Spectroscopic studies of thermally activated C-F bonds and photochemically induced haptotropic shifts of π coordinated aromatic ligand systems

by

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ABSTRACT

Jennifer McKenna

The photochemical and thermal activation of C-X (X = F or H) bonds in heteroaromatic compounds

This thesis consists of six chapters. Chapter 1 reviews the development of organometallic chemistry and the bonding and symmetry features dealt with in later chapters.

Chapter two deals with the treatment of *trans*-NiF(C₅F₃RN)(PEt₃)₂, where R =F or H, with a variety of (CH₃)₃SiX compounds (X = N₃, NCO or C=CSi(CH₃)₃), which resulted in the formation of complexes in which the activated fluorine atom was replaced; yielding *trans*-NiN₃(C₅F₃RN)(PEt₃)₂, *trans*-NiNCO(C₅F₃HN)(PEt₃)₂ and *trans*-NiC=CSi(CH₃)₃(C₅F₃HN)(PEt₃)₂. The trifluoropyridylazide complex, *trans*-NiN₃(C₅F₃HN)(PEt₃)₂, is reactive, forming the metal isocyanate complex, *trans*-NiNCO(C₅F₃HN)(PEt₃)₂ upon reaction with CO. Attempts were made to effect reductive elimination of the Ni(PEt₃)₂ fragment and form fluoropyridines substituted at the 2-position with the functionalities, N₃, NCO and C=CSi(CH₃)₃.

Previous studies have shown that $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe has an extensive photochemistry that is dominated by haptotropic shifts of the coordinated pyrrolyl ligand. In an attempt to control the degree to which the hapticity of the pyrrolyl ligand can be altered, the photochemistry of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe has been investigated. The results of matrix isolation studies of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe are presented in chapter three. The photochemistry of this analogue is also dominated by haptotropic shifts. Both monochromatic and broad-band irradiation of this complex in CO doped Ar matrixes at 20 K gives rise to three species characterised as $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO) (2), $(\eta^5-C_5H_5)(\eta^1-N (CH_3)_2C_4H_2N)$ Fe(CO)₂ (3) and $(\eta^5-C_5H_5)(\eta^3-N-(CH_3)_2C_4H_2N)$ Fe(CO) (4). Subsequent annealing of the matrix results in a conversion of the η^1 -monocarbonyl complex to the dicarbonyl complex and an isomerisation of the aza-allyl species to the corresponding π -allyl complex $(\eta^5-C_5H_5)(\eta^3-C-(CH_3)_2C_4H_2N)$ Fe(CO) (5).

Chapter four presents the results of matrix isolation studies of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in inert (Ar and CH₄) and reactive (CO and N₂) matrixes at 20 K. The results indicate that the η^5 -coordinated selenophene ring undergoes haptotropic shifts upon photolysis. The photoproducts observed depend on the host matrix employed. In all four matrixes, short wavelength irradiation ($\lambda_{exc} = 405$ nm) yields a three carbonyl band pattern that has been assigned to ($\eta^4-C_4H_4Se$)Cr(CO)₃, whereby the selenophene ring has undergone a ring slip from $\eta^5 \rightarrow \eta^4$ coordination, [($\eta^4-C_4H_4Se$)Cr(CO)₃N₂ in N₂ matrixes]. Subsequent photolysis of this photoproduct in inert matrixes produces the CO loss product, ($\eta^4-C_4H_4Se$)Cr(CO)₂. In N₂ matrixes subsequent photolysis of the primary photoproduct results in the formation of the dicarbonyl species, [(η^5 -C₄H₄Se)Cr(CO)₂N₂]. In CO matrixes the initial photoproduct yields Cr(CO)₆ upon

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extended photolysis. There is evidence to support a possible photochemical $\eta^5 \rightarrow \eta^4 \rightarrow \eta^2$ stepwise exchange of the selenophene ring.

Chapter five deals with the steady state photolytic studies of the complex, $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$. These studies indicate that the arene ring undergoes replacement when donor ligands are present in solution and the metal complex undergoes decomposition in their absence. CO was employed as the ligand of choice. $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$ was formed upon photolysis in CO purged acetone and dichloromethane solutions while $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]PF_6$ was produced in CO purged acetonitrile solutions. The decomposition products include ferrocene, 'free' arene and Fe²⁺. These results along with laser flash photolysis studies point to a mechanism involving a solvated intermediate of the type $[(\eta^5-C_5H_5)Fe(solv)_3]^+$. In addition preliminary steady state photolysis studies were carried out on the heteroaromatic complex, $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$.

Outlined in Chapter 6 are the experimental details and suggestions for future work.

.

Abbreviations

ABBREVIATIONS

aq	aqueous
bipy	bipyridine
C*	carbon radical
COD	1,5-cyclooctadiene
Cum	cumene
Ср	cyclopentadiene
d	doublet
DBT	dibenzothiophene
depe	diethylphosphinoethane
dfpe	$(CF_3)_2PCH_2P(CF_3)_2$
diphos	$(CH_2)_2[P(Ph_2)_2]$
dmpe	dimethylphosphinoethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DPA	diphenylanthracene
¹ DPA	singlet excited state of diphenylanthracene
³ DPA	triplet excited state of diphenylanthracene
2,6-DMP	2,6-dimethylphenanthrene
dppe	diphenylphosphinoethane
Δ	heat
H^{\bullet}	hydrogen radical
Hg●	mercury radical
hν	photon
HDS	hydrodesulfurisation
НОМО	highest occupied molecular orbital
HMPT	hexamethylphosphoric triamide
Io	initial intensity
Ι	intensity
J	coupling constant (Hz)
LUMO	lowest occupied molecular orbital
(m)	medium

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Abbreviations

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m	multiplet
Methf	methyltetrahydrofuran
M-C bond	metal carbon bond
M-CO bond	metal carbonyl bond
M-F bond	metal fluorine bond
M-L bond	metal ligand bond
M-M bond	metal metal bond
M-PR ₃ complex	metal phosphine complex
[Ni]-F	NiF(PEt ₃)(C ₅ F ₃ RN)
Nuc	nucleophile
OTf	triflate
pCP	para-cyclophane
PhCN	benzonitrile
Phen	1,10-phenanthroline
PNN	2-(p-pyridyl)-4,4,5,5-tetramethylimidazole-1-oxyl-3-
	oxide
δ	chemical shift in ppm
π^* orbital	pi antibonding orbital
q	quintet
(s)	strong
S	singlet
σ orbital	sigma bonding orbital
σ^* orbital	sigma antibonding orbital
solv	solvated
Red Al	$Na[H_2AI(OCH_2CH_2OCH_3)]$
t	triplet
td	triplet of doublets
d ₈ -thf	deutrated tetrahydrofuran
tol	toluene
tpy	terpyridine
triphos	$CH_3(C(Ph_2)_3)$

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Introduction

Abstract

A brief overview of the development of organometallic chemistry is provided in addition to a discussion of the bonding modes observed throughout this thesis and the symmetry of the reactants encountered. Finally, a description of the techniques employed is presented.

Introduction

1. INTRODUCTION

1.1 Definition of an organometallic compound

An organometallic compound is defined as a compound that contains at least one direct metal to carbon bond and as such organometallic chemistry is at the interface between organic and inorganic chemistry. Many applications of organometallic chemistry make use of the various properties of the metal-carbon bond such as the Ziegler-Natta catalyst. Discovered in the 1950s, this catalyst consisting of a mixture of titanium tetrachloride and an alkyl derivative of aluminium enabled the polymerisation of ethylene to be achieved at atmospheric pressure. This method has been extended to other olefins and modified catalysts involve many mixtures of halides of transition metals, such as titanium, chromium, vanadium, and zirconium, with organic derivatives of non-transition metals, particularly alkyl aluminium compounds.

1.2 The development of organometallic chemistry

The field of organometallic chemistry is relatively new with widespread study of the subject beginning only in the 1950s.¹ Despite this, the first organometallic compounds were produced in the nineteenth century.

The first organometallic complex to be synthesised was $[(CH_3)_2As]_2O$, cacodyloxide, by the French scientist Cadet in Paris.² This was followed with the first olefin-transition metal complex, $[(C_2H_4)PtCl_3]^*K^+$, isolated by Zeise in 1827 (Eqn. 1.1).³

$$C_2H_4 + K_2PtCl_4(aq) \longrightarrow [(C_2H_4)PtCl_3]K^+ + KCl Eqn. 1.1$$

Frankland first synthesised organo-zinc compounds by treating organo-halides with zinc metal (Scheme 1.1).⁴

$$4C_{2}H_{5}I + 3Zn \longrightarrow C_{2}H_{5} + 2C_{2}H_{5} + (C_{2}H_{5})_{2}Zn + ZnI_{2}$$

Scheme 1.1

Introduction

Subsequent work led to the preparation of alkyl mercury compounds *via* alkyl transfer type reactions (Eqn. 1.2).

$$2CH_{3}X + 2NaHg \longrightarrow (CH_{3})_{2}Hg + 2NaX Eqn 1.2$$

In 1890, Mond isolated nickel tetracarbonyl. This research led to the discovery of the first transition metal hydride complex, $Fe(CO)_4H_2$ in 1931.⁵

The most important development in organometallic chemistry was the synthesis and discovery of ferrocene, $(\eta^5-C_5H_5)_2Fe$, the first sandwich complex, which was prepared independently by Pauson and Miller in 1951.⁶ A reaction between cyclopentadienyl magnesium bromide and anhydrous Fe^(III) chloride in ether was carried out in an attempt to synthesise fulvalene *via* oxidation of the Grignard reagent (Scheme 1.2). The expected product was not produced, instead a new complex, ferrocene, was formed.

$$3C_5H_5MgBr + FeCl_3$$

(C_5H_5)₂Fe + $\frac{1}{2}C_{10}H_{10}$ + $3MgBrCl$

Scheme 1.2

Simultaneously Miller reported the formation of orange crystals, $(C_5H_5)_2Fe$, by the direct reaction of cyclopentadiene with iron in the presence of aluminium, potassium or molybdenum oxides at 300 °C (Eqn. 1.3).

 $2C_{5}H_{6} + Fe \longrightarrow (C_{5}H_{5})_{2}Fe + H_{2}$ Eqn. 1.3

Using chemical, physical and spectroscopic techniques, the precise structure of ferrocene was elucidated. The structure of ferrocene involves equal bonding between all of the ten carbon atoms of the cyclopentadienyl rings and the Fe centre. The stability of ferrocene results from the strong overlap between the metal d-orbitals and the π electrons in the p-orbitals of the cyclopentadienyl ligands. Subsequent research revealed that this type of structure was not unique to iron and many analogues were

synthesised, such as nickel and cobalt sandwich complexes. The entire class of transition metal dicyclopentadienyl complexes has become known as 'metallocenes' and accounts for a large portion of organometallic chemistry.

1.3 The 18 electron rule

In 1927 Sidgwick proposed the 18 electron rule. Since the noble gases are relatively inert and have filled s and p shells it was proposed that metal complexes with 18 electrons might exhibit similar stability. There are two methods to count electrons, the neutral/covalent method and the ionic method.

In the ionic method all the ligands are removed from the metal centre and the proper number of electrons are added to each ligand to bring it to a closed shell state. For example, when a methyl group is removed from the metal centre with a closed shell configuration it is formally CH_3^- , a two-electron donor. The metal centre must be oxidised by one to maintain complex neutrality; thus its electron count is reduced by one.

In the covalent method all the ligands are removed from the metal centre and made neutral. For the methyl group, neutrality is achieved with a neutral methyl radical, a one-electron donor. The metal centre retains its full set of d electrons, as the oxidation state is never changed from zero. This method does not give information about the oxidation state of the metal however.

Table 1.1 provides a summary of the common ligands encountered in transition metal chemistry and the number of electrons donated by each one.

A general trend observed among transition metal centres is that first row transition metals favour 18 electron complexes, although there are exceptions such as the Ni(II) complexes prepared in Chapter 2, which are sixteen electron species. In contrast to first row transition metal complexes, second and third row transition metals tend to form complexes with < 18 electrons that are stable, for example $PtCl_2[P(CH_3)_3]_2$.

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Introduction

	Ionic method	Covalent method
R (H, CH ₃ , C ₂ H ₅), -CN, OH	2	1
CO, PR ₃ , amines, NH ₃ , RCN, olefins, alkynes	2	2
arenes	6	6
cyclopentadiene	6	5
$(\eta^{1}-N-(CH_{3})_{2}C_{4}H_{2}N)$	2	1
$(\eta^3 - N - (CH_3)_2 C_4 H_2 N)$	4	3
$(\eta^3 - C - (CH_3)_2 C_4 H_2 N)$	4	3
$(\eta^{5}-(CH_{3})_{2}C_{4}H_{2}N)$	6	6
$(\eta^2 - C_4 H_4 Se)$	2	2
$(\eta^4$ -C ₄ H ₄ Se)	4	4
$(\eta^5-C_4H_4Se)$	6	6

 Table 1.1: The number of electrons donated to a metal centre for the ionic method and covalent method of electron counting

1.4 Bonding encountered in this thesis

1.4.1 M-L ($L = CO \text{ or } PR_3$) bonding

The CO molecule constitutes the most common and the most important π -bonding ligand. In this thesis, the complexes investigated are transition metal complexes of the type NiN₃(PEt₃)₂(η^1 -C₅F₃HN), (η^5 -C₄H₄Se)Cr(CO)₃ and sandwich complexes of the type (η^5 -C₅H₅)Fe(η^5 -(CH₃)₂C₄H₂N) or [(η^5 -C₅H₅)M(η^6 -arene)]⁺ (M = Fe or Ru and arene = C₆H₅(C₃H₇), C₆H₅Cl, C₆H₄Cl₂ or (CH₃)₂C₄H₂S). Their photochemistry is conducted in various environments and under different photolytic conditions. The arene molecules undergo ring slippage upon photolysis, leaving a vacant site on the metal atom. In the presence of CO, a CO molecule occupies the vacant site. The bonding between a metal centre and a carbon monoxide molecule is discussed below and diagrams are included to illustrate this [Fig. 1.1(a) and 1.1(b)].

The bonding between a metal centre and a carbon monoxide molecule involves overlap of the σ orbital of the carbon atom with a σ type orbital on the metal. The donation of two electrons from the carbon to the metal leads to a build up of electron density on the metal (if its oxidation state is +2 or less). To reduce the electron density, the metal

engages in a backbonding interaction with vacant antibonding orbitals of low enough energy on the carbonyl ligand [Fig. 1.1(a)]. Thus the bonding between the metal and a CO molecule is described as being synergistic in nature. The net effect of this bonding is that the C-O bond strength is weakened while the M-C bond is strengthened. Spectroscopically, the effect of M-CO bonding is evident in the carbonyl region of the IR spectrum, where the carbonyl stretching frequencies occur at lower wavenumbers compared to uncoordinated CO (2143 cm⁻¹).



Fig. 1.1: (a) the synergistic bonding between a carbon monoxide molecule and a transition metal, (b) the molecular orbital diagram of the bonding in a M-CO complex

For carbonyl complexes of the type (η^6 -arene)M(CO)₃, one photochemical pathway available is CO loss. Dissociation of one CO molecule from the parent complex means that the electron density, originally 'off-loaded' onto three CO ligands, is now 'offloaded' onto the remaining two CO ligands. The C-O bond strengths of these are reduced compared to the parent complex. Hence the dicarbonyl stretching frequencies occur at lower wavenumbers than in the parent complex.

Another possible photochemical pathway for $(\eta^6\text{-arene})M(CO)_3$ complexes is an haptotropic shift of the arene ring. In the presence of CO, a CO molecule will occupy the vacant sites on the metal produced by arene ring slippage. Thus, in the IR spectrum, this photoproduct will have a different set of carbonyl bands associated with it compared to the parent complex.

Another ligand encountered in this thesis is the phosphine ligand, denoted by the general formula PR₃ where R = alkyl, aryl, H, halide etc. Phosphines are neutral two electron donors that coordinate to metals *via* their lone pair. The bonding is similar to that for M-CO complexes and consists of two components as illustrated in Fig. 1.2. Initial σ donation of the lone pair on the phosphorus atom to an empty σ type orbital on the metal is followed by back donation of a filled metal orbital to an empty orbital on the phosphorus atom.





1.4.2 M-arene bonding

The molecular orbital diagram for ferrocene is illustrated below (Fig. 1.3). The lowest energy orbital, a_1 interacts to a small extent with the metal d_z^2 orbital. The e_{1g} set of degenerate orbitals overlap with d_{xy} and d_{xz} to form a set of π bonds. The e_{1u} interaction between the metal p_x and p_y also gives some stabilisation. Although the metal $d_x^2 \cdot y^2$ and d_{xy} can overlap with the e_{2g} orbitals on the ligand, the degree of overlap is not very large and these levels are essentially non-bonding. The eighteen electrons of ferrocene are accommodated in the bonding and non-bonding molecular orbitals, giving a closed shell

configuration. This is reflected in the stability of the ferrocene molecule towards further reaction, especially photochemical pathways.



Fig. 1.3: The molecular orbital diagram of the bonding in ferrocene in the staggered conformation $(M = Fe)^{1}$

In the case of azaferrocene, the introduction of a nitrogen atom in the place of one of the carbon atoms and a hydrogen atom of one of the cyclopentadiene rings reduces the symmetry of the molecule. The degeneracy of the valence orbitals is lifted and thus, photochemical pathways that are not available to ferrocene now become possible.

1.5 Symmetry of the complexes encountered in this thesis

The most common oxidation state for nickel complexes is the +2 state. This is due to the instability of higher oxidation states. In addition, lower oxidation states of nickel are rare unless the complex contains strongly π bonding ligands. An example of a Ni(0) complex is Ni(COD)₂. This air and moisture sensitive yellow complex is the starting material for the C-F activation reactions studied in Chapter two. This eighteen-electron d¹⁰ complex has C_{2v} symmetry and adopts a tetrahedral configuration [Scheme 1.3(i)].

Reaction with PEt₃ and fluoropyridines produces the sixteen electron d⁸ complexes NiF(PEt₃)₂(C₅F₃RN) (R = H or F). These complexes adopt square planar geometry, with the two phosphine groups *trans* to each other. These complexes belong to the C_S point group [Scheme 1.3(ii)].



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Niam

(i)

Introduction



(ii)



(iii)











(vi)

(vii)

(viii)

Scheme 1.3

1.6 Techniques employed in this thesis

1.6.1 Matrix Isolation

Low temperature photochemical studies have the advantage of extending the lifetimes of reactive intermediates such that their spectroscopic properties can be recorded. Initially low temperature studies were confined to emission studies at 77 K⁷ because of the poor optical quality of the solutions frozen or cooled to this temperature. With the development of solutions that did form clear glasses at 77 K, absorption photochemistry of many complexes could be determined. This method is still used today. The photochemistry of $[(\eta^5-C_5H_5)Mn(CO)_3]$ and $[(\eta^5-C_5(CH_3)_5)Mn(CO)_3]$ was studied by Braterman et al.⁸ in a variety of glasses cooled to 77 K. Photolysis of these complexes at low temperature produces the CO loss products, $[(\eta^5-C_5H_5)Mn(CO)_2]$ and $[(\eta^5-C_5H_5)Mn(CO)_2]$ C_5H_5)Mn(CO)] and the pentamethylcyclopentadiene analogues. In the case where reactive solvent glasses were used, coordination of the solvent molecules was observed, the products include $[(\eta^5-C_5H_5)Mn(CO)(thf)_2]$, $[(\eta^5-C_5H_5)Mn(CO)_2(C_2H_5OH)]$ and $[(\eta^5-C_5(CH_3)_5Mn(CO)_2(Methf)]$. However, the development of matrix isolation by Pimentel⁹ has allowed even lower temperatures to be obtained (12 K) and has enabled inert gases to be used, which has put this technique at the forefront of low temperature photochemical techniques.

Matrix isolation stabilises reactive species by trapping them in a solid unreactive matrix such as argon. The lifetime of the intermediate is extended for sufficient time for the determination of their spectral properties. The use of solidified noble gases has the advantage of (i) extreme chemical inertness, (ii) transparency throughout the UV-visible-IR region and (iii) the tendency to form clear glasses at very low temperatures (\approx 12 K). Reactive species can be prepared by *in situ* photolysis of an appropriate matrix isolated precursor (Chapter six includes a description of the apparatus). Individual molecules are trapped and isolated from each other at very low temperatures. The very cold environment restricts the movement of the trapped molecules. They do not rotate and cannot diffuse through the inert host. Under these conditions bimolecular reactions are precluded. In addition the trapped molecules only interact weakly with the surrounding inert matrix. This technique is well suited to the study of highly reactive chemical species such as ions and free radicals that cannot be detected at room

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temperature, in addition to photochemically generated intermediates with vacant sites on the metal. Reaction of the trapped molecules with the matrix can occur when a reactive gas (CO, N₂) is employed as the host. This technique allows the observation of intermediates, which may play a role in many room temperature chemical reactions. Note that in matrix isolation experiments N₂ usually acts as an inert host but in the experiments carried out on (η^5 -C₄H₄Se)Cr(CO)₃, N₂ acts as a reactive host.

1.6.2 UV-vis laser flash photolysis

UV-vis laser flash photolysis, developed by Porter,¹⁰ generates a transient species when a short but intense laser pulse is absorbed by a sample (Chapter six includes a description of the apparatus). A transient is an excited state of an absorbing molecule or a reactive intermediate generated from it. Transient species can be detected by a number of spectroscopic techniques:

- (i) The decay or growth of the transient is monitored by a second light source of longer duration but lower intensity than the laser. This method is selective for a single wavelength allowing the kinetics of the reaction to be determined.
- UV-vis absorption allows detection of the transient over the complete wavelength range (280-800 nm).

This technique is suitable for the detection of metal-carbonyl complexes since they give rather intense UV-vis absorptions.

Very often matrix isolation and laser flash photolysis studies are used together to probe the photochemistry of transition metal complexes. Perutz *et al.*¹¹ employed laser flash photolysis to determine the kinetic data for the reaction of $Ru(Y)_2$ with H_2 while matrix isolation provided evidence for the formation of the $Ru(Y)_2$ fragment (Y = depe, dppe and dfpe).

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C-F activation of fluoropyridines with Ni(0) complexes

Abstract

Treatment of trans-NiF(C₅F₃RN)(PEt₃)₂, where R = F or H, with a variety of (CH₃)₃SiX compounds ($X = N_3$, NCO or C=CSi(CH₃)₃) resulted in the formation of complexes in which the activated fluorine atom was replaced; yielding trans-NiN₃(C₅F₃RN)(PEt₃)₂, trans-NiNCO(C₅F₃HN)(PEt₃)₂ and trans-NiC=CSi(CH₃)₃(C₅F₃HN)(PEt₃)₂. The trifluoropyridylazide complex, trans-NiN₃(C₅F₃HN)(PEt₃)₂, is reactive, forming the metal isocyanate complex, NiNCO(C₅F₃HN)(PEt₃)₂ upon reaction with CO. Attempts were made to effect reductive elimination of the Ni(PEt₃)₂ fragment and form fluoropyridines substituted at the 2-position with the functionalities, N₃, NCO and $C=CSi(CH_3)_3$.

2.1 LITERATURE SURVEY

There are numerous examples of metals that can cleave C-H bonds,¹ but reagents that break C-F bonds are more rare. However, advances have been made in this area with the discovery that transition metal reagents can successfully activate C-F bonds.

2.1.1 Physical and chemical properties of perfluorocarbons

Fluorine is the most electronegative element. Moreover, the van der Waals radius of fluorine is 1.50 Å and the complete replacement of hydrogen by fluorine is possible, resulting in many compounds analogous to the perhydrocarbons being available. However, the chemical properties of fluorocarbons differ substantially from their hydrogen derivatives. Fluorocarbons have lower boiling and melting points, are non-polar and have very low polarisability. They have the lowest dielectric constants and refractive indices of any liquids at room temperature and have found application in the pharmaceutical, agrochemical and medical industries. Perfluoroalkanes and their derivatives are good solvents for oxygen and have been used as blood substitutes,² while the low hydrocarbon solubility of perfluoroalkyl chains has found application in the fluorous biphase system.³

Despite their numerous applications, fluorocarbons are noted for their chemical inertness. This is a manifestation of the strength of the C-F bond, as the C-F bond is the strongest single bond formed to carbon (Table 2.1). The bond dissociation energy has been cited as being as high as 546 kJ mol⁻¹ for the F_3 C-F bond.⁴ Fluorocarbons are highly resistant to oxidative degradation with some species having atmospheric lifetimes exceeding two thousand years. Fluorocarbons have ozone depletion potential; hence interest lies in the conversion of these compounds into disposable products. The activation of the C-F bond provides a chemical challenge. While fluorocarbons can be destroyed by strong reducing agents such as sodium in liquid ammonia,⁵ it is the selective activation of a C-F bond that proves difficult.

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Chapter 2

Literature survey

X	CH ₃ X	CH ₂ X ₂	CHX ₃	CX ₄
F	459.8	499.9	533.5	546.0
Cl	353.9	335.1	324.7	305.9
Br	296.6	267.7	259.4	235.1
I	239.3	214.6	191.2	-

Table 2.1: Halomethane bond dissociation energies⁴ (kJ mol⁻¹)

Interest in the organometallic chemistry of fluorocarbons has grown with the discovery that perfluorocarbons undergo selective C-F activation with electron rich transition metal complexes. An example is the room temperature oxidative addition of a pentafluorophenyl group to W(0), involving oxidation of the metal to W(II) (Eqn. 2.1).⁶



Eqn. 2.1

2.1.2 Activation of perfluoroaliphatic compounds by transition metal reagents Coordination of perfluoroalkyl groups to transition metal centres reduces the reactivity of these compounds. The C-F bonds α to the metal centre are weakened, as illustrated by longer bond lengths and lower stretching frequencies in the infrared spectra. However, reactions of perfluoroalkanes are still very rare compared to perfluoroaromatics and perfluoroalkenes. It is the absence of π orbitals in these saturated compounds that eliminate many modes of attack common to the arenes and alkenes. The high electron affinity of aliphatic compounds, however, enables them to be attacked by reducing agents. Electron transfer to a C-F σ^* orbital can result in facile C-F bond cleavage and loss of fluoride.

2.1.3 C-F activation via reducing agents

Tatlow *et al.*⁷ reported the first example of high temperature metal catalysed defluorination of saturated cyclic perfluorocarbons to perfluoroaromatics in 1959. Perfluorobiphenyl, perfluoro-*p*-xylene and perfluoroethylbenzene were prepared from the corresponding saturated perfluorocarbons. Iron pieces or nickel turnings (in the temperature range 400-600 °C) were used as the reducing agents. Over twenty years later the same research group discovered milder defluorination processes.⁸ Using CsCoF₄ as the organometallic reductant in the temperature range, 380-400 °C, perfluoromethyl-cyclohexane and perfluoro-1,4-dimethylcyclohexane were converted to octafluorotoluene and perfluoro-*p*-xylene in 90 % and 45 % yield respectively (Eqns. 2.2 and 2.3). A mechanism for these reactions was not proposed, however.



Milder conditions have been used by Bennett *et al.*⁹ to synthesise perfluorotoluene. The more strongly reducing decamethylcobaltocene catalyses this reaction (Eqn. 2.4). LiO_3SCF_3 acts as a fluoride acceptor and six molecules of LiF are liberated. A mechanism for this reaction has not been determined, although electron transfer is believed to be involved. The parent cobaltocene complex, (η^5 -C₅H₅)₂Co, also catalyses C-F activation reactions. Although less reactive than the decamethyl analogue, cobaltocene defluorinates perfluorodecalin at room temperature (Eqn. 2.5).



McAlexander *et al.*¹⁰ reported that perfluorodecalin is converted to perfluorotetralin and perfluoronaphthalene in the presence of sodium oxalate. It is believed that the decomposition products of $Na_2C_2O_4$ (which are carbon and Na_2CO_3) are the active species. In the presence of activated carbon only, perfluorodecalin is converted to perfluoro-9,10-octalin or perfluorotetralin.¹⁰ In the presence of carbon and Na_2CO_3 significant yields of perfluoronaphthalene and small amounts of perfluorotetralin are formed (Eqn. 2.6).



perfluorodecalin

perfluoronaphthalene

perfluorotetralin Eqn. 2.6

2.1.4 Catalytic C-F activation

Kiplinger and Richmond¹¹ showed that group four metallocenes function as catalysts in the conversion of perfluorodecalins to perfluoronaphthalene (Eqn. 2.7). Using $(\eta^5-C_5H_5)MF_2$ (M = Ti or Zr), with activated Mg or Al as the reductant, turnover numbers of up to twelve have been recorded. Low valent zirconocene and titanocene have been postulated as intermediates in this catalytic cycle.



The C-F activation step is proposed to involve the low valent zirconocene fragment, $[(\eta^5-C_5H_5)_2Zr].$

The corresponding dihydride complex $(\eta^{5}-C_{5}(CH_{3})_{5})_{2}ZrH_{2}$ has recently been shown to be an effective C-F activation reagent. Kraft *et al.*^{12a} have reported that the reaction between $(\eta^{5}-C_{5}(CH_{3})_{5})_{2}ZrH_{2}$ and monofluorinated aliphatic complexes, produces the complex, $(\eta^{5}-C_{5}(CH_{3})_{5})_{2}ZrHF$ and the hydrogenated product. More recently,^{12b} research has shown that the $(\eta^{5}-C_{5}(CH_{3})_{5})_{2}Zr^{(111)}H$ complex is the reactive species in this process (Eqn. 2.8).

$$(\eta^{5}-C_{5}(CH_{3})_{5})_{2}ZrH_{2} + \swarrow F \xrightarrow{C_{6}D_{12}} (\eta^{5}-C_{5}(CH_{3})_{5})_{2}ZrHF + \swarrow F$$

Eqn. 2.8

Fluorocyclohexane was found to yield similar products upon reaction with $(\eta^5-C_5(CH_3)_5)_2ZrH_2$. A radical mechanism for the C-F activation reaction is proposed and is supported by the reaction of $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ with cyclopropylcarbinyl fluoride. The cyclopropylcarbinyl radical is known to ring open irreversibly to give the butenyl radical.¹³ Reaction of this fluoride with $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ produces a mixture of $(\eta^5-C_5(CH_3)_5)_2ZrHF$ and $(\eta^5-C_5(CH_3)_5)_2Zr(n-butyl)H$. These products can be accounted for by the following mechanism (Scheme 2.1). A small amount of $(\eta^5-C_5(CH_3)_5)_2Zr(^{(III)}H)$ abstracts a fluorine atom to give the cyclopropylcarbinyl radical. Rapid ring opening yields the butenyl radical that abstracts an II atom from a second molecule of $(\eta^5-C_5(CH_3)_5)_2ZrH_2$, continuing the radical chain. Insertion of butene into a third molecule of $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ gives the butenyl hydride complex with H₂ produces $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ and butane that has also been characterised by NMR and GC/MS.



Scheme 2.1

2.1.5 Photochemical C-F activation of perfluoroaliphatic compounds

Some metal-based photochemical systems have proved to be useful for the C-F activation of saturated perfluorocarbons. Burdeniuc and Crabtree^{14, 15} reported that the use of mercury photosensitization enables perfluoroaliphatic compounds to react with ammonia. Products include amine, imine and cyano derivatives (Eqn. 2.9).



Although initially believed to be restricted to tertiary bonds, recent studies have shown that secondary C-F bonds are also reactive under similar conditions.^{15a} Research revealed that the first step of the reaction involves an exciplex, $[Hg(NH_3)_2]^{\bullet}$, that acts as an electron donor and fluoride acceptor. The following mechanism, involving initial electron transfer accounts for the product formation (Scheme 2.2). A subsequent

mulitstep dark reaction of NH₃ with the exocyclic perfluoromethylenecyclohexane yields the nitrogen-containing product.



Scheme 2.2

A second photolytic process^{15b} converts perfluoroalkanes to perfluoroalkenes upon irradiation in the presence of decamethylferrocene. Cyclic aliphatics are activated with this reagent, although in this case a tertiary bond is a requirement. The catalytic process is illustrated below (Scheme 2.3).


Scheme 2.3

LiO₃SCF₃ acts as a fluoride acceptor and the system can be made catalytic with the introduction of zinc to reduce $[(\eta^5-C_5(CH_3)_5)_2Fe]^+$.

2.1.6 Perfluoroarenes and perfluoroalkenes

Perfluoroarenes and alkenes are more reactive than their saturated analogues. They undergo nucleophilic attack or accept electrons from a reductant. The driving force for conversion to analogous saturated derivatives is the stabilisation obtained upon coordination to a saturated carbon atom compared to an unsaturated carbon atom.^{16, 17}

There are a number of common pathways available for activation reactions of perfluoroarenes and alkenes.³

- Nucleophilic pathways: preferential route of attack for perfluoroarenes involving non-transition metal reagents. In contrast, perhydroarenes tend to undergo electrophilic attack. The intermediate perfluoroalkyl carbanion reacts with the perfluoroarene.
- 2. Electron transfer pathways: the initial step of many C-F activation reactions is the electron transfer from the reductant (Eqns. 2.10a and 2.10b).



3. Homolytic pathways: involving radical formation

 $C-F + H^* \longrightarrow H-F + C^*$ Eqn. 2.11

4. Electrophilic pathways: removal of F^- from perfluorocarbons

5. Oxidative pathways: insertion of the metal into the C-F bond. It is unknown whether this process is concerted or is primarily electron transfer.

In many cases the activation process is a combination of the above pathways. There are many organometallic reagents that participate in the C-F activation processes of fluoroarenes and fluoroalkenes. They can be divided into electron deficient (transition metal groups three to five) and electron rich (transition metal groups six to nine) transition metal reagents.

2.1.7 C-F activation reactions of electron deficient transition metal reagents

C-F activation reactions have been observed with a variety of electron deficient transition metal reagents (d^0 , d^1). Early transition metal centres are highly electrophilic and quite often the processes of defluorination involve electron transfer as the initial step. Alternatively, α -fluorine abstraction by a coordinatively unsaturated metal centre occurs. Formation of a strong M-F bond is often the driving force behind these abstractions. One of the earliest reports of C-F activation in a d^0 metal complex came

from Stone *et al.*^{18, 19} They observed that $(\eta^5 - C_5 H_5)_2 Ti(C_6 F_5)_2$ underwent intramolecular fluorine migration upon pyrolysis producing the C-F activated product (Eqn. 2.12).

$$(\eta^{5}-C_{5}H_{5}) \xrightarrow{Ti} C_{6}F_{5} \xrightarrow{I50^{\circ}C} (\eta^{5}-C_{5}H_{5}) \xrightarrow{Ti} F_{5} \xrightarrow{C_{6}F_{5}} Eqn. 2.12$$

A mechanism was not determined for this reaction. However, in the reaction of tetrakis(trifluoromethyl)cyclopentadienone with d^0 bis(C₅H₅)₂)Ti(C₅H₁₀), a radical mechanism has been proposed (Eqn. 2.13).²⁰



Burk *et al.* postulated the initial formation of a radical ion pair (Scheme 2.4), followed by reductive elimination of dimethyl cyclopropane. Subsequent collapse of the ion pair produces a titanocene-dienone complex (3a-b) (Scheme 2.4).



Scheme 2.4

Coordination through the oxygen directly is quite probable as it places the titanium cation in close contact with the CF_3 group. Fluoride migration to the electrophilic titanium centre can easily be achieved.

Zr has been shown to be equally effective as Ti as an activation reagent. While defluorinating perfluoroaliphatic compounds it also catalytically activates a variety of perfluoroaromatics. Edelbach *et al.*²¹ have shown that $[(\eta^5-C_5H_5)_2ZrH_2]_2$ and $(\eta^5-C_5H_5)_3ZrH$ react with hexafluorobenzene yielding $(\eta^5-C_5H_5)_2Zr(C_6F_5)F$, $(\eta^5-C_5H_5)_2ZrF_2$ and C_6F_5H . Initial interaction between the $Zr^{(IV)}$ centre and a fluorine atom of fluorobenzene is believed to occur, forming an intermediate in which one of the aryl carbon bonds is coordinated to the hydride of the Zr complex (Fig. 2.1).



Fig. 2.1: (i) possible transition state for the reaction with $(\eta^{5}-C_{5}H_{5})_{2}ZrH_{2}$ (ii) possible transition state for the reaction with $(\eta^{5}-C_{5}H_{5})_{3}ZrH$

Further work by this group²² reported the formation of $(\eta^5-C_5H_5)_2Zr(C_6F_5)F$ via the thermal reaction of $(\eta^5-C_5H_5)_2Zr(C_5F_5)_2$ with C_6F_6 . By-products of the reaction include high molecular weight oligomers of perfluorobenzene and tetrafluorobenzyne. A dual mechanism was proposed for the formation of the products. A radical chain reaction accounts for the formation of oligomers that contain varying numbers of monomer units (n = 2-13) (Scheme 2.5).



Radical Initiator (Q) Step 1

$$(\eta^{5}-C_{5}H_{5})_{2}Zr^{*}(C_{6}F_{5})$$



Q = 1,1'-azobis(cyclohexacarbonitrile)



In addition to the radical mechanism, a slower process involving formation of tetrafluorobenzyne proceeds (Eqn. 2.14).



Eqn. 2.14

Once the radical mechanism has terminated the reaction rate decreases and the slower process proceeds only.

