SPECTROSCOPIC STUDIES OF η^5- CYCLOPENTADIENYL IRON DICARBONYL KETONE COMPLEXES

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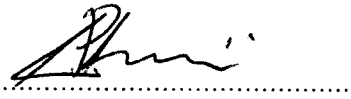
A Dissertation Submitted to the University of Zambia in partial fulfillment of the Requirements for theDegree of Master of Science in Organometallic Chemistry.

THE UNIVERSITY OF ZAMBIA

LUSAKA, 1999.

DECLARATION

I, Phiri Lloyd, do hereby declare that this dissertation represents my own work, and that it has not been previously submitted for a degree at this or any other University.



Signature

DATE: 16/04/99

DEDICATION

I dedicate this work to my beloved late wife and mother of my four sons, Annie M. Phiri whose inspiration and encouragement lived on to see this assignment completed.

APPROVAL

This dissertation of **Mr. Lloyd Phiri** is approved as fulfilling part of the requirements for the award of the degree of Master of Science in Chemistry by the University of Zambia.

Signature:	Date:
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S. J. Phiri	22.10.97
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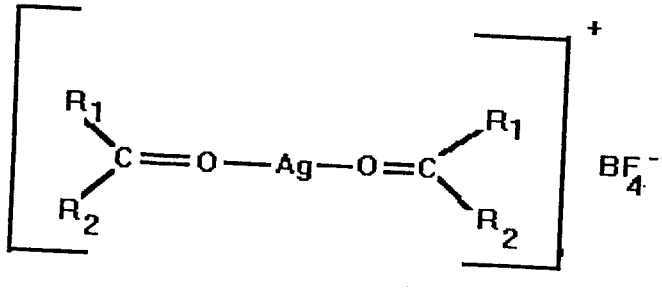
Finally, I would like to thank my late wife Annie, to whom this works is dedicated, and my sons, Azere, Lloyd (Junior), Luseshelo and Ignatius, my mum and dad, for their love, patience and support during the course of this work.

ABSTRACT

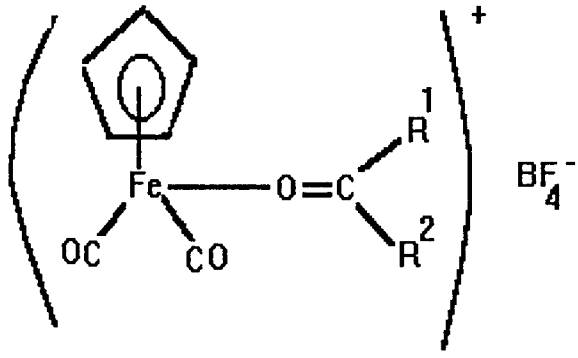
This dissertation is focused on the spectroscopic characterization of cyclopentadienyl iron dicarbonyl ketone complexes **42**. The ketone silver tetraflouroborate complexes **32** are initially prepared. The formation of **32** is supported by the enhanced solubility of the silver tetraflouroborate salt in the ketone dichloromethane solution and the infrared shifts of the ketone carbonyl bands to lower wavenumbers. The ketone silver tetrafluoroborate **32** are reacted with cyclopentadienyl iron dicarbonyl iodide to produce cyclopentadienyl iron dicarbonyl ketone complexes **42.** These complexes (**42**) are characterised by infrared (IR), proton and carbon-13- nuclear magnetic resonance ($^{1}H/^{13}CNMR$) spectroscopies. The infrared shifts of carbonyl bands to lower wavenumbers is observed in **42**.

Carbon-13-nuclear magnetic resonance ($^{13}CNMR$) of cyclopentadienyl iron dicarbonyl cyclopentanone **42vi** also compares very well with cyclopentadienyl iron dicarbonyl complexes prepared by Ganson. The two terminal carbonyls of **42vi** are less by $\Delta\delta$ 2.2 from Gansons range ofδ211.4 - 216.2. The two terminal carbonyls of **42vi** appear atδ209.2.

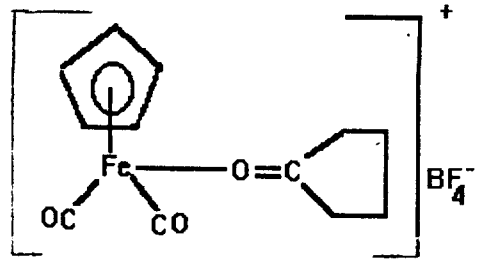
Mass spectroscopy further shows cyclopentadienyl iron dicarbonyl ketone cation, i.e **49,** as a dorminant dissociation product.



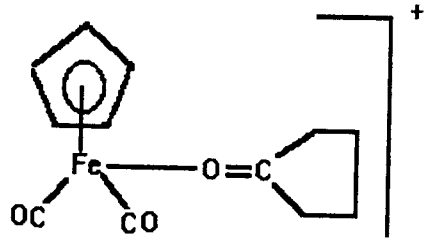
32



42



42vi



m/z 261

49

ABBREVIATIONS

Cp	=	Cyclopentadienyl
Fp	=	Cyclopentadienyl iron Dicarbonyl
Ph	=	Phenyl
L	=	Ligand
M	=	Metal
Sec	=	Secondary
me	=	Methy l
R	=	Alky l

The following abbreviations are used in spectrosopy.

a) Infrared Spectroscopy

w	=	weak
br	=	broad
m	=	medium
s	=	strong
vs	=	very strong

b) Nuclear magnetic resonance

s	=	singlet
m	=	multiplet
d	=	doublet
q	=	quartet

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Appendix 3. Spectroscopic Characterisation of Ketone Complexes

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CHAPTER 1

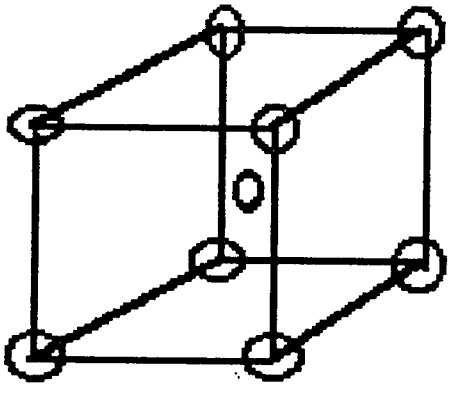
INTRODUCTION

1.1 Iron metal

Since iron is the major inorganic metal component in this study, it is important to briefly look at its structure and chemistry. Iron is a relatively soft silvery metal. It melts at 1528 °C and boils at 2880 °C.[1,2] At ordinary temperatures it possesses the body centred cubic structure (fig 1). In a body centred cubic structure, all the corners of a cube are occupied by an atom each and one atom at the centre of the cube.[3]

Fig. 1

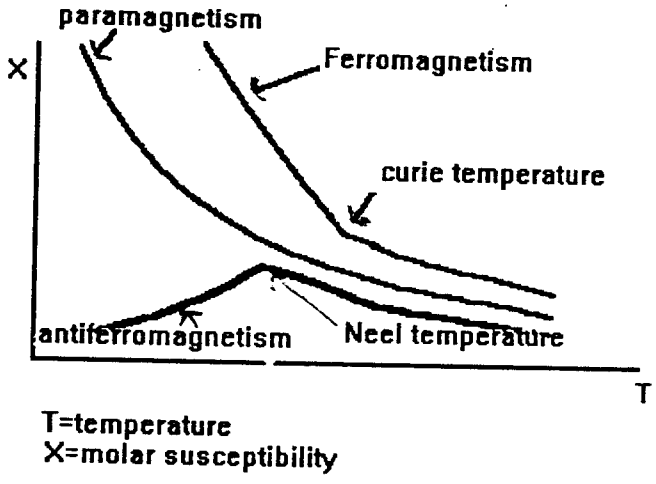
A body centred cubic unit cell of iron.



Iron exhibits ferromagnetism. Ferromagnetism is a special case of paramagnetism. The spins of unpaired electrons of individual atoms in a body centred cube of a unit cell couple and form one unit cell moment when subjected to a magnetic field. This behaviour is experienced up to a temperature of 728°C.[2] This temperature is called curie temperature. Above the curie temperature, the substance behaves just like any other ordinary paramagnetic substance.

Fig. 2

Variation of molar susceptibility with temperature



The reverse of ferromagnetism is a phenomenon called antiferromagnetism.

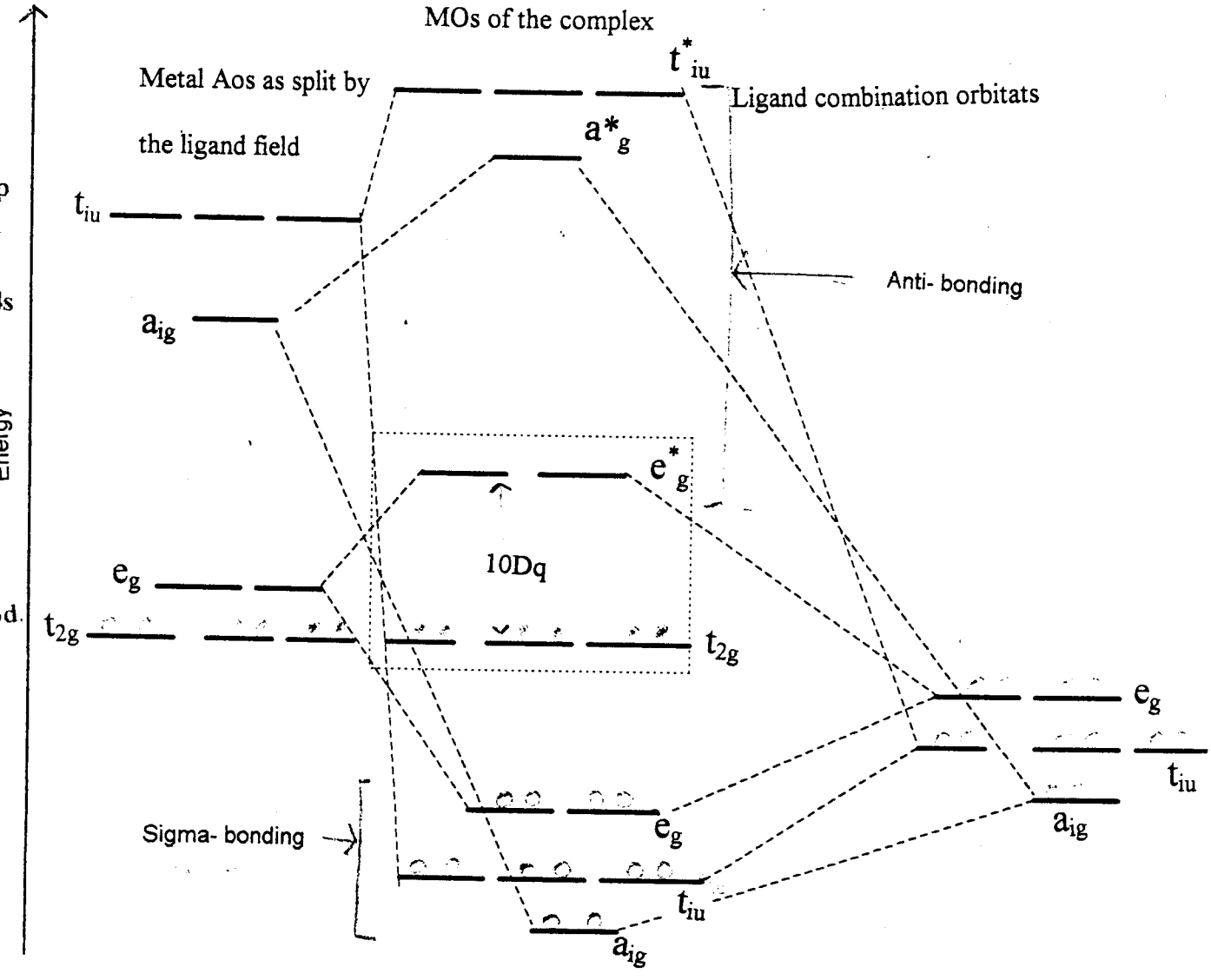
In this case, spins of electrons are anti-parallel. Therefore, these electrons do not couple to produce a resultant moment. But as temperature is increased their thermal motions increase hence χ is seen to rise up to the Neel temperature after which the substance behaves just like any other paramagnetic substance.

Iron, just like other transition metals has a big range of oxidation states. The maximum oxidation state being +6. This is observed in ferrate iron FeO_4^{2-}. But the most important oxidation states are +3 and +2. Like most transition metals, iron has an extensive chemistry associated with low oxidation states.

Iron has at its disposal the 4s, 4p and 3d orbitals available for bonding. The ground state electronic configuration is $[Ar]4s^2 3d^6$. When it is subjected to a ligand field the configuration changes to $[Ar]3d^8$. The 4s electrons shift to the 3d orbital. A closer look at the new configuration reveals that its the 3d, 4s and 4p are available for bonding of iron to other chemical species. This is better explained by valence bond theory,crystal field theory and molecular orbital theory. Below is a molecular orbital scheme for an octahedral d^6 complex.

Fig. 3

Sigma molecular orbital scheme for an octahedral d^6 complex

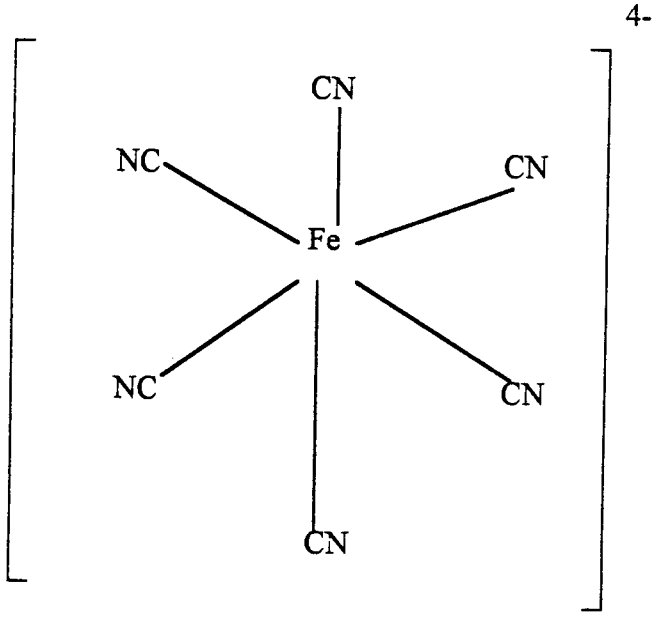


0 Ligand electron

• Metal electron

As seen from the diagram (Fig. 3) the 3d level is more stable than the 4s level which is below 4p. Moreover, in an octahedral setting, it is the d - level which have proper symmetry for d - bonding with ligands are dx^2-y^2 and dz^2. It is also assumed that the energy levels of those d levels which point away from ligands (dxy, dxz, dyz) is unaffected by the ligand field. This concept is derived from a bonding theory which is based on point charges, the "crystal field theory" and its extension to covalent bonding, the ligand field theory.[4] On the left hand side of the diagram are shown the combinations of ligand atomic orbital. For example, filled orbitals of cyanide. The geometry is shown below in figure 4.

Fig. 4. **Geometry of iron (II) hexacyanide**



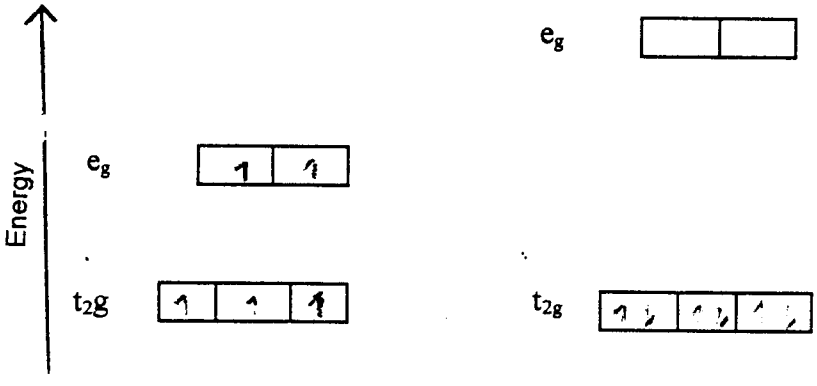
Looking at the molecular orbitals on the diagram in fig 3, at least one molecular orbital is more stable (bonding) and one is less stable (antibonding) than atomic orbitals which are used to form molecular orbitals. Where an overlap occurs, for example in t_{2g} level in octahedral complexes (dxy, dxz and dyz) no net energy change is caused by forming the sigma bonding molecular orbital network, so that these particular t_{2g} molecular orbitals are metal localised and non bonding.

The tetrahedral geometry is commonly prevalent with co-ordinatively saturated d^{10} complexes of nickel (O) palladium (O) and platinum (O). In this type of geometry, there are more orbitals available than required for both sigma and pi bonding.

The 18 electron rule is another concept that assist a lot in determining whether a particular compound is capable of being stable or not. Looking at the molecular orbital diagram in fig 3, the metal has nine (9) metal valence shells s, p. d orbitals which are completely filled. These are usually bonding. Complexes in which these nine orbital are completely filled are stable. A complex with more than 18 valence electrons must generally put some of them into anti-bonding levels and therefore be less stable. For example $Ni(H_20)_6^{2+}$, a d^8 nickel (11). The extra electrons have to be put into the e*g molecular orbital.

The separation between the t_{2g} and e*g levels for the octahedral complex shown in the diagram in fig 3 is designated 10Dq. 10Dq is the crystal field energy which is merely the difference between t_{2g} and e*g. This is different for different ligands. This is very important for classic chemistry of transition metal cation. If the 10Dq is smaller than the energy required to pair electron in the same orbital, the d - electrons may be distributed equally among t_{2g} and e*g levels with minimum pairing. For example, Fe (11), d^6 complexes: $[Fe(CN)_6]^{-4}$ having no unpaired electrons (from measurement of magnetic moment or electron spin resonance) and $[Fe(H_2O)_6]^{+2}$ having four unpaired elections.

Fig. 5 High and low spin Fe (II)complexes



High spin Fe(II)
complex e.g. $Fe(H_20)_6^{2+}$
4 unpaired electron

Low spin Fe(II)
complex e.g. $(Fe(CN)_6)^{4-}$
diagmagnetic
no unpaired electron

The one with all electrons paired is said to be low spin and the one with some unpaired electrons is said to be high spin. The majority of organotransition metal complexes are spin paired; that is 10Dq is usually large.[5]

1.2 Ferrocene

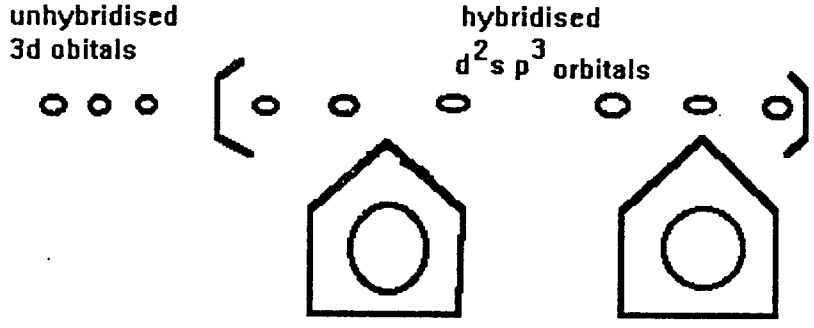
The importance of discussing ferrocene in this research is to try and bring out some of its characteristics and compare them to our complexes 42 which happen to contain the same cyclopentadienyl group which is equally present in ferrocene.

