for the dimer in the FT IR and proton NMR spectra. Thus the likely fate of the cyclopentadienyl radical is hydrogen abstraction from the starting material, which forms cyclopentadiene and a metallocene radical:

\[
\text{M} + \text{Cp}^* \quad \rightarrow \quad \text{Cp} + \text{M}^+ \text{Cp}
\]

(6.7)

Note that the unpaired electron, shown as a dot on Cp in the reaction (6.7), should not be taken to imply that the unpaired electron is localised at particular carbon, i.e. it is merely convenient notation.
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Having lost one of its hydrogen atoms, the metalloocene radical formed subsequently decomposes to give ethyne, cyclopentadienyl radical and presumably metal carbide (MC). A route of this type has already been discussed in Chapter 5.

\[
\begin{align*}
M & \rightarrow \text{C}_2\text{H}_2 + \text{MC} + 2\text{C}_2\text{H}_2 \\
\end{align*}
\]  

(6.8)

Cyclisation of ethyne is a well-known reaction, i.e. under catalytic conditions ethyne undergoes a trimerisation reaction to form benzene. 

\[
\begin{align*}
3\text{C}_2\text{H}_2 & \rightarrow \text{C}_6\text{H}_6 \\
\end{align*}
\]  

(6.9)

A reaction of this type is presumably the source of the benzene observed in our experiments. Perhaps the most unusual product in the pyrolysis process was naphthalene. With the aid of Dr P. R. Jenkins in the Department of Chemistry, Leicester University, a reaction mechanism has been proposed for the formation of naphthalene from the IR LPHP of ferrocene and chromocene. The route suggested naphthalene is as follows. After losing one of its hydrogen atoms to abstraction by a cyclopentadienyl radical (see reaction 6.7), the metalloocene radical is formed. Then follows the dimerisation of the two rings, most likely while both are coordinated to the metal atom. In a sense, the metal centre acts as a catalyst for the dimerisation reaction.
Evidence for the catalytic role of the metal comes from the IR LPHP of cyclopentadiene dimer alone, since this yields no naphthalene.

\[ \text{M} \rightarrow \text{cyclopentadiene dimer} \rightarrow \text{naphthalene radical} \]

This is followed by the rearrangement of dicyclopentadienyl radical to the azulene radical.

\[ \text{dicyclopentadienyl radical} \rightarrow \text{azulene radical} \]

Once this stage is reached the azulene radical isomerises to afford the naphthalene radical, which subsequently forms naphthalene by the loss of a hydrogen atom. There is precedent for a similar process in the organic chemistry literature, since it is known that azulene can isomerise to form naphthalene at temperatures above 540 K.\textsuperscript{21}
If this route occurs, one might expect to observe azulene bands in the IR spectra. In fact we have not observed any trace of azulene in either FT IR or $^1$H NMR spectra. One reason for this could be the relative stabilisation energies of azulene and naphthalene. Although the aromatic stabilisation energy of azulene (72 kJ mol$^{-1}$) is considerably less than naphthalene which is (133 kJ mol$^{-1}$), however the greater structural strain in azulene makes it a less stable isomer, and for that reason naphthalene is preferred.

As for the isomerisation mechanism of azulene, there have been two different propositions. One is a radical process and the other is a unimolecular isomerisation mechanism; these are shown in Schemes 1 and 2 below. It is believed that the radical route is more likely to be operative in our work, for the simple reason that the pyrolysis of metallocenes is consistent with a radical based mechanism as already mentioned earlier. Supporting evidence comes from the work of Alder et al who investigated the pyrolysis of azulene in an oxygen free conditions. They concluded that initial radical generation from azulene is via wall reactions, but the bulk of the rearrangement occurs in the gas phase by a radical reaction mechanism which is summarised below.
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Scheme 1

The molecular isomerisation mechanism was suggested by Scott and Agopian following a flash pyrolysis study (1308 K) of the conversion of azulene to naphthalene. They suggested that isomerisation proceeds via a bicyclobutane intermediate, i.e.

Scheme 2
In addition to the already identified role of free radicals, it would seem unlikely that this process was the source of naphthalene under our conditions because our pyrolysis temperature are very much lower than those employed by Scott and Agopian.