Further research on the system, $(\eta^5-C_5(CH_3)_5)_2ZrH_2$, has been carried out by Kraft *et al.*²³ Reaction of $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ with fluorobenzene produces the complex, $(\eta^5-C_5(CH_3)_5)_2Zr(C_6H_5)F$. This group postulated that hydride attack on the aromatic ring leads to formation of a C-H activated complex. Subsequent fluoride abstraction occurs generating a benzyne complex that quickly inserts into the Zr-H bond, forming $(\eta^5-C_5(CH_3)_5)_2Zr(C_6H_5)F$, (Scheme 2.6).

$$(\eta^{5}-C_{5}(CH_{3})_{5})ZrH_{2} \xrightarrow{C_{6}H_{5}F}_{-H_{2}} \xrightarrow{(\eta^{5}-C_{5}(CH_{3})_{5})}Zr \xrightarrow{F}_{F}$$

Scheme 2.6

Literature survey

In this case C-H activation is initially selective over C-F activation. This selectivity was also observed in the reaction of $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ with 1-fluoronaphthalene. Hydride attack on the aromatic ring followed by subsequent fluoride abstraction is believed to produce the observed products, namely, naphthalene and $(\eta^5-C_5(CH_3)_5)_2ZrHF$. This mechanism is also believed to occur for the C-F activation reaction of fluorobenzene in addition to benzyne formation.

The most recent work carried out by this group has been on the reaction between $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ and $C_6F_6^{23}$ Reaction products include $(\eta^5-C_5(CH_3)_5)_2ZrHF$, H and $(\eta^5-C_5(CH_3)_5)_2Zr(C_6F_5)H$. A nucleophilic hydride attack on C_6F_6 followed by fluoride elimination accounts for formation of C_6F_5H and one equivalent of the complex $(\eta^5-C_5(CH_3)_5)_2ZrHF$. Formation of $(\eta^5-C_5(CH_3)_5)_2Zr(C_6F_5)H$ and the second equivalent of $(\eta^5-C_5(CH_3)_5)_2ZrHF$ can be accounted for by two possible mechanisms. The first possibility involves a metal to cyclopentadienyl ring hydride transfer, followed by attack of the Zr intermediate on the C_6F_6 , to form the Zr-C bond with hexafluorobenzene. Deprotonation of the cyclopentadiene molecule by the fluoride ion would produce $(\eta^5-C_5(CH_3)_5)_2Zr(C_6F_5)H$ and HF. Reaction of HF with $(\eta^5-C_5(CH_3)_5)_2ZrH_2$ accounts for the formation of $(\eta^5-C_5(CH_3)_5)_2ZrHF$ (Scheme 2.7). An alternative mechanism involves homolytic cleavage of a C-F bond in C_6F_6 by a hydrogen depleted dimer such as $[(\eta^5-C_5(CH_3)_5)_2ZrH]_2$.



Scheme 2.7

Literature survey

2.1.8 C-F activation reactions of electron rich transition metal reagents Group nine metals have been studied as possible C-F activation reagents. Perutz *et al.*²⁴ showed that the complex, $(\eta^5-C_5(CH_3)_5)RhP(CH_3)_3(C_2H_4)$ enabled hexafluorobenzene to undergo C-F activation (Scheme 2.8). Reaction with the cyclopentadienyl complex, $(\eta^5-C_5H_5)RhP(CH_3)_3(C_2H_4)$, produced the η^2 -coordinated complex, $(\eta^5-C_5H_5)RhP(CH_3)_3(\eta^2-C_6F_6)$ only.



Scheme 2.8

The extra electron donating ability of the $(\eta^5-C_5(CH_3)_5)$ group promotes the insertion reaction. Subsequent studies by the same group compared the reactivities of the $(\eta^5-C_5H_5)Ir(P(CH_3)_3)H_2$ and the $(\eta^5-C_5(CH_3)_5)Rh(P(CH_3)_3)H_2$ complexes with C_6F_6 . The thermal reaction of the Rh complex also yielded the C-F activated product, while the reaction of the Ir complex with C_6F_6 produced the hydride product rather than the expected fluoride complex. Two possible mechanisms for these processes were proposed (Scheme 2.9).







Recently Aizenberg and Milstein²⁵ reported the use of Rh for the homogeneous transition metal catalysed C-F activation of hexafluorobenzene (Scheme 2.10). Step two and three involve H-H oxidation and C-H reductive elimination processes. Step one is thought to occur *via* electron transfer from the complex to the substrate with subsequent release of the fluoride ion.



Scheme 2.10

Literature survey

Ni has been found to be an effective reactive reagent especially for polyfluorobenzenes and polyfluoropyridines. The reaction between $C_{10}F_8$ and $Ni(COD)_2$ takes several weeks to reach completion. The mechanism of activation is believed to occur *via* initial coordination of the fluorinated aromatic ring to the Ni(0) centre, forming a sixteen electron intermediate (Scheme 2.11).²⁶



Scheme 2.11

Oxidative addition of C_5F_5N at a Ni centre is complete within hours of addition of the reagents. The product has been assigned as *trans*-[NiF(C_5F_4N)(PEt₃)₂].^{26, 27} Coordination of the metal occurs at the carbon *ortho* to the pyridine nitrogen. The discovery of this process has led to the activation of a variety of fluoroarenes by Ni(0) complexes, some of which are outlined in Scheme 2.12.





Further reaction of the activated complex provides a convenient route to many new compounds (Eqns. 2.15 and 2.16).



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2.1.9 Assignment of the Ni C-F activated complexes

Perutz *et al.*²⁷ characterised their first C-F activated fluoropyridine nickel complex [(**a**), Fig. 2.17] on the basis of the characteristic Ni-F resonance at $\approx \delta$ -370 (¹⁹F NMR), the chemical shift data for free pentafluoropyridine and the data for the C-F activated fluorobenzene products documented in the literature.



Fig. 2.17

Pentafluoropyridine [(**b**), Fig. 2.17] gives three resonances in the ¹⁹F NMR. In d₈-thf multiplets are observed at δ -83.98 representing F^{2,6} (J_{2,4} = 14), at δ -129.86 representing F⁴ (J_{3,4} = 19, J_{2,4} = 14) and at δ -157.35 representing F^{3,5} (J_{2,3} = 19). Since ¹⁹F has a spin number S = $\frac{1}{2}$, the coupling to other ¹⁹F atoms or other atoms with S = $\frac{1}{2}$ is the same as that observed for proton coupling. For the [Ni]-F complex (complex (**a**) Fig 2.17, [Ni] = Ni(C₅F₄N)(PEt₃)₂), the resonance observed at δ -370 in the ¹⁹F NMR spectrum is characteristic of the metal fluoride, with coupling to both phosphorous nuclei (which are equivalent, J_{PF} = 48 Hz) and the F³ nucleus of the [Ni](C₅F₄N) group. The four fluorine resonances of the aromatic ring are observed in the fluoroaromatic region of the ¹⁹F NMR and are as follows:²⁸ a multiplet at δ -84.70, a triplet of doublets at δ -131.33, a multiplet at δ -150.75 and a multiplet at δ -173.38. The fluorine atom *ortho* to the ring nitrogen is deshielded, as is a fluorine atom *ortho* to the site of metallation. By comparison to the chemical shifts for free pentafluoropyridine, the chemical shift of δ -84.70 was assigned to F⁶ (J_(3,6) = 28, J_(3,6) = 28, J_(3,4) = 28, J_{3,100ride} = 6). The

Literature survey

remaining resonances were assigned based on the shifts for the free ligand: δ -150.75 representing F⁴ (J_(3,4) = 28, J_(4,5) = 16, J_(4,6) = 14), δ -173.38 representing F⁵ (J_(5,6) = 28, J_(4,5) = 16, J_(3,5) = small). The C-F activated complexes prepared in this chapter have been assigned their fluorine resonances by comparison with pentafluoro and tetrafluoropyridyl Ni(PEt₃)₂ complexes²⁴ and by comparison with data for the 'free' pyridines.

2.2 **RESULTS**

2.2.1 Synthesis of trans-NiF(C₅F₄N)(PEt₃)₂ and trans-NiF(C₅F₃HN)(PEt₃)₂

The synthesis of *trans*-NiF(C₅F₄N)(PEt₃)₂ (1) and *trans*-NiF(C₅F₃HN)(PEt₃)₂ (2) was accomplished *in situ* during the preparation of subsequent complexes. Synthesis of the [Ni]-F complex ([Ni] = Ni(C₅F₃RN)(PEt₃)₂, R = F or H) involved treatment of Ni(COD)₂ in hexane with PEt₃. A red solution was obtained immediately upon addition of the phosphine. A yellow solution was obtained within a few minutes of addition of the fluoropyridine to the solution containing Ni(COD)(PEt₃)₂. Isolation and characterisation of the *trans*-[Ni]-F complexes has previously been reported.²⁶

2.2.2 Synthesis of trans-NiN₃(C₅F₄N)(PEt₃)₂ and trans-NiN₃(C₅F₃HN)(PEt₃)₂

The complexes *trans*-NiN₃(C₅F₄N)(PEt₃)₂ (**3**) and *trans*-NiN₃(C₅F₃HN)(PEt₃)₂ (**4**) were prepared by the addition of $(CH_3)_3SiN_3$ to solutions of (**1**) or (**2**) in hexane. After stirring for 2 hours the tetrafluoropyridylazide derivative (**3**) was isolated in 62 % yield while the trifluoropyridylazide derivative (**4**) was obtained in 71 % yield. Both complex (**3**) and (**4**) exhibit an azide IR stretching band at 2054 cm⁻¹ (Fig. 2.2). The starting material, $(CH_3)_3SiN_3$, exhibits an IR stretching band at 2130 cm⁻¹. NiF(C₅F₃RN)(PEt₃)₂ (R = F, H) does not have any IR stretching bands in the 2000-2200 cm⁻¹ region of the IR spectrum.



Fig. 2.2: The azide absorption band of Ni(N₃)(C₅F₃HN)(PEt₃)₂ obtained in hexane solution

Illustrated in Fig. 2.3 is the numbering of the carbon atoms in the metallated polyfluoropyridine complexes with respect to the nitrogen ring atom. This is necessary to discuss the signals observed in the NMR spectra.



 $X = N_3$, NCO or C \equiv CSi(CH₃)₃

Fig. 2.3: The numbering of the [Ni]-X complexes with respect to the nitrogen ring atom. Structure A refers to the tetrafluoropyridyl derivatives and structure B refers to trifluoropyridyl derivatives.

The ³¹P NMR spectrum of complex (3) contains a singlet at δ 16.09 indicating that the two phosphorus nuclei are equivalent and that the *trans* isomer is exclusively formed. For the trifluoropyridylazide complex (4), the phosphorus signal appears at a lower chemical shift of δ 15.76 (Fig. 2.4).



Fig. 2.4: ³¹P NMR spectrum of complex (4) obtained in C_6D_6 solution

For complex (3), the ¹⁹F spectrum contains four peaks (refer to Fig. 2.3 for ring fluorine labels): a multiplet at δ -85.25 (F⁶), a triplet at δ -132.91 (F³), a multiplet at δ -150.32 (F⁴) and a multiplet at δ -172.64 (F⁵) (Fig. 2.5).



Fig. 2.5: ¹⁹F NMR spectrum of complex (3) obtained in C_6D_6 solution

Meanwhile for complex (4), the ¹⁹F NMR spectrum contains three peaks: a triplet of doublets at δ -90.91 (F⁶), a doublet at δ -111.45 (F³) and a multiplet at δ -150.63 (F⁵) (Fig. 2.6). There is no signal corresponding to position 4 on the ring observed in the ¹⁹F NMR. The proton signal is observed at δ 6.25 in the ¹H NMR spectrum. In the ¹⁹F NMR spectra of complex (3) and (4), integration ratios of 1:1:1:1 and 1:1:1 respectively were recorded for the fluorine substituents on the ring.



Fig. 2.6: ¹⁹F NMR spectrum of complex (4) obtained in C_6D_6 solution

2.2.3 Molecular structure of *trans*-NiN₃(C₅F₃HN)(PEt₃)₂

Crystals of *trans*-Ni(N₃)(C₅F₃HN)(PEt₃)₂ (**4**) suitable for x-ray structural determination were obtained from hexane at $-20 \,^{\circ}$ C.²⁹ The molecular structure of this complex confirms the *trans*-square planar geometry (Fig. 2.7). Coordination of the pyridyl ring to the nickel centre occurs at position 2, *i.e.* adjacent to the ring nitrogen atom, while the proton is at position 4. The angles between the adjacent ligands at nickel vary from 89.78(8)° to 90.55(7)°. The N(1)-Ni(1)-C(1) bond angle is 170.4(1)° and is smaller than the corresponding bond angle in other C-M-N₃ complexes. For example, in NiF(C₆F₅)(PEt₃)₂, F(1)-Ni(1)-C(1) = 177.4(3)° and in NiF(C₅F₃HN)(PEt₃)₂, F(1)-Ni(1)-C(1) = 176.58(12)°.²⁶ The Ni(1)-N(1) bond length is 1.923(2) Å while the N(1)-N(2) and N(2)-N(3) bond distances are 1.185(3) Å and 1.160(3) Å respectively. The azide ligand is not linear with a N(1)-N(2)-N(3) bond angle of 175.3(3)° and the Ni(1)-N(1)-N(2) bond angle is 132.3(2)°. Further crystallographic data for complex (**4**) is included in the appendix.





Chapter	r 2
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Resul	lts
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Bond	Length	Bond	Length	Bond	Angle (°)
	(Å)		(Å)		
Ni(1)-C(1)	1.88(2)	C(4)–F(2)	1.35(3)	Ni(1)–N(1)–N(2)	132.3(2)
Ni(1)–P(1)	2.205(9)	C(5)–F(3)	1.35(3)	N(1)-Ni(1)-C(1)	170.4(1)
Ni(1)-P(2)	2.200(9)	N(4)-C(1)	1.35(3)	P(1)-Ni(1)-P(2)	174.35(3)
Ni(1)-N(1)	1.92(2)			N(1)-N(2)-N(3)	175.3(3)
N(1)–N(2)	1.185(3)			C(1)-Ni(1)-P(1)	90.54(8)
N(2)N(3)	1.16(3)			C(1)–Ni(1)–P(2)	90.55(7)
C(2)–F(1)	1.35(3)			N(1)–Ni(1)–P(1)	89.78(8)
N(4)-C(5)	1.30(3)			N(1)-Ni(1)-P(2)	90.08(8)

Table 2.2: Principal bond lengths (Å) and bond angles (°) of

 $trans-NiN_3(C_5F_3HN)(PEt_3)_2(4)$

2.2.4 Synthesis of trans-NiNCO(C₅F₃HN)(PEt₃)₂

The isocyanate complex, *trans*-NiNCO(C_5F_3HN)(PEt₃)₂ (**5**) was synthesised by adding Me₃SiNCO to a solution of complex (**2**) in hexane. After stirring for 2 hours the trifluoropyridyl derivative was isolated in 79 % yield. This complex was also observed as a product of the photolysis reaction between complex (**4**) and CO (to be discussed later). Complex (**5**) exhibits a strong isocyanate band in the IR spectrum at 2225 cm⁻¹ (Fig. 2.8). Multinuclear NMR data confirms that the isocyanate derivative is isostructural with the azide analogue; resonance signals occur at similar chemical shifts in the ¹⁹F NMR spectrum to those of complex (**4**).





In complex (5) a singlet is observed at δ 15.76 in the ³¹P NMR spectrum (Fig. 2.9), while peaks in the ¹⁹F NMR spectrum appear at δ -90.95, δ -111.53 and δ -150.72 confirming the presence of three fluorine atoms. The ¹H NMR spectrum exhibits signals at δ 0.85 (CH₂ protons of PEt₃ groups), δ 1.05 (CH₃ protons of PEt₃ groups) and δ 6.25 (the ring proton).



Fig.2.9: ³¹P NMR spectrum of complex (5) obtained in C_6D_6 solution

2.2.5 Synthesis of trans-Ni(C=CSi(CH₃)₃)(C₅F₃HN)(PEt₃)₂

Treatment of NiF(C₅F₃HN)(PEt₃)₂ (**2**) with (CH₃)₃SiC=CH and stirring for two weeks resulted in the formation of *trans*-Ni(C=CSi(CH₃)₃)(C₅F₃HN)(PEt₃)₂ (**6**). In the presence of the base Et₃N, the preparation of the trimethylsilyl acetylene derivative is complete after one week with stirring. The IR spectrum of the product contains a carbon-carbon triple bond absorption band at 2023cm⁻¹ (Fig. 2.10). A singlet at δ 19.90 is observed in the ³¹P spectrum (Fig. 2.11).







Fig. 2.11: ³¹P NMR spectrum of complex (6) obtained in C_6D_6 solution

The ¹⁹F NMR spectrum exhibits three peaks confirming that the fluorine atom coordinated to the Ni centre in the starting material complex (**2**) has been replaced. The ring fluorine resonances occur at δ -91.57, δ -112.18, and δ -151.15. A singlet is observed at δ 0.25 in the ¹H NMR spectrum and is assigned to the protons of the three methyl groups attached to the Si atom. Peaks for the ethyl groups of the phosphine molecules and the proton in the position 4 of the pyridyl ring appear at δ 0.97 (CH₃ groups), δ 1.4 (CH₂ groups) and δ 6.4 respectively. Integration is as expected: 18:12:9:1 (methyl protons of the ethyl group: methylene protons of the ethyl group: methyl proton respectively).

2.2.6 Reaction of *trans*-NiN₃(C₅F₃HN)(PEt₃)₂ (4) with CO

Azides are known for their lability and in fact undergo facile loss of N_2 .^{30, 31} It was because of this reactivity that the reaction of NiN₃(C₅F₃HN)(PEt₃)₂ (4) with CO was studied. The azide complex was prepared as discussed previously using Ni(COD)₂ as the starting material. The hexane solution containing (4) was divided into two NMR tubes (samples A and B) fitted with Youngs stopcocks. Both were purged with CO. Tube A was placed in front of a mercury lamp for a total of 30 h while tube B was left in the dark for the same length of time. IR spectra of both solutions were obtained before the addition of CO, during and after the reaction. For both samples the IR spectra are identical at the start, during and after the reactions. The IR spectra of the starting material exhibit one band, the characteristic azide stretch at 2054 cm⁻¹ (Fig.

2.12a). After several hours of photolysis in the case of sample A and several hours in the dark for sample B, five bands were observed (Fig. 2.12b): the starting material band at 2054 cm⁻¹, along with four new bands at 2225, 2066, 1992 and 1937 cm⁻¹. After completion of the reaction (Fig. 2.12c), the starting material band had disappeared as had the band at 1937 cm⁻¹ and only three bands remained, those at 2225, 2066 and 1992 cm⁻¹.



Fig. 2.12: (a) IR stretching frequency of Ni(N₃)(C₅F₃HN)(PEt₃)₂ (2), (b) IR stretching frequency of the reaction mixture after 6 h stirring, indicating that both starting material and product are present, (c) IR stretching frequencies of the final products indicating that the starting material band at 2054 cm⁻¹ has disappeared. IR spectra were obtained in hexane solution.

Once the reaction was determined as being complete from the IR spectrum, the volatiles were removed *in vacuo* and the residues were redissolved in C₆D₆. ¹H, ¹⁹F and ³¹P NMR spectra of the product solutions were obtained. The ³¹P NMR spectra of both samples A and B contained two singlets at δ 15.76 and δ 21.05 (Fig. 2.13). The ¹⁹F NMR spectra of both samples A and B exhibited six peaks, one set of three signals occurring at almost identical chemical shifts to the starting material complex (4) (Fig. 2.14): a triplet at δ -89.60, a doublet at δ -111.45 and a multiplet at δ -150.5. The other

Results

set of three appears with smaller intensities but with the same splitting pattern: a triplet at δ -88.50, a doublet at δ -121.90 and a multiplet at δ -132.10. Further IR spectra of the two samples in C₆D₆ were taken and three bands at 2228, 1985 and 1922 cm⁻¹ were observed. The products associated with these three bands in C₆D₆ also refer to the bands at 2225, 2066 and 1992 cm⁻¹ in hexane. The shift of these frequencies compared to those taken in hexane is consistent with a change in solvent. The rate of formation of products was faster for the photolysed solution compared to the solution left in the dark (note the solution left in the dark was at room temperature). The complex characterised by bands at δ -89.60, δ -111.45 and δ -150.5 in the ¹⁹F NMR spectrum, by the absorption band at 2225 cm⁻¹ in the IR spectrum and by the signal at δ 15.76 in the ³¹P NMR spectrum is assigned as the isocyanate complex, Ni(NCO)(C₅F₃HN)(PEt₃)₂ (**5**). An assignment for the remaining bands was not made.



Fig. 2.13 (a) ³¹P NMR spectrum of the starting material Ni(N₃)(C₆F₃HN)(PEt₃)₂ (4)
(b) ³¹P NMR spectrum of the reaction products from the reaction of complex
(4) with ¹²CO. ³¹P NMR spectra were obtained in C₆D₆ solution



Fig. 2.14: (a) ¹⁹F NMR spectrum of the starting material Ni(N₃)(C₆F₃HN)(PEt₃)₂ (4)
(b) ¹⁹F NMR spectrum of the reaction products from the reaction of complex (4) with ¹²CO. ³¹P NMR spectra were obtained in C₆D₆ solution

The reaction between the azide complex (4) and CO was repeated by stirring a sample of NiN₃(C₅F₃HN)(PEt₃)₂ (4) in hexane under a ¹³CO atmosphere (≈ 0.6 atm). The experiment was repeated to confirm whether the IR bands that were unassigned in the ¹²CO experiment were metal carbonyl bands. After allowing the solution to stir for five days an IR spectrum of the hexane solution exhibited three bands at 2166, 1949 and 1892 cm⁻¹ (Fig. 2.15).



Fig. 2.15: IR spectrum of the reaction products of complex (4) with ¹³CO after five days of stirring in hexane solution

Results





The stretching band at 2166 cm⁻¹ has an absorbance of 0.75 and is assigned as the isocyanate IR absorption band, while the other two bands have lower absorbance values, 0.04 and 0.05 for 1949 and 1892 cm⁻¹ respectively. The volatiles were removed *in vacuo* and the residue was redissolved in C₆D₆. ¹H, ¹⁹F, ³¹P and ¹³C NMR spectra were recorded. The carbonyl stretch of the isocyanate complex was observed at δ 202.80 as a triplet in the ¹³C NMR spectrum indicating coupling to the two phosphorus nuclei (Fig. 2.16a). The ¹H, ¹⁹F, ³¹P NMR spectra contained signals similar to those observed for the isocyanate complex (Fig. 2.16b). The unassigned bands observed in the reaction with ¹²CO (at δ -88.50, δ -121.90 and δ -132.10 in the ¹⁹F NMR spectrum, at δ 21.05 in the ³¹P NMR spectrum and at 2066 and 1992 cm⁻¹ in the IR spectrum) did not appear to be present in the multinuclear NMR spectra for the experiment with ¹³CO.

Com	plex	¹ H	³¹ P{H}	¹⁹ F	IR
(3)	(C_6D_6)	0.90 (t, 18H, CH ₃)	16.10 (s)	-88.25 (m, 1F, CF)	2054
		1.05 (s, 12H, CH ₂)		-132.91 (t, 1F, CF)	
				-150.32 (q, 1F, CF)	
				-172.64 (m, 1F, CF)	
(4)	(C_6D_6)	0.93 (m, 18H, CH ₃)	15.76 (s)	-90.91 (td, 1F, CF)	2054
		1.10 (m, 12H, CH ₂)		-111.45 (d, 1F, CF)	
		6.25 (m, 1H, aryl-H)		-150.63 (m, 1F, CF)	
(5)	(C ₆ D ₆)	0.88 (m, 18H, CH ₃)	15.76 (s)	–90.95 (m, 1F, CF)	2228
		1.40 (m, 12H, CH ₂)		-111.53 (d, 1F CF)	
		6.25 (m, 1H, aryl-H)		-150.72 (m, 1F, CF)	
(6)	(C_6D_6)	0.26 (s, 9H, Si–CH ₃)	19.90 (s)	-91.56 (m, 1F, CF)	2039
		0.97 (m, 18H, CH ₃)		-112.14 (d, 1F, CF)	
		1.40 (s, 12H, CH ₂)		-151.12 (m, 1F, CF)	
		6.40 (m, 1H, aryl-H)			

Table 2.3: Spectroscopic data recorded at 298 K. NMR data are reported in ppm and IR data are reported in cm⁻¹

2.3 DISCUSSION

2.3.1 Complexes (1), (2), (3), (4) and (5)

The reaction of Ni(COD)₂ with PEt₃ and fluoropyridines leads to the formation of NiF(C₅F₃RN)(PEt₃)₂, [(1) R = F, (2) R = H], within minutes. This is in contrast to the reaction with hexafluorobenzene, which takes several weeks to reach completion.²⁷ Fahay and Mahan³² have reported that Ni(PEt₃)₄ can be used as a more reactive precursor than Ni(COD)(PEt₃)₂, where Ni(PEt₃)₃ is believed to be the active reagent. Both mono- and dihalobenzenes react rapidly with this triphosphorus reagent affording high yields of organonickel products. However, as the substitution of the ring increases, the reaction time lengthens and yields decrease. The same holds true for the reagent, Ni(COD)(PEt₃)₂. Hence, the reaction time of several weeks for the formation of the C-F activated product of hexafluorobenzene.

Compared to the reaction with pentafluorobenzene, the rate of the reaction of Ni(COD)₂ and PEt₃ with pentafluoropyridine is much faster. Since the C-F activation reactions were complete within a few minutes with Ni(COD)₂ and two molar equivalents of PEt₃, it was not necessary to use Ni(PEt₃)₄. The reaction is believed to proceed through an oxidative addition mechanism. For the perfluorobenzenes, initial coordination to the Ni centre *via* an η^2 -interaction with a diene fragment of the benzene ring is postulated. Perutz *et al.*²⁶ reported the formation of a Ni- η^2 -octafluoronaphthalene complex, [Ni(η^2 -1,2-C₁₀F₈)(PEt₃)₂], upon the addition of PEt₃ and octafluoronaphthalene to a room temperature solution of Ni(COD)₂ (Scheme 2.11, literature survey). Crystallography confirmed the η^2 -coordination mode. Furthermore, heating this η^2 complex, in toluene for 24 hours resulted in the conversion of the η^2 -complex, [Ni(η^2 -1,2-C₁₀F₈)(PEt₃)₂], to the C-F activated product, *trans*-[NiF(2-C₁₀F₇)(PEt₃)₂]. For the perfluoropyridines, initial coordination to the Ni centre *via* an η^1 -interaction with the pyridine N atom is postulated (Eqn. 2.17).²⁷ Intermediates of this type have not been observed however.



These NiF(C₅F₃RN)(PEt₃)₂ complexes were prepared *in situ* in the reactions described above and are highly air sensitive. In contrast, the analogous metal chloride product is air stable.³³

The reaction of 2,3,5,6-tetrafluoropyridine with Ni(COD)(PEt₃)₂ is selective for C-F activation and there is no trace of the C-H activated product. Some transition metal reagents can discriminate between C-H and C-F bonds. For example hexafluorobenzene undergoes C-F activation at the Rh(η^5 -C₅Me₅)(PMe₃) fragment³⁴ while pentafluorobenzene only undergoes C-H activation with this reagent. In contrast, Ru(dmpe)₂H₂ forms C-F activated products with both hexafluorobenzene and pentafluorobenzene.³⁵ Incidentally, reactions of fluoropyridines with Ni(0) centres are also selective for C-Cl over C-F bonds. This is most likely due to the weaker bond strength of the C-Cl bond (the dissociation energy for a C-Cl bond in CH₃Cl is 353 kJ mol⁻¹ compared with 454 kJ mol⁻¹ for C-F bond in CH₃F).

This selectivity is observed with the complexes described here, for example in the complex NiN₃(C₅F₃HN)(PEt₃)₂ (4). The crystal structure confirms that activation has taken place at the 2-position of the pyridine ring. The azide molecule has subsequently replaced the fluorine atom in complex (4). Tetrafluoropyridines substituted at the 2-

position represent a difficult synthetic problem and so this work is of great interest.³³ Due to the presence of a proton in position 4, disorder about the Ni(1)-C(1) bond is not observed. Disorder would be expected for complex (**3**); hence the determination of a crystal structure was not attempted. Disorder has been observed in other Ni complexes prepared from pentafluoropyridine.²⁷

The Ni(1)-N(1)-N(2) bond angle of complex (4) is $132.3(2)^{\circ}$ and compares favourably with other metal azide complexes. The complex $Co(N_3)_2(PNN)_4^{36}$ contains two azide ligands with a Co(1)-N(1)-N(2) bond angle of 128.91° ; the $[Ru(tpy)(PPh_3)(N_3)]^+$ cation³⁷ has a Ru(1)-N(1)-N(2) bond angle of $139.6(4)^{\circ}$. An example of an azide molecule bridging two metals is observed in the polymeric $[Cu(py)_3(N_3)]^+$ cation.³⁸ A bond angle of $124.0(9)^{\circ}$ for the Cu(1)-N(1)-N(2) bond is observed. Coordination to two Cu metal centres does not cause a great deal of change in the bond angle of the three nitrogen atoms of the bridging ligand. The bond angle for N(1)-N(2)-N(3) of the Cu complex is $176.7(7)^{\circ}$ while the analogous bond angle for the monocoordinated azide in the NiN₃(C₅F₃HN)(PEt₃)₂ complex is $175.3(3)^{\circ}$.

2.3.2 Synthesis of Ni(C=CSi(CH₃)₃)(C₅F₃HN)(PEt₃)₂ (6)

The presence of the triple bond makes alkynes very reactive. Alkynes undergo electrophilic addition of hydrogen, halogens and hydrogen halides to the triple bond. It was because of their potential for further reaction that the metal alkynyl derivative (**6**) was prepared. The driving force behind this reaction is the formation of HF. HF has a bond energy of 568 kJ mol⁻¹ compared to a terminal alkyne proton (acetylene) that has a bond energy of 525 kJ mol⁻¹. The presence of base in this reaction merely reduces the stirring time required and the reaction is successful even in the absence of Et₃N. A number of possible pathways were available to (CH₃)₃SiC=CH when reacted with the metal fluoride complex (**2**):

 (i) Formation of the strong Si-F bond and coordination of the -C≡CH fragment to the Ni centre.

Discussion

- (ii) Reaction of the acidic acetylenic proton with the metal fluoride to form the strong H-F bond and coordination of the -C≡CSi(CH₃)₃ group to the Ni centre.
- (iii) Competition between (i) and (ii).

Only one process was observed to occur in both the presence and absence of base. Data obtained from the IR and multinuclear NMR spectroscopy of the reaction between $(CH_3)_3SiC\equiv CH$ and $NiF(C_5F_3HN)(PEt_3)_2$ (2) confirmed that process (ii) had occurred. The starting alkyne material exhibits two characteristic absorptions in the IR spectrum, a C=C stretch at 2039 cm⁻¹ and a C-H stretch at 3279cm⁻¹ (Fig. 2.18). A stretch at 2023 cm⁻¹ corresponding to the C=C stretch was observed in the product IR spectrum. ¹H NMR spectra further confirmed that process (ii) had occurred. The acetylenic proton that appears at δ 2.5 in the ¹H NMR of the starting material complex does not appear in the product ¹H NMR spectrum. A signal is observed at δ 0.27 in the ¹H NMR spectrum corresponding to the nine protons of the trimethylsilyl group. The reaction of $(CH_3)_3SiC=CH$ is completely regioselective for the trimethylsilyl acetylenic derivative.



Fig. 2.18: (i) (a) alkyne C-H stretch of the starting material complex (CH₃)₃SiC≡CH
(i) (b) IR spectrum of the product showing the absence of an alkyne C-H stretch (ii) (a) C≡C stretch of the starting material complex (CH₃)₃SiC≡CH
(ii) (b) IR spectrum of the product (6) showing the C≡C stretch

2.3.3 Reaction of NiN₃(C₅F₃NH)(PEt₃)₂ (4) with CO

Azides are rather labile ligands and undergo a number of reactions. Photolysis of phenyl azides results in the formation of azepines and hydrazines (Eqn. 2.18). Azepine formation occurs *via* ring closure away from the substituent.³⁹



Studies involving reactions of metal azides have been carried out for Co and Pt complexes. Rehorek *et al.*³¹ have reported that upon photolysis with a mercury lamp $[Co(NH_3)_5N_3]Cl_2$ gives rise to azide radicals. Knoll *et al.*³⁰ exposed Pt^(II)(N₃)₂- $(P(C_6H_5)_3)_2$ to photolysis with a mercury lamp. The major reaction taking place is the photoreduction of the complex to the azide free product Pt^(II)(P(C_6H_5)_3)_2(2-Methf)_n, when carried out in 2-Methf. As a result of the photolability of azides, further studies on the chemistry of Ni(N₃)(PEt₃)₂(C₅F₃HN) (**4**) were undertaken.

The reaction of complex (4) with CO produces the isocyanate complex (5). The difference spectrum shown below (Fig. 2.19) illustrates a decrease in the intensity of the starting material (band at 2054 cm⁻¹) and the appearance of the new bands (already discussed in the results section). A sample of the isocyanate complex, prepared by an independent method, exhibited identical spectroscopic parameters to one of the products observed in the photolysis reaction. The dark and photolysed reactions give rise to the same products. Conversion of the [Ni]-N₃ into the [Ni]-NCO occurs both thermally and photochemically. Photolysis merely increases the speed of formation of the isocyanate complex (5) (note that filters were not used for photolysis; a UV lamp was the light source). ¹⁹F NMR data is almost identical to the ¹⁹F NMR data for the [Ni]-N₃ complex (4). These two complexes are isoelectronic having the same number of electrons and have the same number of and connectivity of atoms.



Fig. 2.19: IR spectrum for the reaction of complex (4) under ¹²CO subtracted from the starting material spectrum, in hexane solution.

To determine whether the remaining peaks observed in the reaction of complex (4) with CO arose from azide or carbonyl containing compounds, the reaction was repeated under a ¹³CO atmosphere. ¹³CO is a heavier molecule than ¹²CO and the stretching frequencies due to ¹³CO complexes absorb at lower energy, hence they occur at lower frequencies in the IR spectrum.

The reaction solution was stirred for 5 days to allow for maximum conversion to products. The resulting IR spectrum confirmed that all the peaks (1992 and 1937 cm⁻¹) were due to metal carbonyl containing compounds. NMR spectroscopy suggests that the major product formed was the isocyanate derivative (**5**). The ¹³C NMR spectrum showed a triplet at δ 202.80 corresponding to the carbonyl group of the isocyanate complex. The signal is observed as a triplet because of the coupling to the two phosphorus nuclei. In the ³¹P NMR spectrum the signal is split to a small extent by coupling to the ¹³C of the carbonyl group. The wavenumbers at which the IR peaks appeared in the ¹³CO spectrum were determined using the reduced masses ratio (Fig. 2.20).

Discussion

$\mu = \frac{m_1 * m_2}{m_1 + m_2}$	
	$\mu_{13} = \frac{13 * 16}{29}$
$\mu_{12} = \prod_{\mu_{12}} \mu_{12} = \prod_{\mu_{13}} \mu_{\mu_{13}}$	$\mu_{12} = \frac{12 * 16}{28}$
μ_{12} = 0.977 μ_{13}	

Fig. 2.20: μ = reduced mass, μ_{12} = reduced mass of ¹²CO, μ_{13} = reduced mass of ¹³CO

By multiplying the carbonyl peaks in the ¹²CO IR spectrum by 0.977 (the ratio of the reduced masses), the positions of the new peaks can be calculated. For example, the carbonyl peak that was observed at 1992 cm⁻¹ in the ¹²CO IR spectrum is calculated to appear at 1947 cm⁻¹ in the ¹³CO IR spectrum. This carbonyl peak is actually observed at 1949 cm⁻¹ in the ¹³CO IR spectrum. The isocyanate peak will shift to a lesser extent in the ¹³CO experiment. This peak in the ¹²CO IR spectrum is multiplied by a factor of 0.972 to give the corresponding peak in the ¹³CO spectrum (Table 2.4). The remaining peaks that are observed in the ¹²CO experiment are not observed in the ¹³CO IR spectrum.

v_{exp}^{12} (cm ⁻¹)	v_{exp}^{13} (cm ⁻¹)	v^{13}_{calc} (cm ⁻¹)	Assignment
2225	2166	2163	Ni–NCO
1992	1949	1947	Carbonyl
1937	1892	1894	Carbonyl

 Table 2.4: Summary of peaks observed in ¹²CO spectrum and their analogous peaks in the ¹³CO spectrum

While the multinuclear NMR data indicates that the main product in the ¹³CO experiment is the isocyanate complex (5), the IR spectrum indicates that the species represented by the band at 1992 cm⁻¹ is the major product. However, without knowing the identity of these metal carbonyl complexes and their extinction coefficients, the

major product cannot be confirmed. Whether these carbonyl bands are intermediates in the preparation of the metal isocyanate assuming a three membered or five membered ring structure is unknown (azides are known to form three and five membered rings upon photolysis).

2.3.4 Reductive elimination reactions

The aims of this project were twofold. Firstly, to prepare novel C-F activated complexes where the activated F atom is replaced by a new functional group. Three new fluoropyridine-Ni-X complexes; $X = N_3$, NCO, C=CSi(CH₃)₃ were successfully prepared. The second aim was to reductively eliminate the Ni(PEt₃)₂ fragment to produce novel 2-substituted fluoropyridine complexes [Fig. 2.21 complexes (c), (d), (e)]. However, attempts at reductively eliminating the Ni(PEt₃)₂ fragment have been unsuccessful to date. Possible reasons will be discussed below.



Fig. 2.21: The novel 2-substituted fluoropyridines that would be expected if reductive elimination was successful

The reaction of Ni(COD)(PEt₃)₂ with fluoropyridines is an oxidative process as already mentioned earlier in the discussion. Reductive elimination is essentially the reverse of oxidative addition. However, reductive elimination requires that the groups being eliminated be in a mutual *cis* position. Gillie and Stille⁴⁰ undertook a number of experiments to test this hypothesis. In this experiment, the authors examined a system that was known to reductively eliminate and synthesised an analogue where the alkyl groups had to be mutually *trans*. The complex with the *trans* methyl groups did not undergo reductive elimination (Fig. 2.22):



Fig. 2.22: Illustration of the complexes investigated by Gille and Stille to demonstrate that reductive elimination requires that the fragments to be eliminated be in a mutually *cis* position

In the complexes (4), (5) and (6) the two PEt₃ groups are in a mutual *trans* position. It is necessary for them to rearrange into a mutually *cis* orientation if reductive elimination is to be successful. Two attempts were made to force the PEt₃ groups in complex (4) into a *cis* position. Initially a sample of complex (4) was heated in hexane. Often thermal agitation is sufficient to bring about a change in stereochemistry of the molecules. However, this attempt was unsuccessful. Multinuclear NMR data revealed there was no conversion of the starting material complex to the *cis* isomer.