Iron, perse, occupies a very special role in the development of organometallic chemistry. The use of iron pentacarbonyl in organic synthesis from acetylene and the independent discoveries of ferrocene by Kealy and Pauson, then Miller, Tebboth and Traiman respectively enhanced the development of organometallic chemistry,[6,7,8.] Kealy and Pauson treated cyclopentadienyl magnesium bromide with iron (III) chloride in an attempt to couple the cyclopentadienyl rings and instead produced ferrocene. Miller, Tebboth and Traiman passed cyclopentadiene over nitrogen at 300°C over reduced iron catalyst. Reduced iron catalyst is the one existing in the presence of Alumina and potassium oxide. It is the same reduced iron used in the Haber process. In the minds of the three gentleman (Miller, Tebboth and Traiman) the intention was to produce a cyclopentadienyl amine but instead ferrocene was produced. This was an accidental discovery.

The structure of ferrocene was latter proposed by Wilkinson, Whiting and Woodward[9] but the most recent is the molecular orbital theory.

In terms of Valence Bond Theory, each cyclopentadienyl anion donates 3 pairs of electrons into the vacant set of d^2sp^3 hybrid orbitals on iron (II)[12].

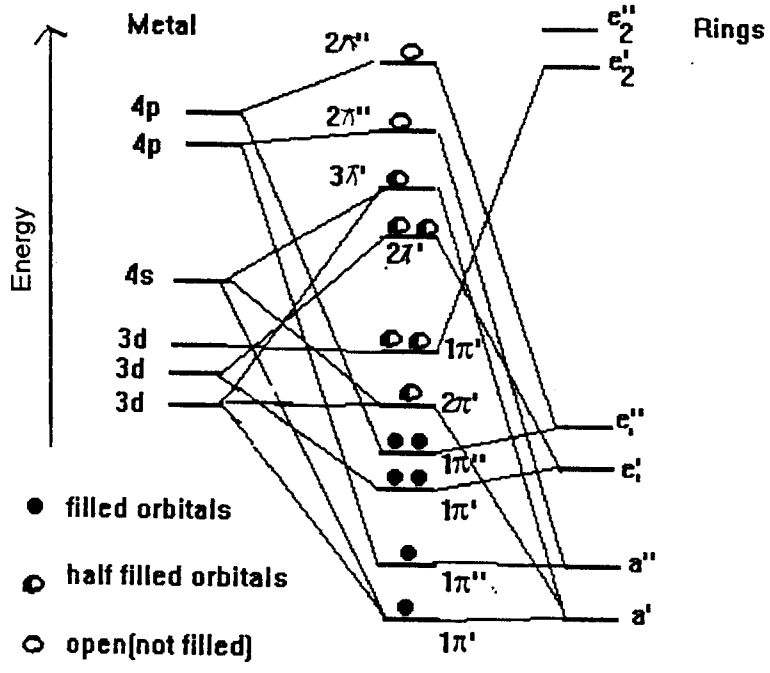
Fig. 6. **Structure of ferrocene according to valence bond theory**



$Fe(C_5H_5)_2$

For the construction of the molecular orbital diagram of ferrocene, it is important to know the orientation of the molecular orbitals of cyclopentadienyl rings and the atomic orbitals of the metal so that they are able to overlap. A cyclopentadienyl ring has five p atomic orbitals on each carbon atom which are at right angles to the plane of the ring. These are the orbitals which delocalise to produce 5π molecular orbitals on the ring which are equally at right angles to the the ring. Now for the metal, atomic orbitals which are properly orientated to the 5π molecular orbitals of cyclopentadienyl rings are one 4s , two 4p (Px , Py) and three 3d (dxt, dxz, dxy) atomic orbitals. $3dz^2$, $3dx^2\text{-}y^2$ and 4Pz lie along the axis x, y, z and therefore are not properly orientated to overlap with the 5π molecular orbitals of the cyclopentadienyl rings. The resulting molecular orbitals between cyclopentadienyl rings and the metal atomic orbitals are all π-molecular orbitals because overlap of the orbitals occur sideways and not head on as is the case for sigma-bonding. On the molecular orbital diagram (fig.7), there are π'

Fig. 7 **Molecular orbital diagram for ferrocene**



molecular orbitals resulting from one cyclopentadienyl ring and π''molecular orbitals resulting from the other since ferrocene contains two cyclopentadienyl rings.

By filling the eighteen electrons into the ferrocene orbitals, the 9 bonding orbitals are filled. Twelve of the electrons are in the strongly bonding orbitals while six, two are in non bonding dz^2 orbital and four are in the weakly bonding (E_{2g}) orbitals. Its the 3dyz and 3dxz which contribute most to the metal - ring bonding (E_{1g}).

1.2.1 Infrared spectroscopy of ferrocene

Ferrocene is a π - bonded complex with a local symmetry C_{5v}.[14] It has six fundamental IR models. These are given in Table 1.

Table 1

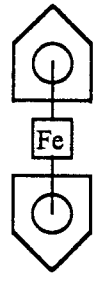
Local symmetry	**Band assignment**
, C_{5v}	CM^{-1}
υ(CH)	3086
	2909
υ (CC)	1408
	1101
σ(CH)	1001
π (CH)	854
	814
ring tilt	490
	478
δ(M - R)	170

1.2.2 Proton nuclear magnetic resonance (^{1}HMR).

The chemical shift δ of ring protonsappear at 4.04 ppm.[15] This means that all protons are equivalent as a result of fluxional behaviour of molecules.[16]

Structure

Ferrocene **1** is a sandwich compound and has a staggered configuration. This structure was established by electron difraction.[17] Ferrocene **1** is diamagnetic.[12] By sandwich it means an atom of iron is bound both at the top and from the bottom by two identical groups. In this case the groups are the cyclopentadienyl [**1**].



1

1.3 Metal carbonyls

Iron forms a wide range of compounds both from inorganic to organo iron compounds. In this review, we are interested in organo iron compounds and in particular cyctopentadienyl iron dicarbonyl complexes.

Transitional metal carbonyls are usually volatile and many are unreactive towards water and air but decompose upon heating and all are violently poisonous. Metal carbonyls are often used for preparing sandwich compounds. The first carbonyl to

be prepared was mond compound ($Ni(C0)_4$, a colourless liquid boiling at 43°C and highly soluble in organic solvents.[18] This is formed by direct combination of nickel and carbon monoxide, Iron also forms $Fe(C0)_5$ by direct combination with carbon monoxide. This is a liquid and boils at 103°C.[18]

Infrared spectroscopy is the single most useful tool for the characterisation of the carbonyl ligand. The intense IR carbonyl bands occur in a region of IR spectrum which is largely free of other strong bands. Possible interfering modes are IR bands of nitrogen, nitrosyl and metal hydrydes. The number and frequency of CO stretching bands are useful in assigning structure and in following the course of a reaction.[19, 20]

Table 2

IR frequency modes for carbonyl groups of metal carbonyl complexes

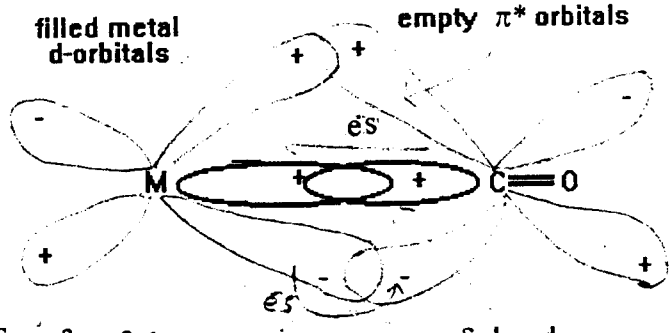
Type of carbonyl	IR range (cm^{-1})
Free carbon Monoxide	2143
Terminal carbonyl	2140 - 1800
Doubly bridging carbonyl	1850 - 1700
Triply bridging	~1625

The major difference between iron carbonyl and cyclopentadienyl iron dicarbonyl lies in the type of ligands linked to the iron metal centre. In iron carbonyl complexes the ligands

are only carbonyl groups whilst in cyclopentadienyl iron dicarbonyl there is a cyclopentadienyl ligand apart from the carbonyl ligands.

Carbon monoxide has low lying vacant anti-bonding orbitals of correct symmetry to the filled metal d - orbital after it has formed a sigma bond with the metal. These vacant orbitals have correct symmetry to form π - bonds by accepting electrons from filled metal d - orbital. This is a phenomena known as back bonding. This phenomena contributes to the stabilisation of the complex. Stabilisation is achieved by the reduction of electron density on the metal centre as a result of the π-bonds so formed.

Fig. 8. **Back bonding of carbon monoxide**



1.4 Cylopentadienyl metal dicarbonyl compounds

$C_5H_5Mo\ (CO)_5\ Mo\ C_5H_5$ and $C_5H_5W\ (CO)_6\ W\ C_5H_5$ were the first binuclear compounds with CO_5/CO_6 bridges. containing one cyclopentadienyl ring bonded to a transition metal to be synthesised.[21, 22]

Wilkinson and Piper confirms that mono or binuclear cyclopentadienyl ring is bonded to the metal atom in a manner similar to the bond in bis cyclopentadienyl compounds.[23, 24] The symmetry of cyclopentadienyl ring per metal is different from symmetrical bis cyclopentadienyl metal compound.[25] Further, metal to ring bond is due to overlap of π electrons of the ring with d electrons of the metal atom. The orbitals both having E_1 symmetry with respect to the local symmetry of C_5H_5 ring. The metal orbitals need not be exactly the same as in bis-cyclopentadienyl compounds. This type of bond is refered to as sandwich even though it is not for compounds with single cyclopentadienyl rings.[25] Upon accepting the above view, this leads us to take all metal carbonyls as diamagnetic whether with even atomic numbers (binuclear) or old Atomic numbers (Mononuclear).[26]

Cyclopentadienyl iron carbonyl compounds could be said to possess almost all the IR active bands of bis cyclopentadienyl iron. In addition, $[CpFe(CO)_x]$ have peaks for the carbonyls around 2100 and 2000 cm^{-1}. The C-H IR stretching frequency is found between 3200 and 3000 cm^{-1}. The C-C IR ring breathing frequency is between 1500 and 1400 cm^{-1}. The C-O IR stretching frequency is found between 22000 and 2000 cm^{-1}. The rest are similar to the peaks of bis cyclopentadienyl iron. For comparison, Table 3 is given below.[51]

Table 3 Infrared spectroscopy of cyclopentadienyl Metal carbonyls

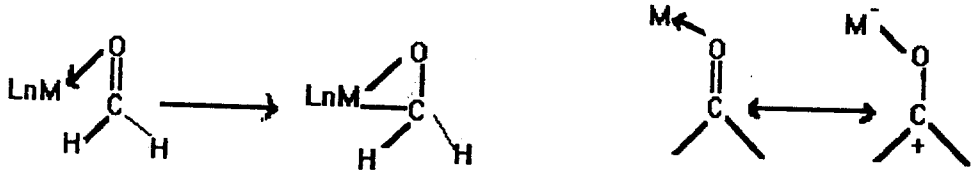
IR	υC-H cm^{-1}	υC=O cm^{-1}					**The**	**rest**			
CpV(CO)₄	3110 *m*	2119 *vs*	1951 *vs*	1919	1430 *m*	1370 *w*	1120 *vw*	1060	1010 *m*	840 *s*	
CpFe(CO)Cl	3110 *m*	2050 *vs*	2010 *vs*		1430 *m*	1365 *w*	1118 *w*	1070 *w*	1003 *s*	874 *s*	835 *s*
CpFe(CO)₂CN	3120 *m*	2060 *vs*	2020 *vs*		1420 *m*	1360 *w*	1115 *w*	1075 *w*	1010 *s*	854 *s*	726 m
CpCo(CO)₂	3110	2028	1967		1405 *s*	1360 *w*	1110 *w*	1051 *w*	1010 *m* 990 *m*	955 *w* 917	754 *w*
CpFeCp	*3085*				1411		1108 s	1051 *w*	1002 s	811 s	

SOURCE: T.S. piper and F.A. Cotton; J. Inorg and Nuclear Chem. 1 (1955), 166.

1.5. Aldehyde and ketone transition metal complexes

The successful isolation of $Os(CO)_2(PPh_3)_2(\eta\text{-}H_2C{=}O)$ in 1971 led to the wide exploration in this field. The major hindrance was the intrinsic thermal instability the complexes possess.[28] The organic carbonyl of both aldehydes and ketons are easily activated to nucleophlic attack when complexed to a transition metal (scheme 1, complex 5).[29] The above is achieved as a result of their behaviour as ligands in metal complexes.[28] The oxygen atom on the carbonyl donates a pair of electrons to the metal to form a sigma (η^1) bond or the π electrons in the C = O double bond are donated to form a π bond (η^2).

Scheme 1

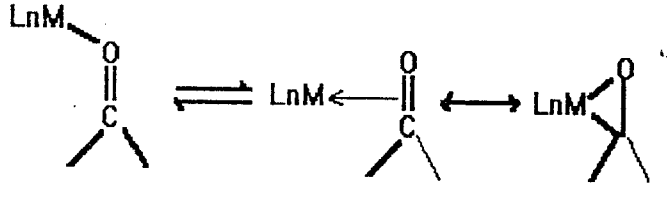


2 **3** **4** **5**

2 and **3** are the two resonance forms of π (η^2) binding. **3** signifies a substantial donation of d orbital electrons to the empty C=O π^* orbital (back - bonding).[28,30] forming an oxametallacyclopropane. **4** and **5** are the two resonance forms of a sigma (η^1) binding. The formation of sigma (η^1) and π (η^2) bonds is greatly

influenced by steric factors in the molecules involved. Simple adehydes, for example, formaldehyde form π bonds in transition metal complexes where as substituted aldehydes and ketones usually form sigma (η^1) bonds. This is so because the carbonyl carbon and substituents are held away from the metal fragment in sigma (η^1) bonding where as in π bonding the carbonyl carbon and substituents are held very close to the metal.[31] So far, its only in aromatic aldehyde complexes where both pi and sigma isomers have been found to exist in equilibrium quantities.[32] This has been observed in seleno benzaldehyde, azo benzene and related complexes. The quantitative ratios of sigma to pi are very much dependent on the electron donating or withdrawing ability of the substituent on the aromatic group. Electron withdrawing groups increase the π - bound isomer and vice verse for electron donating groups.[33, 34]

Scheme 2



6 **7** **8**

σ - bound **π - bound**

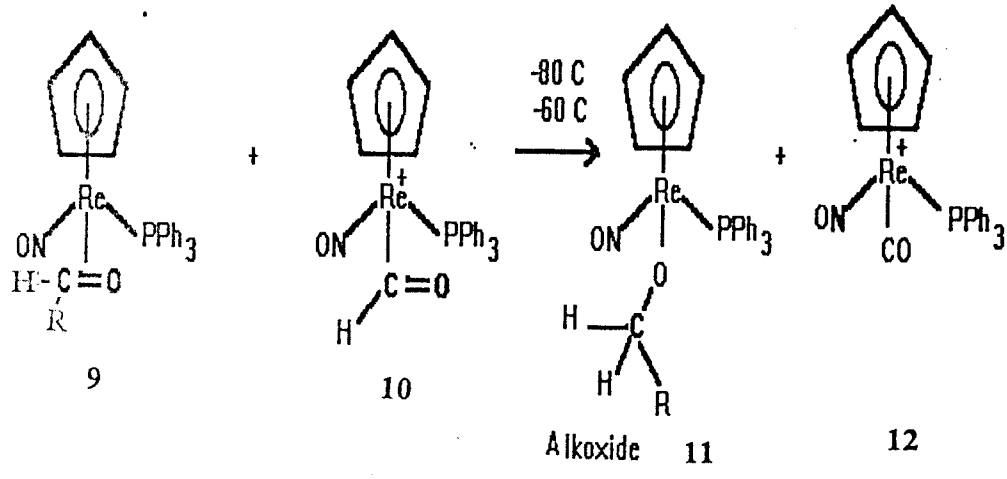
1.5.1 Diagnostic spectroscopic assays for binding modes of aldehyde and ketone transition metal complexes.

The infrared carbonyl absorption of a complexed carbonyl from uncomplexed carbonyl is rarely less by 100 cm^{-1} from the uncomplexed carbonyl upon sigma (η^1) co-ordination where as its completely absent upon π (η^2) co-ordination.

In carbon nuclear magnetic resonance (^{13}CNMR) spectra of sigma (η^1) aldehyde ligand, the carbonyl resonance appear in the normal downfields range of organic carbonyl groups. For π (η^2) aldehyde ligand, the carbonyl resonance appear upfields at 45 - 111 ppm.[28] In ^{1}HNMR spectra, the aldehydic protons appear in the normal range when in sigma (η^1) binding mode and shifted upfield when in the pi (η^2) binding mode (Appendix 2, 3)

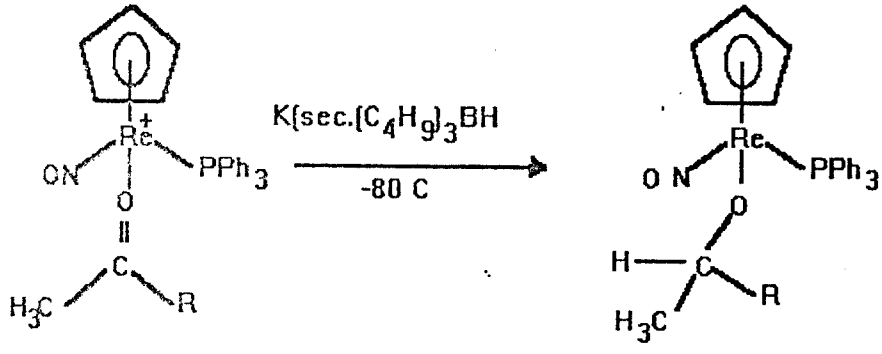
The sigma (η^1) and π bound organic carbonyl complexes undergo a variety of reactions.[34, 35] Gladysz and group have shown that these complexes undergo reduction to form alkoxide complexes.

Scheme 3



9 10 Alkoxide 11 12

Scheme 4.