In order to obtain more information about the pyrolysis mechanisms of the metallocenes, substituted ferrocenes were also subjected to IR LPHP study. In fact these provided little information, since in fact the first stage of pyrolysis always seemed to involve decomposition of the substituent before M-Cp bond fission. In the laser pyrolysis of acetyl ferrocene cyclopentadiene, ethyne, benzene, and carbon dioxide were formed. This is characteristic of carboxylic acids, which eliminate carbon dioxide at high temperature and presumably leaving methyl ferrocene:

\[
\begin{align*}
\text{CH}_2\text{COOH} & \rightarrow \text{M}_{-}\text{Cp} + \text{CO}_2 \\
\text{CH}_3 & \rightarrow \text{M}_{-}\text{Cp} + \text{CO}_2
\end{align*}
\]  

(6.15)

Cyclopentadienyl radicals are most likely to abstract a hydrogen atom from either starting material or from an intermediate to form cyclopentadiene. If the methyl cyclopentadienyl radical is afforded from the decomposition of methyl ferrocene, it may rearrange subsequently to give benzene. The source of benzene also can be the trimmerisation of ethyne (see reaction 6.9).

Pyrolysis of methanol ferrocene was very much like the pyrolysis of ferrocene, the only difference being the formation of water and that pyrolysis took place at lower temperature. A possible reason for the pyrolysis of methanol ferrocene taking place at
lower temperature could be the initiation of pyrolysis by the elimination of water from starting material. This reaction may result in the formation of carbene (this must be regarded as speculation, for which there is no firm evidence):

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{Fe} \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}
\end{align*}
\]

(6.16)

Having formed the carbene, it decomposes further to yield cyclopentadiene and benzene which has already been shown in Chapter 5.

\[
\begin{align*}
\text{Fe} + \text{C}_5\text{H}_5\text{Fe} & \rightarrow \text{C}_5\text{H}_5 + \text{Fe} + \cdot\text{CH} \\
\text{C}_5\text{H}_5 + \cdot\text{CH} & \rightarrow \text{C}_5\text{H}_4 + \text{Fe}
\end{align*}
\]

(6.17)

6.7 Conclusions

The aim of the work described in this chapter was to pyrolyse metallocene compounds of iron, cobalt and chromium in order to determine their gas phase thermal decomposition mechanisms.
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Metalloocene compounds of iron, cobalt, and chromium were successfully pyrolysed in the gas phase using IR LPHP and reaction products were identified by employing a combination of different analytical techniques, notably FT IR and proton NMR spectroscopies and GC-MS. Gas phase reaction products were cyclopentadiene, benzene, ethyne, and naphthalene in the case of ferrocene and chromocene. Cobaltocene only gave cyclopentadiene and benzene as reaction products. A reaction mechanism was proposed for the production of naphthalene, which involves azulene radical formation followed by isomerisation to naphthalene radical. The source of benzene is most likely to be the trimerisation of ethyne.
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6.6 REFERENCES

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Conclusions and Future Work
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The results obtained from the pyrolysis of butadiene iron tricarbonyl, by employing the technique of IR LPHP, compared with those obtained with an SFR approach reported elsewhere, were quite different in terms of reaction products. While SFR pyrolysis was consistent with butadiene and carbon monoxide as the major gaseous products, IR LPHP of the same compound showed that butadiene, cis-butene-2 and trans-butene-2, carbon monoxide, and benzene were formed, along with other unidentified reaction products and evidence of polymers of butadiene. A reaction mechanism has been proposed for the production of benzene from butadiene and this might include involvement of cyclisation of butadiene while coordinated to an iron atom followed by bond breakage to yield ethyne. Benzene is formed from the trimerisation of ethyne in a process which is probably catalysed by butadiene iron tricarbonyl. Another interesting result was that the concentration of cis-butene-2 was higher than that of the trans-butene-2. This suggests that hydrogenation of butadiene takes place while butadiene is still coordinated to the iron atom. However, in order to firmly establish this and other aspects of the reaction mechanism, including the formation of benzene, more work needs to be done on the pyrolysis of similar systems, e.g. dibutadiene iron carbonyl and/or labelled butadiene iron carbonyl compounds.