An attempt to replace the two PEt₃ groups with chelating phosphines containing short alkyl chains between the two phosphine molecules was unsuccessful. The idea behind this attempt was that a short chelating phosphine would have to assume the *cis* orientation. The alkyl chain length between the phosphine atoms would not be long enough to permit the *trans* structure. A sample of complex (4) was dissolved in hexane in the presence of 1 mol. equivalent of PPh₂-CH₂-PPh₂ or 1 mol. equivalent of PPh₂-

Discussion

 CH_2 - CH_2 - PPh_2 (Eqn. 2.19). A sample of each phosphine was stirred for several days in a hexane solution containing complex (4) and a second sample of each phosphine under similar conditions was heated to 70° C for several days. Multinuclear NMR data of all samples revealed only starting material.



Eqn. 2.19

Although the attempts to obtain novel fluoropyridines substituted at the 2-position have been unsuccessful, three new complexes were prepared. Should a general method of reductively eliminating the Ni centre from the complexes be achieved a relatively simple route to preparing the substituted pyridines will be available.
2.4 CONCLUSION

Three new Ni complexes have been prepared; NiN₃(PEt₃)₂(C₅F₃HN), NiNCO(PEt₃)₂(C₅F₃HN) and Ni(C=CSi(CH₃)₃)(PEt₃)₂(C₅F₃HN), with yields in the range 62-79%, although crystals of the metal-acetylene complex could not be obtained. A molecular structure for NiN₃(PEt₃)₂(C₅F₃HN) was determined confirming the *trans* geometry and providing details on relevant bond angles and bond lengths (see discussion and appendix). Conversion of the trifluoropyridyl nickel azide complex to the analogous isocyanate derivative was observed upon stirring of the metal azide complex under CO. Experiments under an enriched ¹³CO atmosphere aided in the assignment of the IR peaks and NMR signals. It was noted that the metal isocyanate and metal azide complexes have very similar NMR resonances.

Unfortunately attempts to eliminate the Ni(PEt₃)₂ fragment have failed to date. Attempts to replace the two phosphine groups coordinated to the nickel centre with chelating phosphines were also unsuccessful. Stirring solutions of the metal azide complex in the presence of diphenylphosphino methane and ethane resulted only in the recovery of starting material. Even with heating, product formation was not observed.

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Matrix Isolation Studies

of 2,5-dimethylazaferrocene

Abstract

Previous studies have shown that $(\eta^5 - C_5H_5)(\eta^5 - C_4H_4N)$ Fe has an extensive photochemistry that is dominated by haptotropic shifts of the coordinated pyrrolyl ligand. In an attempt to control the degree to which the hapticity of the pyrrolyl ligand can be altered, the photochemistry of $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ Fe has been investigated. The photochemistry of this analogue is also dominated by haptotropic shifts. Both monochromatic and broad-band irradiation of this complex in CO doped Ar matrixes at 20 K gives rise to three species, which have been characterised as $(\eta^5 - C_5H_5)(\eta^1 - N - (CH_3)_2C_4H_2N)$ Fe(CO) (2), $(\eta^5 - C_5H_5)(\eta^1 - N - (CH_3)_2C_4H_2N)$ Fe $(CO)_2$ (3) and $(\eta^5 - C_5H_5)(\eta^3 - N - (CH_3)_2C_4H_2N)$ Fe(CO) (4). Subsequent annealing of the matrix results in a conversion of the η^1 -monocarbonyl complex to the dicarbonyl complex and an isomerisation of the aza-allyl species to the corresponding π -allyl complex $(\eta^5 - C_5H_5)(\eta^3 - C - (CH_3)_2C_4H_2N)$ Fe(CO) (5). These changes will be discussed in the following chapter.

Literature Survey

Chapter 3

3.1 Literature Survey

3.1.1 Photochemistry of (n⁶-arene)Cr(CO)₃ complexes

The photochemistry of $(\eta^6$ -arene)Cr(CO)₃ complexes is dominated by CO loss (Eqn. 3.1).

$$(\eta^{6}\text{-arene})Cr(CO)_{3} \xrightarrow{hv} (\eta^{6}\text{-arene})Cr(CO)_{2}L + CO$$
 Eqn. 3.1

In the presence of two-electron donor ligands, novel dicarbonyl complexes can be prepared photochemically.¹ Interestingly, the analogous W derivatives appear to be photoinert, despite the similarity of the photochemistry of the group six (M = Cr, Mo or W) hexacarbonyl complexes.²

Early studies indicated that these CO loss reactions occurred by dissociative CO loss.^{3, 4} The overall reaction is one of CO substitution, where the ligand occupies the vacant site on the metal created by CO dissociation. Wrighton *et al.*³ reported that photolysis of $(\eta^{6}\text{-arene})Cr(CO)_{3}$ (arene = C₆H₃(CH₃)₃ or C₆H₆), in the presence of pyridine forms the substituted dicarbonyl complex, $(\eta^{6}\text{-arene})Cr(CO)_{2}(\eta^{1}\text{-}C_{5}\text{H}_{5}\text{N})$.

Transient species observed during laser flash photolysis studies of $(\eta^6-C_6H_6)Cr(CO)_3$ in cyclohexane were tentatively assigned as the dicarbonyl complex, $(\eta^6-C_6H_6)Cr(CO)_2$.⁴ Matrix isolation studies of $(\eta^6-C_6H_6)Cr(CO)_3$ in inert and reactive matrixes (CH₄, Ar and N₂ respectively) confirmed the formation of this coordinatively unsaturated intermediate upon UV-vis photolysis.⁵ Under inert conditions the intermediate dicarbonyl complex was characterised by two CO stretching frequencies at 1937, 1885 cm⁻¹ (Ar matrix). In the N₂ matrix, a N₂ molecule occupies the vacant site on the coordinatively unsaturated complex (Eqn. 3.2) (M = Cr and L = C₆H₆).

$$[ML(CO)_2] \xrightarrow[hv]{\text{Ar matrix}} [ML(CO)_3] \xrightarrow[hv]{\text{N}_2 \text{ matrix}} [ML(CO)_2N_2] \qquad \text{Eqn. 3.2}$$

Scheme 3.1

The $v_{N=N}$ of $(\eta^6\text{-arene})Cr(CO)_2N_2$ was observed at 2145 cm⁻¹ while v_{CO} were observed at 1940 and 1899 cm⁻¹. The mechanism suggested by Rest *et al.*⁵ is illustrated below (Scheme 3.1).

$$(\eta^{6}-C_{6}H_{6})Cr(CO)_{3} \xrightarrow{hv} [(\eta^{6}-C_{6}H_{6})Cr(CO)_{3}]^{*}$$

$$\longrightarrow [(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}] + CO$$

$$\downarrow L$$

$$[(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}L]$$

If the mechanism of formation of the dicarbonyl complexes were to involve a ring slip intermediate, a dependence on the incoming nucleophile would be observed. No such dependence was recorded however.

TRIR studies⁶ further confirmed the formation of this dicarbonyl intermediate as the main photoproduct upon photolysis of the (η^6 -arene)Cr(CO)₃. Room temperature irradiation of (η^6 -C₆H₆)Cr(CO)₃ in alkane solution produces (η^6 -C₆H₆)Cr(CO)₂(s) (s = alkane solvent), which exhibits v_{CO} IR bands at wavenumbers similar to those observed in the matrix experiments.

Wrighton *et al.*⁷ exploited this reactivity by oxidatively adding alkyl silanes to the photogenerated (η^6 -arene)M(CO)₂ complex. The sixteen electron species generated by UV-vis photolysis of low temperature hydrocarbon glasses, containing the complex (η^6 -C₆H₆)Cr(CO)₃, reacts with a series of silanes to form the oxidative addition products (η^6 -C₆H₆)Cr(CO)₂(H)(SiR₃), R = Et₃, Ph₃, *i*-Pr₃, EtMe₂ and *n*-Pr₃. Each is assigned the *cis* structure.

While irradiation of $(\eta^6\text{-arene})Cr(CO)_3$ in condensed phases results in the dissociation of one of the ligand molecules, UV photolysis of gas phase metal complexes leads to the loss of more than one ligand. Wang *et al.*⁸ reported the formation of the species,

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 $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}$, upon 355 nm excitation, while both $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}$ and the related monocarbonyl $(\eta^{6}-C_{6}H_{6})CrCO$, in the ratio 2:5, are produced upon 266 nm excitation in the gas phase. Photolysis with higher energy photons produces the more highly unsaturated species. Zheng *et al.*⁹ studied the coordination reactions of these intermediates in the gas phase. TRIR spectra indicated the addition of N₂ and H₂ to $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}$ upon 355 nm excitation of $(\eta^{6}-C_{6}H_{6})Cr(CO)_{3}$, $([(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}N_{2} has v_{CO} = 1922 and 1963 cm⁻¹ and <math>(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}H_{2} has v_{CO} = 1917 and 1967 cm⁻¹])$. Excitation at 266 nm of $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}L$ and $(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}L$ and $(\eta^{6}-C_{6}H_{6})Cr(CO)(H_{2})_{2} has v_{CO} = 1917 cm⁻¹])$. The hydrides are of the non-classical type for all photoproducts. In all studies in the presence of CO, no evidence for arene ring slippage was obtained as the decay of all intermediate species, $(\eta^{6}-arene)Cr(CO)_{x}$ (x = 1 or 2), returns to the pre-irradiated absorbance without the appearance of further absorption features resulting from ring slip intermediates.

Although the primary photochemical route for $(\eta^{6}\text{-arene})Cr(CO)_{3}$ complexes is ligand dissociation, there is also evidence for arene exchange, albeit as a minor process.^{10, 11} Strohmeier *et al.*¹² observed exchange of the C₆H₆ molecule in $(\eta^{6}\text{-}C_{6}H_{6})Cr(CO)_{3}$ during photolysis of ¹⁴C benzene and CO labelling experiments. Wrighton *et al.*³ found that CO substitution was six times more efficient than exchange of C₆H₆ in $(\eta^{6}\text{-}C_{6}H_{6})Cr(CO)_{3}$ with C₅H₅N. CO substitution proceeds with a quantum efficiency of 0.72. Gilbert *et al.*⁴ reported that exchange of C₆H₆ in $(\eta^{6}\text{-}C_{6}H_{6})Cr(CO)_{3}$ was suppressed by CO and confirmed the quantum efficiency of CO substitution obtained by Wrighton.

In the absence of other ligands, the interaction of $(\eta^6-C_6H_6)Cr(CO)_3$ with UV-vis light results in the decomposition of the parent complex.¹³ The products of this reaction are 'free' C_6H_6 and $Cr(CO)_6$. The rate of decomposition of $(\eta^6-C_6H_6)Cr(CO)_3$ was found to follow first order kinetics. Substituents on the C_6H_6 ring were not found to affect the decomposition rate, although replacement of one of the CO ligands with a phosphine molecule increases the rate by an order of magnitude. A multistep process was proposed but no further mechanism was presented for this decomposition process.

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3.1.2 Photochemistry of $(\eta^6-C_5H_5N)Cr(CO)_3$

Long *et al.*¹⁴ have successfully characterised ring slipped intermediates in a variety of matrixes for the class of compounds (η^{6} -2,6-X₂C₅H₃N)Cr(CO)₃ (X = H, Me or Me₃Si). The C₅H₅N ring can coordinate to a metal centre *via* its π system or through the lone pair on the N atom, which can trap ring slip intermediates. Moreover, the HOMO and LUMO energies of pyridine are lower than the corresponding orbitals in benzene. As a result, pyridine is a poorer π -donor but a better π -acceptor molecule. Thus, the photochemistry of (η^{6} -2,6-X₂C₅H₃N)Cr(CO)₃ varies greatly from the photochemistry of (η^{6} -C₆H₆)Cr(CO)₃.

Matrix isolation studies following photolysis of $(\eta^6-C_5H_5N)Cr(CO)_3$ in inert (CH₄) and reactive (N₂) matrixes reveal the formation of both the CO loss product and the ring slipped product where the pyridine molecule coordinates as an η^1 ligand to the Cr centre (Eqn. 3.3)



Eqn. 3.3

The photochemistry of $(\eta^6-C_5H_5N)Cr(CO)_3$ is wavelength dependent. Long wavelength irradiation ($\lambda_{exc} = 460$ nm) produces the η^1 -complex only, while short wavelength photolysis results in the formation of both the η^1 -complex as well as the CO loss product. In CO doped matrixes prolonged photolysis of ($\eta^6-C_5H_5N)Cr(CO)_3$ produces $Cr(CO)_6$ and free pyridine. Evidence for a stepwise process was not observed.

TRIR studies of $(\eta^6-C_5H_5N)Cr(CO)_3$ in CO saturated cyclohexane solution suggest that CO loss is the principal route, as observed in the $(\eta^6\text{-arene})Cr(CO)_3$ systems. $(\eta^1-C_5H_5N)Cr(CO)_3$ is observed although in minor amounts. Laser flash photolysis with UV-vis detection supports this, reporting a biphasic process, *i.e.* CO recombination and an $\eta^1 \rightarrow \eta^6$ slippage, reforming the parent complex. CO loss appears as the predominant process in room temperature solutions because of the very fast reversal of the aromatic coordination from $\eta^1 \rightarrow \eta^6$.

3.1.3 Photochemistry of $(\eta^5-C_5H_5)_2$ Fe complexes

 $(\eta^{5}-C_{5}H_{5})_{2}Fe$ is photo inert in dry alkane solvents but is readily photo-oxidised in chlorinated solutions. Decomposition of substituted ferrocenes is observed in solvents such as acetonitrile, methanol, DMSO, decalin, chloroform and carbon tetrachloride.¹⁵ Latif *et al.*¹⁶ reported the decomposition of $(\eta^{5}-C_{5}H_{5})Fe(\eta^{5}-C_{5}H_{4}(COC_{6}H_{5}))$ upon photolysis in 'wet' solvents. In DMSO decomposition occurs forming monocyclopentadienyliron (II) benzoate salt, free cyclopentadiene and $(\eta^{5}-C_{5}H_{5})_{2}Fe$ (Eqn. 3.4).¹⁶



The above products are observed upon photolysis in a variety of solvents including pyridine, DMF and HMPT. Hydrolysis of the carbonyl group followed by Fe-(π -C₅H₅) cleavage is proposed as a likely mechanism. Decomposition was not observed in these solvents when properly dried.

3.1.4 Photochemical reactions of $(\eta^5-C_5H_5)$ -metal complexes

In contrast to the relative photoinertness of $(\eta^5-C_5H_5)_2Fe$, haptotropic shifts of the cyclopentadienyl ligand have been observed for many $(\eta^5-C_5H_5)M$ complexes M = Rh or Ir. The cyclopentadienyl ligand can adopt a variety of bonding modes; all ten illustrated below have been observed (Fig. 3.1). The most interesting are the η^5 , η^3 and η^1 bonding modes because of their ability to interconvert.



Fig. 3.1: The different coordination modes observed between a cyclopentadienyl ligand and one or two metal centres

Crichton *et al.*¹⁷ have reported the photochemical generation of $(\eta^3-C_5H_5)Co(CO)_3$ in a pure CO matrix. Irradiation of $(\eta^5-C_5H_5)Co(CO)_2$ (280 > λ_{exc} > 500 nm) causes the η^5 -bound cyclopentadienyl ring to undergo ring slippage to the η^3 -coordination mode, thus creating a vacant site on the metal centre, which is occupied by a host CO molecule (Eqn. 3.5).



Eqn. 3.5

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The CO stretching frequencies shift to higher wavenumber as expected for an increase in the number of CO ligands. Similarly, photochemically generated η^3 -bound cyclopentadienyl complexes have been reported for a number of Re systems.¹⁸ Photolysis of (η^5 -C₅H₅)₂ReH in a CO matrix produces the η^3 -intermediate, (η^3 -C₅H₅)(η^5 -C₅H₅)Re(CO)H (Eqn. 3.6).



The η^3 -intermediate was formulated on the basis of the monocarbonyl stretch observed at 1918 cm⁻¹. This interconversion chemistry of (η^x -C₅H₅)-metal complexes is of great interest, because of their possible applications in catalytic systems.

3.1.5 Photochemistry of (n⁵-pyrrole)ML₃ complexes

King and Efraty ¹⁹ reported that photolysis of $(\eta^5-C_4H_4N)Mn(CO)_3$ in the presence of triphenyl phosphine derivatives results in the substitution of a CO molecule by a triphenyl phosphine group, $(C_4H_4N)Mn(CO)_2(PPh_3)_2$. The IR spectrum of the starting material contained three carbonyl frequencies in comparison to the two frequencies observed for the analogous cyclopentadienyl derivative, $(\eta^5-C_5H_5)Mn(CO)_3$. Introduction of the nitrogen atom in place of one of the carbon atoms in the cyclopentadienyl ring changes the symmetry of the molecule from $C_{3\nu}$ for $[(\eta^5-C_5H_5)Mn(CO)_3]$ to C_s for the $\eta^5-C_4H_4N$ derivative. The manganese- π -C₄H₄N bond is no longer cylindrical causing a noticeable effect on the v_{CO} IR frequencies. The substitution of a CO molecule in $(\eta^5-C_4H_4N)Mn(CO)_3$ by a triphenyl group following UV irradiation is a substitution reaction similar to that observed for $(\eta^6-arene)Cr(CO)_3$ complexes.

3.1.6 Photochemistry of $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe

The only reported photochemical studies on $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe and $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)$ Fe(CO)₂have been carried out by Heenan.^{20, 21} In the sandwich complex $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe, the presence of the pyrrole group reduces the symmetry of this molecule compared to the symmetrical ferrocene molecule. This asymmetry results in the lifting of the degeneracy of the valence orbitals and permits photochemical routes that are not available to the more symmetrical $(\eta^5-C_5H_5)_2$ Fe.

Photolysis of $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe in a CO matrix at 12 K, with long wavelength irradiation ($\lambda_{exc} > 495$ nm) produces $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)$ Fe(CO)₂ (2053 and 2008 cm⁻¹, an 18 electron species) and $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)$ Fe(CO), (1974 cm⁻¹, a 16 electron species). The identity of the dicarbonyl species was confirmed by comparison of the spectrum to that of an authentic sample of $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)$ Fe(CO)₂ prepared by published procedures. Formation of the monocarbonyl complex was confirmed by comparison with matrix experiments on a sample of the dicarbonyl complex, which upon irradiation produces the monocarbonyl species (1974 cm⁻¹) and 'free' CO (2138 cm⁻¹).

Monochromatic photolysis ($\lambda_{exc} = 538 \text{ nm}$) followed by broadband irradiation ($\lambda_{exc} > 495 \text{ nm}$) produces two additional products assigned to the *exo*-(η^5 -C₅H₅)(η^3 -C-C₄H₄N) Fe(CO) (1949 cm⁻¹, an 18 electron species) and the η^3 -allyl species (η^5 -C₅H₅)(η^3 -N-C₄H₄N)Fe(CO) (1962 cm⁻¹, an 18 electron species) (Scheme 3.2).

Solution photochemical studies performed on $(\eta^5 - C_5H_5)(\eta^5 - C_4H_4N)$ Fe are summarised in Eqn. 3.7. Irradiation of an Ar saturated cyclohexane solution of $(\eta^5 - C_5H_5)(\eta^5 - C_4H_4N)$ Fe does not cause any observable change in the UV-vis spectrum. Subsequent addition of CO to the reaction mixture leads to the formation of the dicarbonyl complex, $(\eta^5 - C_5H_5)(\eta^1 - N - C_4H_4N)$ Fe $(CO)_2(2048$ and $2002 \text{ cm}^{-1})$. Steady state photolysis of the parent complex in CO saturated cyclohexane results in formation of the dicarbonyl complex and the π -allyl species, $(\eta^5 - C_5H_5)(\eta^3 - C - C_4H_4N)$ Fe(CO) (1949 cm⁻¹). Subsequent photolysis of this solution reduces the intensity of the π -allyl species while

increasing the intensity of the dicarbonyl bands. This illustrates that the η^3 complex is itself photosensitive.



Scheme 3.2: Photoproducts observed from matrix isolation studies of $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe in a CO matrix at 12 K²⁰



Eqn. 3.7

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3.1.6 Photochemistry of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$

Similarly to $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe, irradiation of the dimethyl-substituted derivative in cyclohexane solution also gives rise to a number of carbonyl containing species following irradiation in the presence of CO.²¹ For the disubstituted pyrrolyl ligand, the presence of the two electron donating methyl groups makes it a stronger donor to the iron centre. Thus the backbonding of the extra electron density from the iron centre to the antibonding orbitals of the carbonyl groups will be greater. Hence, the carbonyl stretches occur at lower frequency in the IR spectra.

Heenan²¹ has carried out room temperature solution studies on this dimethylated azaferrocene analogue. Room temperature photolysis of $(\eta^5-C_5H_5)(\eta^5-2,5 (CH_3)_2C_4H_2N$)Fe under CO reveals that the formation of photoproducts is wavelength dependent. Low energy photolysis ($\lambda_{exc} > 500 \text{ nm}$) of (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe in a CO saturated cyclohexane solution produces four carbonyl complexes; the dicarbonyl $(\eta^{5}-C_{5}H_{5})(\eta^{1}-N-(CH_{3})_{2}C_{4}H_{4}N)Fe(CO)_{2}$ (2041 and 1995) cm⁻¹), the iron dimer $[(\eta^5-C_5H_5)Fe(CO)_2]$ (2004, 1961 and 1793 cm⁻¹), the methylene complex, $(n^{5}-C_{5}H_{5})(CH_{2}C_{4}H_{2}(CH_{3})NH)Fe(CO)_{2}$ (2015 and 1966 cm⁻¹) and the acyl complex $(n^5-C_5H_5)(COCH_2C_5H_6NH)Fe(CO)_2$ (2022 and 1973 cm⁻¹). The acyl IR band was not observed, while an IR band at 3482 cm⁻¹ was tentatively assigned as the N-H stretch. Higher energy photolysis ($\lambda_{exc} > 410$ nm) precludes formation of the methylene and acyl complexes but produces a significant amount of iron dimer and the dicarbonyl complex. Monochromatic irradiation at $\lambda_{exc} = 355$ nm however, results in the formation of the complexes observed following photolysis with $\lambda_{exc} > 500 \text{ nm}$ (*i.e.* $(\eta^5 - C_5 H_5)(\eta^1 - \eta^5)$ $N-(CH_3)_2C_4H_4N)Fe(CO)_2$, $[(\eta^5-C_5H_5)Fe(CO)_2], (\eta^5-C_5H_5)(CH_2C_4H_2(CH_3)NH)Fe(CO)_2]$ and $(\eta^5-C_5H_5)(COCH_2C_5H_6NH)Fe(CO)_2$. The bulky CH₃ groups do not prevent formation of the η^1 complex but this complex is less stable than the azaferrocene analogue as attempts to isolate it failed. The formation of the acyl and methylene complexes is a secondary thermal process. A summary of the solution photochemistry of $(\eta^5-C_5H_5)(\eta^5-(CH_3)_2C_4H_2N)$ Fe is given in Scheme 3.4.

The assignments of the allyl complexes have been made by comparison with earlier published work²¹ and with other allyl systems synthesised and characterised by Green and coworkers.²² Green prepared π -allyl complexes (η^3 -C₃H₄R)(η^5 -C₅H₅)Fe(CO);

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R = H, Me; by UV irradiation of the related η^1 complexes. The carbonyl stretches for the two complexes are: R = H, $v_{CO} = 1950$ cm⁻¹ and R = Me, $v_{CO} = 1948$ cm⁻¹. The π allyl complexes are usually formed as two isomers, namely the *endo* and *exo* forms. Green *et al.* did not characterise the stereoisomer present in their sample, but from the subsequent studies it can be concluded that it was the *exo* isomer, which was formed.





Belmont *et al.*²³ reported that the *exo* isomer is the more stable M-(η^3 -allyl) isomer, with a carbonyl absorbance for (η^5 -C₅H₅)(η^3 -C₃H₅)Fe(CO) at 1962 cm⁻¹. The *endo* isomer exhibits a carbonyl stretch at a lower frequency in the IR spectrum of 1940 cm⁻¹.

It has been shown by Fish *et al.* that the *endo* species thermodynamically isomerises to the *exo* isomer at a moderate rate at ambient temperature.²⁴ Furthermore, for the

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analogous η^3 -allyl complexes of Mo and W, the carbonyl-stretching trend is reversed. The carbonyl stretch of the *exo* isomer occurs at a lower frequency in the IR spectrum. Downs *et al.*²⁵ have shown that the complex (η^5 -C₅H₅)(η^3 -C₃H₅)Mo(CO)₂, exists as two isomers (*exo* and *endo*) in an Ar matrix at 10 K: the *exo* isomer having lower carbonyl stretching frequencies than the *endo* species (Fig. 3.2). In this case the process is irreversible. In a solid CO matrix the η^1 complex cannot be generated. The M-(η^3 allyl) bond is stronger than the M- σ bond;²⁶ hence the former coordination mode is favoured. Photolysis of matrixes (both CO and Ar) containing the *endo* and *exo* isomers possibly weakens the Mo-allyl π bond, while the σ bond remains intact. The allyl species can rotate more freely and interconvert.



Fig. 3.2: Structures of the $(\eta^5-C_5H_5)(\eta^1-C_3H_5)Mo(CO)_3$ species and the corresponding *endo* and *exo* η^3 -allyl species

The only other documented example of a mononuclear Fe-*aza*-allyl species is that reported by Nakanishi *et al.*²⁷ With selective dimerisation of α -bromoamines, (η^3 -1-*aza*-allyl)(nitrosyl)Fe(CO)₂ complexes are formed. The presence of the weaker donating nitrosyl ligand and second CO group result in the higher stretching frequencies observed for the carbonyl groups [2036 and 1977 cm⁻¹ for (CO)₂Fe(NO)(η^3 -C₂H₃NOMe)]. All other reported (η^3 -1-*aza*-allyl) complexes of Fe are of dinuclear complexes.^{28, 29}

The results presented in this chapter are a continuation of the study into the photochemistry of $(\eta^5-C_5H_5)(\eta^5-(CH_3)_2C_4H_2N)Fe$. Matrix isolation experiments were carried out in inert Ar matrixes and reactive CO matrixes and monitored with UV-vis and IR spectroscopy.

Results

3.2 **RESULTS**

The IR spectroscopic data for $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ Fe and all its photoproducts obtained during these matrix experiments is given in Table 3.1.

COMPLEX	v_{CH}/v_{CN}	MATRIX	TEMP.
	(cm ⁻¹)		(K)
$(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)Fe$ (1)	950-1500	Ar	20
	$v_{\rm CO} ({\rm cm}^{-1})$		
$(\eta^{5}-C_{5}H_{5})(\eta^{1}-N-(CH_{3})_{2}C_{4}H_{2}N)Fe(CO)$ (2)	1999	5 % CO/Ar	20
$(\eta^{5}-C_{5}H_{5})(\eta^{1}-N-(CH_{3})_{2}C_{4}H_{2}N)$ Fe(CO) ₂ (3)	2044, 1992	5% CO/Ar	20
$(\eta^{5}-C_{5}H_{5})(\eta^{3}-N-(CH_{3})_{2}C_{4}H_{2}N)$ Fe(CO) (4)	1957	5 %CO/Ar	20
$(\eta^{5}-C_{5}H_{5})(\eta^{3}-C-(CH_{3})_{2}C_{4}H_{2}N)$ Fe(CO) (5)	1947	5 % CO/Ar	20

Table 3.1: Spectroscopic data for $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) and all photoproducts observed

The IR and UV-vis spectra for $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in an Ar matrix at 20 K are represented in Figs. 3.1 and 3.2 respectively. The IR spectrum of the starting material exhibits bands in the region 950-1500 cm⁻¹. The UV-vis spectrum of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe in an Ar matrix exhibits an intense band below 200 nm due to diene absorption in both the Cp and disubstituted pyrrole ring $(\pi \rightarrow \pi^*$ transition). The band at 325 nm is due to $n \rightarrow \pi^*$ transitions in the heterocyclic ring, while the absorption at 423 nm is due to charge transfer transition between the iron centre and aromatic rings.



Fig. 3.1: IR spectrum of $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ Fe (1) in an Ar matrix at 20 K following deposition



Fig. 3.2: UV-vis spectrum of $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ Fe (1) in an Ar matrix at 20 K following deposition

Results





Fig. 3.3: IR spectra obtained following broadband photolysis of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) in an Ar matrix at 20 K

Photolysis of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) with broadband irradiation ($\lambda_{exc} = > 550, > 500, > 410$ and > 320 nm) in an Ar matrix resulted in the changes illustrated in Fig. 3.3. The spectroscopic changes are similar for all irradiation wavelengths and have been assigned as depletion of the starting material complex (1) with concomitant formation of a ring slipped product of the type ($\eta^{5}-C_{5}H_{5}$)($\eta^{x}-2,5-(CH_{3})_{2}C_{4}H_{2}N$)Fe. A similar result is obtained following monochromatic irradiation ($\lambda_{exc} = 546, 436, 405$ and 365 nm) of ($\eta^{5}-C_{5}H_{5}$)($\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N$)Fe (1) in an Ar matirx (Fig. 3.4). The hapticity change of the disubstituted pyrrole ring is uncertain however, as the IR data cannot provide conclusive evidence.



Fig. 3.4: IR spectra obtained following monochromatic photolysis in an Ar matrix at 20 K of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1)

When the difference spectra obtained following both broadband and monochromatic photolysis of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in an Ar matrix are contrasted it is clear that broadband photolysis gives sharper peaks and a greater depletion of the parent complex (Fig. 3.5). The Xe-arc lamp used for broadband irradiation provides greater intensity photons compared to the Hg-Xe lamp, which is used for monochromatic irradiation. Hence broadband photolysis produces a higher concentration of photoproducts within a given timescale compared to monochromatic irradiation.



Fig. 3.5: The difference spectra obtained after (a) broadband photolysis and (b) monochromatic photolysis of (η⁵-C₅H₅)(η⁵-2,5-(CH₃)₂C₄H₂N)Fe (1) in an Ar matrix at 20 K

A general increase in absorption in the region 300-450 nm is observed in the UV-vis spectrum along with the appearance of a new, broad and intense band centred at 660 nm (Fig. 3.6) following irradiation of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$ (1) in an Ar matrix. Comparing the changes observed with the UV-vis data obtained for the analogous azaferrocene reaction,²⁰ the band centred at 660 nm is associated with the η^3 -allyl species $(\eta^5-C_5H_5)(\eta^3-N-(CH_3)_2C_4H_2N)Fe$ and $(\eta^5-C_5H_5)(\eta^3-C-(CH_3)_2C_4H_2N)Fe$. As a result of the lack of information provided by photolysis in Ar matrixes, the majority of experiments were carried out in CO doped matrixes.



Results



Fig. 3.6: The UV-vis difference spectrum recorded following monochromatic irradiation of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in an Ar matrix at 20 K. A similar spectrum was recorded following broadband photolysis.



Fig. 3.7: The assigned structures for complex (1) and species (2)-(5)

3.2.2 Photolysis ($\lambda_{exc} > 410 \text{ nm or } \lambda_{exc} = 436 \text{ nm}$) of (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe at 20 K in Ar matrixes containing 5 % CO



Fig. 3.8: The carbonyl containing species produced upon photolysis with $\lambda_{exc} = 436$ nm of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in a 5 % CO/Ar matrix at 20 K

Photolysis of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in 5 % CO/Ar matrixes with $\lambda_{exc} > 410$ nm or $\lambda_{exc} = 436$ nm for 60 min produces three species, one with $\nu_{CO} = 1999$ cm⁻¹, a second with $\nu_{CO} = 2044$ cm⁻¹ and a third with $\nu_{CO} = 1957$ cm⁻¹ (Fig. 3.8). The ratio of the bands at 1999 cm⁻¹ to 2044 cm⁻¹ is dependent on the irradiation used. With $\lambda_{exc} > 410$ nm the band at 1999 cm⁻¹ is five times as intense as the band at 2044 cm⁻¹ while with $\lambda_{exc} = 436$ nm the band at 1999 cm⁻¹ is ten times as intense as the band at 2044 cm⁻¹. Within individual experiments this ratio remains constant (Fig. 3.9).



Fig. 3.9: Spectrum illustrating that photolysis of $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ Fe (1) in 5 % CO/Ar matrix with $\lambda_{exc} = 436$ nm produces the η^1 monocarbonyl species and the dicarbonyl species in the same ratio

The species absorbing at 1999 cm⁻¹ is assigned to the η^1 -monocarbonyl species $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)$ (2). This assignment is based on a number of arguments, which will be described in detail in the discussion. Alternative structures for this monocarbonyl species at 1999 cm⁻¹ that were considered are presented and discounted in the discussion. The band at 2044 cm⁻¹ is assigned to the dicarbonyl species $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)_2$ (3). The lower energy band of the dicarbonyl species absorbs at 1992 cm⁻¹. At 20 K it is masked by the broad and intense band of the monocarbonyl species at 1999 cm⁻¹ and only becomes apparent upon annealing. The assignment of the dicarbonyl species is based on comparison with the azaferrocene analogue, $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)Fe(CO)_2$, which has $v_{CO} = 2053$ and 2007 cm⁻¹.²⁰ A third band is observed to have formed with both $\lambda_{exc} > 410$ nm and $\lambda_{exc} = 436$ nm and has $v_{CO} = 1957$ cm⁻¹. This band is assigned to the *aza*-allyl species,

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 $(\eta^5-C_5H_5)(\eta^3-N-(CH_3)_2C_4H_2N)Fe(CO)$ (4) by comparison with the azaferrocene analogue, $(\eta^5-C_5H_5)(\eta^3-N-C_4H_4N)Fe(CO)$, which has $v_{CO} = 1962 \text{ cm}^{-1}$.²⁰

3.2.3 Monochromatic photolysis ($\lambda_{exc} = 546, 436, 405$ and 365 nm) of (η^{5} -C₅H₅)(η^{5} -2,5-(CH₃)₂C₄H₂N)Fe in an Ar matrix containing 1% CO



Fig. 3.10: Difference spectrum observed following monochromatic photolysis of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) in a 1 % CO/Ar matrix

Initial photolysis of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in a 1 % CO/Ar matrix with $\lambda_{exc} = 546$ nm for 20 min did not result in any new bands being observed in the matrix. Changing to shorter wavelength photolysis ($\lambda_{exc} = 436$ nm for 30 min) produced a band at 1999 cm⁻¹, which is related to the η^1 -monocarbonyl species ($\eta^5-C_5H_5$)(η^1-N -(CH₃)₂C₄H₂N)Fe(CO) (**3**). Further shorter wavelength photolysis ($\lambda_{exc} = 405$ nm for 20 min and 365 nm for 180 min) increases the intensity of this band but did not produce any of the other bands *i.e.* 2044 or 1957 cm⁻¹, observed in previous experiments.

3.2.4 Initial photolysis ($\lambda_{exc} = 436 \text{ nm}$) of ($\eta^5 \cdot C_5 H_5$)($\eta^5 \cdot 2, 5 \cdot (CH_3)_2 C_4 H_2 N$)Fe at 20 K in Ar matrixes containing 5 % CO and subsequent monochromatic photolysis ($\lambda_{exc} = 405 \text{ and } 365 \text{ nm}$)



Fig. 3.11: Spectral changes observed following monochromatic irradiation of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in a 5 % CO/Ar matrix

Initial photolysis of a 5 % CO doped Ar matrix with $\lambda_{exc} = 436$ nm containing $(\eta^5 - C_5H_5)(\eta^5 - 2,5 - (CH_3)_2C_4H_2N)Fe$ (1) produced three carbonyl containing species with bands at 2044, 1999 and 1957 cm⁻¹ respectively. Subsequent shorter wavelength photolysis with $\lambda_{exc} = 405$ nm changed the ratio of the products (Fig. 3.11). The intensity of the band at 1999 cm⁻¹ increases more rapidly than those at 2044 or 1957 cm⁻¹. This suggests that the dicarbonyl species is undergoing photoinduced CO loss at this excitation wavelength (Scheme 3.5).



Scheme 3.5

Additional photolysis of this matrix with $\lambda_{exc} = 365$ nm changes the ratio of the products further. The intensity of the band at 1999 cm⁻¹ increases while the intensity of the band at 2044 cm⁻¹ decreases. This result suggest that the dicarbonyl species is undergoing photoinduced CO loss to a greater extent at this excitation wavelength than with $\lambda_{exc} =$ 405 nm. During this experiment the species absorbing at 1957 cm⁻¹ increases in intensity with all excitation wavelengths employed.

3.2.5 Initial photolysis ($\lambda_{exc} > 410 \text{ nm}$) of (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe at 20 K in an Ar matrix containing 5 % CO and subsequent broadband photolysis ($\lambda_{exc} > 390 \text{ nm}$)



Fig. 3.12: Spectral changes illustrating the effect of short wavelength broadband photolysis on the photoproducts produced in a 5 % CO/Ar matrix

Initial photolysis of (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe (1) with $\lambda_{exc} > 410$ nm produced three carbonyl bands at 2044, 1999 and 1957 cm⁻¹. Subsequent photolysis of this matrix with $\lambda_{exc} > 390$ nm increased the intensity of the three bands at 2044, 1999 and 1957 cm⁻¹ but did not change the ratio of the η^1 -monocarbonyl species to the dicarbonyl species (Fig. 3.12). This is in contrast to the previous experiment where monochromatic irradiation affected the ratio of the η^1 -monocarbonyl species to the dicarbonyl species. All photolyses carried out in CO matrixes (either monochromatic or broadband in nature) give similar UV-vis spectra with a general increase in absorption in the region 300-800 nm (Fig. 3.13).