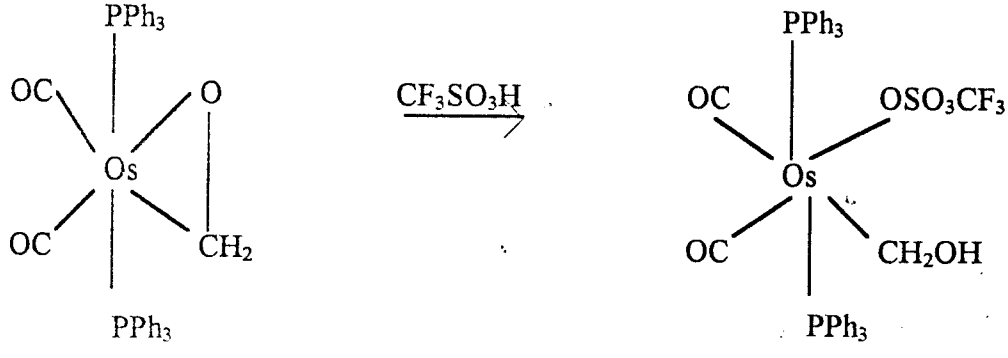


13 14

Some of the reactions are summarised below.[28]

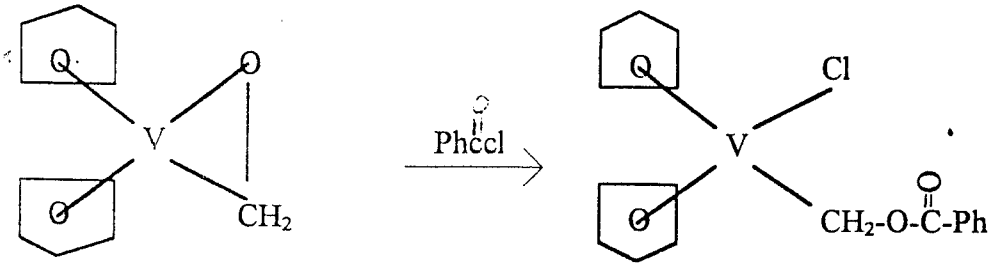
Reactions with electrophiles

Scheme 5



15 16

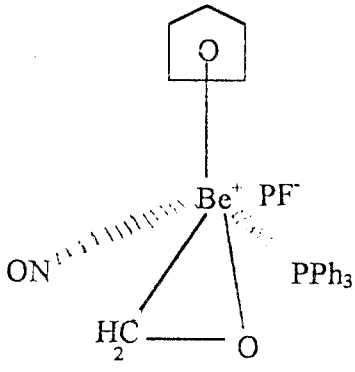
Scheme 6



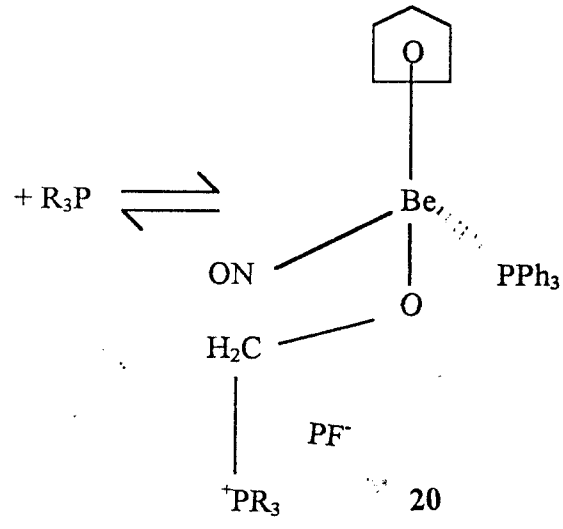
17 18

Reactions with nucleophiles

Scheme 7

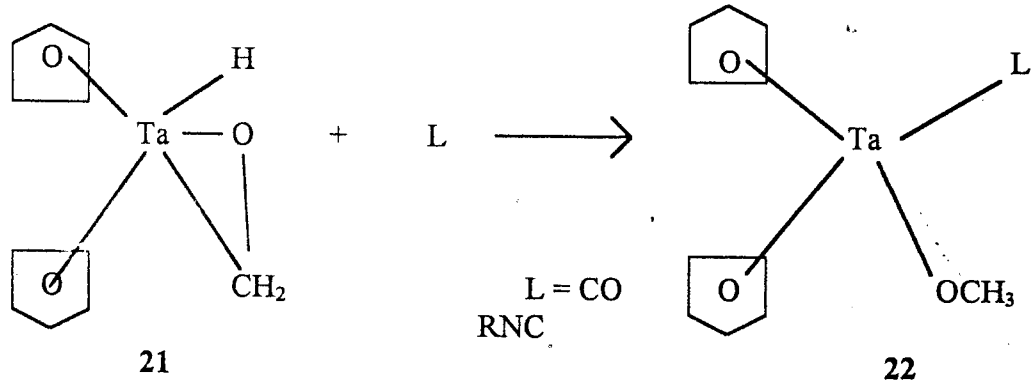


19



20

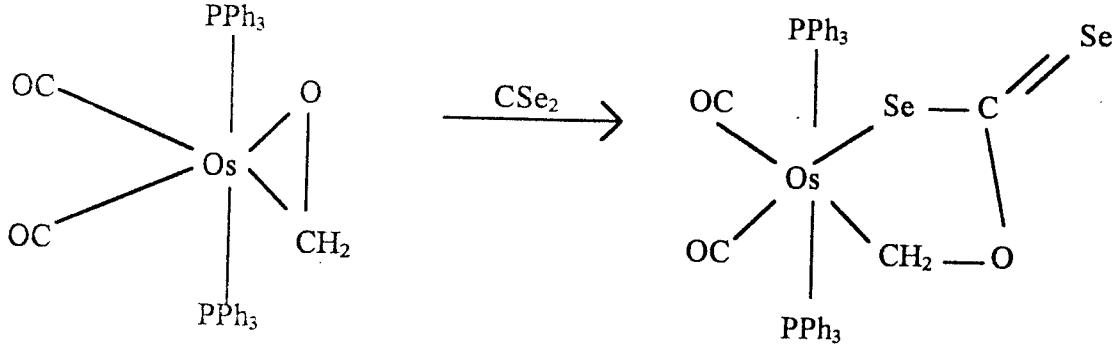
Scheme 8



21 22

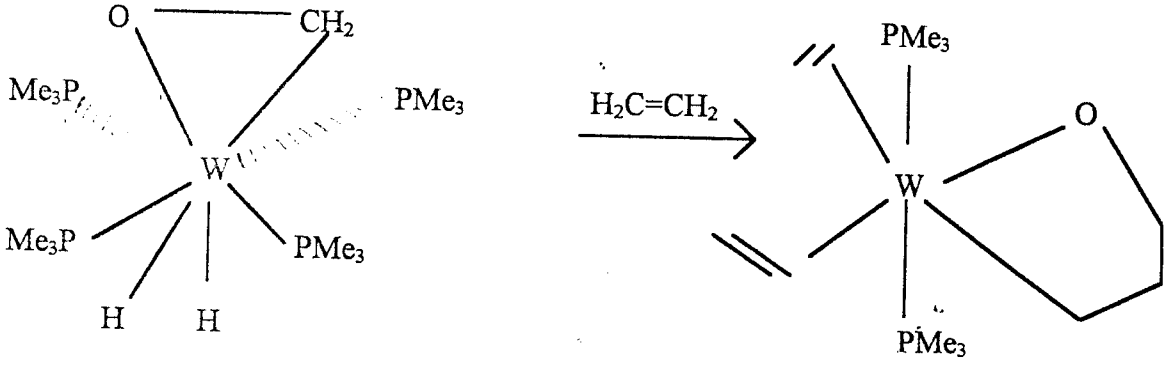
Insertion reactions

Scheme 9



23 **24**

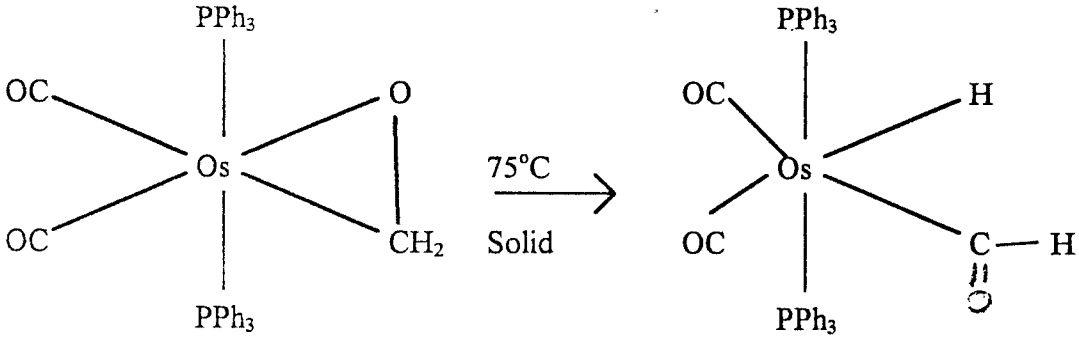
Scheme10



25 **26**

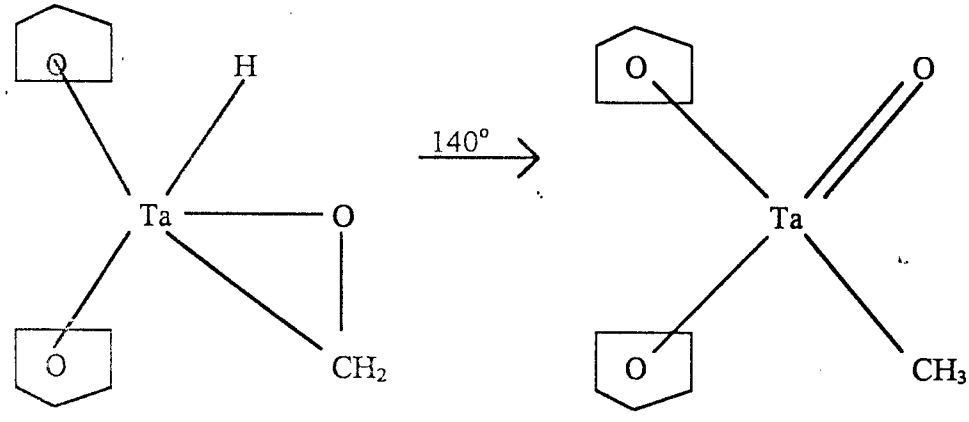
Thermal reactions

Scheme 9



27 28

Scheme 10



29 30

1.6 Cyclopentadienyl iron dicarbonyl aldehyde and ketone complexes

A systematic study of aldehyde and ketone complexes of $[CpFe(CO)_2-(O=CR^1R^2)]BF_4$ has not commanded much attention as the Rhenium complex counterpart. It was only in 1971 when Johnson encountered a complex of the type

$[C\rho Fe(CO)_2\ (O = CR^1R^{11})]$ by accident through the use of acetone as a solvent.[36] He observed that actually, acetone was forming a complex with $[C\rho Fe(CO_2]_2$. Its ^{1}HNMR gave 1.42 ppm (solvent), 1.70 ppm (singlet, co-ordinated acetone) and 4.60 ppm (singlet, π - C_5H_5). The acetone bound complex was found to have a weakly bound ligand which could be displaced easily by a variety of neutral and anionic ligands to give the complex $(\pi\text{-}C_5H_5)Fe(CO)_2\ L^+$; L = neutral ligand and $(\pi\text{-}C5H5)Fe(CO)_2X$; X = anionic ligand. This work was followed up by Williams in 1973 and Rosenblum in 1974 respectively.[37, 38, 39] These managed to make cyclopentadienyl iron dicarbonyl complexes of acetone, 3- methyl cyclohexanone and cyclohexanone. They used $AgPF_4$ as an oxidant. All the cyclopentadienyl iron dicarbonyl complexes discussed above showed sigma (η^1) mode of bonding, surprising enough even the aldehyde complexes of $CpFe(CO)_2$ showed sigma mode of bonding.

In our research, the intended products were the cyclopentadienyl iron dicarbonyl Ketone complexes 42. To justify the feasibility of their existence and structure [42], the valence bond and the molecular orbital theories could be used.

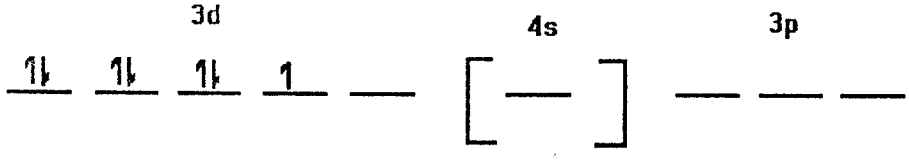
Valence Bond Theory[12]

Here, the electron donors to the iron metal centre are identified as the cyclopentadienyl, the two terminal carbonyl and the ketone carbonyl. The cyclopentadienyl donates 5 electrons, the two terminal carbonyls donate 2 pairs of electrons and the ketone carbonyl

donates one pair of electrons. The total number of electrons donated comes to eleven (11). What this means is that seven (7) electrons must come from the metal in order to satisfy the eighteen electron rule. Since iron is a d^8 species in its ground state, in a d^7 electron configuration it should carry one positive charge. The diagramatic representation of the metal orbital is shown below.

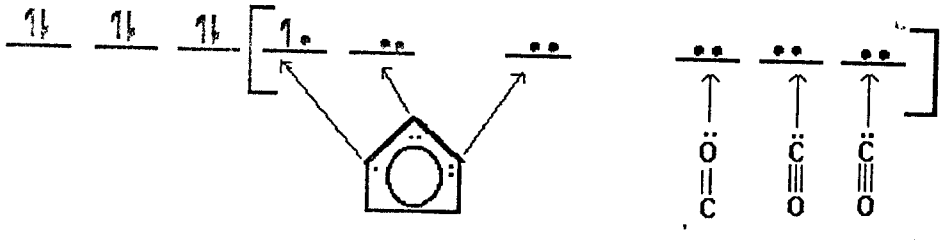
Fig. 11

Iron Orbitals in a d^7 electron configuration.



The ligands donate electrons to the hybridised iron orbitals ($d^2 s\, p^3$) as shown in fig 12:

Fig. 12



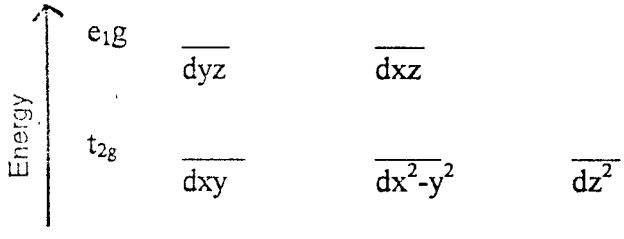
Molecular orbital diagram for a $CpFe(CO)_2$ (O = C R^1R^{11}) BF_4 according to the valence bond theory.

The above diagram satisfies the eighteen electron rule and hence is suggesting that the complex **42** might exist.

Molecular orbital theory. [11, 12]

The validity of the proposed structure **42** could also be supported by applying the molecular orbital theory. The proposed structure could be assumed to be tetrahedral. The number of available valency orbitals on the metal centre should be nine (9). These are s, p_x, p_y, p_z, dxy, dxz, dyz, dx^2-y^2 and dz^2. The orbitals involved in bonding on the metal centre are S, P_x, P_y, P_z, d_{yz}, and d_{xz}. These orbitals have proper orientation in space to overlap with ligand orbitals. The orbitals that point directly to the ligands are raised in energy whilst those that point away remain unaffected. A picture of this perturbationon the d orbitals is shown in fig 13.

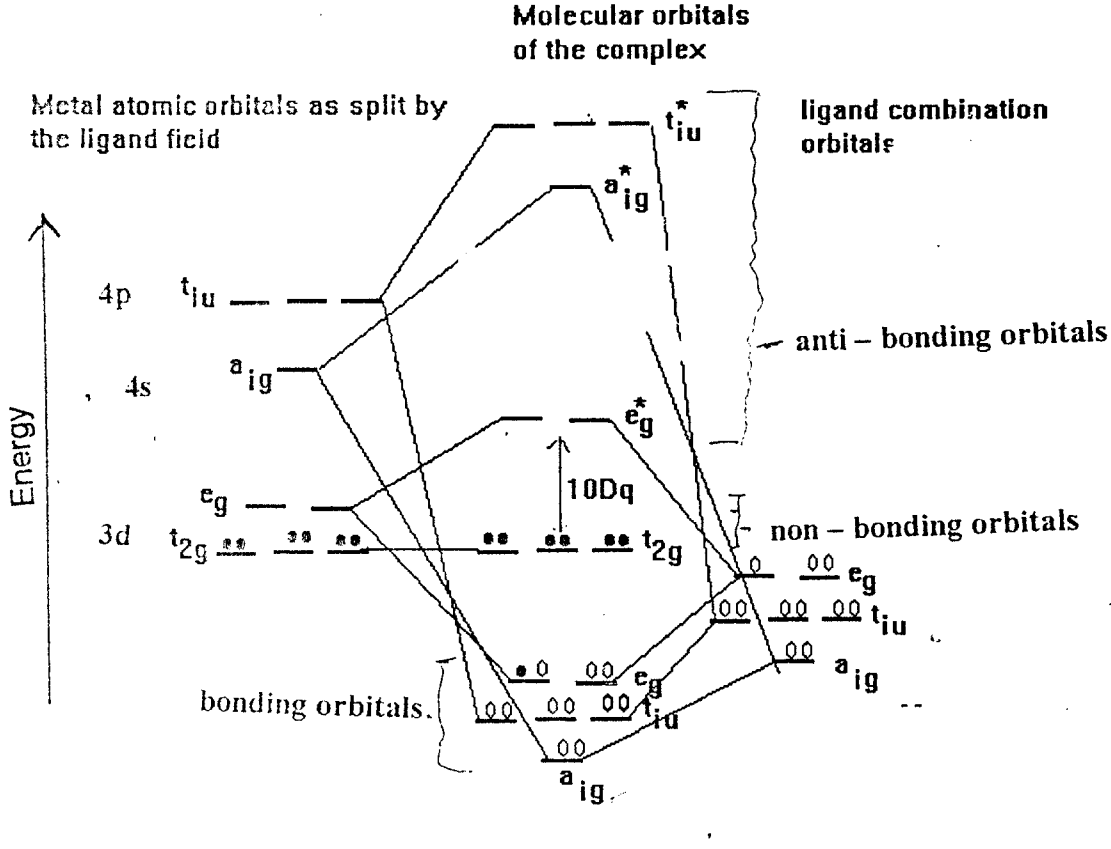
Fig. 13 Perturbation of metal d orbitals by ligands



The metal iron was said to have a d^7 electron configuration while the electron donors were said to be donating eleven electrons to the hybridised orbitals. Therefore, the molecular orbital diagram could be represented as in Fig. 14.

Fig. 14.

Molecular orbital scheme for $CpFe(CO)_2$ (O = CR^1R^{11}) BF_4 complex (tetrahedral, d^7).



- Metal orbital electron

0 ligand orbital electron.

The molecular orbital diagram has all the six (6) bonding molecular orbitals and the three non-bonding molecular orbitals filled. This brings to 18 the number of elctrons. The eighteen electron rule is satisfied indicating that the proposed structure **42** is feasible.

CHAPTER 2

REVIEW OF ALDEHYDE AND KETONE - η^5- CYCLOPENTADIENYL METAL COMPLEXES.

2.1 Brief introduction

Before Gladysz research group not much had been done involving carbonyl cyclopentadienyl metal complexes. Now, Gladysz research group has almost exhausted the carbonyl cyclopentadienyl rhenium nitrosyl phosphino complexes. The objective of this chapter is to review some work done so far on carbonyl cyclopentadienyl metal complexes by Gladysz and Protasiewicz with their groups.

2.2 Review of ketone silver complexes.[41]

The objective in this research was to demonstrate whether ketones reacted with silver tetrafluoroborate and that the product complex so formed could react with cyclopentadienyl iron dicarbonyl iodide to form other new complexes. The reactions were monitored by use of infrared spectroscopy. The ketones dealt with were:

(a) Acetone
(b) 2 - butanone
(c) 3 - pentanone
(d) Benzyl methyl ketone
(e) Benzophenone

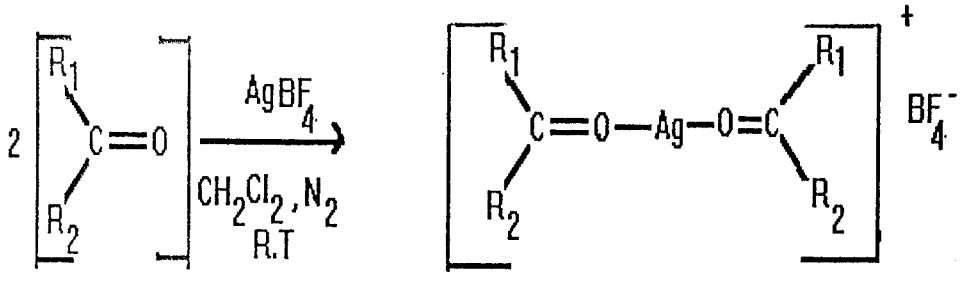
All the reactions were carried out under nitrogen. The above named ketones were done as separate experiments.

Each ketone was measured in the mole ratio of 2 to 1 with silver tetrafluoroborate.They were combined in dichloromethane as a solvent,then manually shaken. All the silver tetrafluoroborate dissolved to produce a clear solution. In the case of benzophenone, a white solid was produced. When infrared

absorption spetroscopy was taken, it was observed that the ketone carbonyls shifted to lower wavenumbers after the reaction with silver tetrafluoroborate (Appendix I).