Laser pyrolysis of acetyl manganese pentacarbonyl and methyl manganese pentacarbonyl have been studied on their own and in co-pyrolysis with trimethyl silane. The results obtained for acetyl manganese showed that pyrolysis takes place in two steps, the first one at low temperature with the elimination of CO from the acetyl group, thus yielding methyl manganese pentacarbonyl. Methyl manganese pentacarbonyl then decomposes at higher temperatures, to yield methane, carbon monoxide, and presumably manganese and manganese carbide. The transformation from acetyl manganese pentacarbonyl to methyl manganese pentacarbonyl has been
observed for the first time in the gas phase and was found to be a reversible reaction. Co-pyrolysis reactions of both acetyl and methyl manganese pentacarbonyl with trimethyl silane led to the formation of trimethyl silane manganese pentacarbonyl and methane. Carbon monoxide also been observed in the case of co-pyrolysis of acetyl manganese pentacarbonyl with trimethyl silane. Co-pyrolysis of trimethyl silane with perdeuteriomethyl manganese pentacarbonyl showed that the fourth hydrogen of methane comes from trimethyl silane, not from acetyl or methyl manganese pentacarbonyl. Reaction mechanisms have been proposed for acetyl manganese pentacarbonyl and methyl manganese pentacarbonyl both with and without trimethyl silane. Once again, by investigating the pyrolysis of similar alkyl manganese compounds, especially with substituted alkyl ligands, a greater understanding of the mechanistic processes should be attainable.

Pyrolysis of cyclopentadienyl manganese tricarbonyl and the methyl cyclopentadienyl analogue gave interesting results. The principal reaction products were cyclopentadiene, benzene, ethyne, carbon monoxide, manganese carbide, and manganese from cyclopentadiene manganese tricarbonyl, and cyclopentadiene, methylcyclopentadiene, carbon monoxide, manganese carbide and manganese in the case of cyclopentadiene manganese tricarbonyl. It was suggested that the pyrolysis reaction is initiated by the sequential loss of carbon monoxide followed by homolytic cleavage of the cyclopentadiene-manganese bond. The cyclopentadienyl radical then abstracts a hydrogen atom from unreacted starting material to form cyclopentadiene, and causes subsequent decomposition of the remaining cyclopentadiene manganese tricarbonyl radical to form ethyne, carbon monoxide and presumably manganese carbide. In addition, as a result of trimerisation of ethyne, benzene is formed. Co-pyrolysis of perdeuteriomethyl manganese pentacarbonyl with cyclopentadiene and methylcyclopentadiene manganese tricarbonyl compounds resulted in reaction at lower temperatures than in the absence of perdeuteriomethyl manganese pentacarbonyl; the
products, however, were the same apart from the additional formation of CD₃H and the absence of benzene. Thus observation supports the idea of a radical-based mechanism. Benzene was not observed in the co-pyrolysis reactions presumably because the temperature was not high enough for trimerisation of ethyne.

Perhalogenated analogues of half sandwich η⁵-bonded compounds of transition metal carbonyls could be good candidates for future work to enable us to clearly establish the role of hydrogen abstraction. In addition, σ-bonded compounds of cyclopentadienyl compounds of transition metal compounds or heterocyclic compounds along with substituted cyclopentadienyl metal complexes would be interesting to look at from the point of view of both reaction products and reaction mechanism.

Gas phase pyrolysis studies of the metalloccenes of iron, cobalt, and chromium gave surprising reaction products. Ethyne and benzene were observed and particularly intriguing was the observation of naphthalene from LPHP of ferrocene and chromocene. We failed to see naphthalene amongst the reaction products from the pyrolysis of cobaltocene, either because it did not form or its concentration was too low to detect. A reaction mechanism has been suggested for the production of naphthalene, and it is believed that the dimerisation of two five-membered rings while they are still coordinated to the metal atom is a key step. The ejected cyclopentadiene dimer radical then isomerises to azulene radical followed by a series of radicalic isomerisation steps to form naphthalene. However, the exact nature of the formation of naphthalene has not been firmly established in this work. More work needs to be done on the pyrolysis of metalloccenes; the use of labelled metalloccenes would be particularly informative, especially data from ¹³C substitution. An obvious extension would be the investigation of other metalloccenes in addition to the ones already been
completed. Other sandwich compounds, such as $C_5$, $C_7$ or higher ring systems would also be intriguing.

Another aspect of future work that ought to be investigated is the nature of films deposited during IR LPHP. The chemical composition of the films produced by IR LPHP would be of particular interest. Are impurities formed in such films, like carbon and metal carbide involvement. Assignment of metal carbide formation has been made tentatively in this work but, since carbon incorporation can be a severe problem in the formation of practical films it would be interesting and important to quantify this in films formed solely via a gas phase pyrolysis route. If metal carbide formation is indeed established, how this can be eliminated or minimised by the use of other compounds in the co-pyrolysis reactions would be of very considerable practical interest for those employing transition metal precursors in MOCVD and other techniques.