Fig. 3.13: The difference UV-vis spectrum obtained following photolysis of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) in a 10 % CO doped Ar matrixes

Wavelength (nm)

0.3

However, the band at 660 nm previously observed in Ar matrixes is not observed in CO doped Ar matrixes. In all of the photolysed CO matrixes at 20 K, the dominant photoproduct is the η^{1} -monocarbonyl species, $(\eta^{5}-C_{5}H_{5})(\eta^{1}-N-(CH_{3})_{2}C_{4}H_{2}N)Fe(CO)$ (2), characterised by the IR band at 1999 cm⁻¹. The η^{3} species characterised by a band at 1957 cm⁻¹, $(\eta^{5}-C_{5}H_{5})(\eta^{3}-N-(CH_{3})_{2}C_{4}H_{2}N)Fe(CO)$ (4) is only present in very small amounts.







Photolysis of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) in 10 % CO doped Ar matrixes at 20 K produces three products: the monocarbonyl species characterised by a band at 1999 cm⁻¹, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO) (4), the dicarbonyl complex characterised by a band at 2044 cm⁻¹, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO)₂ (3) (the low energy band at 1992 cm⁻¹ is masked by the band of the monocarbonyl species at 1999 cm⁻¹), and the η^3 -species $(\eta^5-C_5H_5)(\eta^3-N-(CH_3)_2C_4H_2N)$ Fe(CO) (4) characterised by the band at 1957 cm⁻¹.

Gradually annealing the matrix to 40 K causes the η^1 -monocarbonyl species to convert to the dicarbonyl species and the η^3 -*aza*-allyl species isomerises to the more thermodynamically stable species (η^5 -C₅H₅)(η^3 -C-(CH₃)₂C₄H₂N)Fe(CO) (**5**), which is

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characterised by a band at 1948 cm⁻¹ (Fig. 3.14). Upon annealing an additional band at 2061 cm⁻¹ is observed to have formed and represents a third carbonyl species. An assignment has not been made, however.

Similar results were obtained upon annealing of a 10 % CO/Ar matrix to 40 K that had been initially photolysed with monochromatic irradiation (λ_{exc} = 405 and 365 nm). Fig. 3.15 illustrates the difference spectra between the matrix at 20 K and the matrix at 40 K. It is clear that the band at 1999 cm⁻¹ has decreased while the bands at 2044 and 1992 cm⁻¹ have increased significantly. In addition the band at 1957 cm⁻¹ has shifted to a lower frequency with ν_{CO} = 1947 cm⁻¹. The negative peak refers to the depletion of the monocarbonyl species.



Fig.3.15: Spectral changes observed upon annealing of a 10 % CO/Ar matrix from 20 K to 40 K following monochromatic irradiation

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At 40 K the second band of the dicarbonyl $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)_2$ (3) becomes apparent (Fig. 3.16).



Fig. 3.16: 5 % CO/Ar matrix annealed to 40 K after photolysis illustrating the two bands of the dicarbonyl complex, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)_2$ (3)





Fig. 3.17: Spectra obtained at various time intervals during the photolysis of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe (1) for the first 11 min with $\lambda_{exc} = 436$ nm of a 5 % CO/CH₄ matrix at 30 K

A 5 % CO/CH₄ matrix containing (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe (1) was photolysed at 30 K to confirm that these bands at 2044 and 1992 cm⁻¹ belong to the same species, that is (η^5 -C₅H₅)(η^1 -*N*-(CH₃)₂C₄H₂N)Fe(CO)₂ (**3**). At 30 K, the η^1 monocarbonyl species is no longer the dominant species. The dicarbonyl species is the major photoproduct formed at this temperature. (Note a CO doped CH₄ matrix gives sharper peaks compared to a CO doped Ar matrix). Photolysis of this matrix with λ_{exc} = 436 nm results in the two bands at 2044 and 1992 cm⁻¹ growing in at the same rate (Fig. 3.17), thus confirming that they represent the same species. The two bands for the dicarbonyl species should be of nearly equal intensity,²¹ by comparison with the IR spectrum for the azaferrocene dicarbonyl species, (η^5 -C₅H₅)(η^1 -*N*-C₄H₄N)Fe(CO)₂, but from Fig. 3.17 it can be seen that the band at 1992 cm⁻¹ has a higher intensity than the band at 2044 cm⁻¹. This is because at 30 K the η^1 monocarbonyl species is formed to a

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small extent and its band (1999 cm⁻¹) overlaps with the low energy band of the dicarbonyl complex.





Fig. 3.18 illustrates the rate of growth of the two dicarbonyl bands at longer time intervals. Note that at 30 K both η^3 species are present. At 30 K, the band at 2061 cm⁻¹ is not yet visible.

3.2.8 Photolysis ($\lambda_{exc} = 436 \text{ nm}$) of (η^5 -C₅H₅)(η^5 -2,5-(CH₃)₂C₄H₂N)Fe in a CH₄ matrix containing 0.2 % CO at 40 K



Fig. 3.19: Photolysis of $(\eta^5 - C_5 H_5)(\eta^5 - 2, 5 - (CH_3)_2 C_4 H_2 N)$ Fe (1) in a 0.2 % CO/CH₄ matrix at 40 K with $\lambda_{exc} = 436$ nm for 145 min

A sample of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) was deposited in a 0.2 % CO/CH₄ matrix at 40 K. Photolysis with $\lambda_{exc} = 436$ nm produced the η^1 -monocarbonyl complex, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO) (2) (1999 cm⁻¹) as the dominant photoproduct as illustrated in Fig. 3.19. Thus, at very low CO concentrations, the η^1 -monocarbonyl species is formed in significant amounts regardless of the temperature of the experiment.

The ratio of the dicarbonyl species to the η^3 -species is roughly 2:1 at 40 K. However, at 30 K in a 5 % CO/Ar matrix the ratio of the dicarbonyl species to the η^3 -species is roughly 10:1 (Fig. 3.17). Thus at lower concentrations of CO, the formation of the η^3 -species is favoured while at higher concentrations (Fig. 3.18), the formation of the dicarbonyl complex dominates.

3.2.9 Cyclic voltammetry measurements

Cyclic voltammetry measurements were carried out in N₂ purged acetonitrile solutions of $(\eta^5-C_5H_5)_2Fe$, $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$ and $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$ in order to compare the electrochemical properties of these three complexes. The voltammograms measured at a scan rate of 100 mV per sec are illustrated below and will be followed with an explanation of the results.

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Fig. 3.20: Cyclic voltammogram illustrating the oxidation potential of ferrocene in acetonitrile






Fig. 3.21: Cyclic voltammogram illustrating that although $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe undergoes oxidation in acetonitrile for the first few cycles, thereafter the electrode is pacified



Fig. 3.22: Cyclic voltammogram recorded in acetonitrile illustrating the oxidation potential of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$



Results



Fig. 3.23: Cyclic voltammogram obtained in acetonitrile illustrating the reduction potential of $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$



Fig. 3.24: Cyclic voltammogram obtained in acetonitrile illustrating the reduction potential of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$

Fig. 3.20 illustrates the oxidation of ferrocene in acetonitrile. As the potential of the potentiostat is scanned to positive potential the ferrocene molecules near to the electrode are oxidised to ferrocenium at 0.42 V. On the reverse scan ferrocenium is reduced back to ferrocene at 0.35 V. Comparing the current for the oxidation and reduction process it can be seen that they are equal in amplitude; hence the oxidation of ferrocene is a reversible process. The ferrocenium ion produced is stable enough to exist in solution until it is reduced by the electrode. The potential of this process is equal to the half wave potential (E_{1/2}) and has a value of 0.38 V (E_{1/2} = $\frac{1}{2}(0.42 \text{ V} + 0.35 \text{ V}))$. When a C and H atom of the ferrocene molecule are replaced by a N atom the electrochemistry of the compound changes significantly. Fig. 3.21 illustrates the oxidation of $(\eta^5-C_5H_5)(\eta^5-\eta^5)$ C_4H_4N)Fe in acetonitrile, carried out for several scans. The potential is scanned to positive potential and the azaferrocene molecules are oxidised at 0.7 V. On the reverse scan these oxidised molecules are reduced at -0.1 V. Relative to ferrocene, this compound is more difficult to oxidise as a more positive potential is required to effect oxidation. However, with successive cyclic scans, the electrode becomes pacified as the azaferrocene polymerises. There is a precedent for the polymerisation of pyrrole.³⁰ In the case of the dimethylazaferrocene complex, $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$, (Fig. 3.22), it is oxidised at 0.7 V, which is similar to the oxidation potential of the azaferrocene complex on its first cycle. When the potential is scanned to more positive potentials, further oxidations occur at 0.85 and 1.2 V. On the reverse scan a positive current is not detected. The cyclic voltammogram for dimethylazaferrocene represents an irreversible process. The oxidised species is not stable enough to survive until the reverse scan of the electrode. The oxidised species has decomposed and there is nothing to reduce. Fig. 3.23 illustrates the reduction of $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$. Scanning the potential to negative potential results in the reduction of azaferrocene at -1.55 V. On the reverse scan the reduced species is oxidised at -1.4 V. The reduction of azaferrocene is not fully reversible, as the currents for each process are not equal. Note that the species being reduced at -0.8 V is O_2 , which was present because of inefficient purging with N₂. The cyclic voltammogram for the reduction of $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)$ Fe is illustrated in Fig. 3.24. A more negative potential is required to effect reduction in dimethylazaferrocene compared to azaferrocene as it undergoes reduction at -1.6 V. It is more difficult to reduce. This reduced species undergoes oxidation at -1.4 V on the reverse scan.

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3.3 **DISCUSSION**

Matrix isolation studies of $(\eta^5 - C_5H_5)(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)Fe(1)$ in CO doped Ar matrixes in the temperature range 20 K \rightarrow 40 K, produce a number of carbonyl containing intermediates. The band at 1999 cm⁻¹ has been assigned to the intermediate $(\eta^5 - C_5H_5)(\eta^1 - N - (CH_3)_2C_4H_2N)Fe(CO)$ (2). This assignment will be discussed below. The bands at 2044 and 1992 cm⁻¹ have been assigned to the dicarbonyl species $(\eta^5 - C_5H_5)(\eta^1 - N - (CH_3)_2C_4H_2N)Fe(CO)_2$ (3) based on comparison with the analogous $(\eta^5 - C_5H_5)(\eta^1 - N - (CH_3)_2C_4H_2N)Fe(CO)_2$, which has $v_{CO} = 2053$ and 2007 cm⁻¹. Bands at 1957 and 1948 cm⁻¹ have been assigned to the η^3 -intermediate species, $(\eta^5 - C_5H_5)(\eta^3 - N - (CH_3)_2C_4H_2N)Fe(CO)$ (4) and $(\eta^5 - C_5H_5)(\eta^3 - C - (CH_3)_2C_4H_2N)Fe(CO)$ (5) respectively based on the studies carried out by Green *et al.* on related systems.²²

The major photoproduct formed when $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)$ Fe (1) is irradiated in a CO doped Ar matrix at 20 K, with either monochromatic or broadband photolysis, is the η^1 -monocarbonyl species, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO) (2), characterised by a band at 1999 cm⁻¹. Experimental results show that for low or high CO concentrations (1, 5 or 10 % CO/Ar) this η^1 -monocarbonyl species is the dominant product.

For the analogous azaferrocene derivative, $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe, an IR stretching frequency for $(\eta^5-C_5H_5)(\eta^1-N-C_4H_4N)$ Fe(CO) was observed at 1974 cm⁻¹ following irradiation under similar conditions.²⁰ The methyl substituted η^1 -monocarbonyl species, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)$ Fe(CO) (2) would be expected to have a carbonyl stretching frequency lower than 1974 cm⁻¹ as the methyl groups are electron donating and a weakening of the carbonyl bond is anticipated. Therefore the assignment of the band at 1999 cm⁻¹ seems unrealistic. However, the following arguments serve to support this assignment.

Restricted and unrestricted Hatree-Fock calculations were carried out to investigate if the spin states for the monocarbonyl species could be different for the substituted complex compared to the unsubstituted complex and whether this variation could

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explain the differences in the IR spectroscopic features for $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)$ Fe and $(\eta^{5}-C_{5}H_{5})(\eta^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}N)Fe(1)$.³¹ The STO-3IG basis set was chosen. For restricted Hatree-Focke calculations the structure was optimised through several cycles until an energy minimum was reached. At each cycle of the geometry optimisation the calculations were monitored for spin contamination. There was evidence for spin contamination for each cycle ($S^{**}2 \neq 0$). When the structure reached stationary point the S^{**}2 value was zero. This showed that at the optimised geometry the species appeared to be low-spin. However, upon testing the stability of the wavefunction at the optimised geometry an instability was observed, indicating that there are other wavefunctions, perhaps with higher spin, that have energies very close to the lowest energy wavefunction. Unrestricted Hartree-Focke calculations were carried out to determine if a different lowest energy wavefunction, possibly with higher spin, was produced. The system was optimised to the same structure as for the restricted Hartree-Focke calculation. The S^{**}2 value was zero at the optimised geometry but there was evidence for spin contamination during the geometry optimisation. These results show that although the wavefunction was low spin at the optimised geometry, there were other high spin wavefunctions, which were very close in energy to the lowest energy wavefunction. Thus the assignment of the band at 1999 cm⁻¹ as $(\eta^5 - C_5 H_5)(\eta^1 - N_5)$ $(CH_3)_2C_4H_2N)Fe(CO)$ (2) is not improbable.

Yang *et al.*³² reported the detection of intermediate singlet and triplet states upon photolysis of (η^5 -C₅H₅)Mn(CO)₃ in Et₃SiH. Photolysis of (η^5 -C₅H₅)Mn(CO)₃ in Et₃SiH produced (η^5 -C₅H₅)Mn(CO)₂SiEt₃H and intermediate triplet and singlet states of the type, (η^5 -C₅H₅)Mn(CO)₂, were detected. The singlet dicarbonyl species was found to have carbonyl IR stretching frequencies at 1889 and 1946 cm⁻¹ while the triplet intermediate dicarbonyl was found to have carbonyl IR stretching frequencies at 1870 and 1967 cm⁻¹. The triplet low energy carbonyl band is shifted to lower wavenumbers by 19 cm⁻¹ compared to the low energy band of the singlet species while the high energy carbonyl band of the triplet species is shifted to higher wavenumbers by 21 cm⁻¹ compared to the corresponding singlet carbonyl band. Thus, the shift of the η^1 monocarbonyl complex, (η^5 -C₅H₅)(η^1 -(CH₃)₂C₄H₂N)Fe(CO) (**2**) (1999 cm⁻¹), by 25 cm⁻¹ compared to the azaferrocene η^1 -monocarobnyl complex, (η^5 -C₅H₅)(η^1 -*N*-C₄H₄N)Fe(CO) (1974 cm⁻¹) does not seem implausible.

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Furthermore, an experiment was carried out in an attempt to produce the ground state η^{1} -monocarbonyl complex *in situ* in the matrix by firstly forming the (η^{5} -C₅H₅)(η^{1} -(CH₃)₂C₄H₂N)Fe(CO)₂ (**3**) species. A 0.2 % CO/CH₄ matrix containing (η^{5} -C₅H₅)(η^{5} -(CH₃)₂C₄H₂N)Fe (**1**) at 40 K was initially photolysed with $\lambda_{exc} = 436$ nm (preparatory photolysis) to produce the dicarbonyl complex (Fig. 3.19). A low concentration of CO was employed to ensure that during the preparatory photolysis phase, the uncoordinated host CO molecules were consumed by forming the metal carbonyl species. Therefore, supplementary CO molecules would not be present in the matrix to recombine with the ground state monocarbonyl species should it form. Subsequent photolysis with monochromatic filters did not produce a new band in the spectral region of 1974 cm⁻¹ however. These results aid the assignment of the band at 1999 cm⁻¹ as the η^{1} -monocarbonyl species.

Experimental results indicate that at high CO concentrations (5% or higher) the formation of the η^1 -monocarbonyl species and the dicarbonyl species is simultaneous. This suggests that both of these photoproducts are formed concomitantly by the reaction of CO with the fourteen electron species, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe$. In contrast at low CO concentrations at 20 K (1 % CO/Ar), photolysis with monochromatic irradiation produced the η^1 -monocarbonyl species only, suggesting that the η^1 monocarbonyl species is the precursor to the dicarbonyl species. The experimental results presented here cannot determine if the η^1 -monocarbonyl species is the precusor to the dicarbonyl species or not. Furthermore the observation of the η^3 -species, $(\eta^5-C_5H_5)(\eta^3-N-(CH_3)_2C_4H_2N)(CO)$ (4), in the matrix experiments carried out at 20 K suggest the possibility of a stepwise ring slip of the dimethyl pyrrole ring from $\eta^5 \rightarrow \eta^3$ $\rightarrow \eta^1$ coordination. However, there is no definitive evidence for such a mechanism.

The conversion of the η^{1} -monocarbonyl species to the dicarbonyl species can be controlled thermally. Annealing CO doped Ar matrixes, containing 5 % CO or higher concentrations, converts the η^{1} -monocarbonyl species to the dicarbonyl species (Fig.3.15). The dicarbonyl species, $(\eta^{5}-C_{5}H_{5})(\eta^{1}-(CH_{3})_{2}C_{4}H_{2}N)Fe(CO)_{2}$ (3), is the more thermodynamically stable species. This is confirmed by room temperature photolysis solution studies,²⁰ where the dicarbonyl species is produced but there is no observation of the η^{1} -monocarbonyl species.

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The two bands of $(\eta^5 - C_5H_5)(\eta^1 - (CH_3)_2C_4H_2N)Fe(CO)_2$ (3) have different intensities; this is in contrast to the azaferrocene analogue, $(\eta^5 - C_5H_5)(\eta^1 - C_4H_4N)Fe(CO)_2$, whose related carbonyl bands ($v_{CO} = 2053$ and 2007 cm⁻¹) are almost equal in intensity.²¹ At 40 K a further band is observed at 2061 cm⁻¹. The intensity of this band increases significantly when the CO doped matrix is annealed from 20 K \rightarrow 40 K (cf. Fig. 3.14). The band at 2061 cm⁻¹ possibly represents an additional metal carbonyl species produced during the matrix isolation studies of $(\eta^5 - C_5H_5)(\eta^5 - (CH_3)_2C_4H_2N)Fe$ (1). The intense carbonyl band at 2044 cm⁻¹ masks the accompanying band. An assignment for this additional carbonyl species has not been made.

The η^3 -intermediate, $(\eta^5 - C_5H_5)(\eta^3 - N - (CH_3)_2C_4H_2N)Fe(CO)$ (4) characterised by a band at 1957 cm⁻¹ is present at 20 K but undergoes isomerisation to the more thermally stable η^3 -species, $(\eta^5 - C_5H_5)(\eta^3 - C - (CH_3)_2C_4H_2N)Fe(CO)$ (5) ($\nu_{CO} = 1948$ cm⁻¹) upon annealing of the matrix to 40 K (cf. Fig. 3.17). At 32 K both allyl species are observed. In contrast, the azaferrocene analogue ($\eta^5 - C_5H_5$)($\eta^3 - N - C_4H_2N$)Fe(CO) (4) ($\nu_{CO} = 1948$ cm⁻¹) is observed in CO matrixes at 12 K along with the second allyl species, ($\eta^5 - C_5H_5$)($\eta^3 - C - (CH_3)_2C_4H_2N$)Fe(CO) ($\nu_{CO} = 1962$ cm⁻¹).

Conversion to the more thermally stable product upon matrix annealing is also observed with Fe(CO)₃(η^2 -ethene).³³ Photolysis of an argon matrix containing Fe(CO)₄(η^2 ethene), (which has trigonal bypyramidal geometry) with $\lambda_{exc} = 260$ nm, produces the coordinatively unsaturated CO loss products (Fig. 3.25). At 10 K geometric isomers (**a**) and (**b**) exist whereby the ethene molecule occupies the equatorial and apical positions respectively. Structure (**a**) is the more thermodynamically stable product and complex (**b**) isomerises to the former upon annealing of the matrix to 50 K.



Fig. 3.25: Structures of the isomers of $Fe(CO)_3(\eta^2-C_2H_4)$, in which the ethene molecule occupies an equatorial position (**a**) and an axial position (**b**)

The species absorbing at 1999 cm⁻¹ has been assigned the structure $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)$ based on the arguments given earlier. There were other possible structures that the monocarbonyl complex could have assumed (Fig. 3.26). These are described below and discounted for the following reasons.



Fig. 3.26: The other possible structures that were considered for the η^1 -monocarbonyl species at 1999 cm⁻¹

Structure (c) involves the C-H activated product, where a C-H bond of one of the methyl groups of the 2,5-dimethyl pyrrole has been cleaved. Consequently an Fe-H bond is formed and the remaining methylene group is coordinated to the metal, along with the nitrogen atom, which acts as a one electron donor to the eighteen-electron Fe centre. In effect, the initially activated proton would have to migrate to the methylene group to reform the methyl group before the dicarbonyl species is produced. In addition, the M-CH₂ bond would have to be broken to allow this reformation to take place. It is rather unusual for a proton of a M-H bond to return to its original site. Typically, after transferral to the metal centre, the proton is subsequently lost. The η^1 -monocarbonyl

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band at 1999 cm⁻¹ compares well with results reported by Rest *et al.*³⁴ who found that photolysis of (η^5 -C₅Me₅)Ir(CO)₂ in a methane matrix at 12 K produced the photoactivated product, (η^5 -C₅Me₅)Ir(CO)MeH ($\nu_{CO} = 1992 \text{ cm}^{-1}$ and $\nu_{Ir-H} = 2150 \text{ cm}^{-1}$) (290 < λ_{exc} < 370 nm, $\lambda_{exc} > 550$ nm). In the experiments no M-H bond was observed in the IR spectra in any of the CO doped matrix experiments. It is possible that the Fe-H stretch falls within the range 2125-2150 cm⁻¹, which is masked by the intense and broad band of the host matrix. However, experiments carried out in a methane matrix²¹ did not show any evidence of an Fe-H stretch in the IR spectrum either. Without the observation of an IR Fe-H band, the assignment of the band at 1999 cm⁻¹ to (η^5 -C₅H₅)Fe(η^1 -*N*- μ_2 -CH₂C₄H₂NCH₃)(CO)(H) is unlikely.

Structure (**d**) involves the C-H activated product where the Fe atom is coordinated to the methylene group of the pyrrolyl ligand. The third hydrogen atom of the CH₃ group is coordinated to the nitrogen atom of the disubstituted pyrrole ring. This structure is a plausible sixteen electron intermediate. The analogous azaferrocene dicarbonyl derivative has been characterised in solution studies, with $v_{CO} = 2015$ and 1966 cm⁻¹. Structure (**d**) would be expected to have a lower carbonyl stretching frequency. For the disubstituted pyrrolyl ligand the presence of the two methyl groups makes it a stronger donor to the Fe centre. Backbonding of the extra electron density from the Fe centre to the antibonding orbital of the carbonyl group will be greater. Hence a carbonyl stretch should occur at lower frequency in the IR spectra. Thus a methylene monocarbonyl complex is unlikely.

Structure (c) contains the ring slipped (η^5 -C₅H₅) moiety. Ring slippage of a cyclopentadienyl group is well documented, although in all cases the complexes contain either another cyclopentadienyl ring or acyclic ligands only (Fig. 3.27).^{23, 35} There are no reports of haptotropic shifts of the cyclopentadienyl ring in the presence of other π -coordinated heterocycles. Thus there is no precedent to assign the η^1 -monocarbonyl complex as a cyclopentadienyl ring slipped monocarbonyl species.

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Fig. 3.27: Transition metal carbonyl complexes containing an η^1 -coordinated cyclopentadienyl ligand

Cyclic voltammetry studies of the three related complexes, $(\eta^5-C_5H_5)_2Fe$, $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$ and $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2C_4H_2N)Fe$ revealed different electrochemical properties for each of these complexes. Cyclic voltammetry showed that the oxidation of ferrocene is a reversible process. The $E_{1/2} = 0.38$ V vs SCE. The unsubstituted complex, $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$ was shown to undergo polymerisation when the potential is scanned to positive potential, while $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2-C_4H_2N)Fe$ undergoes a number of oxidations followed by decomposition. The presence of the two methyl groups prevents the polymerisation of the pyrrole ring in the disubstituted complex. In contrast to the cyclic voltammetry results, the presence of the two methyl groups in the $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2-C_4H_2N)Fe$ does not effect the photochemistry of this complex greatly compared to the unsubstituted complex, $(\eta^5-C_5H_5)(\eta^5-C_4H_4N)Fe$; as both produce η^1 - and η^3 - monocarbonyl species upon photolysis in CO matrixes. Although, the dimethylated η^1 - monocarbonyl species is proposed to be a high spin state species.

As already mentioned in the literature survey, $(\eta^5-C_5H_5)_2Fe$ has a distinct lack of photochemical activity compared to azaferrocene and its substituted derivative. The difference in chemistry between these sandwich complexes, $(\eta^5-C_5H_5)_2Fe$ and $(\eta^5-C_5H_{5-x}(CH_3)_x)(\eta^5-C_4H_4N)Fe$, is further illustrated by these cyclic voltammetry studies.

3.4 CONCLUSION

Matrix isolation studies of $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2-C_4H_2N)$ Fe (1) illustrate that the photochemistry of this disubstituted complex is similar to its unsubstituted analogue and is dominated by haptotropic shifts of the disubstituted pyrrole ring. The presence of the two CH₃ groups does not prevent the formation of the η^1 -monocarbonyl or the η^1 dicarbonyl species as both, $(\eta^5-C_5H_5)(\eta^1-N-(CH_3)_2C_4H_2N)Fe(CO)$ (2) and $(n^{5}-C_{5}H_{5})(n^{1}-N-(CH_{3})_{2}C_{4}H_{2}N)Fe(CO)_{2}$ (3) are observed when CO doped matrixes are photolysed. Furthermore the η^1 -monocarbonyl species (η^5 -C₅H₅)(η^1 -N- $(CH_3)_2C_4H_2N)Fe(CO)$ (2) is proposed to exist in the triplet state in these matrix isolation studies. The observation of the η^3 -intermediates in these studies might indicate that a photoinduced stepwise process from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ occurs upon irradiation of the complex $(\eta^5-C_5H_5)(\eta^5-2,5-(CH_3)_2-C_4H_2N)$ Fe (1). However, there is no definitive evidence for such a mechanism. Despite the similar photochemistry of both (η^5 - C_5H_5)(n^5 - C_4H_4N)Fe and (n^5 - C_5H_5)(n^5 -2,5-(CH₃)₂- C_4H_2N)Fe the electrochemistry of these two complexes is very different. With increasing positive potential, azaferrocene is observed to polymerise while the presence of the two methyl groups in dimethylazaferrocene prevent polymerisation.

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Chapter 3

3.5 REFERENCES

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Matrix Isolation Studies

of $(\eta^5 - C_4 H_4 Se)Cr(CO)_3$

Abstract

Matrix isolation studies of $(\eta^5 - C_4H_4Se)Cr(CO)_3$ in inert (Ar and CH₄) and reactive (CO and N₂) matrixes at 20 K reveal that the selenophene ring undergoes haptotropic shifts. The photoproducts observed depend on the host matrixn employed. In all four matrixes, short wavelength irradiation ($\lambda_{exc} = 405$ nm) yields a three carbonyl band pattern that has been assigned to ($\eta^4 - C_4H_4Se$)Cr(CO)₃, where the selenophene ring has undergone a ring slip from $\eta^5 \rightarrow \eta^4$ coordination, [($\eta^4 - C_4H_4Se$)Cr(CO)₃N₂ in N₂ matrixes]. Subsequent photolysis of this photoproduct in inert matrixes produces the CO loss product, ($\eta^4 - C_4H_4Se$)Cr(CO)₂. In N₂ matrixes subsequent photolysis of the primary photoproduct (($\eta^4 - C_4H_4Se$)Cr(CO)₃N₂) results in the formation of the dicarbonyl complex, ($\eta^5 - C_4H_4Se$)Cr(CO)₂N₂. In CO matrixes the initial photoproduct yields Cr(CO)₆ upon extended photolysis.

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Chapter 4

4.1 LITERATURE SURVEY

4.1.1 Hydrodesulfurisation process

During the hydroprocessing of petroleum, crude oil is treated with high pressures of H_2 (150-3000 lb in⁻²) over a hot heterogeneous catalyst (Co or Ni promoted Mo or W sulfides supported on Al₂O₃, 500-825°C) to remove nitrogen, residual metals and sulfur before further processing.¹ HDS can be illustrated by the following equation (Eqn. 4.1):

$$C_{x}H_{y}S + 2H_{2} \longrightarrow C_{x}H_{y+2} + H_{2}S$$
 Eqn. 4.1

The contaminant H_2S causes SO_2 pollution and poisons the Pt catalysts that are used to upgrade feedstocks to product fuels. There is interest in developing new catalysts and processes for the removal of sulfur from organosulfur components in petroleum.

The mechanism for HDS is unknown to date. Non-aromatic sulfur compounds, such as thiols, sulfides and disulfides readily undergo desulfurisation. Aromatic sulfur compounds such as thiophene and their substituted derivatives are much less reactive. As part of an effort into understanding the HDS mechanism of thiophenes, research has explored the possible modes of coordination of thiophenic molecules to transition metal centres and their subsequent reactivities. Six modes of coordination of the thiophene molecule have been reported and are illustrated below (Fig. 4.1).

Under particular conditions the various bonding modes activate the thiophene to further reaction. Each coordination mode of thiophene will be discussed below and its relevance to the HDS process reviewed.

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Fig. 4.1: The six modes of metal coordination to a thiophene molecule that have been reported

4.1.2 η^1 - thiopene transition metal complexes

 η^{1} -coordination of thiophenes to a metal centre is often suggested as the initial step in the HDS process. It is thought that η^{1} -S coordination activates the thiophene ring to give H₂S and C₄ hydrocarbon products.² However, there is little experimental evidence to support this.

In the thiophene complexes, $[(\eta^5-C_5H_5)Fe(CO)_2(\eta^1-C_4H_4S)]^+$ and $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C_4H_4S)]^+$, the thiophene ligands are so weakly bound that further reaction of these complexes results in the dissociation of the thiophene ligand from the metal centre.^{3,4}

In the dibenzothiophene complex, $(\eta^5-C_5H_5)Fe(CO)_2(\eta^1-S-C_4S(C_6H_4)_2)]^+$, the dibenzothiophene is also weakly bound. Reaction of this complex with two equivalents of CH₃CN in CD₃NO₂ results in the replacement of the dibenzothiophene ligand by a CH₃CN molecule (Eqn. 4.2).³



The η^1 -S coordinated complex $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-S-C_4H_4S)]BF_4$,⁴ converts with loss of PPh₃ within hours to the more stable η^5 -complex $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]BF_4$ upon standing (Eqn. 4.3)



The use of a thiophene molecule containing a chelating group enabled the η^1 -S coordination mode to be determined crystallographically (Fig. 4.2). The presence of the methylene bridge prevents the formation of the η^5 -thiophene complex.⁴



Fig. 4.2: Structure of $(\eta^1:\eta^5-C_4H_3SCH_2C_5H_4)Ru(PPh_3)_2$ illustrating the chelating effect of the cyclopentadienyl ligand

Fultz *et al.*⁵ exploited the stabilising effect of chelation by reacting the bidentate 4-R₂P(η^{5} -C₄S(C₆H₄)₂) ligand, (R = Ph or *p*-tol), with RuCl₂(PPh₃)₃ to produce Cl₂Ru[4-R₂P(η^{5} -C₄S(C₆H₄)₂)]₂ (Eqn. 4.4). The two η^{1} -S-DBT complexes illustrated here are rather unique as the majority of DBT ligands coordinate to transition metals in an η^{6} fashion *via* one of the benzene rings.

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 $RuCl_2(PPh_3)_2 + 2(4-PR_2(DBT))_2 \longrightarrow RuCl_2(\eta^1-4-PR_2(DBT))_2 + 2PPh_3$ Eqn. 4.4

Despite the stability imparted to the η^1 -complexes through chelation, the η^1 -thiophenes in $[(\eta^1-S-C_4H_3SCH_2C_5H_4)Ru(PPh_3)_2]BF_4$ and $Cl_2Ru(4-R_2P(\eta^1-S-C_{12}H_8S))_2$ are readily replaced by CH₃CN and CO respectively.

The rate of displacement of η^1 -thiophene ligands from rhenium transition metal complexes was investigated by Angelici *et al.*⁶ They found that the rate of displacement depended on the degree of substitution present on the thiophene ring, with unsubstituted thiophene having the highest rate of displacement. These results indicate that increasing methyl substitution on the thiophene ring strengthens the S-Re bond. Equilibrium studies⁶ on the replacement of thiophene by substituted thiophene molecules show that all methyl substituted thiophenes bind more strongly to the metal centre. The extra electron density provided by the methyl groups makes the S atom a better donor to the metal centre.

There are reports that some complexes activate transition metal η^1 -S thiophene complexes to further reaction.^{7, 2} The reaction of $(\eta^5-C_5(CH_3)_5)(CO)_2Re(\eta^1-S-C_4H_4S)$ with Fe₂(CO)₉ produces the bridged complex $(\eta^5-C_5(CH_3)_5)(CO)_2Re(\mu-S-C_4H_4S)Fe(CO)_3$ (Eqn. 4.5). In this complex the thiophene ring is coordinated to the Re metal centre through the S atom while the diene fragment is bound to the Fe(CO)₃ moiety.



Eqn. 4.5

Coordination of the thiophene S atom to the Re centre disrupts the aromaticity of the thiophene ring, activating the diene fragment. Free thiophene does not react with

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Fe₂(CO)₉ under similar conditions. The v_{CO} values for the dinuclear complex are lower than in the mononuclear complex, indicating that S is a better donor when the thiophene is η^4 -coordinated to Fe(CO)₃. When the thiophene is 2,5-dimethylthiophene or tetramethylthiophene no reaction occurs with Fe₂(CO)₉. This observation can be explained in terms of a two-step mechanism (Eqn. 4.6).



Eqn. 4.6

The first step involves initial coordination of $Fe(CO)_4$ to one of the double bonds of the thiophene ring. Subsequent CO loss followed by coordination of the diene produces the final product. In the case of the 2,5-dimethylthiophene and tetra substituted thiophenes, the α -methyl groups inhibit formation of the η^2 -intermediate.

A bridging benzothiophene ligand is observed in the complex $(\eta^5-C_5(CH_3)_5)(CO)_2Re-(\eta^2:\eta^1(S)-\mu_2-C_8H_6S)W(CO)_5$.⁸ The W(CO)₅ moiety is coordinated to the benzothiophene ligand *via* the S atom. This coordination activates the benzothiophene ligand to coordinate to a Re centre in an η^2 -fashion at the C(2)-C(3) double bond of the benzothiophene ligand.

Novel thiophene complexes containing both thiophene and hydride ligands on the same metal centre, $[IrH_2(\eta^1-S-Th)_2(PPh_3)_2]PF_6$, where Th = thiophene, benzothiophene or dibenzothiophene, have been reported by Sanchez-Delgado *et al.*⁹ X-ray crystal

structures confirmed the η^1 -S coordination of both thiophene ligands to the Ir metal centre. For the thiophene and benzothiophene derivatives, the poorly coordinating solvent CD₂Cl₂ easily displaces the heteroaromatic ligands. Ligand exchange was not observed for the dibenzothiophene derivative however. Reaction between the hydride and the coordinated thiophene molecules is not observed. The strong Ir-H bond may be the reason for the lack of reactivity of these complexes.

Crystal and molecular crystal structures of many η^1 -S-thiophene complexes have been reported.^{6,10} Although the thiophene ligand may vary from one complex to another, they all have some general points in common (Fig. 4.3 for thiophene numbering).



Fig. 4.3: The numbering system for thiophene ligands

In all complexes the S adopts a pyramidal geometry, the angle between the S atom and the two adjacent carbons ranging from $119 - 132^{\circ}$. In the bridged complexes, the C(2)-C(3) and C(4)-C(5) bond lengths are longer than the C(3)-C(4) bond length. This is in contrast to free thiophene where the C(3)-C(4) bond length is longer than the other two bond lengths. In the bridging complex (η^5 -C₅H₅)(CO)₂Re(μ -C₄H₄S)Fe(CO)₃, the thiophene ring is no longer planar as in the case of η^1 -S complexes. Coordination of the Fe centre to the diene fragment of the thiophene ring causes the ring to fold with a dihedral angle of 143.1(4)° between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes.

 η^{1} -coordination of a thiophene molecule to a metal centre of a HDS catalyst was believed to be such that the thiophene ring would coordinate to a metal centre perpendicularly through the sulfur atom. In this arrangement if α -methyl groups were present they would sterically weaken the M-S coordination. However, it is now known that η^{1} -coordination of the thiophene ligand occurs in a 'bent' fashion, where the metal does not lie in the plane of the thiophene ligand and the S atom has pyramidal geometry. Based on these results, it is possible that HDS could occur following η^{1} -coordination of the thiophene ligand to the catalyst. However, there is very little evidence to suggest

that this type of coordination can activate the ring to undergo C-S bond cleavage. In most complexes, the η^1 -S coordinated thiophene molecule is so weakly coordinated to the metal centre that it undergoes substitution upon further reaction. In complexes where further reaction of the η^1 -S coordinated thiophene molecule occurs, bridged complexes are formed.

4.1.3 η⁵-thiophene transition metal complexes

The η^5 -coordination mode represents the second most common bonding mode of thiophene to transition metal centres. These undergo three main types of reaction, namely, (i) nucleophilic reactions, (ii) reduction and (iii) deuterium exchange.