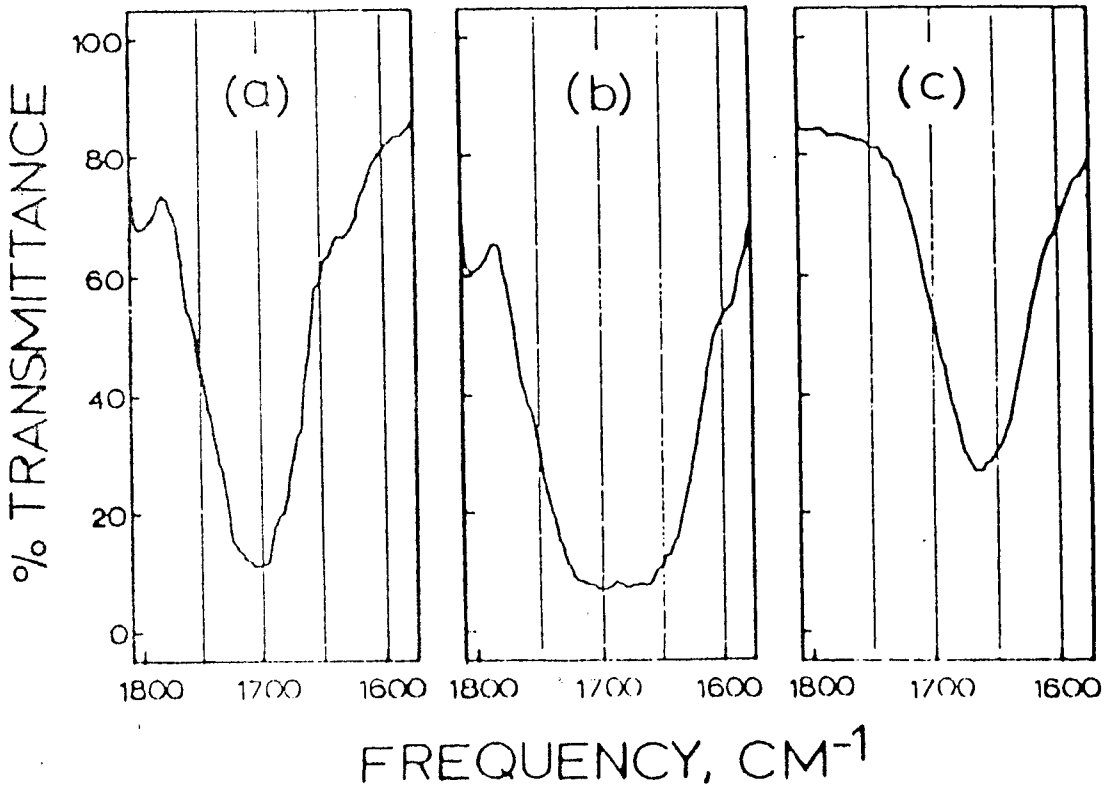
The conclusion from the above work was that the shift in the IR carbonyl absorption peak to lower wave numbers was due to the carbonyl groups in the ketones being bonded to the silver metal ion. The fact that infrared carbonyl wave numbers ($IR_{\upsilon}C=0$) shifted was evidence enough that complexation took place.[42] The broadening of the IR cabonyl absorption peaks and a small $\Delta\upsilon$ suggested that complexation was via the carbonyl oxygen and that carbonyl-oxygen silverbond was weak.The formation of oxygen-silver bond resulted in lowering of the CO force constant leading to the reduction in -bond order of theCO.[42,43]

Scheme 13



31 32

Fig.10



Effect of $AgBF_4$ on the carbonyl stretching frequency of cyclohexanone in methylene chloride. Mole ratios of [$AgBF_4$]/[ketone] were: (a) 0.0; (b) 0.105; (c) 0.443.

Source:Crist, B.D., J. Am. Chem. 1974, 95 4933

2.3 Review of acetone - η^5- cyclopentadienyl iron dicarbonyl complex[41]

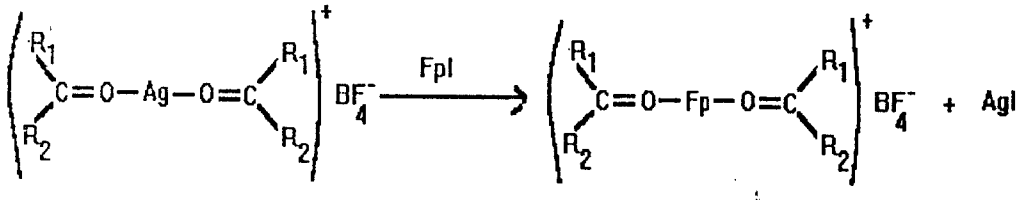
Synthesis of acetone - η^5- cyclopentadienyl iron dicarbonyl complex[41] involved the preparation of acetone silver tetrafluroborate complex as follows: η-^{5} cyclopentadienyl iron dicarbonyl iodide was added to the acetone silver complex solution. The colour of the solution changed to red. The red reaction mixture was filtered and a red filtrate was collected. The solvent was removed by a stream of nitrogen and a red semi-solid substance was obtained. Infrared spectroscropy was taken and the most pronounced peaks were 1960 cm^{-1}, 1980 cm^{-1}. The others were observed at 1712, 1670, 1712 and 1670 cm^{-1}.

2.3.1 Review of benzophenone-η^5 cyclopentadienyl iron dicarbonyl complex [41]

Benzophenone - silver tetrafluuroborate was prepared in the same way as follows: The benzophenone - silver tetrafluoroborate complex was combined with η^5 - cyclopentadienyl iron - dicarbonyl iodide in dichloromethane. A red reaction mixture was obtained. A grey precipitate settled at the bottom of the flask. Upon filtration, a grey precipitate was removed and a red reaction mixture filtrate was collected. The filtrate was dried by a stream of nitrogen and a red solid was obtained. The infrared spectrum of the red solid had three most pronounced peaks. These were 1980 cm^{-1}, 1960 cm^{-1} and 1600 cm^{-1}.

The infrared spectrum of the two ketone - η^5 - cyclopentadienyl iron dicarbonyl complexes both had peaks between 2000 cm^{-1} and 1900 cm^{-1}. The two peaks suggested the presence of carbonyl groups. Then the peaks between 1700 cm^{-1} and 1600 cm^{-1} suggested the presence of the ketone carbonyl from the ketone silver complex. The grey precipitate obtained after combining the ketone silver complex **32** and cyclopentadienyl iron dicarbonyl iodide could have been silver iodide.

Scheme 14.



32 **33**

The two ketone - η^5 - cyclopentadienyl iron dicarbonyl complexes of benzophenone and acetone suggested that binding of the ketone carbonyl to the iron metal was sigma (η^1) due to the presence of the IR absorption peaks.[28]

2.4. Review and characterisation of $[(\eta^5 - C_5H_5)\ Re(NO)\ (PPh_3)(\eta^2 - 0 = CHR)]^+PF_6^-$

The starting point in this synthesis was to synthesis a dichloromethane complex $[\eta^5 - C_5H_5)\ Re(NO)\ (PPh_3)\ (Cl\ CH_2Cl)]^+X^-$ **35 or 37** by combining a methyl complex $[(\eta^5 - C_5\text{-}H_5)\ Re(NO)\ (PPh_3)\ (CH_3)$ and $HPF_6\ .0(C_2H_5)_2$ in dichloromethane at -80°C. Then three (3) equivalent amounts of the following aldehydes were added with stirring.

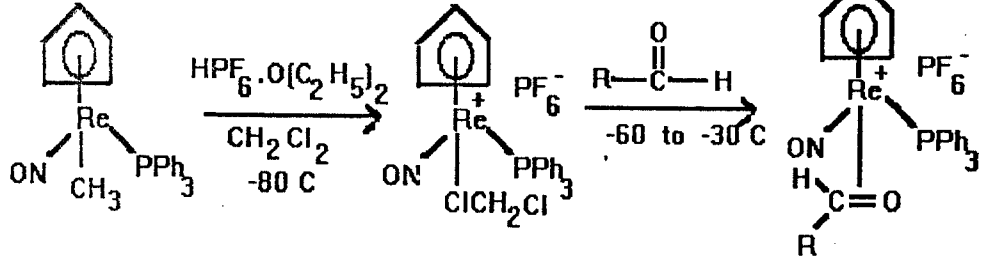
(a) acetaldehyde (b) propionaldehyde

(c) butyraldehyde (d) isobutyraldehyde

(e) benzaldehyde (f) phenyl acetaldehyde

The above named aldehydes were done as separate experiments. Work up of each of them produced yellow microcrystalline crystals or powders. The yield ranged between 77% to 91%.

Scheme 15.



34 **35** **36**

All the $[(\eta^5 - C_5H_5)\ Re\ NO)\ (PPh_3)\ (\eta^2\text{-}0 = CHR)]PF_6$ complexes **36** did not have the infrared carbonyl peaks ($IR_{\upsilon}C=0$). But they had an upfield $^{31}PNMR$ shift of the aldehydic carbon (δ79 - 98). They also had an upfield ^1HNMR shift of the aldehydic protons (δ5-2 - 5-4) for aliphatic aldehydes and δ6.8 for benzaldehyde.

The above characteristics signified $\pi(\eta^2)$ binding between Rhenium metal centre and the aldehyde carbonyl for benzaldehyde, the IR nitrosyl absorption band showed two peaks (1739 cm^{-1} and 1702 cm^{-1}). The minor was attributed to η^1 and the major band to $\pi(\eta^2)$ complexation. This was as result of equilibrium quantities of both η^1 and η^2present in the reaction mixture. When Gladysz used HBF_4 $0(C_2H_5)$ in place of $HP_6.0(C_2H_5)_2$ similar results were obtained.[34] The yields ranged between 85-89%. However, the IR nitrosyl peaks (1707 - 1710) of the complexes made out of $HBF_4 \cdot O(C_2H_5)_2$ were lower by 27-39 cm^{-1}. [31] PNMR chemical shift (δ7.8 - 9.5) were also slightly upfield of those from the complex made out of HPF_6 $O(C_2H_5)_2$ (Appendix 2).

2.4.1 Review and characterisation of rhenium ketone complexes [35]

$[(\eta^5\text{-}C_5H_5)\ Re(NO)\ (PPh_3)\ (\eta^1\text{-}0{=}C(CH_3)\ R)]^+X^-$

The starting point in this synthesis was to synthesise dichloromethane complex. This was synthesised by combining the methyl complex $(\eta^5\text{-}C_5H_5)$ Re(NO) (PPh_3) (CH_3) **34** and $HB.F_4.0$ $(C_2H_5)_2$ in dichloromethane at -80°C. Then the following methyl ketones were added (3 equivalent amounts).

(a) acetone

(b) 2 - butanone

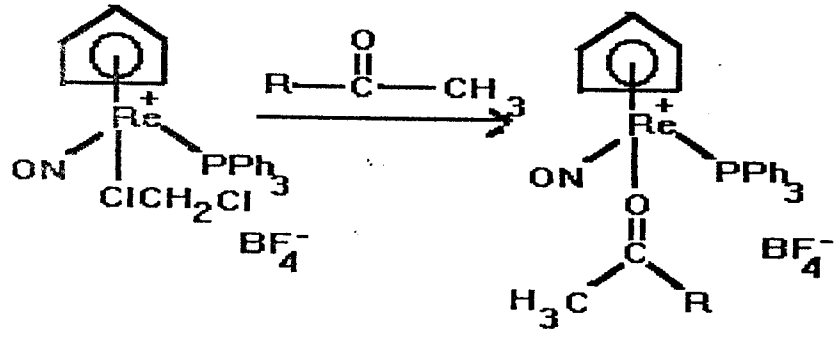
(c) 3 - methyl - 2-butanone

(d) 3, 3-dimethyl - 2 butanone

(e) acetophenone

Workup produced orange or red powders. The yields ranged between 79-86%. The hexafluorophosphate salts were also prepared in a similar way. All the Ketone complexes had infrared spectra band (IRυC=0) at 1554 cm^{-1} to 1620 cm^{-1} as compared to the aldehyde in which this band was absent. ^{13}CNMR resonance was at 216-240 ppm as compared to the aldehyde in which this band was at 79 - 89 *ppm*. . Absence of ν(CO) suggests that the bond between the metal and the carbonyl is pie bonding and not sigma bonding.

Scheme 16



37 13

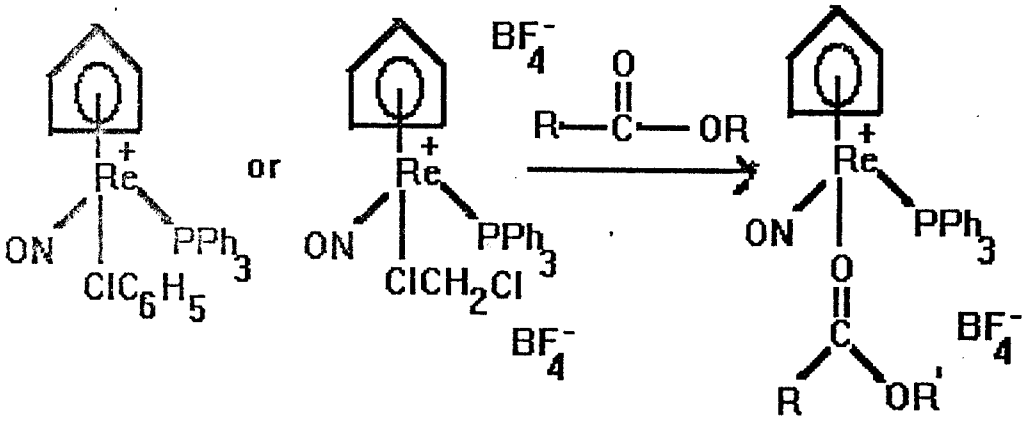
The IR nitrosyl absorption peaks of ketone complexes (1677 - 1697 cm^{-1}) were lower as compared to those of aldehyde complexes (1729 - 1740 cm^{-1}). ^{31}PNMR of the ketone complexes (18.4 - 18.9 ppm) were also downfield of those of aldehydes (10.0 - 10.2 ppm). Now, examining the ^{1}HNMR and the ^{13}CNMR resonances of cyclopentadienyl protons and carbons in both cases ^{1}HNMR and ^{13}CNMR resonances for ketones were upfield to those of aldehydes. ^{1}HNMR resonances for Ketones were 5.59 - 5.71 *ppm* while for aldehydes were 5.83 - 5.96 *ppm*. ^{13}(CNMR) resonances for Ketones were 92.9 - 93.3 ppm while for aldehydes were 98.3 - 99.2 ppm. The above characteristics signified sigma (η^1) binding in the Ketone complexes (Appendix 3) .

2.4.2 Review and characterisation of rhenium carboxylic and carbonic acid ester complexes.[44]

$[(\eta^5 - C_5H_5)\ Re(NO)\ (PPh_3)\ (\eta^1 - 0{=}C(x)\ (x^1)]^+\ BF_4^-$.

As before, its the chlorocarbon complexes to be made first since they are the starting materials in these synthesis. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ **37** and $[(\eta^5\text{-}C_5H_5)\ Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ **34** were made at -80°C in dichloromethane and chlorobenzene as solvent (binding solvents) respectively. Then 2 - 10 equivelent of (a) methyl formate (b) methyl acetate (c) ethyl acetate and (d) phenyl acetate were added. It must be noted here that each one was a separate experiment.

Scheme 17



38 37 39

Work up produced the described complexes **39** which were tan to orange powder. The yields were in the range of 63 - 83%. All the rhenium ester complexes exhibited the sigma binding mode by the presence of the IRυc=o values between 1611 - 1625 cm^{-1}. These values were lower than those of free esters (1700 - 1800). The IR nitrosyl peaks were also lower (1674 - 1708 cm^{-1}) to those of the aldehydes complexes (1729 - 1740 cm^{-1}). ^{13}CNMR of the complexed ester carbonyl was at 179 - 247 ppm as compared to 79 - 89 ppm for complexed aldehyde carbonyl. The rest of other spectroscopic properties were very similar to those reported for δ -ketone complexes $[(\eta^5\text{-}C_5H_5)\ Re(NO)\ (PPh_3)_3\ (\eta^1\text{-}0{=}C(R)R^1)]^+BF_4^-$ (Appendix 4, 5).

The significant similarity between the complexes of (a) methyl formate, (b) 3 methyl acetate, (c) ethyl acetate (d) phenyl acetate was that all formed sigma bonds through the carbonyl oxygen to the metal centre as suggested by the presence of the infrared frequency values between 1611cm^{-1} to 1625cm^{-1} which was lower to that of free ester carbonyls.

Accordingly, ester complexes of rhenium are δ bound considering the above spectroscopic evidence. Lactone and γ - butyrolactone were also generated as described for the carbonylic esters. These came out as orange powders. The yields ranged between 59 - 78%. Table

2.5 Review and characterisation of aromatic aldehyde complexes Of the $[CpFe(CO)_2]^+$ Cation. [40]

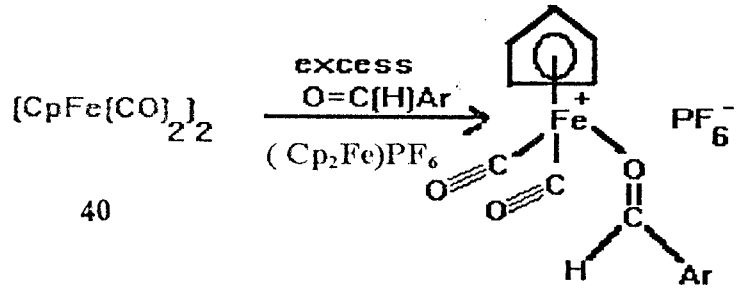
$[CpFe(CO)_2]_2$ and an aromatic aldehyde were combined and stirred for 10 minutes in dichloromethane. Then $AgPF_6$ was added. A colour change was observed from red to black with a precipitate settling at the bottom. The mixture was stirred for 20 minutes and warmed to room temperature and afterwards filtered. The red filtrate was treated by adding 20 ml of diethyl ether in 0.5 ml portions. Red crystals were produced. The crystals were collected by filtration and washed with diethyl ether.

The $[CpFe(CO)_2]^+$ aromatic aldehyde complexes which were prepared constituted the following aldehyde.

(a) benzaldehyde
(b) p - toluadehyde
(c) P - (dimethylamino) benzaldehyde
(d) p - anisaldehyde
(e) p - (trifluoromethyl) benzaldehyde
(f) p - chlorobenzaldehyde
(g) p - (dimethylamino) cinnathaldehyde

The yield ranged between 30.7 to 36.7%. However, the yields improved greatly when $(Cp_2Fe)PF_6$ was used in place of $AgPF_6$. For $(Cp_2Fe)PF_6$, the yields ranged between 46.3 to 77.8%

Scheme 18



40

41

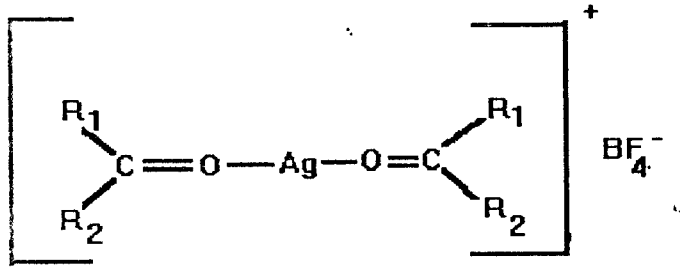
Infrared spectroscopy for all the $[CpFe(CO)_2]^+$ cation aromatic aldehyde complexes **41** showed the the IR carbonyl peaks indicating η^1 binding between the aldehyde carbonyl and iron metal centre on the $[CpFe(CO)_2]^+$ cation see Scheme **18**. Crystallography also confirmed η^1 binding between aldehyde carbonyl and iron metal centre on $[CpFe(CO)_2]^+$ (Appendix 6).