(i) Nucleophilic reactions

There are two general types of nucleophilic reaction of the η^5 -thiophene complexes (Scheme 4.1). In cationic complexes nucleophiles most often add to the 2 or 5 positions of the ring producing thioallyls, butadienothiolates or S coordinated complexes. Neutral η^5 -complexes typically undergo deprotonation with strong bases.



Scheme 4.1

Angelici *et al.*¹¹ reported that the π -thiophene ligand in $[Mn(CO)_3(\eta^5-C_4H_4S)]^+$ undergoes nucleophilic attack at the 2 position with a range of nucleophiles (Nu = CN⁻, OMe⁻, C₆H₅⁻, SC₄H₃⁻ or H⁻). In the case of the hydrido complex further reaction with HCl forms the unstable 2,3-dihydrothiophene complex (Eqn. 4.7). These results support a mechanism, which is thought to be the initial step in the HDS process, where a C-C double bond of the η^5 -ring is hydrogenated.





A second plausible step in the HDS process involves cleavage of a C-S bond. Evidence for this comes from the nucleophilic reactions of $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]^+$. A variety of nucleophiles including OMe⁻, SMe⁻, SEt⁻, S(i-Pr)⁻, CH(COOMe)₂⁻ or H⁻ activate the thiophene ring to produce a ring opened butadienethiolate structure (Eqn. 4.8).



In the case of thiophenes methylated at the 2 or 5 positions, nucleophilic addition occurs at the non-methylated carbon. It is thought that formation of the butadienethiolate products occurs after initial formation of the allyl sulfide intermediate (Fig. 4.4). This is reasonable since butadienethiolates are often produced from allyl sulfides in organic reactions.



Fig. 4.4: Structure of the Ru allyl sulfide (η^5 -C₅H₅)Ru(η^4 -C₄H₄S•Nuc)

The butadienethiolate complex where R = H and Nu = SEt, reacts with one equivalent of dppe to produce the η^1 -S bound complex illustrated below (Eqn. 4.9).



Eqn. 4.9

Further support for C-S bond cleavage comes from work carried out by Birri *et al.*¹² Reaction of the Os(II) complex $[Os(\eta^6-p-(CH_3)C_6H_4C_3H_7)(\eta^5-C_4H_4S)]^{2+}$ with hydroxide produces the zwitterionic S-oxide complex (Fig. 4.5). Elution of this complex through a silica column converts the S-oxide complex to the C-S cleaved product. Similar Ru complexes have been reported by Rauchfuss.¹³



Fig. 4.5: Structures of the zwitterionic S-oxide complex and the acyl thiolate complex reported by Rauchfuss

For the neutral complex $(\eta^5-C_4H_4S)Cr(CO)_3$ reaction with n-BuLi leads to deprotonation of the thiophene ring at position 2. This intermediate has been used in the formation of a number of bridged complexes (Eqn. 4.10).⁸



Eqn. 4.10

While the dinuclear complex can undergo an extraordinary interchange (Eqn. 4.11), there are no reports of C-S bond cleavage with these neutral complexes.



(ii) Reduction reactions

Angelici *et al.*¹⁴ have reported that C-S bond cleavage of cationic η^5 -thiophene complexes can be achieved reductively. Reduction of $[(\eta^5-C_5(CH_3)_5)Ir(\eta^5-C_4H_4S)]^{2+}$ by two equivalents of Na[H₂Al(OCH₂CH₂OMe)₂] produces an η^4 -complex whereby the Ir centre is coordinated to the diene of the thiophene ring. Further reaction of this complex with basic Al₂O₃ produces a ring-opened complex in which the Ir centre has inserted into the C-S bond of the thiophene molecule (Eqn. 4.12).



Rauchfuss *et al.*¹⁵ reported that reduction of the cationic complex $[(\eta^5-C_5(CH_3)_5)Rh(\eta^5-C_5)Rh(\eta^5-C_5$ $C_4(CH_3)_4S$]²⁺ by cobaltocene produced the η^4 -bound thiophene complex similar to the

Ir complex above. Further reaction of this neutral complex with $Fe_3(CO)_{12}$ leads to desulfurisation to form the complex (η^5 -C₅(CH₃)₅)Rh(C₄(CH₃)₄)Fe(CO)₃ (Eqn. 4.13).



This reaction is unique as most other η^4 -thiophene complexes form the dinuclear bridged complexes when reacted with Fe₃(CO)₁₂.

(iii) Deuterium exchange

Thiophene undergoes deuterium exchange on HDS catalysts before desulfurisation if D₂ is used in the reaction.¹⁶ The η^5 -coordination to the Ru metal centre in the complex, $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]^+$ activates the thiophenic molecule to deuterium exchange. The rate of exchange of protons on the thiophene ring with deuterium follows the trend $H_{2,5} \ge H_{3,4} > CH_3$ (in substituted derivatives). In the presence of CD₃OD, the $H_{2,5}$ in $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]^+$ exchange readily (within three minutes) while there is no exchange of $H_{3,4}$ within 20 hours. In the presence of KOH, reaction times are reduced to 6 h for $H_{3,4}$. A first order dependence on OH⁻ is observed. The following mechanism is postulated (Eqn. 4.14).

The OH⁻ deprotonates the thiophene molecule at position 2 in a slow step. Rapid deuterium transfer to the intermediate follows giving the deutrated product. The rapid exchange of $H_{2,5}$ is possibly due to the stabilisation of the negative charge by vacant d orbitals on the sulfur atom.

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Eqn. 4.14

4.1.4 Ring opened isomerisation reactions

Benzothiophene and dibenzothiophene represent the most difficult thiophenes to desulfurise. C-S bond cleavage of these thiophenes is achieved using the reactive fragment [triphosIrH]⁺ (Scheme 4.2).¹⁷



Scheme 4.2

The Ir inserted benzothiophene complex converts to the thermodynamically more stable 2-vinylthiophenolate complex at 20 °C, while the Ir inserted dibenzothiophene complex is thermally stable up to 170 °C.

C-S bond cleavage, where the metal inserts into the C(vinyl)-S bond of thiophene and benzothiophene, has been observed for many complexes.^{18,19,20} In the systems η^1 -precoordination is believed to weaken the C(vinyl)-S bond and insertion follows

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readily. Recent studies have found that precoordination of a Mn centre in an η^6 -fashion to the benzene ring activates C(aryl)-S bond cleavage.²¹ C-S bond cleavage is observed in the complex $[(\eta^6-C_8H_6S)Mn(CO)_3]^+$ when it is reacted with a further Mn centre. The bimetallic complex $[(\eta^6,\eta^4-C_8H_6S)Mn_2(CO)_7]^+$ is produced whereby the second Mn atom has inserted into the C(aryl)-S bond (Eqn. 4.15).



When the benzene ring is substituted at C(7) with a Me or Et group (Fig. 4.5), the kinetic products (which contain the cleaved C(aryl)-S bond) convert readily to the thermodynamic products (which contain the metal inserted into the C(vinyl)-S bond²² (Eqn. 4.16). Prolonged heating of this complex when R = H does not lead to isomerisation of the kinetic product to the thermodynamic product. Similar results are obtained when $M = Rh^{23}$ or Ru.²⁴



Fig. 4.5: The numbering system for the benzothiophene molecule coordinated to a $Mn(CO)_3$ fragment in an η^6 -fashion through the benzene ring

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Eqn. 4.16



The presence of two metal atoms in these complexes renders the S atom highly nucleophilic and it reacts readily with MeOTf, HBF_4^- and $W(CO)_5$ to produce the S substituted products.²⁴ Hydrogenation of S-substituted complexes (R = CH₃ or H) with a 95:5 mixture of H₂:CO leads to desulfurisation as shown in Eqn. 4.17. In contrast, hydrogenation of the unsubstituted S complex results in cleavage of the Mn-C σ bond and formation of a bridged complex.



Eqn. 4.17

Usually, coordination of a metal fragment to the benzene ring of benzothiophene in an η^6 -fashion activates the benzene ring to nucleophilic addition reactions. The reaction of complex (d) with a metal nucleophile Pt(PPh₃)₃²⁵ results in insertion of Pt(PPh₃)₃ into the C(vinyl)-S bond of [(CO)₃Mn(η^6 -C₈H₆S)]⁺ (Eqn. 4.18).



Precoordination of any of the electrophilic fragments $\text{Ru}(\text{C}_6\text{Me}_6)^{2+}$, $\text{Mn}(\text{CO})_3^+$, Fe(C₅H₅)⁺, Ru(C₅H₅)⁺ or Cr(CO)₃ to the benzene ring of benzothiophene activates the thiophene ring to C(vinyl)-S bond cleavage by Pt(PPh₃)₃. Free benzothiophene does not react with Pt(PPh₃)₃ however. C(vinyl)-S bond cleavage is preferred due to the greater steric interaction that would be present at the C(aryl)-S bond. However, when C(2) of the benzothiophene ligand is substituted C(aryl)-S bond cleavage is observed. Furthermore the S atom is highly nucleophilic and coordinates to the Mn metal centre with loss of CO (Fig. 4.6).



Fig. 4.6: Structure of C(aryl)-S bond inserted Pt(PPh₃)₂ complex

Insertion of the Pt metal centre into 'free' thiophene, benzothiophene and dibenzothiophene has been reported in the literature for Pt.^{26,27} A study by Bianchini *et al.*²⁸ indicated that the activation energy to metal insertion is much greater for dibenzothiophene than for benzothiophene. This barrier accounts for the relatively few literature reports on metal insertion into the C-S bond of dibenzothiophene. Precoordination of a Mn(CO)₃ fragment to one of the benzene rings of dibenzothiophene aids insertion of Pt(PPh₃)₂C₂H₄ into the C-S bond of the thiophene ring (Eqn. 4.19).²⁹



Complex (f) undergoes a slow decarbonylation and the S atom attacks the Mn centre, forming complex (g). This is analogous to that observed for benzothiophene. When the $[(\eta^6-C_{12}H_8S)Mn(CO)_3]^+$ complex is reduced with cobaltocene, the Mn inserted product is obtained (Eqn. 4.20).⁸



Eqn. 4.20

Electron transfer *via* a mechanism involving ring slippage and arene ligand displacement is postulated.³⁰ Treatment of the tetranuclear complex with HBF₄ in CH_2Cl_2 forms the more usual dinuclear complex (Fig. 4.7).



Fig. 4.7: Product formed when the tetranuclear product in Eqn. 4.20 is reacted with HBF_4

Hydrogenation of the tetranuclear species produces the bridging hydride, while methylation followed by hydrogenation results in the desulfurisation of DBT and $[Mn(CO)_5(SCH_3)]$.

In conclusion, while benzothiophene and dibenzothiophene are known to be the most difficult organosulfur complexes to desulfurise, model complexes containing these thiophenes do suggest that C-S bond cleavage is possible. Precoordination of an electrophilic metal fragment to a benzene ring of these thiophenes activates the thiophene ring to C-S bond cleavage, which is achieved by a second metal fragment. Both homometallic and heterometallic systems are successful. Since HDS catalysts consist of heterometallic surfaces, it is plausible that precoordination to one metal can activate the thiophene ring to desulfurisation by the second metal present.

4.1.5 Selenophene transition metal complexes

Selenium complexes have been studied as model systems for thiophene HDS. The complex $[(\eta^5-C_4H_4Se)Mn(CO)_3]^+$ undergoes reduction with NaBH₄ or Red-Al to give $(\eta^4-C_4H_4Se \cdot H)Mn(CO)_3$.³¹ The analogous products are observed with the nucleophiles CN⁻ and H⁻. Reaction of the Ru complex $[(C_5(CH_3)_5)Ru(\eta^5-C_4H_4Se)]^+$ with Red-Al results in C-Se bond cleavage (Eqn. 4.21).

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A novel selenophene complex was formed when $(\eta^5-C_5(CH_3)_5)Re(CO)_2(\eta^2-C_4H_4Se)$ was reacted with M(CO)₄L(THF), M = W, Cr or Mo and L = CO or PPh₃.³² The 2methyl substituted selenophene complex exists as a pair of linkage isomers, converting between the two forms (Eqn. 4.22).^{32, 33} In the analogous thiophene complexes, the thiophene ring is always coordinated to the Re centre through the S atom.



Electron donating groups on selenophene increase the donor ability of the selenium atom, favouring η^1 -Se coordination. Methyl groups inhibit η^2 -coordination for steric reasons. Increasing methyl substitution on the cyclopentadienyl ring favours η^2 coordination as the Re centre becomes more electron rich and has more electron density to 'offload'. The η^2 -coordination has better π -acceptor properties and hence this structure is favoured. Furthermore, increased electron density on the Re centre increases the basicity of the metal, weakening the Re-Se bond.

The reactivity of the η^2 -Se complex, $(\eta^5-C_5(CH_3)_5)Re(CO)_2(\eta^2-C_4H_4Se)$, is illustrated in Scheme 4.3.



Scheme 4.3 (M = W, Cr or Mo and L = CO or PPh₃)

Three products are formed upon reaction with $Fe_2(CO)_9$, (i) where selenophene is η^2 coordinated to the Re centre and η^1 bound to the $Fe(CO)_3$ (ii) where selenophene is η^1 bound to the Re and η^4 -bound to the $Fe(CO)_3$ (iii) and the complex in which $Fe(CO)_3$ has inserted into the Se-C(5) bond. This chemistry is not observed for selenophene that is not precoordinated.

The reactive fragment (η^5 -C₅(CH₃)₅)RhPMe₃ has been shown to cleave a C-Se bond of selenophene.³⁴ The starting reagent (η^5 -C₅(CH₃)₅)Rh(PMe₃)Ph(H) thermally eliminates benzene and the transition metal fragment formed inserts into the selenophene producing the complex illustrated below (Eqn. 4.23).



4.1.5.1 Photochemical studies of $(\eta^{5}-C_{4}H_{4}S)Cr(CO)_{3}$ and $(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{3}$ To date very few photochemical studies have been carried out on $(\eta^{5}-C_{4}H_{4}S)Cr(CO)_{3}$ and $(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{3}$ in comparison with the many thermal studies that have been conducted. The photochemical studies that have been carried out on $(\eta^{5}-C_{4}H_{4}S)Cr(CO)_{3}$ and $(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{3}$ will be discussed below.³⁵

Under a CO atmosphere, UV-vis laser flash photolysis and matrix isolation studies of $(\eta^5-C_4H_4S)Cr(CO)_3$ indicate that $Cr(CO)_6$ is the dominant photoproduct (Eqn. 4.24). In N₂ matrixes both $(\eta^4-C_4H_4S)Cr(CO)_3N_2$ (1972, 1888, 1881 and 2185 cm⁻¹) and $(\eta^5-C_4H_4S)Cr(CO)_2N_2$ are produced (1932, 1867 and 2154 cm⁻¹).

$$\begin{array}{c} & & & \\ & & \\ OC & \\ & & \\ CO & \\ & \\ CO & \\ \end{array} \end{array} \xrightarrow{h\nu} Cr(CO)_6 + C_4H_4S \qquad Eqn. 4.24$$

In the absence of CO, the thiophene ring undergoes replacement by arene ligands as confirmed by room temperature NMR studies of $(\eta^5-C_4H_4S)Cr(CO)_3$ in C_6D_6 , while under a CO atmosphere the exchange reaction is suppressed and $Cr(CO)_6$ is the only photoproduct observed (Scheme 4.4).



Scheme 4.4

In the presence of trapping ligands such as PPh₃ the thiophene ring does not undergo exchange, instead one of the CO ligands is displaced. TRIR studies further confirmed that CO loss occurs upon photolysis. IR bands have been assigned to $(\eta^5 - C_4H_4S)Cr(CO)_2$ (heptane) and $(\eta^4 - C_4H_4S)Cr(CO)_4$.

Photolysis of a CO saturated C_6D_{12} solution of the related complex $(\eta^5-C_4H_4Se)Cr(CO)_3$ results in the haptotropic shift of the selenophene ring from $\eta^5 \rightarrow \eta^4$ coordination. IR spectroscopy confirms the formation of $(\eta^4-C_4H_4Se)Cr(CO)_4$ (2014, 1956 and 1914 cm⁻¹) along with Cr(CO)_6. The corresponding ¹H NMR spectroscopic studies also reveal the formation of $(\eta^4-C_4H_4Se)Cr(CO)_4$.

Photolysis of the parent complex in the presence of the trapping ligand, C_5H_5N , produces the dicarbonyl species, $(\eta^5-C_4H_4Se)Cr(CO)_2(\eta^1-N-C_5H_5N)$ (1920 and 1859 cm⁻¹) and the tricarbonyl species $(\eta^4-C_4H_4Se)Cr(CO)_3(\eta^1-N-C_5H_5N)$ (1974 and 1854 cm⁻¹), which involves a η^4 -coordinated selenophene ring (Eqn. 4.25). A third carbonyl band for the tricarbonyl species was not observed in the IR spectrum.



TRIR studies ($\lambda_{exc} = 355 \text{ nm}$) of (η^5 -C₄H₄Se)Cr(CO)₃ in CO saturated heptane solution result in the formation of (η^5 -C₄H₄Se)Cr(CO)₂(heptane), (η^4 -C₄H₄Se)Cr(CO)₄ and a species with IR bands at 2046, 2001 and 1957 cm⁻¹.

The results presented in this chapter are a continuation of an earlier study into the photochemistry of $(\eta^5-C_4H_4Se)Cr(CO)_3$. Matrix isolation experiments were carried out in inert (Ar and CH₄) and reactive (CO and N₂) matrices and followed spectroscopically in the UV-vis and IR to provide evidence for ring slip intermediates and the stepwise conversion of $(\eta^5-C_4H_4Se)Cr(CO)_3$ to Cr(CO)₆.
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4.2 **RESULTS**

The IR spectroscopic data for $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) and all the photoproducts obtained during these matrix experiments is given in Table 4.1.

COMPLEX		VN=N	ν _{co}	MATRIX	TEMP.
		(cm ⁻¹)	(cm ⁻¹)		(K)
Deposition bands :					
$(\eta^5-C_4H_4Se)Cr(CO)_3$	(1)	-	1989, 1924, 1906	Ar	20
$(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{3}$	(1)	an.	1982, 1916, 1891	CH_4	20
$(\eta^5-C_4H_4Se)Cr(CO)_3$	(1)		1982, 1914, 1893	N_2	20
$(\eta^5-C_4H_4Se)Cr(CO)_3$	(1)	-	1976, 1905, 1883	CO/Ar	20
Photoproduct bands :					
$(\eta^4$ -C ₄ H ₄ Se)Cr(CO) ₃	(2)	-	2046, 2001, 1957	Ar	20
$(\eta^4$ -C ₄ H ₄ Se)Cr(CO) ₂	(3)		2035, 1934	Ar	20
$(\eta^4$ -C ₄ H ₄ Se)Cr(CO) ₃	(2)		2044, 1997, 1953	CH ₄	20
$(\eta^4$ -C ₄ H ₄ Se)Cr(CO) ₂	(3)	-	2032, 1928	CH ₄	20
$(\eta^4-C_4H_4Se)Cr(CO)_3N_2$	2 (4)	2161	2047, 2001, 1958	N_2	20
$(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{2}N_{2}$	(5)	2171	1936, 1879	N_2	20
$(\eta^4-C_4H_4Se)Cr(CO)_3$	(2)	-	2044, 1996, 1953	CO/Ar	20
$(\eta^4-C_4H_4Se)Cr(CO)_4$	(6)	-	2031	CO/Ar	20
$(\eta^2-C_4H_4Se)Cr(CO)_5$	(7)	-	2068	CO/Ar	20
Cr(CO) ₆	(8)	-	1985	CO/Ar	20

Table 4.1: Spectroscopic data for $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) and all its photoproducts obtained during these matrix experiments

Fig. 4.8 illustrates the IR spectra for $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) in both inert (Ar and CH₄) and reactive (N₂ and CO) matrixes. Depending on the host matrix employed, varying degrees of matrix splitting are observed. CO doped Ar matrixes of varying percentages produce the best IR spectra.



Fig. 4.8: (a) IR spectrum of $(\eta^5-C_4H_4Se)Cr(CO)_3$ following deposition in an Ar matrix

- (b) IR spectrum of $(\eta^5$ -C₄H₄Se)Cr(CO)₃ following deposition in an CH₄ matrix
- (c) IR spectrum of $(\eta^5-C_4H_4Se)Cr(CO)_3$ following deposition in a N₂ matrix
- (d) IR spectrum of (η⁵-C₄H₄Se)Cr(CO)₃ following deposition in a CO/Ar matrix. All are recorded at 20 K.



Fig. 4.9 : Representation of structures of the parent complex (1) and photoproducts (2)-(8) observed during these matrix isolation studies



Fig. 4.10: UV-vis spectrum of (η⁵-C₄H₄Se)Cr(CO)₃ (1), observed in all matrixes at 20 K following deposition

The UV-vis spectrum for $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) is similar for all host matrixes and is shown in Fig. 4.10. $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) contains a λ_{max} at 409 nm due to $n \rightarrow \pi^*$ transition in the carbonyl groups, a band at 360 nm due to $\pi \rightarrow \pi^*$ transition in the carbonyl groups and a broad band is observed at lower energy centred at 500 nm due to metal to charge transfer transition between the Cr centre and the aromatic rings.

4.2.1 Photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in Ar matrixes

A sample of (η^5 -C₄H₄Se)Cr(CO)₃ (1) was deposited in an Ar matrix at 20 K. The metal carbonyl stretching frequencies of the parent complex occur at 1989, 1924 and 1906 cm⁻¹. Irradiation of this sample with long wavelength irradiation either monochromatic or broadband in nature fails to produce any new bands in the IR spectrum. However, photolysis at either $\lambda_{exc} > 410$ nm or $\lambda_{exc} = 405$ nm results in the formation of new bands at 2047, 2001 and 1957 cm⁻¹. These bands have been assigned to the ring slipped η^4 -coordinated complex, (η^4 -C₄H₄Se)Cr(CO)₃ (2) (Fig. 4.11).

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Fig. 4.11: Difference spectrum illustrating the new bands produced following photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (1) with $\lambda_{exc} = 405$ nm in an Ar matrix at 20 K for 100 min

These three bands belong to the same species. This was confirmed when an Ar matrix containing (η^5 -C₄H₄Se)Cr(CO)₃ (1) was photolysed with $\lambda_{exc} = 405$ nm at short time intervals. The three peaks grow in at the same rate and hence are related to each other (Fig. 4.12). The positive peaks represent formation of the photoproduct, while the negative peaks represent depletion of the parent complex. The corresponding UV-vis spectrum for the ring slipped photoproduct is shown in Fig. 4.13. Photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (1) results in a decrease in the absorption of the parent bands in the UV-vis spectrum in the region 350-440 nm while an increase in absorption is observed from 440-475 nm.



Fig. 4.12: IR difference spectra illustrating that the three bands observed upon photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) with $\lambda_{exc} = 405$ nm in an Ar matrix grow in at the same rate and thus are related to each other





When $(\eta^4-C_4H_4Se)Cr(CO)_3$ (2) in an Ar matrix was photolysed with higher energy monochromatic irradiation, $\lambda_{exc} = 365$ nm, a reduction in the bands at 2047, 2001 and 1957 cm⁻¹, and the parent bands in the IR spectrum was observed. In addition, two new carbonyl bands formed at 2035 and 1934 cm⁻¹ (Fig. 4.14). The species characterised by bands at 2035 and 1934 cm⁻¹ is assigned to the CO loss product, $(\eta^4-C_4H_4Se)Cr(CO)_2$ (3). A band representing 'free' CO is observed at 2137 cm⁻¹. An alternative assignment for these bands is the ring inserted complex, where the Cr metal centre has inserted into the C-Se bond. This structure was discounted; the reasons for which are presented in the discussion.



Fig. 4.14: Difference spectrum illustrating the effect of $\lambda_{exc} = 365$ nm on the photoproduct (η^4 -C₄H₄Se)Cr(CO)₃ (**2**) in an Ar matrix at 20 K

Subsequent photolysis of this matrix with $\lambda_{exc} = 334$ nm reduces the intensity of the bands in the IR spectrum due to the tricarbonyl species (2) further while simultaneously regenerating the parent complex. The intensity of the carbonyl bands assigned to the CO loss product (3) is not affected by this irradiation wavelength, however.

The CO loss product (3) is produced most efficiently upon irradiation with the band pass filter, $320 < \lambda_{exc} < 395$ nm. Fig. 4.15 confirms that the bands at 2035 and 1934

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cm⁻¹ grow in at the same rate and hence are assigned to the same species. Irradiation with this filter decreases the intensity of the IR bands of the ring slip product, $(\eta^4-C_4H_4Se)Cr(CO)_3$ (2). The UV-vis spectrum obtained following the photolysis experiments given in Fig. 4.14 is illustrated in Fig. 4.16. The changes in this spectrum are similar to that in Fig. 4.13.





(1) with a band pass filter, $320 < \lambda_{exc} < 395$ nm, in an Ar matrix at 20 K

(* = $(\eta^4 - C_4 H_4 Se)Cr(CO)_3$ (2) and * = $(\eta^4 - C_4 H_4 Se)Cr(CO)_2$ (3))



Fig. 4.15 : (b) Corresponding stretch observed for uncoordinated CO following photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) with a bandpass filter $320 < \lambda_{exc} < 395$ nm in an Ar matrix



Fig. 4.16: UV-vis spectrum of the CO loss product, (η⁴-C₄H₄Se)Cr(CO)₂ (3), in an Ar matrix at 20 K, before and after photolysis

Following the production of both (η^4 -C₄H₄Se)Cr(CO)₃ (**2**) and (η^4 -C₄H₄Se)Cr(CO)₂ (**3**) by photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (**1**) in an Ar matrix, broadband irradiation at λ_{exc} > 550, > 410 or > 300 nm bleaches (η^4 -C₄H₄Se)Cr(CO)₃ (**2**) and reforms the starting material bands (Fig. 4.17). The CO loss product (**3**) (2035 and 1934 cm⁻¹) is unaffected by broadband irradiation at these wavelengths. Once formed the CO loss product (**3**) is stable to broadband irradiation.





4.2.2 Photolysis of $(\eta^5 - C_4 H_4 Se)Cr(CO)_3$ in CH₄ matrixes

Deposition of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) in CH₄ matrixes produces bands at 1982, 1916 and 1891 cm⁻¹. In general photolysis of the CH₄ matrixes yields similar results to those observed in Ar matrixes. Both the ring slip product, $(\eta^4-C_4H_4Se)Cr(CO)_3$ (2) (2044, 1997 and 1953 cm⁻¹) and the CO loss product, $(\eta^4-C_4H_4Se)Cr(CO)_2$ (3) (2032 and 1928 cm⁻¹) are observed upon photolysis with a variety of filters. Long wavelength irradiation (either monochromatic $\lambda_{exc} = 436$ nm or broadband $\lambda_{exc} > 500$ nm) fails to produce either of the photoproducts. Higher energy irradiation however at $\lambda_{exc} > 410$ nm or $\lambda_{exc} = 405$ nm again produces the ring slip product. Monochromatic irradiation with $\lambda_{exc} = 405$ nm is most efficient at producing the ring slip photoproduct (2), with the band pass filter 320 < λ_{exc} < 395 nm being most efficient at producing the CO loss product (3).

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4.2.3 Photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in N₂ matrixes

Following deposition of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) in a N₂ matrix IR bands were observed at 1982, 1914 and 1893 cm⁻¹. Irradiation of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) in a N₂ matrix with $\lambda_{exc} = 405$ nm results in the depletion of the parent bands and appearance of new bands in the IR spectrum at 2047, 2001 and 1958 cm⁻¹ (Fig.4.18) in addition to a N₂ stretch at 2161 cm⁻¹. The presence of the dinitrogen stretch indicates the presence of a coordinatively unsaturated metal fragment. These bands are assigned to the ring slip product, $(\eta^4-C_4H_4Se)Cr(CO)_3N_2$ (4) (Fig.4.19).

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Fig. 4.19: Difference spectrum illustrating the N₂ stretch at 2161 cm⁻¹ following photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (1) with $\lambda_{exc} = 405$ nm for 10 min

When a N₂ matrix is further irradiated with $320 < \lambda_{exc} < 395$ nm, the ring slip product (4) initially increases in intensity and four new bands are observed to form at 2172, 2137 1934 and 1879 cm⁻¹. The bands at 1934 and 1879 cm⁻¹ have been assigned to the CO loss product, (η^5 -C₄H₄Se)Cr(CO)₂N₂ (5). The band at 2172 cm⁻¹ represents the N₂ stretch and the band at 2137 cm⁻¹ is due to 'free' CO (Fig. 4.20). When this N₂ matrix is subsequently photolysed at $\lambda_{exc} > 500$ nm, the bands assigned to the nitrogen species (η^4 -C₄H₄Se)Cr(CO)₃N₂ (4) are bleached and the parent is regenerated. The dicarbonyl bands (5) are unaffected however (Fig. 4.21).





Fig. 4.20: (a) Difference spectrum illustrating the ring slip (4) and CO loss (5) products produced in a N₂ matrix at 20 K upon photolysis with $320 < \lambda_{exc} < 395$ nm



Fig. 4.20: (b) The corresponding difference spectrum illustrating the N₂ and 'free' CO stretches



Fig. 4.21: IR spectrum illustrating the effect of broadband irradiation ($\lambda > 500$ nm) on complexes (4) and (5) in a N₂ matrix

4.2.4 Photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in CO doped Ar matrixes

Deposition of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in CO doped Ar matrixes results in the observation of carbonyl bands at 1976, 1905 and 1883 cm⁻¹. Irradiation of this matrix at 20 K with $\lambda_{exc} = 405$ nm produces bands that are assigned to the ring slip product $(\eta^4-C_4H_4Se)Cr(CO)_3$ (2) at 2044, 1996 and 1953 cm⁻¹ (Fig. 4.22). Subsequent photolysis with $320 < \lambda_{exc} < 395$ nm increases the intensity of these bands while long wavelength irradiation at $\lambda_{exc} > 500$ nm results in the bleaching of the carbonyl bands at 2044, 1996 and 1953 cm⁻¹ (2) and regeneration of the parent complex.



Fig. 4.22: IR spectrum following photolysis of $(\eta^5 - C_4 H_4 Se)Cr(CO)_3$ (1) with $\lambda_{exc} = 405$ nm in a 5 % CO/Ar matrix at 20 K

Extended photolysis of a 5 % CO/Ar matrix with $\lambda_{exc} = 405$ nm or $320 < \lambda_{exc} < 395$ nm produces Cr(CO)₆, which is characterised by the intense band at 1985 cm⁻¹ (Fig. 4.23). These results provide evidence of a possible sequential ring slip of the selenophene ring from $\eta^5 \rightarrow \eta^4 \rightarrow \eta^2$ coordination, which finally undergoes replacement of the selenophene ring with a sixth carbonyl group to produce the hexacarbonyl, Cr(CO)₆ (8).



Fig. 4.23: Difference spectrum illustrating the intense band of $Cr(CO)_6$ (8) at 1985 cm⁻¹ produced after extended photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (1) in a 5 % CO/Ar matrix at 20 K with 320 < λ_{exc} < 395 nm.

4.2.5 Photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in CO doped CH₄ matrixes

Photolysis of a 5 % CO/CH₄ matrix with $\lambda_{exc} = 405$ nm results in formation of three bands at 2044, 1996 and 1953 cm⁻¹, as in the previous experiment. In addition to a band at 2031 cm⁻¹, which was tentatively assigned to (η^4 -C₄H₄Se)Cr(CO)₄ (**6**), a band at 2068 cm⁻¹ (7) was cautiously assigned to (η^2 -C₄H₄Se)Cr(CO)₅ (Fig. 4.24). Accompanying bands for the tetracarbonyl and pentacarbonyl species are masked by the parent bands and the species (η^4 -C₄H₄Se)Cr(CO)₃ (**2**). A discussion regarding these assignments will be given in section 4.3.



Fig. 4.24: Difference spectra illustrating the carbonyl bands that are tentatively assigned to $(\eta^4 - C_4 H_4 Se)Cr(CO)_4$ (6) (*) and $(\eta^2 - C_4 H_4 Se)Cr(CO)_5$ (7) (*), which are produced following photolysis of a 5 % CO/CH₄ matrix with $\lambda_{exc} = 405$ nm

4.3 **DISCUSSION**

4.3.1 N₂ matrixes

Monochromatic irradiation ($\lambda_{exc} = 405 \text{ nm}$) of (η^5 -C₄H₄Se)Cr(CO)₃ (1) in a N₂ matrix at 20 K produces a three band pattern in the carbonyl region of the IR spectrum; 2047, 2001 and 1958 cm⁻¹. A dinitrogen stretch is also observed at 2161 cm⁻¹. The observed photoproduct in the N₂ matrix was assigned the structure (η^4 -C₄H₄Se)Cr(CO)₃N₂ (4). The selenophene ring has undergone a ring slip from $\eta^5 \rightarrow \eta^4$ and donates less electron density to the Cr metal centre in comparison to the electron density donated to the Cr centre in the parent complex, (η^5 -C₄H₄Se)Cr(CO)₃ (1). Hence the carbonyl stretches of the photoproduct occur at higher wavenumber than the starting material carbonyl bands ($\nu_{CO} = 1982$, 1914 and 1893 cm⁻¹). Observation of the N₂ stretch and no evidence for 'free' CO confirms that the selenophene ring has undergone a ring slip. The parent complex (η^5 -C₄H₄Se)Cr(CO)₃ (1) has an electron count of eighteen and there is no vacant metal site for a N₂ molecule to coordinate. The selenophene ring must undergo a haptotropic shift upon irradiation to produce a vacant site that can be occupied by the N₂ molecule, in the absence of CO loss.

Subsequent photolysis of a N₂ matrix containing the photoproduct, (η^4 -C₄H₄Se)Cr(CO)₃N₂ (4) photoproduct, with 320 < λ_{exc} < 395 nm for an extended period of time results in a decrease in the bands associated with (η^4 -C₄H₄Se)Cr(CO)₃N₂ (4) and the appearance of four new bands at 2171, 2137, 1936 and 1879 cm⁻¹. The bands at 2171, 1936 and 1879 cm⁻¹ have been assigned to (η^5 -C₄H₄Se)Cr(CO)₂N₂ (5) by comparison with the analogous thiophene complex, (η^5 -C₄H₄Se)Cr(CO)₂N₂ (ν_{CO} = 1932 and 1879 cm⁻¹ and $\nu_{N=N}$ = 2154 cm⁻¹). While the band at 2137 cm⁻¹ represents 'free' CO. The dicarbonyl dinitrogen thiophene complex was observed to form during photolysis of the complex (η^5 -C₄H₄S)Cr(CO)₃ in a N₂ matrix.³⁵ Solution photochemistry of (η^5 -C₄H₄S)Cr(CO)₃ in the presence of a trapping ligand, PPh₃, with a Xe-arc lamp also provided evidence for the dicarbonyl complex, (η^5 -C₄H₄S)Cr(CO)₂PPh₃, which was observed to have ν_{CO} = 1906 and 1850 cm⁻¹.³⁵ In the dicarbonyl dinitrogen complex, (η^5 -C₄H₄Se)Cr(CO)₂N₂ (**5**), the selenophene ring has maintained its η^5 -coordination mode. There is a greater donation of electron density from the selenophene ring in this

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complex compared to the η^4 -tricarbonyl complex. In addition there is one less carbonyl ligand present in this photoproduct. Therefore the extra electron density is 'off-loaded' onto a reduced number of carbonyl ligands compared to the tricarbonyl complex, resulting in the carbonyl bands of the dicarbonyl complex occurring at lower wavenumber compared to the carbonyl bands of the tricarbonyl complex. The assignment of the bands at 1932 and 1879 cm⁻¹ to the (η^5 -C₄H₄Se)Cr(CO)₂N₂ species are accurate. Carbonyl bands for (η^6 -C₆H₆)Cr(CO)₂N₂ were observed at 1940 and 1899 cm⁻¹ upon photolysis of (η^6 -C₆H₆)Cr(CO)₃ in the presence of N₂.³⁶ These carbonyl bands for the (η^5 -C₄H₄Se)Cr(CO)₂N₂.

4.3.2 Ar or CH₄ matrixes

In Ar or CH₄ matrixes, photolysis of (η^5 -C₄H₄Se)Cr(CO)₃ (1) with high energy irradiation produces the same three band pattern in the carbonyl region of the IR spectrum ($\nu_{CO} = 2047$, 2001 and 1957 cm⁻¹) that was observed upon photolysis of N₂ matrixes. Hence the assignment of the structure of the initial photoproduct in Ar or CH₄ matrixes to (η^4 -C₄H₄Se)Cr(CO)₃ (2), where the two diene fragments each donate two electrons to the Cr metal centre. In these matrixes, Ar and CH₄ act as inert hosts and do not coordinate to the vacant site on the metal centre. At this point however, the photochemistry in N₂ and Ar or CH₄ matrixes diverge.

Subsequent higher energy photolysis ($\lambda_{exc} = 365 \text{ nm}$) of either the Ar or CH₄ matrix results in a decrease in the intensity of the three bands at 2046, 2001 and 1957 cm⁻¹ and the appearance of three new bands at 2137, 2035 and 1934 cm⁻¹. The band at 2137 cm⁻¹ represents uncoordinated CO while the bands at 2035 and 1934 cm⁻¹ correspond to two carbonyl groups. The structure of this species has been assigned to the species, (η^4 -C₄H₄Se)Cr(CO)₂ (**3**). The ring slipped tricarbonyl complex is the precursor to the dicarbonyl species.

It is unusual that the tricarbonyl complexes $(\eta^4-C_4H_4Se)Cr(CO)_3$ (produced upon photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in an Ar matrix) and $(\eta^4-C_4H_4Se)Cr(CO)_3N_2$ (produced upon photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in a N₂ matrix) have similar carbonyl bands in the IR spectrum; v_{CO} for these complexes are ≈ 2046 , 2000 and 1956

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cm⁻¹. Coordination of a N₂ molecule to the metal centre would be expected to cause a shift in the carbonyl bands. The complex (η^4 -2,3-dimethylbutadiene)Cr(CO)₃ has ν_{CO} = 1999, 1942 and 1880 cm⁻¹, while the dicarbonyl complex with a N₂ molecule coordinated to the metal centre, (η^4 -2,3-dimethylbutadiene)Cr(CO)₃N₂ has ν_{CO} = 2004, 1929 and 1909 cm⁻¹.³⁷

An alternative structure that the species (η^4 -C₄H₄Se)Cr(CO)₂ (**3**) might assume involves insertion of the Cr metal centre into the C-Se bond of the selenophene ring. In this structure selenophene acts as a one-electron donor and with the electron donated by the carbon atom of the selenophene ring and the four electrons donated by the two carbonyl groups this complex represents a twelve-electron intermediate. This coordination mode is documented in the literature (Fig. 4.1).

An X-ray crystal structure of the Ir complex, $[(\eta^5-C_5(CH_3)_5)Ir(\eta^4-2,5-(CH_3)_2C_4H_2S)]$,¹⁴ shows that the S atom lies 0.905 Å out of the C(2)-C(3)-C(4)-C(5) plane away from the Ir centre. A crystal structure has not been recorded for the analogous unsubstituted complex however.



Fig. 4.1

Reaction of C₄H₄Se with $[(\eta^5-C_5(CH_3)_5Rh(P(CH_3)_3)(H)Ph)]$, has been shown to form the selenophene ring-opened complex, $[(\eta^5-C_5(CH_3)_5Rh(P(CH_3)_3)(C,Se-C_4H_4Se))]$.³⁴ Vicic *et al.*³⁴ found that this ring insertion reaction was irreversible (in contrast to the analogous reaction with thiophene which reverts to starting material upon heating). Further literature data suggests that the ring inserted complex of $[(\eta^5-C_5(CH_3)_5)Ir(\eta^5 2,5-(CH_3)_2C_4H_2S)]$ is more thermodynamically stable compared to the η^4 analogue.¹⁴ Ring insertion is not observed upon photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ in a N₂ matrix. It

is likely that the matrix is too rigid to allow the necessary rotation for ring insertion to occur.

4.3.3 CO doped Ar matrixes

A similar three band pattern to that observed in Ar, CH₄ and N₂ was observed when $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) was irradiated in CO doped Ar matrixes with short wavelength photolysis ($\lambda_{exc} = 405 \text{ nm or } \lambda_{exc} > 410 \text{ nm}$). Bands at 2045, 1996 and 1953 cm⁻¹ are assigned to ($\eta^4-C_4H_4Se$)Cr(CO)₃ (2). Extended photolysis with $320 < \lambda_{exc} < 395 \text{ nm}$ reveals formation of Cr(CO)₆ (8). The CO loss products, (3) and (5), observed in Ar, CH₄ and N₂ matrixes were not observed in these experiments. The presence of additional CO molecules prevents the formation of the dicarbonyl complexes. If the tricarbonyl complex produces a dicarbonyl complex upon photolysis, the extra CO molecules are small enough to diffuse through the matrix and occupy the vacant site. The net effect is that there is no observation of the formation of any dicarbonyl complexes.

Experiments carried out at short time intervals reveal the presence of tetra and penta carbonyl species. Photolysis of a CO doped Ar matrix with $\lambda_{exc} = 405$ nm results in the formation of a band at 2031 cm⁻¹. The assignment of this band as (η^4 -C₄H₄Se)Cr(CO)₄ (**6**) is based on comparison with the complex (η^2 -C₂H₄)₂Cr(CO)₄, which has $\nu_{CO} = 2036$, 1949 and 1913 cm⁻¹.³⁸ Inspection of Fig. 4.23 in the results section, shows that the remaining peaks for this tetracarbonyl complex could be masked by the depletion of the parent bands or the photoproduct bands for (η^4 -C₄H₄Se)Cr(CO)₃ (**2**). The depletion of the parent band at ≈ 1913 cm⁻¹ contains a shoulder at higher wavenumber (marked by *), which appears to increase in intensity with successive photolyses. This is suggested as evidence of a band growing in *i.e.* the low energy band for the tetracarbonyl species, (η^4 -C₄H₄Se)Cr(CO)₄ (**6**).

A band for the pentacarbonyl complex, $(\eta^2-C_4H_4Se)Cr(CO)_5$ (7), has been tentatively assigned as 2068 cm⁻¹ by comparison with the species $(\eta^2-cis-C_8H_{14})Cr(CO)_5$, which has $v_{CO} = 2070$, 1954 and 1948 cm⁻¹.³⁹ Inspection of Fig. 4.23 illustrates the two remaining absorption bands of the pentacarbonyl species coincide with the absorption

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Discussion

bands of the photoproduct (η^4 -C₄H₄Se)Cr(CO)₄ (6). A shoulder at higher wavenumber than to the tetracarbonyl band at 1953 cm⁻¹ is also assigned to the pentacarbonyl species.

It is possible that because the tetra and penta complexes are intermediates in the formation of $Cr(CO)_6$ (8), they are produced in very small amounts. Or alternatively they have very low molar extinction coefficients. Since these tetra and penta carbonyl species are reactive intermediates, their extinction coefficients cannot be determined.

Experiments carried out in CO doped Ar matrixes suggest that the photolytic removal of the selenophene ring occurs in a stepwise fashion: $\eta^5 \rightarrow \eta^4 \rightarrow \eta^2$. Each successive ring slip occurs with the coordination of an additional CO molecule, so that the process can also be described as stepwise in terms of CO coordination: $M(CO)_3 \rightarrow M(CO)_4 \rightarrow M(CO)_5 \rightarrow M(CO)_6$.

Conclusion

4.4 CONCLUSION

Matrix isolation studies of $(\eta^5-C_4H_4Se)Cr(CO)_3(1)$ have revealed evidence for a stepwise haptotropic shift from $\eta^5 \rightarrow \eta^4 \rightarrow \eta^2$ for the photochemical removal of the selenophene ring from the Cr metal centre.

In CO matrixes at 20 K, short wavelength photolysis, ($\lambda_{exc} = 405$ nm), produces a three carbonyl band pattern assigned to (η^4 -C₄H₄Se)Cr(CO)₃ (**2**). Extended photolysis indicates formation of Cr(CO)₆ (**8**), characterised by an intense carbonyl band at 1985 cm⁻¹.

Photolysis of $(\eta^5-C_4H_4Se)Cr(CO)_3$ (1) in inert matrixes revealed the formation of the three carbonyl band pattern observed in CO matrixes. In addition subsequent photolysis of these matrixes produced the CO loss species $(\eta^4-C_4H_4Se)Cr(CO)_2$ (3). In N₂ matrixes, the initial photoproduct produced is the complex, $(\eta^4-C_4H_4Se)Cr(CO)_3N_2$ (4), with extended photolysis producing the CO loss product $(\eta^5-C_4H_4Se)Cr(CO)_2N_2$ (5) from species (4). Thus the photochemistry of $(\eta^5-C_4H_4Se)Cr(CO)_3$ is dependent on the conditions employed.

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Photochemical studies of $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+X^$ complexes in various solvents

Abstract

Steady state photolytic studies of $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-(CH_{3})_{2}CHC_{6}H_{5})]PF_{6}$ in a variety of solvents show that the arene ring undergoes replacement when ligands are present and the metal complex undergoes decomposition in the absence of ligands. CO was employed as the ligand of choice. $[(\eta^{5}-C_{5}H_{5})Fe(CO)_{3}]PF_{6}$ was formed upon photolysis in CO purged acetone and dichloromethane solutions while $[(\eta^{5}-C_{5}H_{5})Fe(CH_{3}CN)_{2}(CO)]PF_{6}$ was produced in CO purged acetonitrile solutions. The decomposition products include ferrocene, 'free' arene and Fe²⁺. These results along with laser flash photolysis studies point to a mechanism involving a solvated intermediate of the type $[(\eta^{5}-C_{5}H_{5})Fe(solv)_{3}]^{+}$. In addition preliminary steady state photolysis studies were carried out on the heteroaromatic complex, $[(\eta^{5}-C_{5}H_{5})Fe(n^{5}-2,5-(CH_{3})_{2}C_{4}H_{2}S)]BF_{4}$.

5.1 LITERATURE SURVEY

5.1.1 Photochemistry of $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$ complexes

Nesmeyanov *et al.* first reported quantitative photochemical experiments on compounds of the type, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$.¹ Their investigations indicated that complexes of the type, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$, underwent decomposition upon irradiation in various organic solvents (Eqn. 5.1). The products of this reaction were ferrocene, Fe²⁺ and free arene.

$$2[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-arene)]PF_{6} \xrightarrow[\text{organic}]{\text{organic}} (\eta^{5}C_{5}H_{5})_{2}Fe + Fe^{2+} + 2arene \quad \text{Eqn. 5.1}$$

Gill and Mann² extended this work by exchanging the xylene ligand in the complex, $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]PF_6$ with either three two-electron donor ligands or one 6-electron donor ligand (Table 5.1).

Ligand	Product	Yld	Solvent	Method of
		(%)		irradiation
<i>p</i> -CNC ₆ H ₄ CH ₃	$[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-p-CNC_{6}H_{4}CH_{3})]^{+}$	84	Acetone	sunlight
$P(OC_6H_5)_3$	$[(\eta^{5}-C_{5}H_{5})Fe(P(OC_{6}H_{5})_{3})_{3}]^{+}$	52	CH_2Cl_2	sunlight
СО	$[(\eta^{5}-C_{5}H_{5})Fe(CO)_{3}]^{+}$	50	Acetone	Corning052
$(\eta^{6}\text{-}C_{6}(CH_{3})_{6})$	$[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-C_{6}(CH_{3})_{6})]^{+}$	76	~	sunlight
Triphos	$[(\eta^5-C_5H_5)Fe(triphos)]^+$	73	Acetone	436 nm

Table 5.1

Photolysis of $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]PF_6$ in degassed acetone or dichloromethane solutions in the presence of a suitable ligand resulted in the exchange of the three coordination sites occupied by *p*-xylene (Eqn. 5.2). These reactions occur cleanly at room temperature with high conversions.

$$[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-p-xyl)]PF_{6} \xrightarrow{hv} [(\eta^{5}-C_{5}H_{5})FeL_{3}]PF_{6} + p-xylene Eqn. 5.2$$

Literature survey

Application of experimental information³ and extended theoretical models for the system, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$, suggest that the mechanism for *p*-xylene exchange is dissociative.^{4, 2} It is believed that total dissociation of the η^6 -ligand occurs to give $[(\eta^5-C_5H_5)Fe(solv)]^+$ prior to ligand attack (Eqn. 5.3).

$$[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-arene)]PF_{6} \xrightarrow{h\nu} [(\eta^{5}-C_{5}H_{5})Fe(solv)]^{+} \underbrace{3L} [(\eta^{5}-C_{5}H_{5})FeL_{3}]^{+}$$

Eqn. 5.3

An associative mechanism would involve arene ring slippage. The ring slipped intermediate could then reconvert to starting material by expulsion of solvent molecules or could undergo replacement of the solvent molecules by ligand molecules, beginning the sequential replacement of the remaining coordination positions occupied by the arene molecule. However, it is unlikely that the solvated complex in which the arene is bound in an η^2 - or η^4 -fashion would have a lifetime long enough to undergo the second order reaction with the ligands, at the concentrations used in this study.

Schrenk and Mann⁵ have studied the photochemical removal of the *p*-xylene molecule from the $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]X$ complex as a function of solvent and counterion. Quantum yields for the appearance of $[Fe(phen)_3]^{2+}$, formed upon irradiation of solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]X$ and 1,10-phenanthroline, were determined. They found that the quantam yield (ϕ) for arene replacement varied from 0.81 in water to 0.58 in dichloromethane solution for X = BF₄⁻ (Table 5.2). The variation of ϕ is indicative of the assistance of solvent in the chemical step, in which *p*xylene is released from the central iron atom. This effect is more pronounced for X⁻ = SbF₆⁻, where $\phi_{CH_2Cl_2} = 0.084$ and $\phi_{CH_3CN} = 0.72$. Conductivity data for 0.02 M solutions of BF₄⁻ and SbF₆⁻ salts in CH₃CN solutions suggests the almost complete dissociation of these salts into free ions. Thus, for acetonitrile solutions, the assisting component is the solvent.

Chapter 5		Literature survey
Anion	Conditions	φ
BF4	H ₂ O/0.1 M H ₂ SO ₄	0.81
BF ₄	Propylene Carbonate	0.79
BF ₄	Methanol	0.77
BF_4	CH ₃ CN	0.72
SbF ₆	CH ₃ CN	0.72
SbF ₆ ⁻	CH_2Cl_2	0.084
CF ₃ SO ₃ ⁻	CH_2Cl_2	0.60
BF_4	CH_2Cl_2	0.58
PF ₆	CH_2Cl_2	0.12
AsF ₆	CH_2Cl_2	0.087

Table 5.2

In contrast to the results obtained for the irradiation of acetonitrile solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]X$, photolysis of dichloromethane solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]X$ show a strong dependence on counterion: SO₃CF₃⁻ > BF₄⁻ >> PF₆⁻ > AsF₆⁻ \cong SbF₆⁻. Conductivity data for the salts in dichloromethane solutions indicated that substantial fractions of the ions in solution are ion pairs. This variation suggests that the paired anion (*i.e.* the anion is bound to the metal centre) assisted the removal of *p*-xylene as a nucleophile in acetonitrile solutions, decreasing as indicated above.

 PF_6 , AsF_6 and SbF_6 exhibit ion pairing to the same extent as BF_4 . However, their quantum yields are smaller indicating that they are the poorer nucleophiles in the solvent assisted step. This is consistent with the poor coordinating ability of these anions.⁶

The medium assistance involved in these photolysis reactions contrasts with the dissociative behaviour observed for ligand field excited states in other organometallic transition metal systems. The availability of other bonding modes in the metal arene complex⁷ and the higher total metal- η^6 -arene bond energy compared to a M-CO bond,⁸ enables the medium to play an important role in the arene release step.

Literature survey

McNair *et al.*⁹ suggested that exchange occurred *via* the nucleophilic attack of the solvent cage on the excited state of these salts, which consists of a metal coordinated counterion. Studies indicated that the metal arene bond was broken almost completely in the excited state. Nucleophilic attack of the solvent in the transition state effectively controlled the rate of arene release for a given complex.

As well as solvent dependence, the effect of aromatic substitution⁹ on arene exchange was investigated. It has been reported that the quantum yield for the formation of $[Fe(phen)_3]^{2+}$ (ϕ_{phen}) decreases with the increased alkyl substitution on the arene ring. Likewise, the ϕ_{phen} decreases as the size of the alkyl group on the ring increases. In contrast, the ϕ_{phen} increases when chloro substituents are present. Upon deuteration, it was found that the ϕ for the formation of Fe(phen)₃²⁺ upon irradiation of $[(\eta^5-C_5H_5Fe(\eta^6-(CD_3)C_6D_5)]PF_6$ in the presence of 1,10-phenanthroline decreases to 0.35 (0.39 for the hydrogen analogue). The increased steric hindrance introduced by the presence of bulkier substituents reduces the participation of the solvent cage in the transition state. Hence, decreasing the ϕ for arene release.

Low temperature studies of $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-p-(CH_{3})_{2}C_{6}H_{4})]PF_{6}$ in CH₃CN solution revealed the formation of a purple intermediate.¹⁰ A visible absorption spectrum obtained at low temperature exhibited a lowest energy band with $\lambda_{max} = 550$ nm. $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-p-(CH_{3})_{2}C_{6}H_{4})]PF_{6}$ has an absorption peak with $\lambda_{max} = 450$ nm. The absorption peak of the intermediate was shifted to the red of the parent complex absorption. This is consistent with the formation of $[(\eta^{5}-C_{5}H_{5})Fe(CH_{3}CN)_{3}]PF_{6}$. The ruthenium analogue of the parent iron complex, $[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-p-(CH_{3})_{2}C_{6}H_{4})]PF_{6}$ has $\lambda_{max} = 320$ nm, while the thermally stable tris acetonitrile complex has $\lambda_{max} = 365$ nm, which is also shifted to the red of the parent complex. The similarity and positions of the shifts supported the formulation of $[(\eta^{5}-C_{5}H_{5})Fe(CH_{3}CN)_{3}]PF_{6}$ (Eqns. 5.4 + 5.5).

$$\frac{\text{Chapter 5}}{[(\eta^{5}-C_{5}H_{5})\text{Fe}(\eta^{6}-p-xyl)]\text{PF}_{6}} \xrightarrow{h\nu} [(\eta^{5}-C_{5}H_{5})\text{Fe}(\text{CH}_{3}\text{CN})_{3}]\text{PF}_{6}} \xrightarrow{\text{Fe}^{2+}} + (\eta^{5}-C_{5}H_{5})_{2}\text{Fe}}$$

$$\frac{\text{thermally}}{\text{unstable}} + p-xyl \xrightarrow{\text{Eqn. 5.4}}$$

$$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-arene)]PF_{6} \xrightarrow{hv} [(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{3}]PF_{6} + arene Eqn. 5.5$$

thermally
stable

The iron tris acetonitrile complex could not be isolated but the labile acetonitrile ligands readily undergo photolytic exchange. Six compounds were isolated by Gill and Mann¹⁰ *via* photolysis of acetonitrile solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]PF_6$, in the presence of L, giving $[(\eta^5-C_5H_5)Fe(CH_3CN)L_2]PF_6$ as orange crystals. Conversion occurs with high yields. These compounds are air stable, soluble in polar organic solvents and have rather unexceptional properties (Table 5.3).

Ligand	Product	Yield	Length
		(%)	hv (h)
P(O(CH ₃)) ₃	a. $[(\eta^5 - C_5 H_5)Fe(CH_3 CN)(P(OCH_3)_3)_2]^+$	93	1
CNC(CH ₃) ₃	b. $[(\eta^5 - C_5 H_5)Fe(CH_3 CN)(CNC(CH_3)_3)_2]^+$	82	2.25
2,6-DMP	c. $[(\eta^5-C_5H_5)Fe(CH_3CN)(2,6-DMP)_2]^+$	78	1.66
$P(OCH_2(CH_3))_3$	d. $[(\eta^{5}-C_{5}H_{5})Fe(CH_{3}CN)(P(OCH_{2}CH_{3})_{3})_{2}]^{+}$	80	3.66
P(OC ₆ H ₅) ₃	e. $[(\eta^{5}-C_{5}H_{5})Fe(CH_{3}CN)(P(OC_{6}H_{5})_{3})_{2}]^{+}$	60	4.5
Diphos	f. $[(\eta^5-C_5H_5)Fe(CH_3CN)(Diphos)]^+$	96	2

Table 5.3

The third acetonitrile ligand is displaced by heating the disubstituted complex in dichloromethane (Table 5.4).

Chapter 5	Chapter 5 Literature surve			
Product	Ligand	Final	Yield	Length of
Table		product	(%)	Reflux (h)
5.3				
a	2,6-DMP	$[CpFe(P(OCH_3)_3)_2(2,6-DMP)]^+$	90	64
с	P(OCH ₃) ₃	$[CpFe(P(OCH_3)_3(2,6-DMP)_2)^+$	95	18
d	P(OCH ₃) ₃	$\left[CpFe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)\right]^+$	90	22

Table 5.4

Lee *et al.*¹¹ succeeded in photolytically exchanging the chlorobenzene molecule in $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ with more basic arenes. Exchanges were carried out with benzene, toluene, tetralin and 9,10-dihydroanthracene, with yields as high as 85 %. However, exchange reactions involving nitrobenzene, naphthalene and anthracene failed (Scheme 5.1). The nitro group has similar electron withdrawing properties to the chloro atom and is not basic enough to undergo exchange. For naphthalene and anthracene, coordination *via* one of the aromatic rings could result in the loss of aromaticity in the adjacent ring.



Scheme 5.1

In an attempt to investigate whether the cyclopentadienyl ring undergoes exchange, complexes of the type $[(\eta^5-C_5H_4X)Fe(\eta^6-arene)]^+$, where X is an electron withdrawing group, were reacted both thermally and photolytically with P(OR)₃, R = CH₃ or C₂H₅, C₆H₅; X= H, Cl, CH₃CO or COOR. In all cases the aromatic ring was replaced.¹¹ Photolysis provided higher yields than the corresponding thermal reactions. The introduction of heteroaromatics has been achieved by this method.

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Chapter 5

Photolysis of $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ in dichloromethane, in the presence of 2 to 3 equivalents of thiophene or substituted thiophenes, produces the appropriate thiophene derivative (Eqn. 5.6, Table 5.5).



Eqn. 5.6

2)1 ⁺ 75
)] ⁷⁵
$H_3S)]^+$ 70
$H_3S)]^+$ 75
$C_4H_2S)]^+$ 85
(

Jakubek *et al.*¹² have investigated the decomposition of the complex, $[(\eta^5 - C_5H_5)Fe(\eta^6 - (CH_3)_2CHC_6H_5)]^+$, over a range of excitation wavlengths, 355-683 nm. The studies reveal that the decomposition reaction is efficient in the UV and visible regions and results from both the triplet and singlet excited states. Arene exchange was also observed for sensitised reactions of $[(\eta^5 - C_5H_5)Fe(\eta^6 - p - (CH_3)_2C_6H_4)]^+$ in the presence of benzil and anthracene⁹ with both long (578 or 690 nm) and short (366 nm) wavelength irradiation. Irradiation in the 600 nm range corresponds to the region of singlet-triplet absorption.¹³ These experiments have shown that decomposition of the mixed sandwich complexes occurs both *via* singlet and triplet excited states. A possible mechanism is illustrated below (Scheme. 5.2).



Scheme 5.2

Chrisope *et al.*¹⁴ have carried out time resolved experiments on compounds of this kind. Their work confirms a role for triplet-excited states in the arene exchange reaction. Singlet excited states were not investigated. As indicated earlier, irradiation of either the ion pair or the freely solvated ion with 532 nm light (in the presence of a sensitiser) produced the corresponding triplet excited state. The presence of benzonitrile as the sensitiser led to the formation of a new absorbing feature in the UV-vis spectrum.

This transient signal consists of two kinetic phases. The first (intermediate A) is unresolved with a fast growth. It arises from irradiation of the solvated complex. The efficiency of the reaction of intermediate A in PhCN is not affected even when high concentrations of the quencher perylene are present. Therefore it is believed that species A is a ground state species derived from a short-lived triplet excited state. Its structure consists of a ring slipped η^4 -arene, coordinatively unsaturated complex. The transient signal also contains a second growth that is much slower. This intermediate B has been assigned as the ring slipped η^4 -arene-Cp-Fe complex covalently bound to its counterion. It is formed from the reaction of the ion-paired triplet state of the cationic complex. The rate of reaction of intermediate B with an attacking ligand depends on the identity of the counterion.

As both intermediates are produced in sensitisation reactions, they originate from the triplet-excited states. Intermediate A is short lived and is captured at high PhCN concentrations while intermediate B is captured at low PhCN concentrations. Both

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react to give the mononitrile, intermediate C, $[(\eta^5 - C_5H_5)Fe(C_6H_5CN)(\eta^4-arene)]^+$. The coordinatively unsaturated intermediate A reacts rapidly with PhCN to form intermediate C. The reaction of PhCN with intermediate B is slow because the counterion must be displaced. Intermediate B is a neutral species while intermediate C carries a positive charge. Intermediate B having been formed from ion pairs in nonpolar solvents converts to intermediate C slowly because it requires the separation of charge in a medium of low polarity. Both intermediates A and B converge at intermediate C, which in the presence of excess PhCN form the ligand exchanged reaction product $[(\eta^5 - C_5H_5)Fe(PhCN)_3]^+$ (Scheme 5.3).



Scheme 5.3

5.1.2 Photochemistry of $[(\eta^5-C_5H_5)Ru(\eta^6-arene)]^+$ and $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_{4-x}R_xS)]^+$ complexes

 $[(\eta^5-C_5H_5)Ru(\eta^6-arene)]^+$ complexes exhibit similar electronic absorptions to their iron analogues. However, their low solubility means that it is difficult to obtain UV-vis spectra. Those, which have been obtained, consist of an absorption peak on the low energy side of an intense absorption feature. The ligand field bands of the ruthenium complex occur at higher energy to those of the corresponding iron complexes. The highly soluble hexamethylbenzene and 1,3,5–butylbenzene derivatives also exhibit weak absorption shoulders.

The isolable, air stable trisacetonitrile product, $[(\eta^5-C_5H_5)Ru(CH_3CN)_3]^+$ was prepared *via* photolysis of the benzene complex with 406 nm irradiation.¹⁵ This wavelength corresponds to the region of singlet–triplet absorption. This product can also be produced with shorter wavelength irradiation (313 nm) (Eqn. 5.7).

$$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-C_{6}H_{6})]PF_{6} \xrightarrow{hv (\lambda_{exc} = 406 \text{ or } 313 \text{ nm})}{CH_{3}CN} \longrightarrow [(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{3}]PF_{6}$$

Eqn 5.7

For the ruthenium complex the quantum yield for the arene exchange with acetonitrile ligands varied from a high of 0.88 for *p*-dichlorobenzene to a low of 0.0031 for 1,3,5-butylbenzene. As already established for the analogous iron complexes, the presence of chloro substituents¹¹ on the aromatic ring increases the quantum yield for arene exchange. The same holds true for the ruthenium complexes. Interestingly, it has been found that ϕ_{CH3CN} of a given arene complex is always larger for the corresponding iron compound. Deuteration of the arene ring causes a decrease in the ϕ from 0.34 to 0.32 (hydro analogue) for the ruthenium system.

The $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]^+$ complex is the first example of an η^5 -bound, π –coordinated thiophene complex. In this complex the thiophene molecule is strongly bound to the metal. This was confirmed by the slow rate of its displacement in acetone at room temperature¹⁶ (only 33 % of the complex had reacted after 4.5 h). ¹H NMR spectroscopic studies show that the 2, 5 protons undergo deuterium exchange in the presence of KOD within four minutes. There was no evidence for the exchange of the protons in the 3, 4 positions. In the absence of base there was no exchange at the 2, 5 positions.

Photochemical exchange of the arene in the complexes, $[(\eta^5-C_5H_5)Ru(\eta^6-arene)]^+$ has provided routes to complexes that are difficult to synthesise by other means (Table 5.6). As already mentioned, photolysis of $[(\eta^5-C_5H_5)Ru(\eta^6-C_6H_6)]^+$ in acctonitrile solution yields the thermally stable trisacetonitrile product $[(\eta^5-C_5H_5)Ru(CH_3CN)_3]^+$.^{15, 17}

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Chapter 5	Literature survey			
LIGAND	PRODUCT	TIME	YIELD	SOLVENT
		(h)	(%)	
P(OCH ₃) ₃	$[(\eta^{5}-C_{5}H_{5})Ru(P(OCH_{3})_{3})_{3}]^{+}$	4.5	85	CH ₂ Cl ₂
P(OCH ₂ CH ₃) ₃	$[(\eta^{5}-C_{5}H_{5})Ru(P(OCH_{2}CH_{3})_{3})_{3}]^{+}$	5.5	69	CH ₂ Cl ₂
CH ₃ CN	$[(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{3}]^{+}$	22	100	CH ₃ CN

Table 5.6

Replacement of these ligands has proved more difficult than with the iron analogue.¹⁷ The ruthenium complex exerts a selectivity not observed in the iron analogue. Replacement of one acetonitrile ligand is achieved *via* addition of the ligand at room temperature in acetonitrile solution. The second ligand is exchanged upon addition of excess ligand again at room temperature but in dichloromethane solution while the third acetonitrile ligand is replaced upon heating excess ligand in dichloroethane (Table 5.7). Consequently, by varying the reaction conditions the degree of substitution in the ruthenium system can be controlled.

L	Product	t	Yld	Solvent	hν
		(h)	(%)		/Δ
СО	$[(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{2}(CO)]^{+}$	0.33	96	CH ₃ CN	hν
P(OCII ₃) ₃	$[(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{2}(P(OCH_{3})_{3})]^{+}$	3.5	88	CH ₃ CN	hν
$P(OCH_3)_3$	$[(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)(P(OCH_{3})_{3})_{2}]^{+}$	22	100	CH_2Cl_2	Δ
C ₆ (CH ₃) ₆	$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-C_{6}(CH_{3})_{6})]^{+}$	21	60	CH ₃ CHCl ₂	Δ
pСР	$[(\eta^5-C_5H_5)Ru(\eta^6-pCP)]^+$	17.5	85	CH ₃ CHCl ₂	Δ
$pCl_2C_6H_4$	$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-p-C_{6}H_{4}Cl_{2})]^{+}$	15	66	CH ₃ CHCl ₂	Δ

Table 5.7

Under analogous conditons, both the $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]^+$ and $[(\eta^5-C_5H_5)Ru(\eta^6-C_6H_6)]^+$ were irradiated in the presence of tri–isopropylphosphite. In the case of the iron complex, a 100 % conversion to $[(\eta^5-C_5H_5)Fe(P(OCH(CH_3)_2)_3)_3]^+$ was observed while in the case of the ruthenium complex, only 50 % conversion was recorded. However, a 100 % conversion is obtained for both complexes for

trimethylphosphite as the entering ligand. The electronic and steric effects of the ligand can affect the efficiency of ring replacement reactions in this system.

Other photochemical reactions have been attempted, but in the case of $P(OPh)_3$ as a ligand replacement of the η^6 -arene is not observed. While in the presence of $P(OCH(CH_3)_2)_3$ and toluene a mixture of products was obtained (Eqns. 5.8, 5.9 and 5.10).

$$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-C_{6}H_{6})]PF_{6} \xrightarrow[P(OPh)_{3}]{P(OPh)_{3}} \text{ no reaction } Eqn. 5.8$$

$$[(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-C_{6}H_{6})]PF_{6} \xrightarrow{5h \text{ hv}} P(OCH(Me)_{2})_{3} [(\eta^{5}-C_{5}H_{5})Ru(P(OCH(CH_{3})_{2})_{3})]PF_{6}$$

$$CH_{2}Cl_{2} Eqn. 5.9$$

$$[(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)_{2}P(OCH_{3})]PF_{6} \xrightarrow{\begin{array}{c} 19h & hv \\ CH_{3}C_{6}H_{5} \\ \hline CH_{3}CHCl_{2} \end{array}} [(\eta^{5}-C_{5}H_{5})Ru(CH_{3}CN)(P(OCH_{3})_{3})_{2}]PF_{6} + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{3}C_{6}H_{5})]PF_{6} \\ + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{3}C_{6}H_{5})]PF_{6} + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{5})Ru(\eta^{6}-CH_{5}H_{5})]PF_{6} \\ + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})]PF_{6} \\ + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})]PF_{6} \\ + [(\eta^{5}-C_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5})Ru(\eta^{6}-CH_{5}H_{5$$

Eqn. 5.10

Unlike the iron system, irradiation of the ruthenium complex in dichloromethane solution does not lead to decomposition.⁹ The starting material is recovered. The observed differences between the two metals suggest that the intermediates may differ in the coordination modes of the arene ring.

5.2 **RESULTS**

The UV-vis spectrum of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ is presented in Fig. 5.8. It exhibits a λ_{max} at 395 nm with a second band at 480 nm. Initially photochemical experiments on this compound involved steady state photolysis in which the changes in the UV-vis spectrum were monitored to decide which solvent was best suited for the laser flash photolysis studies.



Fig. 5.8: UV-vis spectrum of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in dichloromethane solution.

A sample of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was dissolved in the solvent of choice. The solution was purged with Ar or CO and placed in front of the irradiation source for typically 25 min with UV-vis spectra recorded at regular intervals. A Xe-arc lamp was used as the irradiation source while broadband filters were employed to select the desired wavelength range.

5.2.1 Steady state photolytic studies of [(η⁵-C₅H₅)Fc(η⁶-(CH₃)₂CHC₆H₅)]PF₆ in various solvents under Ar or CO atmospheres

An acetone solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ under a CO atmosphere was subjected to steady state photolysis with $\lambda_{exc} > 410$ nm. A general increase in absorption in the region 330-520 nm of the UV-vis spectrum was observed (Fig. 5.9).



Fig. 5.9: UV-vis spectra of the changes observed when a CO saturated acetone solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was photolysed

An IR spectrum of this solution contained two bands at 2128 and 2074 cm⁻¹ (Fig. 5.10). The lower energy band contains a shoulder at higher wavenumber but an assignment for this feature has not been made. These two bands have been assigned to the formation of $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$ by comparison with literature values for the replacement of p-(CH₃)₂C₆H₄ in $[(\eta^5-C_5H_5)Fe(\eta^6-p-(CH_3)_2C_6H_4)]PF_6$ with three CO molecules.² A precipitate was also formed during the reaction.





A sample of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was dissolved in acetone and purged with Ar. After steady state photolysis with $\lambda_{exc} > 410$ nm, several milligrams of bipy were added to the solution, which immediately turned red. A UV-vis spectrum of the solution revealed the appearance of a new band with $\lambda_{max} = 490$ nm (Fig. 5.11), indicating the formation of $[Fe(bpy)_3]^{2+}$. A sample of $[(\eta^5-C_5H_5)Fe(\eta^6 (CH_3)_2CHC_6H_5)]PF_6$ was dissolved in acetone under an Ar atmosphere and 1,10phenanthroline was added to the solution prior to photolysis. After 1 minute of irradiation with $\lambda_{exc} > 410$ nm the solution had changed colour from yellow to red. The UV-vis spectrum contained a band with $\lambda_{max} = 510$ nm, which is indicative of $[Fe(phen)_3]^{2+}$, confirming that under these conditions, Fe²⁺ is produced *via* photolysis and is scavenged by phenanthroline.



Fig. 5.11: UV-vis spectrum of $[Fe(bipy)_3]^{2+}$ in Ar purged acetone solution

A sample of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was dissolved in acetonitrile, purged with CO and subjected to steady state photolysis with $\lambda_{exc} > 410$ nm. Irradiation for 30 min resulted in an increase in absorbance in the region 320-550 nm of the UV-vis spectrum along with the formation of a broad band centred at 570 nm (Fig. 5.12).



Fig: 5.12: UV-vis spectrum illustrating the formation of the new band at $\lambda_{max} = 570$ nm upon photolysis of a CO purged acetonitrile solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ for 30 min

The IR spectrum of this solution exhibits a carbonyl band at 2008 cm⁻¹ (Fig. 5.13), which has been assigned to the mono carbonyl bis-acetonitrile complex, $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]PF_6$. After irradiation, bipy was added to the solution, which immediately turned red. A UV-vis spectrum exhibited a new band with $\lambda_{max} = 490$ nm indicating the formation of $[Fe(bpy)_3]^{2+}$.



Fig. 5.13: IR spectrum of $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]PF_6$ in the 2080-1930 cm⁻¹ region

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A control reaction, in which a sample of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was dissolved in acetonitrile and purged with CO, was left in the dark for several hours. Spectroscopic data obtained after several hours confirmed that no reaction had taken place.

Steady state photolysis of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in Ar purged acetonitrile solution, in the presence of bipy resulted in the solution changing colour from yellow to red and a new band being producing with a $\lambda_{max} = 490$ nm. In the absence of added ligands, $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ undergoes decomposition to unidentified products. A similar solution was placed in the dark for several hours as a control reaction. Spectroscopic data showed that no reaction had taken place. Decomposition of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ is a photochemical process as is the exchange of the arene ring with CO.

A CO purged dichloromethane solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was irradiated with $\lambda_{exc} > 410$ nm. The UV-vis spectrum was recorded at 5 min intervals. Photolysis resulted in an increase in absorption in the region 300-600 nm in the UV-vis spectrum (Fig. 5.14).



Fig. 5.14: UV-vis spectrum showing the effect of photolysis on [(η⁵-C₅H₅)Fe(η⁶-(CH₃)₂CHC₆H₅)]PF₆ when irradiated in a CO purged dichloromethane solution

Within 5 min of irradiation, the solution had changed colour from orange to green and a precipitate had formed. This can be seen upon inspection of the UV-vis spectrum in Fig. 5.14. In the region 600-800 nm, each successive trace is above the baseline, indicating sample turbidity. An IR spectrum recorded after photolysis revealed the presence of carbonyl bands at 2128 and 2074 cm⁻¹ as in Fig. 5.10 and have been assigned to the formation of $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$. Addition of bipy to the photolysed sample caused an immediate colour change to red. This is accompanied by a band at $\lambda_{max} = 490$ nm in the UV-vis spectrum.

5.2.2 Laser Flash photolysis studies of [(η⁵-C₅H₅)Fe(η⁶-(CH₃)₂CHC₆H₅)]PF₆ in various solvents under Ar and CO atmospheres.

For laser flash photolysis studies to be successful, the solution being photolysed must not become turbid. If a precipitate is formed early in the experiment, the transient signals observed may be the result of light scattering caused by the precipitate or indeed photoacoustic effects. Table 5.9 summarizes the solvents used for steady state photolysis and the irradiation time required before a precipitate is observed.

SOLVENT	λ_{exe} (nm)	COLOUR OF	TIME BEFORE	ATM
		PRECIPITATE	PRECIPITATE	CO/Ar
			OBSERVED	
			(min)	
CH ₃ CN	> 410	brown	29	either
CH ₂ Cl ₂	> 410	brown	4	either
(CH ₃) ₂ CO	> 410	black	21	either

Table 5.9

For both acetonitrile and acetone solutions, it takes more than 20 min of photolysis before a precipitate appears. Consequently, these two solvents are most suited to laser flash photolysis studies. For dichloromethane solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ it only takes 4 min for a precipitate to form upon irradiation. Formation of the precipitate begins long enough after photolysis is started for laser flash photolysis studies to be carried out in dichloromethane solution.