CHAPTER 3

RI SULTS AND DISCUSSION

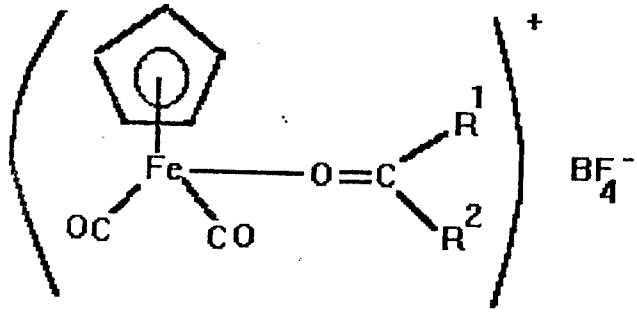
3.1 Introduction

The reaction of a ketone with silver tetrafluoroborate entailed the dissolution of the silver tetrafluoraborate into the ketone dichloromethane solution. Consider the reaction between acetone and silver tetrafluoroborate, here the silver compound was dissolved completely. Only benzophenone produced a white solid in these reactions. The above observations could have been due to the ketone carbonyl bonding to the silver ion 5s orbital to form a co-ordinate bond. The bonding may have been via the carbonyl oxygen atom due to the fact that the carbonyl absorption in the infrared spectrum shifted to lower wave numbers and became broadened.[45, 46 a,b] Accordingly the suggested structure of the complex could be the one shown below:[41]



32

When the complex 32 was reacted with cyclopentadienyl iron dicarbonyl iodide, a red solution and a grey precipitate were produced. A simple substitution of silver from the complex 32 appeared to have taken place. The silver may have precipitated out as silver iodide. Accordingly, the most likely structure of the complex could be the one shown below **42:**



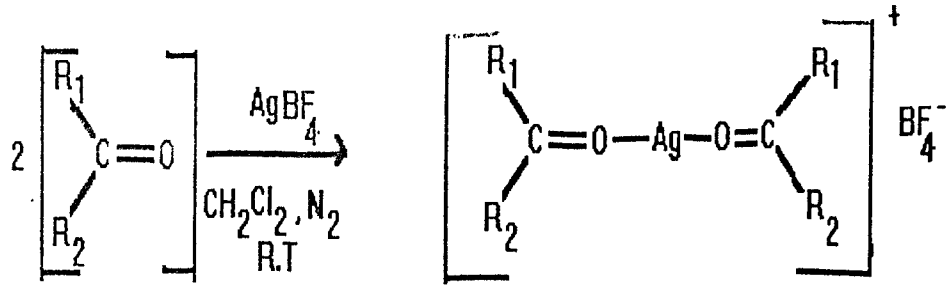
42

The above structure **42** could be explained in terms of the consistent shift of the reacted ketone carbonyl frequency when compared to the free carbonyl ketone (Appendix 7). The shift in the carbonyl wave number once complexed signified the formation of a sigma (η^1) bond between the iron metal centre and the oxygen atom on the ketone carbonyl.[28, 34, 40]

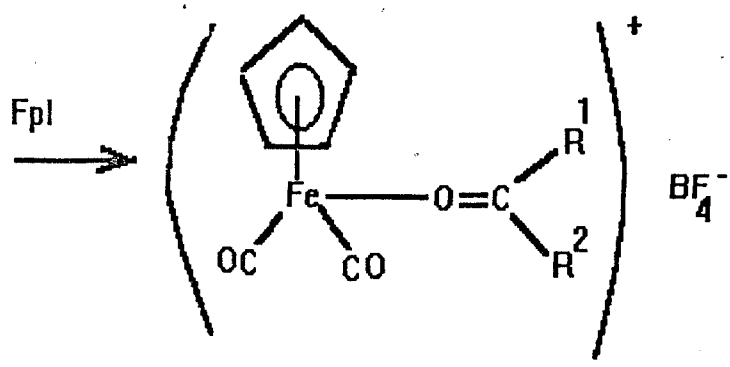
If it were π bonding of the iron metal and the ketone carbonyl, the carbonyl peak should have dissappeared completely.[28] Moreover ketones and the cyclopentadienyl groups are bulky groups that should not permit π - bonding to take place. Its in this light that π bonding could be ruled out from taking place.[28]

3.1.1 Mechanism

Scheme 19



31 32



42

The above scheme provides a likely pathway in the formation of the cyclopentadienyl iron dicarbonyl ketone tetrafluoroborate complexes **42**. The studies carried out by Zulu and Protasiewicz seem to agree very well with the above proposed routes.[40, 41] To test the validity of the structure **42**, two theories could be applied. These are the valence bond and molecular orbital theories respectively.

3.2 Spectroscopic data

The cyclopentadienyl iron dicarbonyl ketone complexes **42** have been observed to show similar patterns of infrared spectra with very slight variations in their actual spectral figures (Appendix 8). Looking at the infrared spectral figures for the cyclopentadienyl group which is expected to be aromatic, its infrared stretching frequency for all the complexes appeared in the range of 3070 cm^{-1} to 3050 cm^{-1}. [47a, b]

For the reacted ketone carbonyl (bound to Fp), the IR absorption peaks appeared in the range of 1670 cm^{-1} to 1600 cm^{-1}. The cyclopentadienyl iron dicarbonyl group had its terminal carbonyl groups appearing between 2100 cm^{-1} to 2000 cm^{-1}. [40, 49] The B-F IR stretching wave number appeared between 1080 cm^{-1} and 1050 cm^{-1}.

In proton nuclear magnetic resonance spectroscopy, the most important groups under investigation were the cyclopentadienyl and ketone carbonyl groups in the cyclopentadienyl iron dicarbonyl ketone complexes (Appendix 4). The chemical shift for cyclopentadienyl protons were coming between δ5.00 and δ5.90[40, 49] For the ketone protons chemical shifts depended on the nature of the ketones. Some ketones were straight chains, some cyclic while others had aromatic groups. in 3 - pentanone, cyclopentanone and benzophenone respectively.

Carbon 13 - nuclear magnetic resonance and mass spectroscopy were done for one compound. This was cyclopentadinyl iron dicarbonyl cyclopentanone complex **42vi**. In carbon-13-nuclear magnetic resonance spectroscopy, the terminal carbonyls appeared at δ 209.2, the ketone carbonyl appeared at δ 247.6 and the cyclopentadienyl appeared at δ 42.0

3.2.1 Cyclopentadienyl iron dicarbonyl 3 - pentanone complex 42i

$[(\eta^5 - Cp)\ Fe(CO)_2\ (\eta^1 - 0 = C\ (CH_2\ CH_3)_2)]^+ BF^-_4$

(a) **Infrared spectroscopy.**

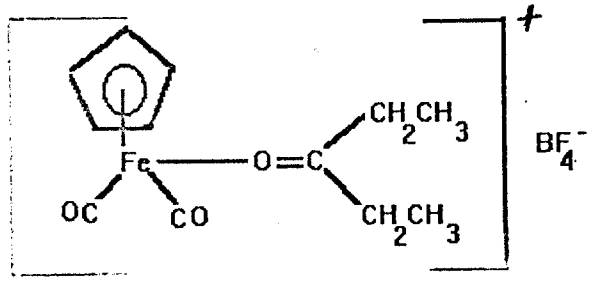
The infrared spectroscopy for this complex was interpretated by considering the cyclopentadienyl, ketone group and the terminal carbonyls (C=O). The cyclopentadienyl group would be characterised by the infrared stretching frequency at 3055 cm^{-1}. The two terminal carbonyls on the iron metal centre were evident by the presence of two strong peaks at 2065 cm^{-1} and 2011 cm^{-1}. Terminal carbonyls absorb between 1850 cm^{-1} to 2125 cm^{-1}.[49] The ketone group would be identified by methyl, methylene and the ketone carbonyl. The two (methyl and methylene) could be assigned the stretchning frequences at

2940 cm^{-1} and 2885 cm^{-1} resepctively.[47(a)] The centre of interest in these complexes were the ketone carbonyl group. For, it were these groups which were indicating whether complexation between cyclopentadienyl iron dicarbonyl and the ketones took place. The free ketone carbonyls absorbed at higher wave number's as compared to reacted ketone carbonyls. 3 - pentanone carbonyl absorbed at 1751 cm^{-1}. But when 3-pentanone was reacted, it absorbed at 1632 cm^{-1}. The wave number difference between the reacted and free 3-pentanone was 119 cm^{-1} (' Appendix 7). Broadening of the peak and the shift to lower wave numbers was due to lengthening of the carbon oxygen double bond as a result of ligation to the iron metal centre.

(b) Proton nuclear magnetic resonance.

Cyclopentadienyl iron dicarbonyl - 3 - pentanone complex **42i** showed its nuclear magnetic resonance peaks at δ1.00 (t, 3-H) J = 7.2 H_z), 2.42 (q, 2, J = 7.2 H_z). The peak at δ1.00 was due to the methyl protons whilst the peak at δ2.42 was due to methylene protons. The coupling constant was 7.2 H_z . Cyclopentadienyl protons appeared at δ5.25 (s, 5 - H). The peak at δ1.00 was a triplet and that at δ2.420 was a quartet. The peak at δ1.00 was a triplet because in the neighbourhood of the methyl protons were two protons on the adjacent carbon. The peak at δ2.420 was a quartet because the neighbouring protons on the adjacent carbon had three protons.

It follows that the most plausible structure which is consistent with IR and ^{1}HNMR spectra is the one proposed below (42i).

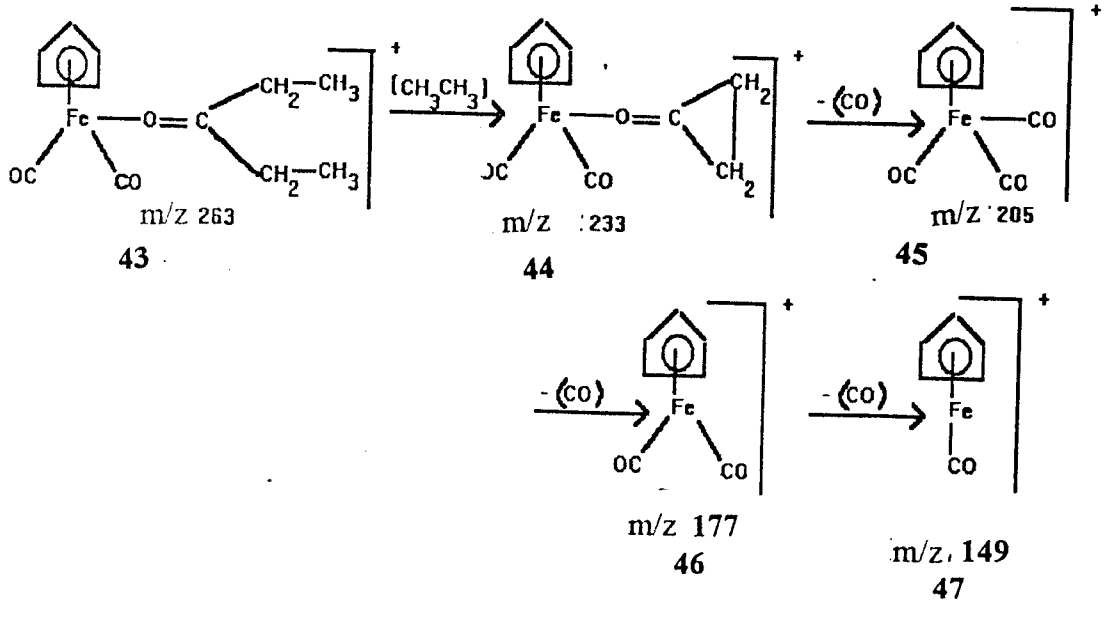


42i

(c) Mass spectroscopy

The mass spectrum of the Fp - 3 - pentanone complex **42I** had the following ion molecular weight peaks m/z 263 (1.7%), 205 (12.1%), 177 (10.3%) and 149 (14.7%). The calculated M^+ for Fp - 3 - pentanone was 350. This was not present. Therefore, these peaks could corresponds to the following partial decomposition pathway (Scheme 18) excluding M^+ which was not present on the mass spectrum.

Scheme 20



m/z 263
43

m/z 233
44

m/z 205
45

m/z 177
46

m/z 149
47

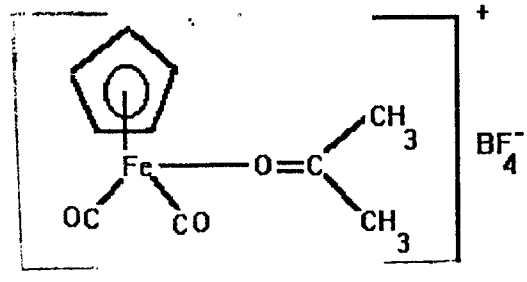
3.2.2 Cyclopentadienyl iron dicarbonyl acetone complex 42ii

$[(\eta^5 - C_p)\ Fe\ (CO)_2\ (\eta^1 - O = C\ (CH_3)_2)]^+\ BF_4^-$

(a) Infrared spectroscopy.

The cyclopentadienyl iron dicarbonyl acetone complex showed a similar pattern of infrared spectrum as the cyclopentadienyl iron dicarbonyl - 3 - pentanone complex. The IR peak for the cyclopentadienyl group appeared at 3065 cm^{-1}. This peak was as a result of C - H stretching. The two terminal carbonyls on the iron metal centre were assigned the infrared wave numbers at 2080 cm^{-1} and 2020 cm^{-1}. As already pointed out, the infrared wave numbers that indicate complexation are the ketone carbonyl wave numbers (Appendix 7). The ketone carbonyls infrared absorption peak appeared at 1640 cm^{-1} when reacted. The free Ketone carbonyl had its infrared peak at 1715 cm^{-1}. This produced a shift of 65 cm^{-1}. The peak for the reacted acetone was broad and medium characteristic of a complexed ketone carbonyl. The two methyls could be assigned 2930 cm^{-1}. Then, the B-F infrared absorption peak appeared at 1050 cm^{-1}.

From the above analysis the structure that is consistent with IR spectra is the one proposed below (**42ii**).



42ii

3.2.3 Cyclopentadienyl iron dicarbonyl cyclohexanone complex 42iii

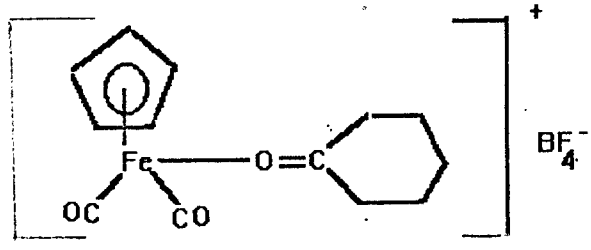
(a) Infrared spectroscopy

The infrared spectrum for cyclopentadienyl iron dicarbonyl cyclohexanone complex **42iii** had all the characteristics for the Fp-ketone complex. The cyclopentadienyl group had an infrared absorption peak at 3055 cm^{-1}. The two terminal carbonyl attached to the iron metal centre had their infrared absorption peaks at 2068 cm^{-1} and 2020 cm^{-1}. The ketone carbonyl had its infrared absorption peak at 1642 cm^{-1}. This wave number indicated a shift of 66 cm^{-1} as compared to the free ketone carbonyl whose infrared absorption peak was 1718 cm^{-1} (Appendix 7). The shift from 1718 cm^{-1} to 1642 cm^{-1} may be an indication that complexation had taken place. The B-F infrared absorption peak showed at 1057 cm^{-1}. The peak at 2857 cm^{-1} in the infrared spectrum were assigned to the C-H stretching for the methylene groups of the cyclohexanone group.

(b) Proton nuclear magnetic resonance spectroscopy (^{1}HNMR)

Cyclopentadienyl iron dicarbonyl cyclohexanone complex **42iii** had the following chemical shifts: δ1.70 (2H, m), 1.84 (2H, m) 2.32 (2H, t) 5.39 (5H, s). The chemical shift at δ1.70 could be associated with methylene protons which were third furthest from the ketone carbonyl on the cyclohexanone component of the complex. The chemical shift at δ1.84 could be associated with methylene protons on the carbon atom which were second furthest from the Ketone carbonyl carbon. The chemical shift at δ2.32 could be associated witht the protons on the carbon atoms just adjacent to the carbonyl carbon atom. The cyclopentadienyl proton showed resonance at δ5.39.

The most plausible structure consistent with IR and ^{1}HNMR Spectra discussed above is the one proposed below (42iii)

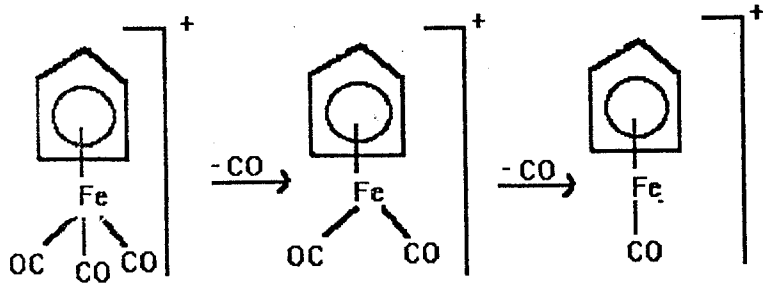


42iii

(c) **Mass spectroscopy**

The mass spectrum for cyclopentadienyl iron dicarbonyl cyclohexanone complex showed the major fragment ions at m/z, 149 (11%), 177 (14%) and 205 (10%). The above peaks were indicative of the original complex **42iii.** The partial disintergration of the complex **42iii** is shown below.

Sheme 21



m/z 205 m/z 177 m/z 49

3.2.4 Cyclopentadienyl iron dicarbonyl benzophenone complex 42iv

$[(\eta^5$ - Cp) Fe $(CO)_2$ $(\eta^1$ - O = C $(Ph)_2)]^+$ BF_4

(a) Infrared spectroscopy

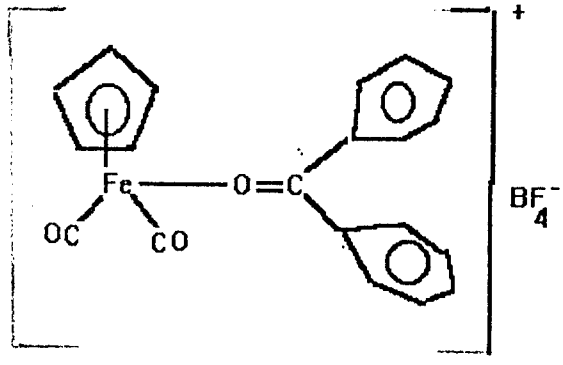
The infrared spectrum of cyclopentadienyl iron dicarbonyl benzophenone complex **42iv** produced relatively adequate information about the structure of the complex. The cyclopentadienyl group could be assigned the infrared absorption peak at 3066cm^{-1} were as the terminal carbonyls on the metal centre could be assigned the infrared absorption peak at 2069 cm^{-1} and 2021 cm^{-1}. The ketone carbonyl group could be assigned the infrared peak at 1600 cm^{-1}. There was a peak at 3088 cm^{-1}. This peak could be assigned to the C - H stretching of the phenyl group. The B - F infrared absorption peaks showed at 1075 cm^{-1}.

(b) Proton nuclear magnetic resonance spectroscopy (^{1}HNMR)

Cyclopentadienyl iron dicarbonyl benzophenone complex **42iv** had its proton nuclear magnetic resonance peaks at δ5.16 (5H, s), 7.78 - 7.47 (10H, m). The cyclopentadienyl group on the complex could be assigned δ5.16 as its chemical shift. The last range of chemical shift could be assigned to the phenyl protons. This range of chemical shifts was δ 7.78 - 7.47. This range was due to the 3 non equivalent protons on the phenyl groups.