A CO purged acetone solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ was subjected to laser flash photolysis studies with $\lambda_{exe} = 355$ nm. Weak UV-vis signals were observed in the range 350 - 400 nm (Fig. 5.15). Despite being weak the signals do not decay to baseline and indicate the formation of a permanent photoproduct. This is confirmed upon inspection of the corresponding UV-vis spectrum recorded during the laser studies. The changes observed in the UV-vis spectrum are similar to those observed in the steady state photolytic studies and hence the photoproduct is assigned to the complex $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$. After laser flash photoysis studies bipy was added to the solution and it turned red immediately. A band at $\lambda_{max} = 490$ nm is observed in the UV-vis spectrum. Laser flash photoysis studies at $\lambda_{exc} = 532$ nm in CO or Ar purged acetone solutions were not performed.



Fig. 5.15: Signal observed at 370 nm following laser flash photolysis at $\lambda_{exc} = 355$ nm of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in CO purged acetone

For CO purged acetonitrile solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$, laser flash photolysis studies with $\lambda_{exc} = 355$ nm produced depletion signals at 420 and 440 nm (Fig. 5.16). These depletions do not recover to the baseline within the timescale of the experiment. Little change is observed in the UV-vis spectrum of the solution however. A slight increase in absorbance is observed in the region 340-480nm in the UV-vis spectrum while there is no evidence for the band at 570 nm as was observed

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during the steady state photolysis experiments. An assignment for this signal has not been made.



Fig. 5.16: Signal observed at 420 nm following laser flash photolysis at $\lambda_{exc} = 355$ nm of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in CO purged acctonitrile

In a CO saturated acetonitrile solution with $\lambda_{exc} = 532$ nm, signals are observed in the 550-700 nm region (Fig. 5.17).



Fig. 5.17: Signal observed at 550 nm following laser flash photolysis at $\lambda_{exc} = 532$ nm of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in CO purged acetonitrile

The signal in Fig. 5.17 consists of two parts. The first part, which occurs within 10 μ s of the laser pulse is assigned as formation of the ring slipped solvated intermediate. This assignment is consistent with literature precedents.¹⁴ The second part of the signal fails to decay to baseline within the timescale of the experiment and it is assigned as formation of the monocarbonyl complex, $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]PF_6$. This is confirmed by the UV-vis spectrum where a new broad band at 520-600 nm is observed similar to that observed in the steady state photolytic studies.

Under an Ar atmosphere and with $\lambda_{exc} = 532$ nm, signals were observed in the 510-600 nm region. The signals observed (Fig. 5.18) contain two parts. The first process illustrated in Fig. 5.18 is assigned as formation of the solvated ring slipped intermediate. The second part of the signal is related to the formation of the decomposition products ferrocene, Fe²⁺ and (CH₃)₂CHC₆H₅. The solution turned red after addition of bipy to the photolysed sample.



Fig. 5.18: Signal observed at 510 nm following laser flash photolysis at $\lambda_{exc} = 532$ nm of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in Ar purged acetonitrile

Dichloromethane solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ were subjected to laser flash photolysis studies. In a CO purged dichloromethane solution and with $\lambda_{exc} =$ 355 nm, signals were observed from 380 to 520 nm (20 nm intervals) (Fig. 5.19). A general increase in absorbance in the region 300-600 nm was observed in the UV-vis spectrum.



Fig. 5.19: Signal observed at 480 nm following laser flash photolysis at $\lambda_{exc} = 355$ nm of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in CO purged dichloromethane

An IR spectrum of the photolysed solution exhibited bands at 2128 and 2074 cm⁻¹. Similar results were obtained when laser flash photolysis studies were carried out at $\lambda_{exc} = 532$ nm under analogous conditions. Signals were observed in the region 380-560 nm, bands at 2128 and 2074 cm⁻¹ were observed in the IR spectrum and an increase in absorbance in the region 300-600 nm of the UV-vis spectrum was observed. The signals observed for the laser studies at $\lambda_{exc} = 355$ or 532 nm are assigned to formation of the tricarbonyl complex, $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$. The transient signals do not return to baseline in the laser studies and are accompanied by an increase in intensity in the UV-vis spectrum similar to that observed for the steady state photolytic studies. Therefore the transient signals represent the formation of a permanent photoproduct. Figs. 5.20 and 5.21 below illustrate the transient absorption spectra following laser

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studies of $[(\eta^5 - C_5H_5)Fe(\eta^6 - (CH_3)_2CHC_6H_5)]PF_6$ in CO dichloromethane solutions at $\lambda_{exc} = 355$ and 532 nm respectively.



Fig. 5.20: Transient absorption spectrum following laser flash photolysis studies of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6 \text{ in CO purged dichloromethane at}$ $\lambda_{exc} = 355 \text{ nm}$



Fig. 5.21: Transient absorption spectrum following laser flash photolysis studies of $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-(CH_{3})_{2}CHC_{6}H_{5})]PF_{6} \text{ in CO purged dichloromethane at}$ $\lambda_{exc} = 532 \text{ nm}$

The figures illustrate that the photoproduct produced during these laser flash photolysis studies has λ_{max} at ≈ 300 and ≈ 500 nm. Only one photoproduct is produced. No new absorption features appear at longer timescales.

5.2.3 Photochemical studies of $[(\eta^5-C_5H_5)Fe(\eta^6-CCl_xC_6H_{6-x})]PF_6$ (x = 1 or 2)

The mono- and di-chloro benzene complexes, $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ and $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$, were prepared following a literature procedure.¹⁸ Their syntheses were readily achieved by reacting ferrocene with the relevant benzene derivative in the presence of AlCl₃ and Al powder at reflux temperature in the relevant dichlorobenzene solvent. Both complexes give similar UV-vis spectra (Fig. 5.22).



Fig. 5.22: UV-vis spectrum of the complexes, $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ and $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_4Cl_2)]PF_6$

Laser flash photolysis studies with $\lambda_{exc} = 355$ nm were carried out on both complexes in Ar purged CH₂Cl₂ solutions. Signals were observed at 390, 400, 420 and 440 nm. A typical signal observed is given in Fig. 5.23.



Fig. 5.23: Signal observed at 420 nm following laser flash photolysis at $\lambda_{exc} = 355$ nm of [(η^5 -C₅H₅)Fe(η^6 -C₆H₅Cl)]PF₆ in Ar purged dichloromethane

The addition of bipy to either solution after photolysis resulted in an immediate colour change from yellow to red. This colour change confirms that under an Ar atmosphere, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$ complexes decompose.

Laser flash photolysis studies with $\lambda_{exc} = 355 \text{ nm on } [(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ and $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$ were carried out in CO purged CH₂Cl₂ solutions. For the dichloro derivative, 1 atmosphere of CO was employed and transients were observed at 500, 480 and 460 nm (Fig. 5.24). The corresponding UV-vis spectrum is shown in Fig. 5.25.



Fig. 5.24: Signal observed at 500 nm when $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$ was photolysed in CO purged dichloromethane solution at $\lambda_{exc} = 355$ nm



Fig. 5.25: UV-vis spectrum recorded during laser flash photolysis at $\lambda_{exc} = 355$ nm of [(η^5 -C₅H₅)Fe(η^6 -1,2-C₆H₄Cl₂)]PF₆ in dichloromethane

For the monochloro derivative, ½ atmosphere of CO was employed and transients at 460, 440 and 420 nm (Fig 5.26). The accompanying UV-vis spectrum is illustrated in Fig. 5.27.



Fig. 5.26: Signal observed at 420 nm when $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ was photolysed in CO purged dichloromethane solution at $\lambda_{exc} = 355$ nm



Fig. 5.27: UV-vis spectrum following laser flash photolysis at $\lambda_{exc} = 355$ nm of [(η^5 -C₅H₅)Fe(η^6 -C₆H₅Cl)]PF₆ in dichloromethane in CO purged dichloromethane solution

For both chlorinated benzene derivatives, laser flash photolysis at $\lambda_{exc} = 355$ nm in dichloromethane solutions leads to formation of a permanent photoproduct. The transient signals do not decay to the baseline within the timescale of the experiment and an increase in absorbance in the UV-vis spectrum similar to that observed for steady state photolytic studies of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ in CO purged dichloromethane studies is observed. By comparison with the laser flash photolysis studies carried out on $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$, the photoproduct is assigned to $[(\eta^5-C_5H_5)Fe(CO)_3]PF_6$.

According to the literature,⁹ the arene in $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+$ complexes can be displaced by a more basic arene. Attempts were made to synthesise $[(\eta^5-C_5H_5)Fe(\eta^6-C_4H_4S)]PF_6$ via this method. The dichorobenzene complex, $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$, was dissolved in dichloromethane and purged with Ar. Excess thiophene was added to the solution and the solution was subjected to steady state photolysis with $\lambda_{exc} > 410$ nm for 4 h. The corresponding UV-vis spectrum is shown in Fig. 5.28. The ¹H NMR spectrum contains two multiplets at δ 7.45 and 7.20 representing uncoordinated dichlorobenzene. Signals were also observed at δ 6.4, 6.48 and 5.3. Integration was as expected: 2:2:1 respectively. These are assigned to the protons of the thiophene ring and the cyclopentadienyl ring. However, the signals were very weak and the product could not be isolated.



Fig. 5.28: UV-vis spectrum following photolysis of $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$ in dichloromethane in the presence of excess thiophene

Results

Chapter 5

5.2.4 Photochemical studies on $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]PF_6$

The preparation of $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ was successfully achieved by bringing $(\eta^5-C_5H_5)Ru(PPh_3)_2Cl$ to reflux temperature in the presence of methanol, AgBF₄ and $(CH_3)_2C_4H_2S$.¹⁹ The UV-vis spectrum of this complex is illustrated in Fig. 5.29.



Fig. 5.29: UV-vis spectrum of $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ in dichloromethane solution

This complex was subjected to steady state photolysis in a variety of solvents: methanol, dichloromethane or acetonitrile. All photolyses employed the $\lambda_{exc} > 300$ nm filter and the solutions were also saturated with CO.

After 26 min steady state photolysis in CO purged methanol, the colour of the solution changed from a pale yellow to a deeper yellow. The UV-vis spectra recorded at intervals during this photolysis are illustrated in Fig. 5.30. An IR spectrum of the final solution in the region 2100-1600 cm⁻¹ contained no new peaks, however.

Results

Chapter 5



Fig. 5.30: UV-vis spectrum of $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ upon photolysis in CO purged methanol

In dichloromethane, almost no change is observed in the UV-vis spectrum after steady state photolysis. According to McNair *et al.*⁹ photolysis of $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ in Ar purged CH₂Cl₂ does not result in decomposition of the cationic complex.

Steady state photolysis of this complex in acetonitrile resulted in an increase in absorption in the region 280-380 nm of the UV-vis spectrum and a decrease in the region 380-480 nm (Fig. 5.31). These changes are accompanied by the appearance of two isobestic points at 340 and 380 nm. Consequently the $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ complex is converted to a second complex cleanly and without formation of side products. This new complex is assigned to $[(\eta^5-C_5H_5)Ru(CH_3CN)_3]BF_4$.



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Fig. 5.31: UV-vis spectrum showing the effect of steady state photolysis on [$(\eta^5-C_5H_5)Ru(CH_3CN)_3$]BF₄ in CO purged acetonitrile

5.3 **DISCUSSION**

Table 5.10 tabulates regions of change in the UV-vis spectra and the appearance of IR bands when $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ was irradiated in CO or Ar saturated solutions in a variety of solvents.

SOLVENT	ATMOSPHERE	UV-vis (nm)	IR (cm ⁻¹)
(CH ₃) ₂ CO	СО	330-520	2182
			2074
	Ar	520 (bipy)	-
CH ₃ CN	СО	320-550	2010
		570	
	Ar	520 (bipy)	-
CH ₂ Cl ₂	СО	300-600	2127
			2074

Table 5.10:

The changes tabulated above are the results of photochemical processes. This was confirmed by control reactions, where $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ was dissolved in the solvent of choice, purged with Ar or CO and left in the dark for several hours. The UV-vis and IR spectra confirmed that no reaction had taken place and only starting material was present.

Hendrickson *et al.*²⁰ have reported that complexes of the type $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+X^-$ exhibit spin allowed ligand field bands in the region 400-500 nm. Irradiation of these complexes with $\lambda_{exc} = 436$ nm yields products which result from ligand field excitation. In these studies, the broadband filter, $\lambda_{exc} > 410$ nm, was employed, as monochromatic filters were not available.

Photolysis of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ in Ar flushed CH₃CN, (CH₃)₂CO or CH₂Cl₂ led to the decomposition of this cationic complex. Decomposition of this type of $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+X^-$ complex is known to yield Fe²⁺, ferrocene and 'free' arene. The formation of Fe²⁺ in these studies was confirmed by the formation of a band

Discussion

at 520 nm associated with $[Fe(bipy)_3^{2^+}]$ in the UV-vis spectrum by the addition of bipy to the photolysed solutions. 1,10-phenanthroline can also be used as an indicator for the decomposition. Addition of 1,10-phenanthroline to an Ar purged acetone solution of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ caused the sample to turn red within 1 min of irradiation, confirming the formation of $[Fe(phen)_3]^{2^+}$. 1,10-phenanthroline and bipy act as cationic scavengers. The decomposition mechanism was proposed to proceed through a $[(\eta^5-C_5H_5)Fe(solv)]^+$ intermediate.

When $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ was photolysed in these solvents under CO atmospheres interesting results were obtained. For CO purged acetone and dichloromethane solutions of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$, photolysis produces the tricarbonyl complex $[(\eta^5-C_5H_5)Fe(CO)_3]^+PF_6^-$, while for CO purged acetonitrile solutions the monocarbonyl complex $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]^+PF_6^$ was produced. This assignment is based on comparison with the analogous Ru complex, $[(\eta^5-C_5H_5)Ru(CH_3CN)_2(CO)]^+PF_6^-$ which has $v_{CO} = 2004 \text{ cm}^{-1}$.¹⁷ Formation of the diacetonitrile complex is in contrast to the reactions carried out by Gill and Mann.¹⁰ They have successfully replaced two acetonitrile ligands in the trisacetonitrile complex $[(\eta^5-C_5H_5)Fe(CH_3CN)_3]^+PF_6^-$ with two molecules of P(OCH_3)_3, 2,6-DMP among others. There are no reports of the synthesis of the Fe bis-acetonitrile complex containing only one CO ligand however.

It has been reported that formation of the trisacetonitrile complex is accompanied by the observation of an intense purple colour.¹⁰ This purple colour fades as the complex either undergoes decomposition or reaction with other ligands present in solution. During the photolytic studies of $[(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$, in acetonitrile solution, a purple colour was not observed for either Ar or CO purged solutions. The ligands used by Gill and Mann to replace the two acetonitrile ligands in the complex, $[(\eta^5-C_5H_5)Fe(CH_3CN)_3]^+PF_6^-$, are rather large molecules in comparison with a CO molecule. Furthermore, acetonitrile ligands in the Fe complex $[(\eta^5-C_5H_5)Fe(CH_3CN)_3]^+PF_6^-$ are very labile and easily replaced. It is therefore surprising that the three CO molecules did not replace all three CH₃CN molecules when $[(\eta^5-C_5H_5)Fe((CH_3)_2CHC_6H_5)]^+PF_6^-$ was photolysed in CO purged acetonitrile. If this were the case, bands at 2128 and 2074 cm⁻¹ would be expected in the IR spectrum.¹⁶

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For ligands such as $P(OCH_3)_3$ and 2,6-DMP it is most likely that steric interactions prevent the replacement of the third acetonitrile ligand.

Photolysed arene exchange of complexes of the type $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+PF_6^$ proceeds through medium assisted intermediates.⁵ In polar solvents, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+PF_6^-$, exist as free ions and solvent assistance is important whereas in nonpolar solvents, $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+PF_6^-$ exists mainly as ion pairs and photolysis of this complex leads to coordination of the counterion to the metal. The solvents used in this study are all polar and the counterion does not change, hence the medium assistance is solvent based. Photolysis of the complex $[(\eta^5-C_5H_5)Fe(\eta^6-arene)]^+PF_6^-$ leads to arene ring slippage from $\eta^6 \rightarrow \eta^4$ coordination.¹⁴ A vacant site on the metal centre becomes solvated and subsequent molecules replace the arene. These solvent molecules can then be replaced by ligand molecules present in the solution. Dichloromethane has been shown to be less nucleophilic than acetonitrile,¹⁷ hence solvating dichloromethane molecules are replaced more easily than acetonitrile molecules. Further experimental evidence supports a solvated mechanism.

For the three solvents employed in this study, bipy was added to the CO purged solutions after photolysis. In all cases, the solutions turned red immediately, indicating the presence of $[Fe(bipy)_3]^{2+}$. This observation supports the proposal that the mechanism proceeds *via* a $[(\eta^5-C_5H_5)Fe(solv)]^+$ intermediate. After formation of this intermediate, CO molecules replace the solvent molecules to form the observed carbonyl complexes. When bipy is added to the photolysed solutions, it is likely that there are $[(\eta^5-C_5H_5)Fe(solv)]^+$ molecules present whose solvent molecules have not been replaced. Molecules of bipy would then replace these solvent molecules to form $[(\eta^5-C_5H_5)Fe(bipy)_n]^+$, which is unstable. Loss of the $(\eta^5-C_5H_5)^-$ ligand and coordination of bipy molecules would yield $[Fe(bipy)_3]^{2+}$. Another possibility is that bipy replaces the ligands in $[(\eta^5-C_5H_5)Fe(CH_3CN)_2(CO)]^+PF_6^-$ and $[(\eta^5-C_5H_5)Fe(CO)_3]^+PF_6^-$

The laser studies show that the formation of the carbonyl complexes are very fast. For the experiments carried out in acetonitrile, the observed transients consist of two phases. The initial phase of the transient is assigned as formation of the trisacetonitrile complex,

 $[(\eta^5-C_5H_5)Fe(CH_3CN)_3]^+PF_6^-$. The lifetime of this intermediate is too short for kinetic data to be determined. For the solvents, acetone and dichloromethane, there is no evidence for the solvated intermediate. The lifetime of these solvated intermediates is too short to be recorded. The laser results presented here do not provide any additional information regarding the mechanism of arene exchange. The laser flash photolysis results presented here are preliminary findings and more detailed and complete studies would be necessary before definite proposals could be made.

Steady state photolysis of $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]^+BF_4^-$ was carried out in a number of Ar purged solvents, methanol, dichloromethane and acetonitrile. Almost no change was observed in the UV-vis spectrum when this complex was photolysed in dichloromethane. This confirms the findings of McNair *et al.*⁹ who found that in dichloromethane solutions $[(\eta^5-C_5H_5)Ru(\eta^6-arene)]^+X^-$ complexes do not exhibit arene release behaviour. In contrast for the analogous Fe complexes, arene exchange is always observed. A further difference between the Fe and Ru complexes was noted when $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]^+BF_4^-$ was photolysed with $\lambda_{exc} > 410$ nm in Ar purged acetonitrile solutions. The UV-vis spectrum recorded during photolysis exhibited isobestic points at 340 and 380 nm. These changes are assigned to the formation of the trisacetonitrile complex $[(\eta^5-C_5H_5)Ru(CH_3CN)_3]^+BF_4^-$. This complex has been reported before¹⁰ and is known to be stable at room temperature in comparison to the Fe analogue.

Conclusion

5.4 CONCLUSION

The photochemical studies presented here of complexes of the type, $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+X^-$, support the suggested mechanisms of arene exchange proposed in the literature. The results obtained point to a mechanism for arene release involving a solvated intermediate such as $[(\eta^5-C_5H_5)M(solv)_3]^+$. After $[(\eta^5-C_5H_5)M(\eta^6-(CH_3)_2CHC_6H_5)]^+PF_6^-$ was photolysed in CO purged acetonitrile, acetone and dichloromethane solutions, the solutions went red immediately upon the addition of bipy to the samples, indicating the formation of $[Fe(bipy)_3]^{2+}$. A possible mechanism for formation of this complex is *via* the above solvated intermediate. Although this work supports such a mechanism it is only preliminary. More studies need to be carried out before any definite proposals can be made.

5.5 **REFERENCES**

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Experimental

Abstract

This chapter describes the synthetic methods used to prepare the complexes studied in this thesis. Also included is a description of the techniques used and their mode of operation. Finally a brief note on future work to be carried out on these complexes is provided.

6. EXPERIMENTAL

6.1 Chapter 2: C-F Activation

6.1.1 General considerations

All manipulations were performed inside an argon filled glovebox or on a Schlenk line $(O_2 \text{ levels in glovebox below 10ppm})$. Solvents used for synthesis were dried over sodium benzophenone ketyl and distilled under argon before use. The main solvents used were hexane, tetrahydrofuran and benzene. Most of the chemicals used were bought from Aldrich Chemical Company Ltd. except pentafluoropyridine and 2,3,5,6-tetrafluoropyridine, which were bought from Apollo Fluorochemicals Ltd. and used as received. Multinuclear NMR spectroscopy for the complexes in Chapter two were carried out on a Bruker AMX-500 NMR spectrometer in the University of York while multinuclear NMR spectroscopy for the remaining chapters was carried out on a Bruker Avance 400 spectrometer in Dublin City University.

6.1.2 Spectroscopy

Compounds were characterised by ¹H (500.13 MHz), ³¹P (202.46 MHz), ¹⁹F (470.4 MHz) and ¹³C (125.76 MHz) NMR spectroscopy on a Bruker AMX-500 NMR spectrometer. NMR samples were prepared in tubes fitted with Youngs stopcocks. Either d_6 -benzene or d_8 -thf was used as solvent for NMR spectroscopy. The deuterated solvents were dried over potassium and transferred on the ultra-high vacuum line. Infrared spectra were recorded on a Unicam Research Series FTIR spectrometer while mass spectra were recorded on a VG Autospec mass spectrometer. Elemental Microanalysis Ltd., Devon, carried out elemental analysis.

6.1.3 Synthesis of Ni(COD)₂

Ni(II)Cl₂ (20 g, 84.1 mmol) was dissolved in ethanol (250 ml). Pyridine (40 ml, 250 mmol) was added and the solution was left to stir for 3 h. The precipitate was filtered to give Ni(II)Cl₂(C₅H₅N)₄. The blue solid was transferred to a Schlenk tube and stored in the glovebox. Ni(II)Cl₂(C₅H₅N)₄ (5 g, 11.2mmol) was suspended in THF (50 ml) in a greaseless Schlenk tube. 1,5-cyclooctadicne (2.5 ml, 20 mmol) and sodium metal (0.5 g, 22 mmol) were added and the solution was stirred under argon for 3 h. The volatiles

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were removed *in vacuo*. Methanol was added and the solution stirred for 15 min to kill the excess sodium. The product was extracted with benzene. The solution was filtered in the glovebox and benzene was removed *in vacuo*. The resulting solid was washed several times with methanol and the solvent was decanted by cannular until a yellow product was obtained. The product was dried *in vacuo*, collected and stored in the glovebox.

6.1.4 Synthesis of *trans*-NiF(C_5F_4N)(PEt₃)₂ (1)



This compound was prepared following literature methods (Eqn. 6.1).¹ Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ l, 0.81 mmol) to give a red solution. Pentafluoropyridine (50 μ l, 0.45 mmol) was added and the solution changed to an orange/yellow colour after approximately 3 min. The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The precipitate was redissolved in hexane and the solution was used without isolation of the NiF(C₅F₄N)(PEt₃)₂ complex for subsequent reactions. The NiF(C₅F₄N)(PEt₃)₂ complex has been isolated and characterised previously in the literature.¹

Experimental

6.1.5 Synthesis of *trans*-NiF(C₅F₃HN)(PEt₃)₂ (2)



This complex was synthesised according to literature methods (Eqn. 6.2).¹ Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ l, 0.81 mmol) to give a red solution. 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50 mmol) was added and the solution changed to an orange/yellow colour after approximately 3 min. The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The precipitate was redissolved in hexane and the solution was used without isolation of the NiF(C₅F₃HN)(PEt₃)₂ complex for subsequent reactions. The NiF(C₅F₃HN)(PEt₃)₂ complex has been isolated and characterised previously in the literature.¹

6.1.6 Synthesis of *trans*-Ni(N₃)(C_5F_4N)(PEt₃)₂ (3)



Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ l, 0.81 mmol) and pentafluoropyridine (50 μ l, 0.45mmol) (Eqn. 6.3). The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The residue was redissolved in hexane and treated with trimethylsilyl azide (50 μ l, 0.38 mmol). The solution was stirred overnight and the volatiles were removed *in vacuo*. The residue was redissolved

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in hexane (5 ml). Crystals formed overnight at -20 °C and were filtered and dried under vacuum. Yield: 111 mg (0.23 mmol, 62 %).

Elemental analysis: calculated for C₁₇H₃₀N₄F₄P₂Ni: C, 41.92; H, 6.21; N, 11.50. Found: C, 42.16; H, 6.32; N, 10.84

IR (nujol): $v_{N_3} = 2054 \text{ cm}^{-1}$ (m)

MS (EI, m/z, relative intensity): 444 (13%) $[Ni(C_5F_4N)(PEt_3)_2]$ 294 (8%) $[Ni(PEt_3)_2]^+$, 118 (51%) $[PEt_3]^+$

¹H NMR (C₆D₆): δ 0.90 (t, 18H, CH₃), δ 1.05 (s, 12H, CH₂). Integration: 2:3 (CH₂:CH₃); ³¹P NMR (C₆D₆): δ 16.10 (s, 2PEt₃); ¹⁹F NMR (C₆D₆): δ -88.25 (m, 1F, CF, J_{3,6} = 30; J_{5,6} = 30; J_{6,4} =16), δ -132.91 (t, 1F, CF, J_{3,6} = 30; J_{3,4} = 30), δ -150.32 (q, 1F, CF, J_{3,4} = 30; J_{4,5} = 18; J_{4,6} = 16), δ -172.64 (m, 1F, CF, J_{5,6} = 30; J_{4,5} = 18). Integration: 1:1:1:1 (F³: F⁴: F⁵: F⁶).

6.1.7 Synthesis of *trans*- $Ni(N_3)(C_5F_3HN)(PEt_3)_2$ (4)



Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ l, 0.81 mmol) and 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50mmol) (Eqn. 6.4). The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The residue was redissolved in hexane and treated with trimethylsilyl azide (50 μ l, 0.38 mmol). The solution was stirred overnight and the volatiles were removed *in vacuo*. The residue was redissolved in hexane (5 ml). Crystals formed overnight at -20 °C and were filtered and dried under vacuum. Yield: 119 mg (0.26 mmol, 71 %).

Elemental analysis: calculated for $C_{17}H_{31}N_4F_3P_2Ni$: C, 43.53; H, 6.66; N, 11.94. Found:

C, 43.13; H, 6.93; N, 11.63

IR (nujol): $v_{N3} = 2054 \text{ cm}^{-1}$ (m)

MS (EI, m/z, relative intensity): 426 (5%) [Ni(C₅F₃HN)(PEt₃)₂], 294 (6%) [Ni(PEt₃)₂]⁺, 118 (46%) [PEt₃]⁺

¹H NMR (C₆D₆): δ 0.93 (m, 18H, CH₃), δ 1.10 (m, 12H, CH₂), 6.25 (m, 1H, aryl-H, J = 6). Integration: 1:12:18 (aryl-H:CH₂:CH₃). ³¹P NMR (C₆D₆): δ 15.76 (s, 2PEt₃); ¹⁹F NMR (C₆D₆): δ -90.91 (td, 1F, CF, J_{5,6} = 31; J_{3,6} = 31, J_{6,H} = 6), δ -111.45 (d, 1F, CF, J = 31), δ -150.63 (m, 1F, CF, J = 31). Integration: 1:1:1 (F³:F⁵:F⁶)

6.1.7 Synthesis of *trans*-Ni(NCO)(C₅F₃HN)(PEt₃)₂ (5)



Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ l, 0.81 mmol) and 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50mmol) (Eqn. 6.5). The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The residue was redissolved in hexane and treated with trimethylsilyl isocyanate (50 μ l, 0.37 mmol). The solution was stirred overnight and the volatiles were removed *in vacuo*. The residue was redissolved in hexane (5 ml). Crystals formed overnight at –20 °C and were filtered and dried under vacuum. Yield: 130 mg (0.28 mmol, 79%).

Elemental analysis: calculated for $C_{18}H_{31}N_2F_3P_2NiO$: C, 46.09; H, 6.66; N, 5.97. Found: C, 46.43; H, 6.72; N, 6.00

IR (nujol): $v_{\rm NCO} = 2225 \text{ cm}^{-1}$ (s)

¹H NMR (C₆D₆): δ 0.88 (m, 18H, CH₃), δ 1.40 (m, 12H, CH₂), 6.25 (m, 1H, aryl-H). Integration: 1:12:18 (aryl-H:CH₂:CH₃). ³¹P NMR (C₆D₆): δ 15.76 (s, 2PEt₃); ¹⁹F NMR (C₆D₆): δ-90.95 (m, 1F, CF, J_{5,6} = 31; J_{3,6} = 31, J_{6,H} = 6), δ -111.53 (d, 1F, CF, J = 31), δ -150.72 (m, 1F, CF, J = 31). Integration: 1:1:1 ($F^3:F^5:F^6$).

Experimental

6.1.9 Synthesis of Ni(C=CSiMe₃)(C₅F₃HN)(PEt₃)₂ (6)



Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 ml) was treated with PEt₃ (140 μ L, 0.81 mmol) and 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50mmol) (Eqn. 6.6). The solution was stirred for 2 h and the volatiles were removed *in vacuo*. The residue was redissolved in hexane and treated with trimethylsilyl acetylene (50 μ l, 0.35 mmol). The solution was stirred for two weeks and the volatiles were removed *in vacuo*. Alternatively, the trimethylsilyl acetylene derivative was prepared by addition of Et₃N (50 μ l, 0.36 mmol) to the reaction flask and stirring for one week followed by removal of volatiles *in vacuo*. The residue was redissolved in hexane (5 mL). However, crystals of the product could not be obtained.

IR (nujol): $v_{C=C} = 2023 \text{ cm}^{-1}(s)$

¹H NMR (C₆D₆): δ 0.26 (s, 9H, Si–CH₃), δ 0.97 (m, 18II, CH₃), δ 1.40 (m, 12H, CII₂), 6.40 (m, 1H, aryl-H). Integration: 1:9:12:18 (aryl-H:Si(CH₃)₃:CH₂:CH₃). ³¹P NMR (C₆D₆): δ 19.90 (s, 2PEt₃); ¹⁹F NMR (C₆D₆): δ -91.56 (m, 1F, CF, J_{3,6} = 31, J_{6,H} = 6), δ -112.14 (d, 1F, CF, J = 31), δ -151.12 (m, 1F, CF, J = 31). Integration: 1:1:1 (F³:F⁵ :F⁶).

6.2 Chapter 3: Matrix isolation studies of $(\eta^5 - C_5H_5)Fc(\eta^5 - (CH_3)_2C_4H_2N)$

6.2.1 General considerations

All manipulations were performed on a Schlenk line. $[CpFe(CO)_2]_2$ was dried at 50 °C and under vacuum before use. $(CH_3)_2C_4H_2N$ was distilled over CaH₂ and under reduced pressure before use. All reactants were bought from Aldrich Chemical Company Ltd.

6.2.2 Spectroscopy

 $(\eta^5-C_5H_5)Fe(\eta^5-(CH_3)_2C_4H_2N)$ was characterised by ¹H (400 MHz) spectroscopy on a Bruker Avance 400 NMR spectrometer. NMR samples were prepared in tubes with non-airtight caps. CDCl₃ was used as solvent for NMR spectroscopy. The deuterated solvent was used as received. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer and UV-vis spectra were recorded on a Perkin Elmer Lambda EZ201 spectrophotometer.

6.2.3 Synthesis of $(\eta^{5}-C_{5}H_{5})Fe(\eta^{5}-(CH_{3})_{2}C_{4}H_{2}N)$



 $(\eta^{5}-C_{5}H_{5})Fe(\eta^{5}-(CH_{3})_{2}C_{4}H_{2}N)$ was synthesised following a literature procedure (Eqn 6.7).² (CH₃)₂C₄H₂N (5 ml, 49 mmol) and [CpFe(CO)₂]₂ (1.42 g, 4 mmol) were brought to reflux temperature under an argon atmosphere for 36 h. After cooling to room temperature, heptane (60 ml) was added. The resulting solid was filtered off. The filtrate was diluted with ether (40 ml) and extracted twice with 5 % aq. HCl. The aqueous layer was shaken with ether (20 ml), separated and made alkaline with solid Na₂CO₃. Extraction with ether (2 x 30 ml), drying with MgSO₄ and evaporation of the solvent gave a red oil, which was purified by column chromatography (SiO₂/CH₂Cl₂/ Et₃N) to afford (η^{5} -C₅H₅)Fe(η^{5} -2,5-(CH₃)₂C₄H₂N). Yield: 620 mg (2.88 mmol, 36 %). IR(nujol): $\nu = 1457$ (s), 1410 (m), 1373 (s), 1334 (s), 1300 (m), 1258 (m), 1106 (s), 1037 (s), 1021 (s), 1002 (s) cm⁻¹

¹H NMR (CDCl₃): δ 4.29 (s, 2H, H_{3, 4}), δ 4.10 (s, 5H, Cp), δ 2.23 (s, 6H, Me). Integration: 1:3:2.5 (pyrrole-H: CH₃: Cp)

UV-vis (Ar matrix): $\lambda_{max} = 423$ nm, also band at 325 nm

6.3 Chapter 4: Matrix isolation studies of $(\eta^5-C_4H_4Se)Cr(CO)_3$

6.3.1 General considerations

All manipulations were performed on a Schlenk line. $n-Bu_2O$ was distilled from CaH₂ before use. THF was distilled from Na/benzophenone using a micro distillation apparatus before use. Cr(CO)₆ and selenophene were used as received. All reactants were bought from Aldrich Chemical Company Ltd.

6.3.2 Spectroscopy

 $(\eta^5-C_4H_4Se)Cr(CO)_3$ was characterised by ¹H (400 MHz) NMR spectroscopy on a Bruker Avance 400 spectrometer. NMR samples were prepared in tubes with nonairtight caps. CDCl₃ was used as solvent for NMR spectroscopy. The deuterated solvent was used as received. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer and UV-vis spectra were recorded on a Perkin Elmer Lambda EZ201 spectrophotometer.

6.3.3 Synthesis of $(\eta^5-C_4H_4Se)Cr(CO)_3$



Eqn. 6.8

 $(\eta^5-C_4H_4Se)Cr(CO)_3$ was prepared following a literature procedure (Eqn. 6.8).³ Cr(CO)₆ (0.22 g, 1.77 mmol) and C₄H₄Se (0.5 ml, 5.43 mmol) were added to a reaction flask containing n-Bu₂O (10 ml) and THF (1 ml). The reaction mixture was brought to reflux temperature for 3.5 h. The volatiles were removed *in vacuo*. The residue was dissolved in cyclohexane/dichloromethane (1:1) and chromatographed on deactivated alumina. After elution from the column the solvent was removed *in vacuo* to give a red crystalline product. Neutral alumina (Brockman, activity I, \approx 150 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for several
Experimental

hours. The alumina was deactivated with 5 % w/w N₂ saturated water and stored under N₂. Yield: 320 mg (1.18 mmol, 67 %). IR (CHCl₃): $v_{CO} = 1967$ (s), 1889 (s), 1867 (s) cm⁻¹ ¹H NMR (CDCl₃): δ 5.95 (s, 2H, H_{3,4}), δ 5.79 (s, 2H, H_{2,5}) ¹³C NMR: (CDCl₃): δ 91.80 (s, C_{3,4}), δ 91.51 (s, C_{2,5}), δ 233 (s, CO). Integration: 1:2.5 (selenophene-H: Cp). UV-vis (Ar matrix): $\lambda_{max} = 409$ nm, also bands at 360 and 500 (br) nm.

6.4 Chapter 5: Study of the photochemistry of $[(\eta^5-C_5H_5)M(\eta^6-C_6H_5X)]$ complexes

6.4.1 General considerations

All manipulations were performed on a Schlenk line. Ethanol (500 ml) was dried by bringing Mg turnings (2.5 g) in the presence of iodine (0.2 g) to reflux temperature until the iodine colour disappeared. The ethanol was distilled immediately before use. Dicyclopentadiene was distilled through a *Vigreux* column. The distilled cyclopentadiene was collected in ice to prevent dimerisation. Methanol was dried over CaH₂ before use, 2,5-dimethylthiophene was dried over KOH and dichloromethane was dried over CaCl₂ before use. RuCl₃•xH₂O, triphenylphosphine, ferrocene, mono- and dichlorobenzene and $[(\eta^5-Cp)Fe(\eta^6-(CH_3)_2CHC_6H_5)]PF_6$ were used as received. All reactants were bought from Aldrich Chemical Company Ltd.

6.4.2 Spectroscopy

All $[(\eta^5-C_5H_5)M(\eta^6-C_6H_5Y)]X$ complexes were characterised by ¹H (500.13 MHz) and ¹³C (125.76 MHz) NMR spectroscopy on a Bruker Avance 400 NMR spectrometer. NMR samples were prepared in tubes with non-airtight caps. CDCl₃ was used as solvent for NMR spectroscopy. The deuterated solvent was used as received. Infrared spectra were recorded on a Unicam Research Series FTIR spectrometer.

Experimental

6.4.3 Synthesis of $[(\eta^5 - C_5H_5)Ru(\eta^5 - 2, 5 - (CH_3)_2C_4H_2S)]BF_4$



 $(\eta^5-C_5H_5)Ru(PPh_3)_2Cl$ was prepared following a literature procedure (Eqn. 6.9).⁴ A solution of RuCl₃•xH₂O (0.52 g, \approx 2 mmol) in dry ethanol (20 ml) was added to a rapidly stirred solution of triphenylphosphine (2.10 g, 8.0 mmol) in ethanol (100 ml). The mixture was brought to reflux temperature. A solution of freshly distilled cyclopentadiene (1-2 ml) in ethanol (20 ml) was immediately added to the reaction flask. The mixture was brought to reflux temperature until the colour change from dark brown to orange was complete. The reaction flask was placed in the refrigerator overnight. The orange crystalline product was filtered and washed with cold ethanol (2 x 10 ml), water (2 x 10 ml), ethanol (2 x 10 ml) and pet. ether (40 - 60° C) (2 x 10 ml). Yield: 790 mg (1.088 mmol, 78 %).