From the above analysis, the structure that is consistent with IR and ^{1}HNMR spectra is the one proposed below (**42iv**);

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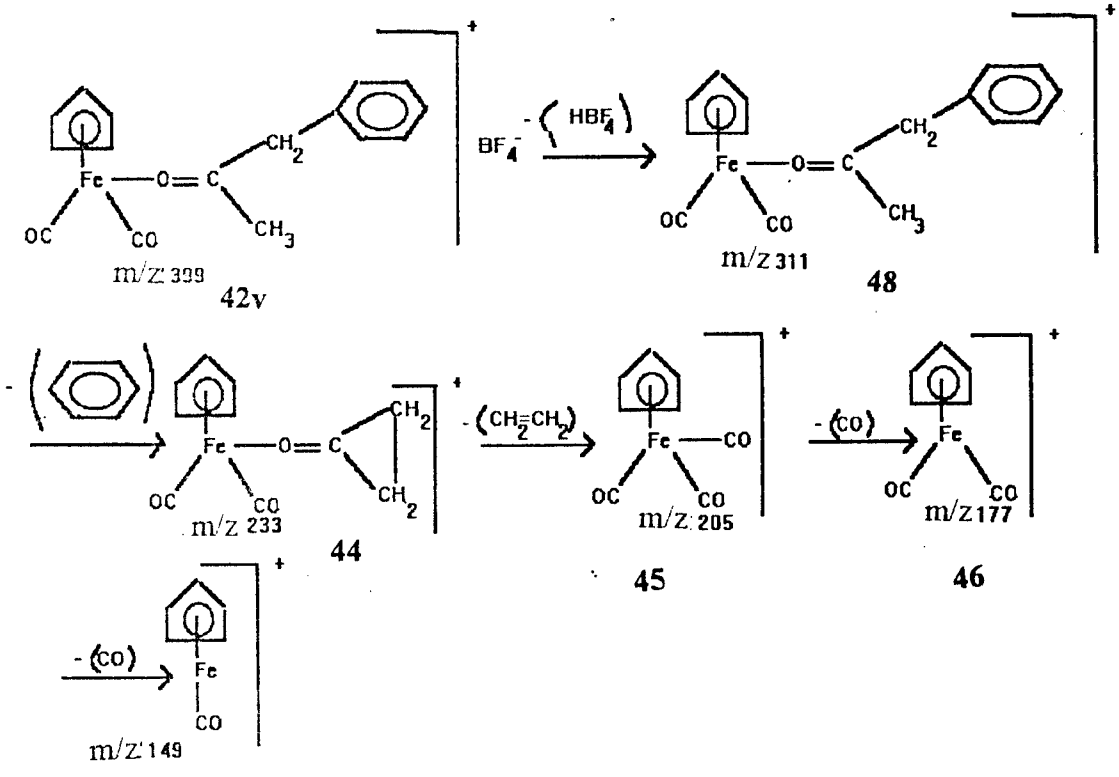
42iv

3.2.5 Cyclopentadienyl iron dicarbonyl benzyl methyl ketone complex 42v

(a) Mass spectroscopy

We only obtained a mass spectrum for this complex **42v.** The M^+ appeared as M^++1 at 399. As already stated before conjugation brings about stabilisation of the ion. The Fp benzyl methyl ketone complex had a phenyl group which could stabilise the ion fragment hence an appreciable intensity was observed at 399 (18%)[47b, 48]. The other peak was at 311 (8.6%) which could have been due to the loss of BF_4 group. The scheme below illustrates the possible mechanism of decomposition.

Scheme 22.



The $M^+ + 1$ which is as a result of the molecular weight ion abstracting an atom of hydrogen from the solvent, should be losing the same abstracted hydrogen atom with the BF_4 group as HBF_4 to produce a peak at m/z 311. From the above explanation, the structure seem to be strongly supported as proposed for **42v** (Sheme 22).

3.2.6 Cyclopentadienyl iron dicarbonyl cyclopentanone complex 42vi

(a) Infrared spectroscopy of cyclopentadienyl iron dicarbonyl cyclopentanonne **42vi** absorption peak for cyclopentadienyl group appeared at 3055 cm^{-1}. The aliphatic part of the ketone group was not clear. The terminal carbonyls on the Fp group showed infrared absorption peak at 2071 cm^{-1} and 2023 cm^{-1}. The ketone carbonyl group bonded to the iron metal centre showed a broad carbonyl absorption at 1680 cm^{-1} where as the BF infrared absorption occured at 1059 cm^{-1}.

(b) Proton nuclear magnetic resonance spectroscopy (^{1}HNMR).

The cyclopentanone complex **42vi** had its proton nuclear magnetic resonance peaks at δ1.85 (m, 2H), 2.00 (t, 2H), and 5.42 (s, 5H). δ1.85 was a multiplet while the one at δ2.00 was a triplet. The nuclear magnetic resonance peak at δ1.85 was due to the protons on the two carbon atoms furthest from the ketone carbonyl carbon atom.

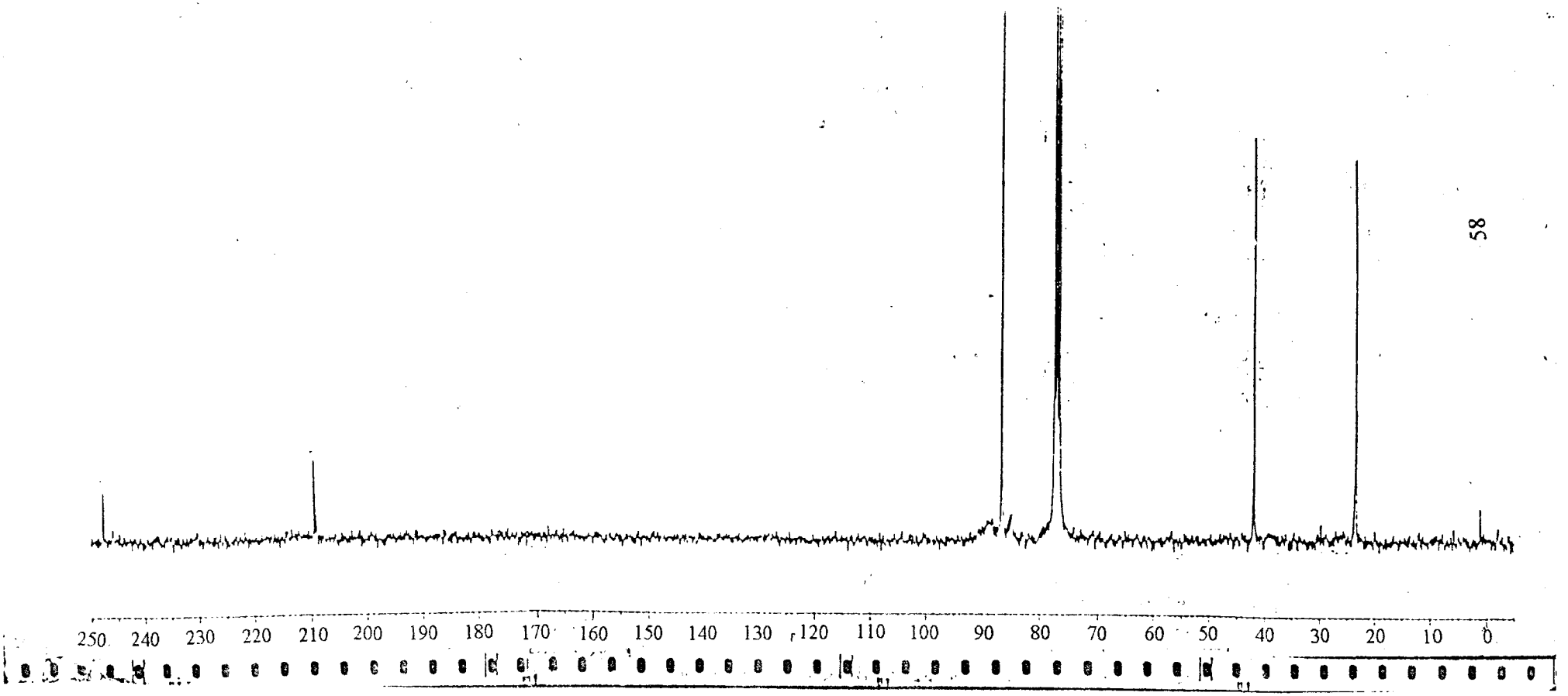
The chemical shift at δ 2.00 ppm was due to the protons on the carbon atom next to the ketone carbonyl carbon atom. This one was a triplet as a result of its interaction to the two protons on the adjacent carbon atom. The cyclopentadienyl proton appeared at δ5. 42 as a singlet. This was the normal position for the cyclopentadienyl protons. The proton nuclear magnetic resonance peak at δ 2.00 was due to protons on the carbon atoms next to the ketone carbonyl carbon atom. The proton nuclear magnetic resonance peak at δ5. 42 was due to the five equivalent protons on the cyclopentadienyl group.

(c) Carbon 13 - nuclear magnetic resonance spectroscopy

Cyclopentadienyl iron dicarbonyl cyclopentanone complex **42vi** had its carbon 13 - carbon nuclear magnetic resonance spectroscopic peaks at δ 23.46 (s), 42.00 (s), 86.63 (s), 209.20 (s), 247.59 (s). The chemical shift at δ23.46 could be assigned to the two methylene carbon atoms third from the ketone carbonyl carbon atom on the cyclopentanone group. The chemical shift at δ 42.00 could be assigned to the two methylene carbon atoms which were adjacent to the carbonyl carbon atom on the cyclopentanone group. The carbon atoms which were adjacent to the carbonyl group were experiencing more deshielding effect from the ketone carbonyl electron withdrawing influence as compared to the methylene carbon atoms responsible for the chemical shift at δ 23.46. The chemical shift at δ86.63 could be assigned to the five equivalent cyclopentadienyl carbon atoms.[49] This was the normal position for the cyclopentadienyl carbons. The two different carbonyl carbon atoms (cyclopentanone carbonyl carbon atom and the two terminal carbonyl on the iron metal centre) present on the complex could be differentiated as follows:

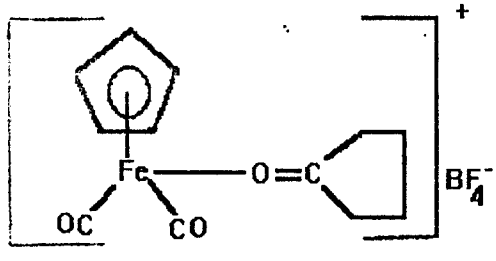
The terminal carbonyl on the metal centre had a high electron density as compared to the ketone carbonyl. Therefore, the terminal carbonyls could be assigned the chemical shift at δ 209.2. The two terminal carbonyls were identical hence their ^{13}CNMR chemical shift was the same. This chemical shift tallied very well with the ^{13}CNMR chemical shift for the various derivatives of Cp Fe $(CO)_2$ X; (x = Cl, Br, etc.) studied by Ganson in 1972.[49] The range of the derivatives of CpFe $(CO)_2$ X in ^{13}CNMR was between δ 211.4 to 216.5. For

Fig. 15 Carbon-13-nuclear magnetic resonance spectra (^{13}C.N.M.R.) for cyclopentadienyl iron dicarbonyl-η^1- cyclopentanone complex 42vi



our product, it meant the ^{13}CNMR chemical shift was below this range by $\Delta\delta$ 2.2. Then the chemical shift at δ 247.6 could be assigned to the ketone carbonyl. The assignment of δ247.6 to the ketone carbonyl of our complex could be justified by comparing to the ^{13}CNMR of $[(\eta^5 - C_5H_5)\ Re(NO)\ (PPh_3)\ (\eta^1 - O = C\ (CH_3)\ B)]^+\ BF_{-4}$ complexes.[35] In these Rhenium complexes, the ketone carbonyl ^{13}CNMR chemical shifts ranged between δ 231.9 to δ240.4. The assignment of δ247.6 to the ketone carbonyl in the $CpFe(CO)_2$ $(O = C\ R^{I}R^{II})^+\ B\ F^-_4$ complexes could further be justified by the infrared spectroscopy in which case it was suggested that our complexes were sigma (η^1) bonding via the oxygen Ketone carbonyl to the metal centre and not π - bonding. If it were π bonding, the chemical shift could have been below δ100.[34, 35]

Therefore, the most plausible structure consistent with IR and ^{1}H/ ^{13}CNMR spectra is the one proposed below (**42vi**).

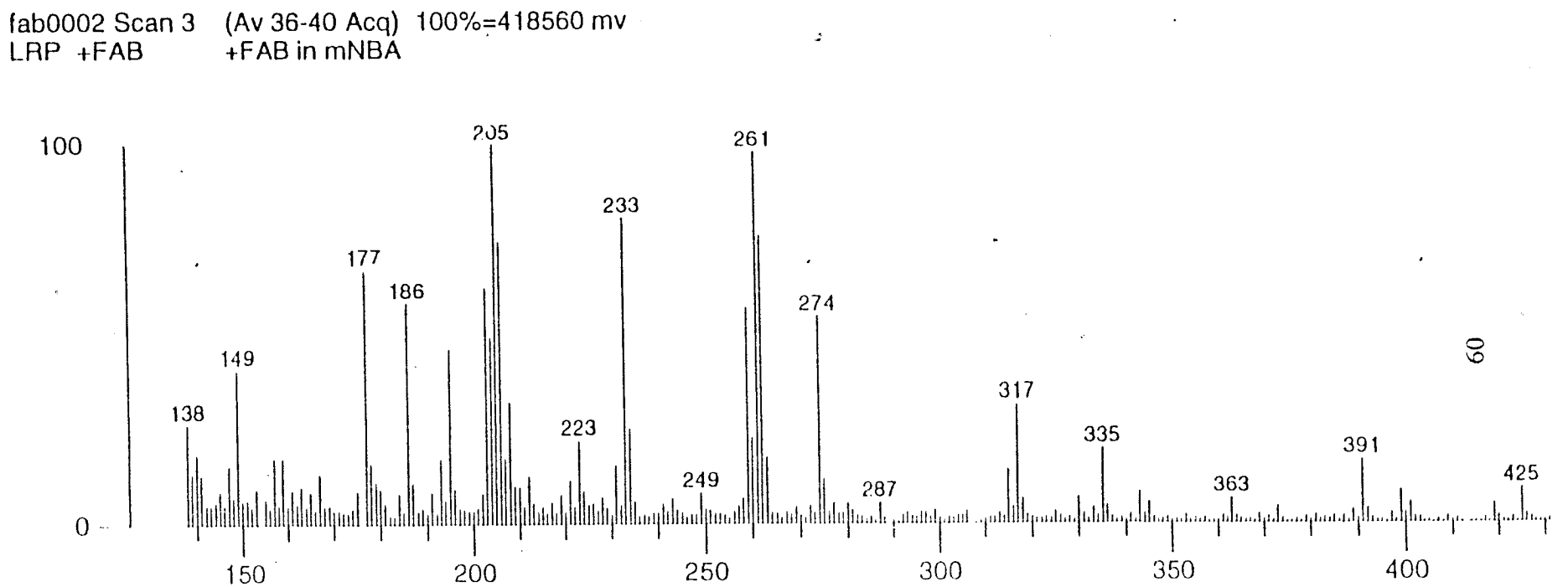


42vi

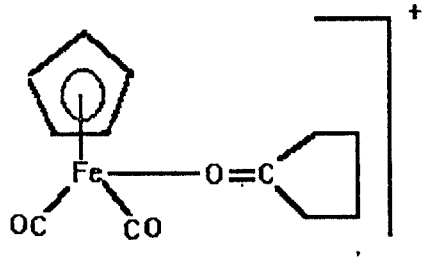
(d) Mass spectroscopy

The mass spectroscopic data for cyclopentadienyl iron dicarbonyl cyclopentanone complex were as follows: m/z 261 (98.3%), 233 (80.2%), 205 (100%), 177 (67.2%) and 149

Fig. 16 **Mass spectra (F.A.B.) for cyclopentadienyl iron dicarbonyl-η^1- cyclopentanone complex 42vi**



(39.7%). The parent peak had a negligible intensity. This was m/z 348 on the mass spectrum. This peak could be justified by considering the next lower fragment peak which had an appreciable intensity. This peak could have been as result of the M^+ losing 3 to 5 hydrogen atoms.[48a, 48b] This could have resulted in an enhanced intensity at m/z 345 (5.2%) and 343 (8.6%). This could be explained in terms of the concept that conjugated systems bring about stabilisation and as such the resulting fragment ion could be expected to be more stable relative to the M^+.[47b, 48] The above concept needed further investigations on our complexes. However, when the mass spectrum was examined further down, there were two most intense peaks. These were at m/z 261 and m/z 205 respectively. The base peak was m/z 205 (100%). The peak at m/z 261 accounted for a major fragment 49.

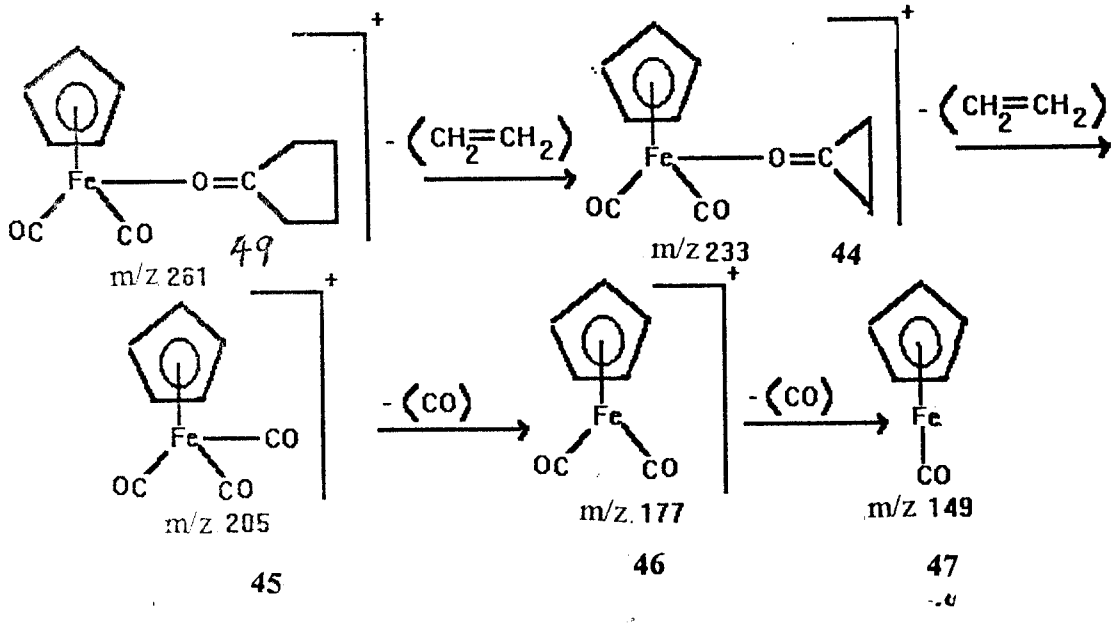


, m/z 261

49

A partial decomposition pathway is given in scheme 22.

Scheme 22



The above mechanism seem to suggest that the proposed general structure **42** was possible with the fragment $[CpFe(CO)_2$ (O = ⬠) $]^+$ at m/z 261. The positive charge in this case could be counter balanced by the tetrafluoroborate anion (BF_4) to produce **42vi.**

3.2.7 Conclusion

The spectral data for the cyclopentadienyl iron dicarbonyl ketone complexes provided enough supportive information for the proposed structure **42.** For example, infrared spectroscopy had shown the infrared absorption peaks for all the major groups in their normal regions as found in similar complexes like $[\eta^5 - C_5H_5Re(NO)(PPh_3)$

$(\eta^{-1}$ - O = C CH_3 R)]X^- and $(\eta^5$ - Cp) Fe $(CO)_2(x^1)$, $X^- = BF^-_4$, PF^-_4, etc and x^1 = Cl, Br, CN^- etc.

The infrared absorption peak for cyclopentadienyl group was consistently between 3070 cm^{-1} 3050 cm^{-1}.[47(a, b)] Those of terminal carbonyls were between 2100 cm^{-1} to 2000 cm^{-1}.[40, 49]

The infrared absorption peak of the two terminal carbonyls were two because of their symetrical and antisymetrical modes of vibration. The BF stretchning infrared absorption peak also came in the region between 1050 cm^{-1} and 1080 cm^{-1}.

In the proton nuclear magnetic resonance, the chemical shift for the major component (cyclopentadienyl) came in the region between δ5 to δ6. Carbon 13 - nuclear magnetic resonance spectroscopy also had its peaks for the different groups appear in their normal regions. For example, the nuclear magnetic resonance spectrum for [CpFe$(CO)_2$ (O = )]$^+$ BF^-_4 **42vi** complex had the chemical shift for Cp at δ86.63. The two terminal carbonyls had their peak at δ209.2. The peak for the two terminal carbonyls had compared very well to the ^{13}CNMR peaks for CpFe $(CO)_2$ x (x = Cl, Br, CN etc), as investigated by Gauson. The above information left the Ketone carbonyl to be assigned the ^{13}CNMR on the [CpFe$(CO)_2$ (O = )]$^+BF^-_4$ **42vi** spectrum which was at δ249.6. This chemical shift was strongly supported by infrared spectroscopy which was

suggesting sigma bonding of the Ketone carbonyl when compared to the $[CpRe(NO)(PPh_3)(O{=}CCH_3R)]^+x^-$ **13.**

For $(CpRe(NO)(PPh_3)\ (O{=}C(CH_3)R)]^+x^-$, **13** the Ketone carbonyl ^{13}CNMR peaks came between δ231.9 to δ240.4. When the above information was taken together with details of the mass fragmentation pattern found in the mass spectrum, especially that of $[CpFe(CO)_2\ (O =$  $)]^+\ BF^-_4$ **42vi,** it was concluded that complexes of the type $[CpFe(CO)_2\ (O = C\ R^1R^{11})]^+\ BF^-_4$ **42** seemed to bind via sigma bonding between the cyclopentadienyl iron dicarbonyl and the Ketone carbonyl as shown in **42**. More information about these complexes could be obtained by running x - ray crystallography. We were not able to obtain x - ray crystallography because of the difficulties in growing appropriate crystals. This could be done in the near future. A lot more similar complexes of the type $[CpM(CO)_2\ CO = C\ R^1R^{11})]^+\ BF^-_4$ could be studied in the future.

EXPERIMENTALS

EXPERIMENTAL

Equipment

IR spectra were recorded on perkin-elmer model 297 grating and perkin-elmer 1710 fourier transform spectrophotometers as CH_2Cl_2 solutions. Routine ^1H / ^{13}CNMR were recorded on a higher field spectra on Bruker AC-300 (300 MHz). All the samples were run in deuterochloroform, unless stated, using tetramethylsilane as an internal standard were applicable. Routine mass spectra were measured with high resolution mass spectra (F.A.B) on a cratos concept SI instrument.

Apparatus

Liquid reagents and products were handled by use of disposable syringes and needles during transfers and mixing. Solid reagents and products were handled by use of small weighing bottles and spatula under a blanket of nitrogen gas. Reactions under magnetic stirring were carried out in schlenk or conical flasks connected to a nitrogen vacuum line at room temperature (r.t).

Materials

Ketones were of reagent grade and were bought from BDH chemicals. Dichloromethane was purified by distillation and dried under calcium oxide. It was bought from BDH chemicals and it was an analytical reagent.

Nitrogen gas was bought from Zamox. It was reagent grade. Silver tetrafluoroborate was bought from Aldrich chemical company. It was 98% pure.

Cyclopentadienyl iron dicarbonyl iodide was bought from Aldrich chemical company. This was reagent grade.

Molecular sieve type 4A(1/8 or 1/16) was used. This was bought from BDH chemicals. It was reagent grade.

Methods

The preparation of the ketone cyclopentadienyl iron dicarbonyl complexes were done by use of a method developed in our laboratory. In this method, the silver ketone complexs were reacted with cyclopentadienyl iron dicarbonyl iodide to produce a red reaction mixture and a grey precipitate.

Air was completely isolated from the reaction mixture by use of a nitrogen blanket. Syringes and needles were used for the addition of solvents and reagents to the reaction mixtures. Draining of liquids from the reation mixtures were also done by syringes and needles.

This method afforded the isolation of pure products which could not have been possible otherwise since Organometallic complexes are usually unstable. Such complexes could only have their NMR and IR spectra compared to those of complexes already characterised such as cyclopentadienyl rhenium nitrophosphino ketone (or aldehyde) and cyclopentadienyl iron dicarbonyl aldehyde complexes.[34, 35, 40]

1. Preparation of 3 - Pentanone - η^5 - cyclopentadienyl iron dicarbonyl tetrafluoroborate 42i

3 - pentanone (0.066 g, 0.77 mmol) was added to 30 ml of dichloromethane in a 250 ml conical flask under a blanket of nitrogen. The flask with its contents was then placed on a magnetic stirrer for 5 minutes. Silver tetrafluoroborate (0.150 g, 0.77 mmol) was added to the flask. This was stirred for 15 minutes.

Cyclopentadienyl iron dicarbonyliodide (0.233 g, 0.77 mmol) was added to the reaction mixture. A red colour appeared. The reaction mixture was stirred for 15 minutes. A grey precipitate formed which settled at the bottom and on the sides of the flask. The red liquid was drained by syringe and transferred to another clean conical flask. The volume of the red liquid was reduced to one quarter (¼) of the original volume by vacuum. Diethyl ether (5ml) was added. A red precipitated formed. The liquid was removed by syringe. Diethyl ether was added again. The mixture was shaken and left to stand for a minute. The liquid portion was drained by syringe. The process of cleaning with diethyl ether was repeated for the third time. The red solid was dried by a stream of nitrogen. The residue was then transferred to a sample holder

The yield was 0.112 g (41.75%).

FTIR: (CH_2Cl_2, cm^{-1}), 3070 (w), 2925 (w), 2885 (w), 2065 (vs, υco) 2011 (vs, υco), 1632 (m, br, $\upsilon_{O=CR^1R^{11}}$), 1472 (m), 1266 (s), 1078 (vs, br), 737 (vs), 703 (s).

^{1}HNMR: δ 5.250 (5H, s), 2.420 (2H, q, J = 7.2 Hz), 1.004 (3H, t, J = 7.2 H_2)

M/Z: 263 (M^+ - BF_4, 1.7%), 205 (12.1%), 177 (10.3%), 149(14.7%).

2. Preparation of acetone - η^5 - cyclopentadienyl iron dicarbonyl tetrafluoroborate 42ii

Acetone (0.128 ml, 1.7 mmol) was added to 30 ml of dichloromethane in a 250 ml conical flask under a blanket of nitrogen. The flask with its contents was then placed on a magnetic stirrer plate and stirred for 5 minutes. Silver tetrafluoroborate (0.150 g, 0.77 mmol) was added to the flask. This was stirred for 15 minutes. Cyclopentadienyl iron dicarbonyl irodide (0.233 g, 0.77 mmol) was added to the reaction mixture. A red colour appeared. The reaction mixture was stirred for 15 minutes. A grey precipitate formed which settled at the bottom and on the sides of the flask. The red liquid was drained by syringe and transferred to another clean conical flask. The volume of the red liquid was reduced to one quarter (¼) of the original volume by vacuum. Diethyl ether (5ml) was added. A red precipitated formed. The liquid was removed by syringe. Diethyl ether was added again. The mixture was shaken and left to stand for a minute. The liquid portion was drained by syringe. The process of cleaning with diethyl ether was repeated for the third time. The red solid was dried by a stream of nitrogen. The residue was then transferred to a sample holder. The yield was 0.097g (39%).

FTIR: (CH_2Cl_2, cm^{-1}): 3065 (w), 2930 (w) 2080 (s), 2020 (s), 1640 (w, br), 1430 (w), 1050 (vs, br), 740 (s) 705 (s).

3. Preparation of cyclohexanone - η^5 - cyclopentadienyl dicarbonyl tetrafluoroborate 42iii

Cyclohexanone (0.066 g, 0.860 mmol) was added to 30 ml of dichloromethane in a 250 ml conical flask under a blanket of nitrogen. The flask with its contents was then placed on a magnetic stirrer plate and stirrred for 5 minutes. Silver tetrafluoroborate (0.15g, 0.77 mmol) was added to the flask. This was stirred for 15 minutes. cyclopentadienyl iron dicarbonyl iodide (0.233 g, 0.77 mmol) was added to the reaction mixture. A red colour appeared. The reaction mixture was stirred for 15 minutes. A grey precipitate formed which settled at the bottom and out the sides of the flask. The red liquid was drained by syringe and transferred to another clean conical flask. The volume of the red liquid was reduced to one quarter (¼) of the original volume by vacuum. Diethyl ether (5ml) was added. A red precipitated formed. The liquid was removed by syringe. Diethyl ether was added again. The mixture was shaken and left to stand for a minute. The liquid portion was drained by syringe. The process of cleaning with diethyl ether was repeated for the third time. The red solid was dried by a stream of nitrogen. The residue was then transferred to a sample holder. The yield was 0.147 g (37%).

FTIR: (CH_2Cl_2, cm^{-1}); 3055 (w), 2930 (w), 2857 (w), 2068 (s, υ_{CO}) 2020 (s, υ_{CO}), 1642 (w, br, $\upsilon_{O=CR^1R^{11}}$), 1266 (s) 1057 (s), 737 (s), 704 (s). υ

^{1}HNMR: δ5.386 (5H, s), 2.316 (2H, t), 1.843 (2H, m), 1.695 (2H, m). M/Z: 205 (10%), 177 (14%), 149 (11%).

4. Preparation of benzophenone - η^5 - cyclopentadienyl dicarbonyl tetrafluoroborate 42iv

Benzophenone (0.561 g, 3 mmol) was dissolved in 30ml of dichloromethane in a 250 ml conical flask under a blanket of nitrogen. The flask with its contents was then placed on a magnetic stirrer plate and stirred for 5 minutes. Silver tetrafluoroborate (0.300 g, 1.5 mmol) was added to the flask. This was stirred for 15 minutes. A white prepitate formed. Cyclopentadienyl iron dicarbonyl iodide (0.233 g, 0.77 mmol) was added to the reaction mixture. A red colour appeared. The reaction mixture was stirred for 15 minutes. A grey solid formed which settled at the bottom and on the sides of the flask.. The red liquid was drained by syringe and transferred to another clean conical flask. The volume of the red liquid was reduced to one quarter (¼) of the original volume by vacuum. Diethyl ether (5ml) was added. A red precipitated formed. The liquid was removed by syringe. Diethyl ether was added again. The mixture was shaken and left to stand for a minute. The liquid portion was drained by syringe. The process of cleaning with diethyl ether was repeated for the third time. The red solid was dried by a stream of nitrogen. The residue was then transferred to a sample holder. The yield was 0.108 g (31%)

FTIR: (CH_2Cl_2, cm^{-1}): 3085 (w), 3066 (w) 2069 (m, υco), 2021 (m, υco), 1600 (s, $\upsilon_{O=CR^{I}R^{II}}$), 1578 (s), 1448 (s), 1276 (vs), 1070 (m), 737 (vs), 701 (vs) υ

^{1}HNMR: δ7.781 - 7.469 (10H, m), 5.157 (5H, s)

5. Preparation of benzyl methyl ketone - η^5 - cyclopentadienyl tetrafluoroborate 42v

Benzyl methyl ketone (0.103 g, 1 mmol) was added to 30 ml of dichloromethane in a 250 ml conical flask under a blanket of nitrogen. The flask with its contents was then placed on a magnetic stirrer plate and stirred for 5 minutes. Silver tetrafluoroborate (0.150g, 0.77 mmol) was added to the flask. This was stirred for 15 minutes. The silver tetrafluoroborate dissolved completely.

Cyclopentadienyl iron dicarbonyl iodide (0.233, 0.77 mmol) was added. A red colour appeared. The reaction mixture was stirred for 15 minutes. A grey precipitate formed which settled at the bottom and on the sides of the flask. The red liquid was drained by syringe and transferred to another clean conical flask. The volume of the red liquid was reduced to one quarter (¼) of the original volume by vacuum. Diethyl ether (5ml) was added. A red precipitated formed. The liquid was removed by syringe. Diethyl ether was added again. The mixture was shaken and left to stand for a minute. The liquid portion was drained by syringe. The process of cleaning with diethyl ether was repeated for the third time. The red solid was dried by a stream of nitrogen. The residue was then transferred to a sample holder.

. The yield was 0.142 g (49%).

^{1}HNMR: δ 7.24 (6H, m), 5.35 (5H, s), 3.68 (2H, s), 2.14 (3H, s)

, m/z : 399 (M^+ + 1, 18%), 311 (M^+ - BF_4, 8.6%), 233 (6.9%), 205 (58%), 177 (82%), 149 (40%).

6. Preparation of cyclopentanone - η^5 - cyclopentadienyl iron dicarbonyl tetrafluoroborate 42vi

Cyclopentanone (0.13g, 1.54 mmol) was added to 10 ml of dichloromethane in a shlenk flask under a blanket of nitrogen. The mixture was swirled. Silver tetrafluoroborate(0.15g, 0.77 mmol) was added to the reaction mixture. The reaction mixture was swirled for 15 minutes. Cyclopentadienyl iron dicarbonyl iodide (0.23g, 0.77 mmol) was added. The reaction mixture turned red immediately. It was swirled for 15 minutes. A grey precipitate settled at the bottom and sides of the flask. The volume of the reaction mixture was reduced by vacuum to 1/4 of the original volume. 5 ml of diethyl ether was added. A red precipitate was formed. The liquid portion was drained out by syringe. 5 ml of diethyl ether was added. This was swirled for 5 minutes. It was left to stand for 5 minutes. The liquid portion was removed by syringe. Washing with diethyl ether was repeated twice with 5 ml portions and the liquid removed by syringe. 5 ml of dichloromethane was added to the reaction mixture. The mixture was swirled for 5 minutes. The liquid extract was removed by syringe and transfered to a clean schenk flask.

Extraction of the product was repeated twice with 5 ml portions of dichloromethane and transfered to the same clean schlenk flask. The volume was reduced by vacuum to ¼ of the original volume. 5 ml of diethyl ether was added. A red precipitate was formed. The liquid was removed completely by vacuum. The red solid was scrapped out by use of a spatula and transfered to a clean sample holder.The yield was 0.18g (69%).

FTIR: (CH_2Cl_2, cm^{-1}), 3055 (w), 2986 (w) 2071 (vs, υ_{CO}), 2023 (vs, υ_{CO}), 1680 (m, br, $\upsilon_{O=CR^{1}R^{11}}$), 1266 (vs), 736 (vs), 705 (vs).

^{1}HNMR: δ 5. (5H, s), 2.00 (4H, m), 1.85 (4H, t)

^{13}CNMR: δ 247.6, 209.2, 86.6, 42.0, 23.5

m/z : 345 (M^+ - 3, 5.2%), 343 (M^+ -5, 8.6%), 261 (M^+ - BF_4, 98.3%), 233 (80.2%), 205 (100%), 177 (67.2%), 149 (39.7%).

Appendix 1

Comparison of reacted carbonyl and free carbonyl of the ketone when reacted with silver tetrafluoroborate

Ketone	**Free Ketone** cm^{-1}	**reacted Ketone** m^{-1}	$\Delta\upsilon$ cm^{-1}
Acetone	1712	1660	45
2 - butanone	1715	1650	65
3 - pentanone	1715	1680	35
Benzyl methyl ketone	1710	1680	30
Benzophenone	1650	1630	20
Sym-dichloroacetone	1730	1650	90

Source:Zulu, G.C. Organometallic chemistry report, UNZA, 1995, pp 7

Spectroscopic Characterisation of Aldehyde Complexes (RS,SR)-([(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CHR)]$^+$ PF_6^-((RS,SR)-$3^+PF_6^-$)

Spectroscopic Characterization of Aldehyde Complexes (*RS,SR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CHR)]$^+PF_6^-$ ((*RS,SR*)-$3^+PF_6^-$)

complex (R)	IR ν_{NO},[a] cm^{-1}	^1H NMR,[b] δ	$^{13}C\{^1H\}$ NMR,[c] ppm	$^{31}P\{^1H\}$ NMR,[d] ppm
(*RS,SR*)-$3a^+PF_6^-$ (CH_3)	1737 (vs)	7.63–7.33 (m, 3 C_6H_5), 5.83 (s, C_5H_5), 5.50 (m, HCO), 2.32 (d, J = 4.0, CH_3)	PPh_3 at[e] 133.8 (d, J = 10.6, *o*), 133.1 (d, J = 2.9, *p*), 129.9 (d, J = 11.5, *m*), 127.6 (d, J = 59.8, *i*); 98.8 (s, C_5H_5), 79.5 (s, CO), 24.6 (s, CH_3)	10.0 (s)
(*RS,SR*)-$3b^+PF_6^-$ (CH_2CH_3)	1738 (vs)	7.67–7.42 (m, 3 C_6H_5), 5.96 (d, J_{PH} = 0.5, C_5H_5), 5.44 (ddd, J = 5.4, 4.2, J_{PH} = 2.3, HCO), 2.88 (ddddq, J = 14.5, 7.4, 4.2, J_{PH} = 0.7, C*HH'*), 1.95 (ddq, J = 14.5, 7.5, 5.5, C*H'*), 1.24 (t, J = 7.5, CH_3)	PPh_3 at 133.6 (d, J = 10.4, *o*), 133.0 (d, J = 2.6, *p*), 129.8 (d, J = 11.4, *m*), 127.4 (d, J = 59.5, *i*); 98.5 (s, C_5H_5), 85.8 (br s, CO), 32.5 (s, CH_2), 13.2 (s, CH_3)	10.0 (s)
(*RS,SR*)-$3c^+PF_6^-$ ($CH_2CH_2CH_3$)	1740 (vs)	7.67–7.42 (m, 3 C_6H_5), 5.92 (s, C_5H_5), 5.37 (ddd, J = 4.4, 5.2, J_{PH} = 2.3, HCO), 2.42 (m, C*HH'*), 2.12 (m, CH*H'*), 1.67 (m, CH_2), 1.02 (t, J = 7.3, CH_3)	PPh_3 at 133.5 (d, J = 9.6, *o*), 133.0 (d, J = 2.2, *p*), 129.8 (d, J = 11.5, *m*), 127.3 (d, J = 60.3, *i*); 98.3 (s, C_5H_5), 83.3 (br s, CO), 41.1 (s, CH_2), 23.6 (s, CH_2CH_3), 14.2 (s, CH_3)	10.1 (s)
(*RS,SR*)-$3d^+PF_6^-$ ($CH(CH_3)_2$)	1740 (vs)	7.67–7.42 (m, 3 C_6H_5), 5.96 (d, J_{PH} = 0.5, C_5H_5), 5.19 (dd, J = 7.2, J_{PH} = 2.3, HCO), 1.68 (pseudooct, J = 6.8, C*H*-(CH_3)$_2$), 1.33 (d, J = 6.6, CH_3), 1.17 (d, J = 6.8, CH_3')	PPh_3 at 133.6 (d, J = 10.4, *o*), 133.0 (d, J = 2.8, *p*), 129.8 (d, J = 10.5, *m*), 127.3 (d, J = 59.9, *i*); 98.5 (s, C_5H_5), 89.0 (br s, CO), 38.2 (s, CH), 25.2 (s, CH_3), 19.5 (s, CH_3')	10.0 (s)
(*RS,SR*)-$3e^+PF_6^-$ (C_6H_5)	1735 (vs)	7.90–7.06 (m, 4 C_6H_5), 6.81 (d, J_{PH} = 1.4, HCO), 5.89 (s, C_5H_5)	PPh_3 at[e] 134.0 (d, J = 10.2, *o*), 133.1 (s, *p*), 130.0 (d, J = 11.2, *m*), 127.9 (d, J = 59.1, *i*); CPh at 139.5 (s, *i*), 130.7 (s), 128.7 (s), 127.1 (s); 99.3 (s, C_5H_5), 89.5 (br s, CO)	10.0 (s)
(*RS,SR*)-$3f^+PF_6^-$ ($CH_2C_6H_5$)	1729 (vs)	7.71–7.27 (m, 4 C_6H_5), 5.84 (s, C_5H_5), 5.44 (br m, HCO), 3.58 (dd, J = 14.2, 5.8, C*HH'*), 3.44 (dd, J = 14.2, 3.9, CH*H'*)[f]	PPh_3 at 134.1 (d, J = 10.9, *o*), 133.9 (s, *p*), 130.5 (d, J = 11.4, *m*), 127.7 (d, J = 60.3, *i*); CPh at 139.5 (s, *i*), 129.7 (s), 129.5 (s), 128.0 (s); 99.0 (s, C_5H_5), 81.0 (br s, CO), 45.5 (s, CH_2)	10.1 (s)

[a] KBr disk. [b] Recorded at 300 MHz in CD_2Cl_2 at ambient probe temperature and referenced to internal $Si(CH_3)_4$. All couplings are in Hz. [c] Recorded at 75 MHz in CD_2Cl_2 at ambient probe temperature and referenced to CD_2Cl_2 (53.8 ppm). All couplings are in Hz and are to ^1H unless noted. Assignments of phenyl carbon resonances were made as described in footnote *c* of Table I in ref 19. [d] Recorded with external lock at 32.2 MHz in CD_2Cl_2 at ambient probe temperature and referenced to external 85% H_3PO_4 unless noted. [e] These spectra were obtained with (+)-(*RS*)-$3a^+BF_4^-$ and (+)-(*RS*)-$3e^+BF_4^-$. The racemates (*RS,SR*)-$3a,e^+X^-$ are poorly soluble in CD_2Cl_2, CD_3CN, acetone-d_6, and THF-d_8. [f] Solvate resonance at δ 5.63 (s, 0.5 CH_2Cl_2) in acetone-d_6.

Source: Gladysz, J.A., J. Am. Chem. Vol.112, # 13, 1990, pp 5147

Appendix 3

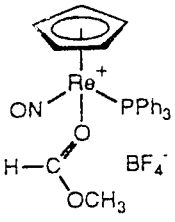
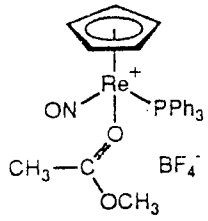
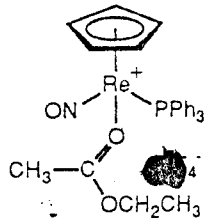
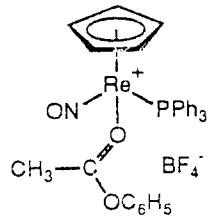
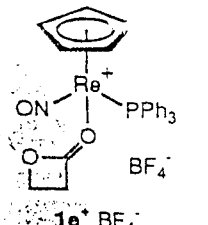
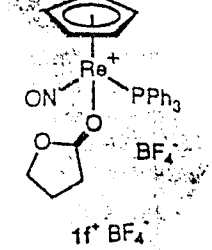
Spectroscopic Characterisation of Ketone Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}CHR)]^+ BF_4^-$ ($3^+PF_6^-$)

Spectroscopic Characterization of Ketone Complexes $[(\eta^5\text{-}C_5H_5)$

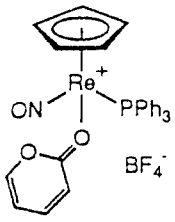
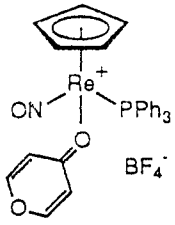
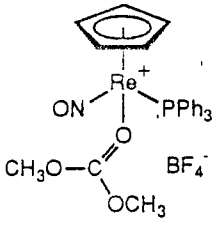
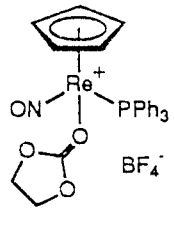
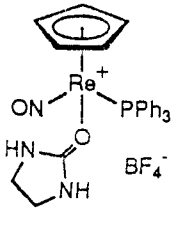
complex (R)	IR (cm^{-1}, KBr/CH_2Cl_2)	^1H NMR[b,c] (δ)	$^{13}C\{^1H\}$ NMR[c,d] (ppm)	$^{31}P\{^1H\}$ NMR[c,e] (ppm)
3a$^+BF_4^-$ (CH_3)	ν_{NO} 1680 vs/1693 vs	7.59–7.30 (m, $3C_6H_5$), 5.61 (s, C_5H_5), 2.34 (d, J_{HP} = 0.7, $2CH_3$)	PPh_3 at 133.7 (d, J = 10.8), 132.0 (s, *p*), 131.6 (d, J = 40.5, *i*), 129.1 (d, J = 10.8); 231.9 (s, CO), 92.9 (s, C_5H_5), 32.3 (s, $2CH_3$)	18.7 (s)
	$\nu_{C=O}$ 1618 m/1622 m			
3b$^+BF_4^-$ (CH_2CH_3)	ν_{NO} 1686 vs/1694 vs	7.61–7.28 (m, $3C_6H_5$), 5.61 (s, C_5H_5), 2.94 (dq, J = 19.3, 7.1, CHH'), 2.51 (dq, J = 19.3, 7.1, CHH'), 2.38 (s, $COCH_3$), 0.75 (t, J = 7.1, CH_2CH_3)	PPh_3 at 133.8 (d, J = 11.0), 132.0 (d, J = 1.5, *p*), 131.8 (d, J = 55.2, *i*), 129.6 (d, 10.7); 234.9 (s, CO), 92.9 (s, C_5H_5), 39.5 (s, CH_2), 31.1 (s, $COCH_3$), 8.2 (s, CH_2CH_3)	18.9 (s)
	$\nu_{C=O}$ 1617 s/1625 m			
3c$^+BF_4^-$ ($CH(CH_3)_2$)	ν_{NO} 1692 vs/1694 vs	7.60–7.25 (m, $3C_6H_5$), 5.59 (s, C_5H_5), 2.93 (m, CH), 2.45 (s, $COCH_3$), 0.86 (d, J = 6.5, $CHCH_3$), 0.69 (d, J = 7.0, $CHCH_3$)	PPh_3 at 133.7 (d, J = 11.1), 132.0 (d, J = 55.4, *i*), 131.9 (d, J = 2.5, *p*), 129.5 (d, J = 10.7); 238.2 (d, J = 2.0, CO), 93.0 (d, J = 1.6, C_5H_5), 44.5 (s, $COCH_3$), 29.7 (s, CH_3CHCH_3), 18.9 (s, $CHCH_3$), 17.7 (s, $CHCH_3$)	18.5 (s)
	$\nu_{C=O}$ 1611 s/1614 m			
3d$^+BF_4^-$ ($C(CH_3)_3$)	ν_{NO} 1684 vs/1697 vs	7.60–7.25 (m, $3C_6H_5$), 5.59 (s, C_5H_5), 2.47 (s, $COCH_3$), 0.87 (s, $C(CH_3)_3$)	PPh_3 at 133.9 (d, J = 11.1), 132.3 (d, J = 55.7, *i*), 132.2 (d, J = 2.4, *p*), 129.8 (d, J = 10.9); 240.4 (s, CO), 93.2 (d, J = 1.5, C_5H_5), 48.1 (s, $C(CH_3)_3$), 27.4 (s, $COCH_3$), 26.6 (s, $C(CH_3)_3$)	18.7 (s)
	$\nu_{C=O}$ 1607 s/1605 m			
3e$^+BF_4^-$ (C_6H_5)	ν_{NO} 1677 vs/1693 vs	7.65–7.25 (m, $4C_6H_5$), 5.71 (s, C_5H_5), 2.62 (d, J_{HP} = 0.5, CH_3)	PPh_3 at 133.8 (d, J = 10.8), 132.0 (d, J = 1.7, *p*), 131.3 (d, J = 55.7, *i*), 129.6 (d, J = 10.8); CPh at 136.4 (s), 135.0 (s), 129.7 (s), 129.3 (s); 215.9 (s, CO), 93.3 (s, C_5H_5), 26.8 (s, CH_3)	18.4 (s)
	$\nu_{C=O}$ 1558 m/1554 m			

Source: Gladysz, J.A., J. Am. Chem. Vol.112, # 25, 1990, 9201

Spectroscopic Characterisation of New Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)O{=}C(X)X')]^+ BF_4^-$ ($1^+BF_4^-$)

complex	IR (cm^{-1})[a]	^1H NMR (δ)[b,c]	$^{13}C\{^1H\}$ NMR (ppm)[c,d]
 **1a**$^+$ BF_4^-	ν_{NO} 1698 vs ν_{CO} 1618 s	8.29 (s, HC=O), 7.61–7.28 (m, 3 C_6H_5), 5.61 (s, C_5H_5), 3.31 (s, CH_3)	179.3 (s, C=O); PPh_3 at 133.0 (d, J = 11.0, o), 131.0 (s, p), 130.2 (i),[f] 128.7 (d, J = 10.3, m); 91.3 (s, C_5H_5), 55.3 (s, CH_3)
 **1b**$^+$ BF_4^-	ν_{NO} 1696 vs ν_{CO} 1611 vs	7.65–7.37 (m, 3 C_6H_5), 5.60 (s, C_5H_5), 3.34 (s, OCH_3), 2.35 (s, CH_3)	186.9 (s, C=O); PPh_3 at 133.8 (d, J = 11.0, o), 132.1 (d, J = 55.(i), 131.9 (d, J = 2.3, p), 129.1 (d, J = 10.8, m); 92.3 (s, C_5H_5), 56.4 (s, OCH_3), 22.5 (s, CH_3)
 **1c**$^+$ BF_4^-	ν_{NO} 1694 vs ν_{CO} 1619 s	7.71–7.19 (m, 3 C_6H_5), 5.58 (s, C_5H_5), 3.89 (m, CHH′), 2.93 (m, CHH′), 2.42 (s, CH_3C=O), 1.03 (t, J = 7.0, CH_3)	185.8 (s, C=O); PPh_3 at 133.5 (d, J = 10.8, o), 131.7 (s, p), 130. (i),[f] 129.4 (d, J = 10.4, m); 92.1 (s, C_5H_5), 66.0 (s, CH_2), 23.2 (CH_3C=O), 13.4 (s, CH_3)
 **1d**$^+$ BF_4^-	ν_{NO} 1703 vs ν_{CO} 1625 s	7.60–7.35 (m, 3 C_6H_5); CPh at 6.91 (br, s, 4 H), 6.40 (d, J = 7.5, 1 H); 5.43 (s, C_5H_5), 2.77 (s, CH_3)	185.8 (s, C=O); PPh_3 at 132.7 (d, J = 9.0, o), 132.1 (d, J = 55.4, i), 131.1 (s, p), 128.9 (d, J = 10.4, m); CPh at 149.1 (s, i), 129.8 (s), 127.0 (s), 120.3 (s); 91.8 (s, C_5H_5), 21.7 (s, CH_3)
 **1e**$^+$ BF_4^-	ν_{NO} 1684 vs ν_{CO} 1719 s	7.64–7.30 (m, 3 C_6H_5), 5.56 (s, C_5H_5), 4.60 (m, OCH), 4.47 (m, OCH′), 3.64 (m, O=CCH), 3.06 (m, O=CCH′)	185.0 (s, C=O); PPh_3 at 133.1 (d, J = 11.1, o), 131.1 (s, p), 130 (d, J = 55.6, i), 128.6 (d, J = 10.5, m); 91.2 (s, C_5H_5), 65.0 (s, OCH_2), 35.5 (s, O=CCH_2)
 **1f**$^+$ BF_4^-	ν_{NO} 1703 vs ν_{CO} 1635 s	7.60–7.27 (m, 3 C_6H_5), 5.51 (s, C_5H_5), 4.63 (m, OCH_2), 2.47–2.06 (m, 2 CH_2)	193.0 (s, C=O); PPh_3 at 133.6 (d, J = 13.9, o), 132.0 (d, J = 5 i), 131.5 (s, p), 129.1 (d, J = 13.2, m); 91.1 (s, C_5H_5), 75.5 (s, OCH_2), 30.4 (s, O=CCH_2), 23.1 (s, $CH_2CH_2CH_2$)

Appendix 4 (Continued)

complex	IR (cm^{-1})[a]	^1H NMR (δ)[b,c]	$^{13}C\{^1H\}$ NMR (ppm)[c,d]	$^{31}P\{^1$ NM (ppn
 1g$^+$ BF_4^-	ν_{NO} 1674 vs ν_{CO} 1638 vs	7.83 (m, OCH), 7.54–7.27 (m, 3 C_6H_5), 6.72 (m, CH), 6.50 (m, CH),[g] 5.53 (s, C_5H_5)	220.7 (s, C═O), 152.9 (s, OCH), 146.3 (s, OC═*C*C); PPh_3 at 133.5 (d, J = 10.0, o), 132.2 (i),/ 131.5 (s, p), 129.1 (d, J = 11.4, m); 116.3 (s, O═*C*C), 110.7 (s, OC═*C*), 91.8 (s, C_5H_5)	18.9
 1h$^+$ BF_4^-	ν_{NO} 1665 vs ν_{CO} 1627 s	8.08 (m, OCH), 7.49–7.31 (m, 3 C_6H_5), 6.70 (m, O═CCH), 5.53 (s, C_5H_5)	220.8 (s, C═O), 159.0 (s, OCH); PPh_3 at 133.6 (d, J = 11.4, o), 132.1 (i),/ 131.4 (s, p), 129.2 (d, J = 11.2, m); 117.4 (s, O═*C*C), 92.3 (s, C_5H_5)	18.5
 1i$^+$ BF_4^-	ν_{NO} 1680 vs ν_{CO} 1622 s	7.68–7.24 (m, 3 C_6H_5), 5.53 (s, C_5H_5), 3.99 (s, OCH_3), 3.27 (s, OC′H_3)	220.0 (s, C═O); PPh_3 at 133.0 (d, J = 10.5, o), 131.0 (d, J = 54.2, i), 130.8 (s, p), 128.5 (d, J = 10.0, m); 91.0 (s, C_5H_5), 59.1 (s, OCH_3), 57.6 (s, OC′H_3)	21.3
 1j$^+$ BF_4^-	ν_{NO} 1708 vs ν_{CO} 1663 vs	7.62–7.30 (m, 3 C_6H_5), 5.48 (s, C_5H_5), 4.72 (s, 2 CH_2)	220.0 (s, C═O); PPh_3 at 132.9 (d, J = 12.0, o), 130.8 (d, J = 56.8, i), 130.8 (s, p), 128.4 (d, J = 13.1, m); 91.0 (s, C_5H_5), 68.9 (s, 2 CH_2)	19.2
 1k$^+$ BF_4^-	ν_{NO} 1690 vs ν_{CO} 1627 vs	7.72–7.37 (m, 3 C_6H_5), 5.46 (s, C_5H_5), 5.41 (br, s, NH), 3.63 (s, 2 CH_2)	247.8 (s, C═O); PPh_3 at 133.8 (d, J = 11.6, o), 132.9 (d, J = 55.3, i), 131.6 (s, p), 129.3 (d, J = 10.9, m); 92.0 (s, C_5H_5), 42.6 (s, 2 CH_2)	18.1

Source: Gladysz, J.A., Organometallics, Vol.11, # 2, 1992, pp 686

Appendix 5

Comparison of Spectrscopic Properties of Free and coordinated ligands in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+ BF_4^-$ ($1^+BF_4^-$)

Comparison of Spectroscopic Properties of Free and Coordinated Ligands in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+BF_4^-$ ($1^+BF_4^-$)

	ligand	IR ($\nu_{C=O}$, cm^{-1})			^{13}C NMR (C=O, ppm)		
		uncoordinated	coordinated[b]	Δ	uncoordinated[c]	coordinated[c]	Δ
a	methyl formate	1724[a]	1618	106	161.1	179.3	18.2
b	methyl acetate	1740[a]	1611	129	169.8[d]	186.9	17.1
c	ethyl acetate	1740[a]	1619	121	170.0[d]	185.8	15.8
d	phenyl acetate	1754[a]	1625	129	168.8	185.8	17.0
e	propiolactone	1835[a]	1719	116	168.6	185.8	17.2
f	γ-butyrolactone	1770[a]	1635	135	177.5	185.0	7.5
g	2*H*-pyran-2-one	1740[b]	1638	102	161.5	220.7	59.2
h	4*H*-pyran-4-one	1658[b]	1627	31	177.7	220.8	43.1
i	dimethyl carbonate	1754[a]	1622	132	155.9	220.0	64.1
j	ethylene carbonate	1800[b]	1663	137	155.5	220.0	64.5
k	imidazolidone	1675[b]	1627	48	165.4	247.8	82.4

[a] Neat. Data from: Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich Chemical Co.: Milwaukee, 1981. [b] KBr. [c] $CDCl_3$, unless noted. [d] Neat. Data from: Breitmaier E.; Haas, G.; Voelter, W. *Atlas of Carbon-13 NMR Data*; Heyden: Bristol, 1979. [e] CD_2Cl_2 at −80 °C (1a,c–e,j$^+BF_4^-$) or ambient (1b,f–h,k$^+BF_4^-$) probe temperature.

Source: Gladysz, J.A., Organometallics, Vol.11, # 2, 1992, pp 691

Appendix 6

Infrared data for $[(CpFe(CO)_2(aldehyde)]PF_6$ 41

COMPOUND	IR $\upsilon_{C=O}$ cm^{-1}	IR $\upsilon_{HC=O}$ cm^{-1}
1. benzaldehyde	2075,2031	1626
2. p - tolualolehyde	2075,2030	1596
3. p - (dimethylamino) benzaldehyde	2070,2024	1619
4. p - anisaldehyde	2074, 2029	1594, 1586
5. p - (trifluoromethyl) benzaldehyde	2077, 2033	1637
6. p - (dimethylamino) cinnamaldehyde	2070,2024	1546

Source: Cicero, R.C.; Protasiezwicz, J.D., Organometallics, 1995, 14, 4792.

Appendix 7

IR frequency **Comparison of reacted carbonyl and unreacted carbonyl of ketones with cyclopentadienyl iron dicarbonyl complex (Fp)**

COMPOUND	KETONE USED	FREE (CM^{-1})	REACTED (CM^{-1})	$\triangleleft$1R (CM^{-1})
42i	3 - pentanone	1716	1632	84
42ii	Acetone	1715	1640	75
42iii	Cyclohexanone	1718	1642	76
42iv	Benzophenone	1664	1600	64
42vi	Cyclopentanone	1751	1680	71

Appendix 8

Infrared spectroscopic wave numbers for the common groups of cyclopentadienyl iron dicarbonyl ketone complexes 42

Compound	Ketone	Cp cm^{-1}	C=O(cm^{-1}) Terminal carbonyl	C=O(cm^{-1}) Bound ketone carbonyl	B-F_4 cm^{-1}
42i	3 - pentanone	3055	2065, 2011	1632	1078
42ii	Acetone	3065	2080, 2020	1640	1050
42iii	Cyclohexanone	3055	2068, 2020	1642	1057
42iv	Benzophenone	3066	2069, 2021	1600	1075
42vi	Cyclopentanone	3055	2071, 2023	1680	1059

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