¹H NMR (CDCl₃): δ 7.15 (m, 30H, PPh₃), δ 4.05 (s, 5H, C₅H₅). Integration 1:6 (Cp: C₆H₅).

 $[(\eta^5-C_5H_5)Ru(\eta^5-2,5-(CH_3)_2C_4H_2S)]BF_4$ was prepared following a literature procedure (Eqn. 6.9).⁵ $(\eta^5-C_5H_5)Ru(PPh_3)_2Cl$ (1.00 g, 1.38 mmol), AgBF₄ (0.29 g, 1.52 mmol), 2,5-(CH₃)_2C_4H_2S (3 ml) were brought to reflux temperature in methanol (20 ml) for 24 h under a N₂ atmosphere. Removing the volatiles *in vacuo*, extracting the residue with CH₂Cl₂ and precipitating the compound from the filtered solution by slow addition of Et₂O isolated the product. Successive recrystallisations from CH₂Cl₂/Et₂O yielded the salts as brown powders. Yield: 2.15 g (0.59 mmol, 43 %).

¹H NMR (CDCl₃): δ 6.46 (s, 2H, H_{3,4}), δ 6.38 (s, 2H, H_{2,5}), δ 5.38 (s, 5H, Cp). Integration: 2:2.5 (thiophene-H: Cp)

UV-vis (CII₂Cl₂): $\lambda_{max} = 485$ nm, also band at 455 nm

Experimental

6.4.4 Synthesis of $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$



Eqn. 6.10

 $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]PF_6$ was prepared following a literature procedure (Eqn. 6.10).⁶ AlCl₃ (1.4 g, 0.10 mmol) and Al powder (0.2 g, 7.41 mmol) were added to a solution of ferrocene (1 g, 5 mmol) in C₆H₅Cl (20 ml). The mixture was brought to reflux temperature with stirring for 6 h. After cooling to room temperature, water (60 ml) was added to the reaction flask and the solution was stirred for several minutes. The aqueous layer was removed and washed with pet. ether (40-60 °C). The solid residue was filtered off and a solution of ammonium hexafluorophosphate was added to the filtrate. A precipitate formed immediately. The solid was filtered off and recrystallised from acetone and ether. Yield: 0.98 g (2.6 mmol, 52 %).

Elemental analysis: calculated for $C_{11}H_{10}CIFePF_6$: C: 34.9; H: 2.66. Found C: 34.6; H: 2.51. ¹H NMR (CDCl₃): δ 6.75 (m, 2H, arene ring), δ 6.55 (m, 2H, arene ring), δ 6.4 (m, 1H, arene ring) J = 3, 7 Hz; δ 5.2 (s, 5H, C₅H₅). Integration: 1:2:2:5 (aryl-H: 2aryl-H: 2aryl-H: Cp). UV-vis (CH₂Cl₂): $\lambda_{max} = 485$ nm, also band at 450 nm.

6.4.5 Synthesis of $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$



Eqn. 6.11

 $[(\eta^5-C_5H_5)Fe(\eta^6-1,2-C_6H_4Cl_2)]PF_6$ was prepared following a literature procedure (Eqn. 6.11).⁶ AlCl₃ (1.4 g, 0.10 mmol) and Al powder (0.2 g, 7.41 mmol) were added to a solution of ferrocene (1 g, 5 mmol) in 1,2-C₆H₄Cl₂ (20 ml). The mixture was brought to

reflux temperature with stirring for 6 h. After cooling to room temperature, water (60 ml) was added to the reaction flask and the solution was stirred for several minutes. The aqueous layer was removed and washed with pet. ether (40-60 °C). The solid residue was filtered off and a solution of ammonium hexafluorophosphate was added to the filtrate. A precipitate formed immediately. The solid was filtered off and recrystallised from acetone and ether. Yield: 0.99 g (2.4 mmol, 48 %).

Elemental analysis: calculated for $C_{11}H_9Cl_2FePF_6$: C: 34.9; H: 2.66. Found C: 32.03; H: 2.05. ¹H NMR (CDCl₃): δ 6.7 (m, arene, J = 3.5 Hz), δ 6.5 (m, arene, J = 3.6 Hz), δ 5.5 (5H, Cp). Integration: 3:2:5 (aryl-H: aryl-H: Cp). UV-vis (CH₂Cl₂): $\lambda_{max} = 485$ nm, also band at 450 nm.

6.5 UV-vis laser flash photolysis

6.5.1 Apparatus

The apparatus for laser flash photolysis is illustrated in Fig. 6.1. The laser source is a Nd-YAG (neodymium yttrium aluminium garnet). It operates at a wavelength of 1064 nm but can be doubled, tripled or quadrupled to produce a second, third or fourth harmonic at 532, 355, 266 nm. Typically at 355 nm the laser has energy of 45 mJ per pulse. The pulse time of the laser is in the region of 10 ns. The laser is directed *via* one Pellin-Broca prism onto the sample cuvette. When the pulse passes through the power meter situated after the prism, the oscilloscope is triggered. The monitoring light source is an air-cooled 275-Watt xenon arc lamp positioned at right angles to the laser beam. The monitoring beam passes through the sample and is directed to the entrance slit of the monochromator *via* a circular lens. UV-vis filters are employed to prevent excessive sample degradation. A photomultiplier is arranged at the exit slit of the monochromator. Absorbance changes of the sample are monitored *via* an IEEE bus and all signals are recorded on disk.



Fig. 6.1: Apparatus for UV-vis laser flash photolysis

6.5.2 Mode of operation

The amount of light passing through the sample before the laser flash is triggered is measured as I_0 . This value is measured by obtaining the difference in the voltage of the amount of light transmitted by the solution when the shutter of the monitoring beam is opened and then closed. After the laser has been triggered the intensity of light passing through the sample is measured and recorded as I. The ratio of I_0/I creates a trace on the screen known as the transient. A standard trace illustrates the change in voltage with time, which corresponds to time resolved absorbance. The resulting transients are analysed by first order kinetics.

6.6 Matrix isolation

6.6.1 Apparatus for IR and UV-vis detected matrixes

The matrix isolation apparatus is described below. The apparatus consists of a closed cycle helium refrigerator, sample window, sample shroud, deposition tube, gas mixing chamber, gas inlet, backing pump, diffusion pump and temperature control unit (Figs. 6.2 and 6.3). Matrixes are deposited *via* the slow 'spray-on' technique onto a CaF_2 window cooled to 20 K. For UV-vis detection, CaF₂ outer windows are used. This allows detection to 950 cm⁻¹ in the IR spectrum. A thermocouple embedded into a cavity beside the window and connected to the temperature control unit maintains the temperature. The window is cooled by a closed cycle helium refrigerator (Air Products) mounted via a double O-ring seal in a stainless steel vacuum shroud. The system pumps to 8 x 10^{-4} mbar prior to cooling and achieves 10^{-7} mbar upon cooling. Host gases (Cryo Service) are deposited onto the window via the needle valve. When a reactive gas such as CO is being deposited, it is mixed with Ar in the correct ratio in the mixing chamber prior to deposition. A ratio of sample molecule to host molecule in the region of 1:2000 is desirable. A BOC gauge controls the rate of gas deposition. Typically a rate of 0.6 torr per min achieves sufficient dilution on the matrix window. Simultaneous with gas deposition, is sample deposition. The sample is kept in a rightangled tube at temperatures below -10 °C until required. When required, the sample is heated with a heating wire to the necessary temperature, where it sublimes onto the CaF₂ window. A temperature of 8 °C was required for the sublimation of $(\eta^{5}-C_{5}H_{5})Fe(\eta^{5}-(CH_{3})_{2}C_{4}H_{2}N)$ onto the CaF₂ window while sublimation of $(\eta^5-C_4H_4Se)Cr(CO)_3$ was achieved at 35 °C *via* a heating coil. Photolysis of the matrix is achieved with either an Oriel 300 Watt Xe-arc lamp or 200 Watt Hg/Xe lamp. Cut off interference filters with $\lambda_{exc} = 546, 436, 405, 365$ nm are employed along with broadband filters with $\lambda_{exc} > 550$, > 410, >390, >310 nm. UV-vis spectra are recorded on a Perkin Elmer Lambda EZ201 spectrophotometer while IR spectra are recorded on a Perkin Elmer Spectrum One instrument.

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Experimental

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Fig. 6.2: Apparatus for matrix isolation



Fig. 6.3: Illustration of the sample shroud, sample container and gas inlet

Experimental

6.7 Cyclic voltammetry

The apparatus for cyclic voltammetry is illustrated in Fig. 6.4. The most important electrode in cyclic voltammetry is the working electrode, which was made from teflon shrouded glassy carbon. The counter electrode was made from platinum wire. The redox of the analyte occurs at this electrode. The auxiliary electrode conducts electricity form the signal SCE into the solution to maintain the correct current. The reference electrode used for these experiments was made from saturated calomel (SCE). The scan rate employed in these studies was 100 mV/s. The potential of this electrode is known and remains constant. The potential that is cycled is the potential difference between the working electrode and the reference electrode. The potential is scanned in the negative direction until it has become negative enough to reduce the analyte at the working electrode. The reaction continues at the electrode until most of the species has been reduced. The current then decays for the remainder of the forward scan until the potential is reversed. The potential is scanned in the positive direction until it sould be completed in the positive direction until it reaches point where the analyte is oxidised. The current then decays from this peak and the potential completes its cycle.



6.7.1 Apparatus

Fig. 6.4: Apparatus for cyclic voltammetry

6.8 Future work

6.8.1 C-F activation

In the chapter presented on C-F activation, success was achieved in producing three new complexes in which the activated fluorine had been replaced by new functionalities. The orientation of these groups is *trans* to the polyfluorinated ring. In order to achieve reductive elimination, a *cis* orientation is required. Work on this project is ongoing and fellow workers in the University of York have succeeded in producing a C-F complex in which the activated fluorine and polyfluorinated pyridine ring are in a *cis* orientation (Eqn 6.11). Dicyclohexylphosphino ethane (dcpe) was employed as the phosphine. Current work is attempting to replace the activated fluorine atom in the complex NiF(dcpe)₂(C₅F₃HN) with an alternative ligand.

6.8.2 Photochemistry of $(\eta^5-C_5H_5)Fe(\eta^5-2,5-(CH_3)_2C_4H_2N)$

Studies of the photochemistry of $(\eta^5 - C_5H_5)Fe(\eta^5 - 2, 5 - (CH_3)_2C_4H_2N)$ are almost complete. Future work involving this complex would be to assign a structure to the metal-carbonyl complex that absorbs at $v_{CO} = 2061 \text{ cm}^{-1}$. Molecular modelling studies would obtain theoretical data about the assignments made for the photoproducts observed in the matrix isolation studies. The observation of a triplet state monocarbonyl complex is rather unusual and further molecular modelling studies will confirm whether its presence is likely. Indeed preliminary studies do indicate that the triplet state complex is a possible intermediate. Details of these initial studies are included in the appendix.

6.8.3 Photochemistry of $(\eta^5-C_4H_4Se)Cr(CO)_3$

Studies of the photochemistry of $(\eta^5-C_4H_4Se)Cr(CO)_3$ have been completed. Theoretical studies could be employed to confirm the assignments made for the photoproducts observed in the various matrixes. Investigation of methyl-substituted derivatives of the parent complex may shed further light on the photochemistry of this complex.

6.8.4 Photochemistry of $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+$ complexes

The photochemical studies of complexes of the type $[(\eta^5-C_5H_5)M(\eta^6-arene)]^+$ are incomplete. Transient absorption spectra need to be completed for $[(\eta^5-C_5H_5)Fe(\eta^6-$

Experimental

 $(CH_3)_2CHC_6H_5)]^+$ in CO and Ar purged acetone and acetonitrile solutions at $\lambda_{exc} = 355$ and 532 nm. Laser flash photolysis studies need to be completed for the complexes, $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_{5-x}Cl_x)]^+$ (where x = 1 and 2). Studies carried out on the heteroaromatic complex $[(\eta^5-C_5H_5)Ru(\eta^5-C_4H_4S)]^+$ need to be subjected to the full set of experiments that have been suggested for the preceeding complexes.

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6.9 **REFERENCES**

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Appendix

Appendix

A.1 CRYSTAL DATA

Table 1: Crystal data and structure refinement for NiN₃(C₅F₃NH)(PEt₃)₂ as obtained from S. Archibald of the University of Hull.

Empirical Formula

 $C_{17}H_{31}N_4F_3P_2N_1$

Unit cell contents	68	H124	F12	N16	Ni4	P8
Formula weight	876.4	13				
Temperature	50 (2) K				
Wavelength	0.710)73 Å				
Crystal system, space group	mono	oclinic, P	2 _{1/c}			
Unit cell dimensions	a = 9	.1396 (12	2) Å	alpha	= 90 de	eg
	b = 1	2.7408 (12) Å	beta =	= 97.383	8 (11) deg
	$\mathbf{c} = 1$	9.819 (3)) Å	gamm	na = 90	deg
Volume	2288	.7 (5) Å ³				
Z (no. of molecules per unit cell),						
calculated density	4, 1.3	861 Mg/r	n^3			
Absorption coefficient	1.020) mm ⁻¹				
F (000)	98 4					
Crystal size	0.05	x 0.12 x	0.17 m	m		
θ range for data collection	2.62	to 34.97	deg			
Index ranges	-14<=	=h<=14,	-19 <k<< td=""><td><=20, -3</td><td>31<=1<=</td><td>=30</td></k<<>	<=20, -3	31<=1<=	=30
Reflections collected/unique	2943	9/ 9834	R(int)	= 0.124	6]	
Completeness to $2\theta = 69.94$	97.8	%				
Refinement method	Full-	matrix le	ast squ	ares on	F^2	
Data/ restraints/ parameters	9834	/ 0 / 245				
Goodness-of-fit on F ²	0.740)				
Final R indices [I>2o(I)]	$R_1 =$	0.0450,	$wR_2 = 0$	0.858		
R indices (all data)	$R_1 =$	0.1477, v	$wR_2 = 0$).10 82		
Extinction coefficient	0.002	26 (3)				
Largest diff. peak and hole	0.728	3 and -1 .	629 e.A	-3		

Appendix

Table 4: Anisotropic displacement parameters (A² X 10³). The anisotropic displacement factor exponent takes the form: -2 π^2 [h² a^{*2} U₁₁ + ... + 2 h k a^{*} b^{*} U₁₂]

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ni(1)	27 (1)	23 (1)	20(1)	-2 (1)	3 (1)	3 (1)
P(1)	33 (1)	28 (1)	24 (1)	-5 (1)	-2(1)	2(1)
P(2)	30 (1)	31 (1)	24 (1)	-2 (1)	-1 (1)	8(1)
F(4)	56(1)	29(1)	48 (1)	4(1)	22 (1)	-2 (1)
F(5)	72 (1)	47 (1)	70(1)	-21 (1)	42 (1)	3 (1)
F(6)	45 (1)	51 (1)	37 (1)	1(1)	17(1)	-5 (1)
N(1)	42 (1)	30 (1)	33 (1)	-6 (1)	11 (1)	7 (1)
N(2)	42 (1)	33 (1)	34 (1)	-5 (1)	6(1)	3 (1)
N(3)	74 (2)	63 (2)	63 (2)	-8 (1)	41 (2)	-3 (2)
N(4)	27 (1)	30 (1)	23 (1)	0(1)	2 (1)	0(1)
C(1)	24 (1)	25 (1)	20 (1)	-2 (1)	1 (1)	4 (1)
C(2)	29(1)	25 (1)	27 (1)	-1 (1)	3 (1)	-2 (1)
C(3)	41 (2)	25 (1)	44 (2)	-8 (1)	8 (1)	1 (1)
C(4)	36(1)	39 (1)	35 (1)	-13 (1)	12(1)	1 (1)
C(5)	26(1)	38 (1)	25 (1)	-3 (1)	4 (1)	-5 (1)
C(6)	41 (2)	35 (1)	44 (2)	-10(1)	-3 (1)	-7 (1)
C(7)	51 (2)	48 (2)	75 (2)	-15 (2)	24 (2)	-14 (2)
C(8)	38 (1)	40 (2)	37 (1)	-7 (1)	-8 (1)	14(1)
C(9)	21 (2)	71 (2)	47 (2)	-11 (2)	-18 (2)	20 (2)
C(10)	54 (2)	42 (2)	22 (1)	-2 (1)	1 (1)	7 (1)
C(11)	102 (3)	46 (2)	44 (2)	7 (2)	26 (2)	-2 (2)
C(12)	41 (2)	56 (2)	26 (1)	-11 (1)	-2 (1)	14(1)
C(13)	52 (2)	115 (4)	38 (2)	-26 (2)	-13 (2)	30 (2)
C(14)	32(1)	66 (2)	44 (2)	-11 (2)	2 (1)	1 (1)
C(15)	56 (2)	73 (3)	89 (3)	17 (2)	29 (2)	1 (2)
C(16)	100 (3)	44 (2)	53 (2)	0 (2)	-19 (2)	34 (2)
C(17)	207 (7)	42 (2)	93 (4)	26 (2)	14 (4)	2 (3)

Appendix

Table 4: Anisotropic displacement parameters ($A^2 \times 10^3$). The anisotropic
displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + + 2 h k a^* b^* U_{12}]$

	x	у	У	U(eq)
Ni(1)	9347 (1)	2996 (1)	1595 (1)	23 (1)
P(1)	11182(1)	2938 (1)	2433 (1)	28 (1)
P(2)	7406 (1)	2937 (1)	814 (1)	29(1)
F(4)	9710 (2)	543 (1)	152 (1)	43 (1)
F(5)	12932 (2)	484 (2)	-147 (1)	60(1)
F(6)	12710 (2)	2596 (1)	-206 (1)	43 (1)
N(1)	8410 (3)	4066 (2)	2073 (1)	35 (1)
N(2)	7562 (3)	4024 (2)	2477 (1)	36 (1)
N(3)	6739 (4)	4057 (2)	2876 (2)	64 (1)
N(4)	11179 (2)	2624 (2)	608 (1)	27 (1)
C(1)	10408 (2)	2138 (2)	1057 (1)	23 (1)
C(2)	10482 (3)	1055 (2)	1085 (1)	27 (1)
C(3)	11306 (3)	454 (2)	700 (2)	37 (1)
C(4)	12070 (3)	992 (2)	255 (1)	36(1)
C(5)	11959 (3)	2068 (2)	234 (1)	30 (1)
C(6)	12202 (3)	4173 (2)	2496 (2)	41 (1)
C(7)	12852 (4)	4452 (3)	1847 (2)	56 (1)
C(8)	12565 (3)	1902 (2)	2422 (2)	40 (1)
C(9)	13806 (4)	1894 (3)	3017 (2)	59 (1)
C(10)	10533 (3)	2811 (2)	3264 (1)	39 (1)
C(11)	9654 (5)	1812 (3)	3320 (2)	62 (1)
C(12)	7554 (3)	2201 (3)	34 (1)	42 (1)
C(13)	6207 (4)	2207 (4)	-514 (2)	70 (1)
C(14)	5788 (3)	2404 (3)	1161 (2)	48 (1)
C(15)	5977 (4)	1296 (3)	1397 (2)	71 (1)
C(16)	6805 (5)	4239 (3)	513 (2)	68 (1)
C(17)	8035 (8)	4770 (3)	170 (3)	114 (2)

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Appendix

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Ni(1)-C(1) $1.881 (2)$ Ni(1)-N(1) $1.923 (2)$ Ni(1)-P(2) $2.2003 (9)$ Ni(1)-P(1) $2.2053 (9)$ P(1)-C(6) $1.825 (3)$ P(1)-C(6) $1.827 (3)$ P(1)-C(8) $1.829 (3)$ P(2)-C(16) $1.823 (3)$ P(2)-C(14) $1.839 (3)$ F(4)-C(2) $1.354 (3)$ F(5)-C(4) $1.354 (3)$ F(6)-C(5) $1.355 (3)$ N(1)-N(2) $1.185 (3)$ N(2)-N(3) $1.160 (3)$ N(4)-C(1) $1.353 (3)$ C(1)-C(2) $1.375 (4)$ C(4)-C(5) $1.375 (4)$ C(4)-C(5) $1.528 (4)$ C(10)-C(11) $1.517 (5)$ C(10)-Ni(1)-P(2) $90.08 (8)$
Ni(1)-N(1) $1.923 (2)$ Ni(1)-P(2) $2.2003 (9)$ Ni(1)-P(1) $2.2053 (9)$ P(1)-C(6) $1.825 (3)$ P(1)-C(10) $1.827 (3)$ P(1)-C(8) $1.829 (3)$ P(2)-C(16) $1.823 (3)$ P(2)-C(12) $1.827 (3)$ P(2)-C(14) $1.839 (3)$ F(4)-C(2) $1.354 (3)$ F(5)-C(4) $1.355 (3)$ N(1)-N(2) $1.185 (3)$ N(2)-N(3) $1.160 (3)$ N(4)-C(5) $1.303 (3)$ N(4)-C(1) $1.353 (3)$ C(1)-C(2) $1.375 (4)$ C(4)-C(5) $1.375 (4)$ C(4)-C(5) $1.528 (4)$ C(10)-C(11) $1.517 (5)$ C(10)-C(11) $1.517 (5)$ C(10)-C(15) $1.490 (5)$ C(10)-C(17) $1.543 (7)$ C(1)-Ni(1)-N(1) $170.40 (10)$ C(1)-Ni(1)-P(2) $90.88 (8)$
Ni(1)-P(2)2.2003 (9)Ni(1)-P(1)2.2053 (9)P(1)-C(6)1.825 (3)P(1)-C(10)1.827 (3)P(1)-C(8)1.829 (3)P(2)-C(12)1.827 (3)P(2)-C(14)1.839 (3)F(4)-C(2)1.354 (3)F(5)-C(4)1.354 (3)F(6)-C(5)1.355 (3)N(1)-N(2)1.185 (3)N(2)-N(3)1.160 (3)N(4)-C(5)1.303 (3)C(1)-C(2)1.383 (3)C(2)-C(3)1.372 (3)C(3)-C(4)1.378 (4)C(4)-C(5)1.375 (4)C(4)-C(1)1.517 (5)C(10)-C(11)1.5134 (4)C(10)-C(11)1.5134 (4)C(10)-C(11)1.534 (7)C(1)-Ni(1)-N(1)170.40 (10)C(1)-Ni(1)-P(2)90.08 (8)
Ni(1)-P(1) 2.2053 (9)P(1)-C(6) 1.825 (3)P(1)-C(10) 1.827 (3)P(1)-C(8) 1.829 (3)P(2)-C(16) 1.823 (3)P(2)-C(12) 1.827 (3)P(2)-C(14) 1.839 (3)F(4)-C(2) 1.354 (3)F(5)-C(4) 1.354 (3)F(6)-C(5) 1.355 (3)N(1)-N(2) 1.185 (3)N(2)-N(3) 1.160 (3)N(4)-C(5) 1.303 (3)N(4)-C(5) 1.303 (3)C(1)-C(2) 1.383 (3)C(2)-C(3) 1.372 (3)C(3)-C(4) 1.378 (4)C(4)-C(5) 1.526 (4)C(6)-C(7) 1.526 (4)C(10)-C(11) 1.517 (5)C(12)-C(13) 1.534 (4)C(14)-C(15) 1.490 (5)C(10)-C(17) 1.543 (7)C(1)-Ni(1)-N(1) 170.40 (10)C(1)-Ni(1)-P(2) 90.08 (8)
P(1)-C(6) $1.825(3)$ P(1)-C(10) $1.827(3)$ P(1)-C(8) $1.829(3)$ P(2)-C(16) $1.823(3)$ P(2)-C(12) $1.827(3)$ P(2)-C(14) $1.839(3)$ F(4)-C(2) $1.359(3)$ F(5)-C(4) $1.354(3)$ F(6)-C(5) $1.355(3)$ N(1)-N(2) $1.185(3)$ N(2)-N(3) $1.160(3)$ N(4)-C(5) $1.333(3)$ C(1)-C(2) $1.383(3)$ C(2)-C(3) $1.372(3)$ C(3)-C(4) $1.378(4)$ C(4)-C(5) $1.528(4)$ C(10)-C(11) $1.517(5)$ C(12)-C(13) $1.534(4)$ C(14)-C(15) $1.490(5)$ C(10)-C(17) $1.543(7)$ C(1)-Ni(1)-N(1) $170.40(10)$ C(1)-Ni(1)-P(2) $90.98(8)$
P(1)-C(10) $1.827 (3)$ P(1)-C(8) $1.829 (3)$ P(2)-C(16) $1.823 (3)$ P(2)-C(12) $1.827 (3)$ P(2)-C(14) $1.839 (3)$ F(4)-C(2) $1.359 (3)$ F(5)-C(4) $1.354 (3)$ F(6)-C(5) $1.355 (3)$ N(1)-N(2) $1.185 (3)$ N(2)-N(3) $1.160 (3)$ N(4)-C(5) $1.333 (3)$ C(1)-C(2) $1.383 (3)$ C(2)-C(3) $1.372 (3)$ C(3)-C(4) $1.378 (4)$ C(4)-C(5) $1.526 (4)$ C(6)-C(7) $1.526 (4)$ C(10)-C(11) $1.517 (5)$ C(12)-C(13) $1.534 (4)$ C(14)-C(15) $1.490 (5)$ C(10)-C(17) $1.543 (7)$ C(1)-Ni(1)-N(1) $170.40 (10)$ C(1)-Ni(1)-P(2) $90.08 (8)$
P(1)-C(8) $1.829(3)$ $P(2)-C(16)$ $1.823(3)$ $P(2)-C(12)$ $1.827(3)$ $P(2)-C(14)$ $1.839(3)$ $F(4)-C(2)$ $1.359(3)$ $F(5)-C(4)$ $1.354(3)$ $F(6)-C(5)$ $1.355(3)$ $N(1)-N(2)$ $1.185(3)$ $N(2)-N(3)$ $1.160(3)$ $N(4)-C(5)$ $1.303(3)$ $N(4)-C(1)$ $1.353(3)$ $C(1)-C(2)$ $1.383(3)$ $C(2)-C(3)$ $1.372(3)$ $C(2)-C(3)$ $1.375(4)$ $C(4)-C(5)$ $1.526(4)$ $C(6)-C(7)$ $1.526(4)$ $C(10)-C(11)$ $1.517(5)$ $C(10)-C(11)$ $1.534(4)$ $C(14)-C(15)$ $1.490(5)$ $C(10)-C(17)$ $1.543(7)$ $C(1)-Ni(1)-N(1)$ $170.40(10)$ $C(1)-Ni(1)-P(2)$ $90.08(8)$
$\begin{array}{ccccccc} P(2)-C(16) & 1.823 (3) \\ P(2)-C(12) & 1.827 (3) \\ P(2)-C(14) & 1.839 (3) \\ F(4)-C(2) & 1.359 (3) \\ F(5)-C(4) & 1.354 (3) \\ F(6)-C(5) & 1.355 (3) \\ N(1)-N(2) & 1.185 (3) \\ N(2)-N(3) & 1.160 (3) \\ N(4)-C(5) & 1.303 (3) \\ N(4)-C(1) & 1.353 (3) \\ C(1)-C(2) & 1.383 (3) \\ C(2)-C(3) & 1.372 (3) \\ C(3)-C(4) & 1.378 (4) \\ C(4)-C(5) & 1.375 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(16)-C(17) & 1.543 (7) \\ \end{array}$
P(2)-C(12) $1.827 (3)$ P(2)-C(14) $1.839 (3)$ F(4)-C(2) $1.359 (3)$ F(5)-C(4) $1.354 (3)$ F(6)-C(5) $1.355 (3)$ N(1)-N(2) $1.185 (3)$ N(2)-N(3) $1.160 (3)$ N(4)-C(5) $1.303 (3)$ N(4)-C(1) $1.353 (3)$ C(1)-C(2) $1.383 (3)$ C(2)-C(3) $1.372 (3)$ C(3)-C(4) $1.378 (4)$ C(4)-C(5) $1.375 (4)$ C(6)-C(7) $1.526 (4)$ C(10)-C(11) $1.517 (5)$ C(10)-C(11) $1.534 (4)$ C(14)-C(15) $1.490 (5)$ C(16)-C(17) $1.543 (7)$ C(1)-Ni(1)-N(1) $170.40 (10)$ C(1)-Ni(1)-P(2) $90.08 (8)$
$\begin{array}{ccccc} P(2)-C(14) & 1.839 (3) \\ F(4)-C(2) & 1.359 (3) \\ F(5)-C(4) & 1.354 (3) \\ F(6)-C(5) & 1.355 (3) \\ N(1)-N(2) & 1.185 (3) \\ N(2)-N(3) & 1.160 (3) \\ N(4)-C(5) & 1.303 (3) \\ N(4)-C(1) & 1.353 (3) \\ C(1)-C(2) & 1.383 (3) \\ C(2)-C(3) & 1.372 (3) \\ C(3)-C(4) & 1.378 (4) \\ C(4)-C(5) & 1.375 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(8)-C(9) & 1.528 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(10)-C(17) & 1.543 (7) \\ \end{array}$
F(4)-C(2) $1.359(3)$ $F(5)-C(4)$ $1.354(3)$ $F(6)-C(5)$ $1.355(3)$ $N(1)-N(2)$ $1.185(3)$ $N(2)-N(3)$ $1.160(3)$ $N(4)-C(5)$ $1.303(3)$ $N(4)-C(1)$ $1.353(3)$ $C(1)-C(2)$ $1.383(3)$ $C(2)-C(3)$ $1.372(3)$ $C(3)-C(4)$ $1.378(4)$ $C(4)-C(5)$ $1.526(4)$ $C(6)-C(7)$ $1.528(4)$ $C(1)-C(11)$ $1.517(5)$ $C(12)-C(13)$ $1.534(4)$ $C(14)-C(15)$ $1.490(5)$ $C(1)-Ni(1)-N(1)$ $170.40(10)$ $C(1)-Ni(1)-P(2)$ $90.08(8)$
F(5)-C(4) $1.354(3)$ $F(6)-C(5)$ $1.355(3)$ $N(1)-N(2)$ $1.185(3)$ $N(2)-N(3)$ $1.160(3)$ $N(4)-C(5)$ $1.303(3)$ $N(4)-C(1)$ $1.353(3)$ $C(1)-C(2)$ $1.383(3)$ $C(2)-C(3)$ $1.372(3)$ $C(3)-C(4)$ $1.378(4)$ $C(4)-C(5)$ $1.375(4)$ $C(6)-C(7)$ $1.526(4)$ $C(6)-C(7)$ $1.528(4)$ $C(10)-C(11)$ $1.517(5)$ $C(12)-C(13)$ $1.534(4)$ $C(14)-C(15)$ $1.490(5)$ $C(16)-C(17)$ $1.543(7)$ $C(1)-Ni(1)-N(1)$ $170.40(10)$ $C(1)-Ni(1)-P(2)$ $90.08(8)$
F(6)-C(5) $1.355(3)$ $N(1)-N(2)$ $1.185(3)$ $N(2)-N(3)$ $1.160(3)$ $N(4)-C(5)$ $1.303(3)$ $N(4)-C(1)$ $1.353(3)$ $C(1)-C(2)$ $1.383(3)$ $C(2)-C(3)$ $1.372(3)$ $C(3)-C(4)$ $1.378(4)$ $C(4)-C(5)$ $1.375(4)$ $C(6)-C(7)$ $1.526(4)$ $C(6)-C(7)$ $1.528(4)$ $C(10)-C(11)$ $1.517(5)$ $C(12)-C(13)$ $1.534(4)$ $C(14)-C(15)$ $1.490(5)$ $C(16)-C(17)$ $1.543(7)$ $C(1)-Ni(1)-N(1)$ $170.40(10)$ $C(1)-Ni(1)-P(2)$ $90.08(8)$
N(1)-N(2) 1.185 (3)N(2)-N(3) 1.160 (3)N(4)-C(5) 1.303 (3)N(4)-C(1) 1.353 (3)C(1)-C(2) 1.383 (3)C(2)-C(3) 1.372 (3)C(3)-C(4) 1.378 (4)C(4)-C(5) 1.375 (4)C(6)-C(7) 1.526 (4)C(8)-C(9) 1.528 (4)C(10)-C(11) 1.517 (5)C(12)-C(13) 1.534 (4)C(14)-C(15) 1.490 (5)C(16)-C(17) 1.543 (7)C(1)-Ni(1)-N(1) 170.40 (10)C(1)-Ni(1)-P(2) 90.08 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
N(4)-C(5)1.303 (3) $N(4)-C(1)$ 1.353 (3) $C(1)-C(2)$ 1.383 (3) $C(2)-C(3)$ 1.372 (3) $C(3)-C(4)$ 1.378 (4) $C(4)-C(5)$ 1.375 (4) $C(6)-C(7)$ 1.526 (4) $C(6)-C(7)$ 1.528 (4) $C(10)-C(11)$ 1.517 (5) $C(12)-C(13)$ 1.534 (4) $C(14)-C(15)$ 1.490 (5) $C(16)-C(17)$ 1.543 (7) $C(1)-Ni(1)-N(1)$ 170.40 (10) $C(1)-Ni(1)-P(2)$ 90.08 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccccc} C(1)-C(2) & 1.383 (3) \\ C(2)-C(3) & 1.372 (3) \\ C(3)-C(4) & 1.378 (4) \\ C(4)-C(5) & 1.375 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(8)-C(9) & 1.528 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(16)-C(17) & 1.543 (7) \\ \hline \\ $
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccc} C(3)-C(4) & 1.378 (4) \\ C(4)-C(5) & 1.375 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(8)-C(9) & 1.528 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(16)-C(17) & 1.543 (7) \\ \end{array}$
$\begin{array}{cccc} C(4)-C(5) & 1.375 (4) \\ C(6)-C(7) & 1.526 (4) \\ C(8)-C(9) & 1.528 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(16)-C(17) & 1.543 (7) \\ \hline \\ \hline \\ C(1)-Ni(1)-N(1) & 170.40 (10) \\ C(1)-Ni(1)-P(2) & 90.55 (7) \\ N(1)-Ni(1)-P(2) & 90.08 (8) \\ \hline \end{array}$
$\begin{array}{cccc} C(6) - C(7) & 1.526 (4) \\ C(8) - C(9) & 1.528 (4) \\ C(10) - C(11) & 1.517 (5) \\ C(12) - C(13) & 1.534 (4) \\ C(14) - C(15) & 1.490 (5) \\ C(16) - C(17) & 1.543 (7) \\ \end{array}$
$\begin{array}{cccc} C(8)-C(9) & 1.528 (4) \\ C(10)-C(11) & 1.517 (5) \\ C(12)-C(13) & 1.534 (4) \\ C(14)-C(15) & 1.490 (5) \\ C(16)-C(17) & 1.543 (7) \\ \end{array}$
$\begin{array}{cccc} C(10) - C(11) & 1.517 (5) \\ C(12) - C(13) & 1.534 (4) \\ C(14) - C(15) & 1.490 (5) \\ C(16) - C(17) & 1.543 (7) \\ \hline \\ \hline \\ C(1) - Ni(1) - N(1) & 170.40 (10) \\ C(1) - Ni(1) - P(2) & 90.55 (7) \\ N(1) - Ni(1) - P(2) & 90.08 (8) \\ \hline \end{array}$
$\begin{array}{cccc} C(10) & C(11) & & & 1.534 \ (4) \\ C(12)-C(13) & & & 1.534 \ (4) \\ C(14)-C(15) & & & 1.490 \ (5) \\ C(16)-C(17) & & & 1.543 \ (7) \\ \end{array}$
$\begin{array}{cccc} C(12) & C(15) & & 1.490 (5) \\ C(14)-C(15) & & 1.543 (7) \\ \hline \\ C(1)-Ni(1)-N(1) & & 170.40 (10) \\ C(1)-Ni(1)-P(2) & & 90.55 (7) \\ N(1)-Ni(1)-P(2) & & 90.08 (8) \end{array}$
C(16)-C(17) 1.543 (7) C(1)-Ni(1)-N(1) 170.40 (10) C(1)-Ni(1)-P(2) 90.55 (7) N(1)-Ni(1)-P(2) 90.08 (8)
C(1)-Ni(1)-N(1) 170.40 (10) C(1)-Ni(1)-P(2) 90.55 (7) N(1)-Ni(1)-P(2) 90.08 (8)
C(1)-Ni(1)-N(1)170.40 (10)C(1)-Ni(1)-P(2)90.55 (7)N(1)-Ni(1)-P(2)90.08 (8)
C(1)-Ni(1)-P(2) 90.55 (7) N(1)-Ni(1)-P(2) 90.08 (8)
N(1)-Ni(1)-P(2) 90.08 (8)
C(1)-Ni(1)-P(1) 90.54 (8)
N(1)-Ni(1)-P(1) 89.78 (8)
P(2)-Ni(1)-P(1) 174.35 (3)
C(6)-P(1)-C(10) 103.72 (14)
C(6)-P(1)-C(8) 105.96 (14)
C(10)-P(1)-C(8) 104.58 (14)
C(6)-P(1)-Ni(1) 110.77 (11)
C(10)-P(1)-Ni(1) 112.24 (10)
C(8)-P(1)-Ni(1) 118.35 (10)
C(16)-P(2)-C(12) 104.01 (16)
C(16)-P(2)-C(14) 103.62 (19)
C(12)-P(2)-C(14) 106.05 (15)
C(16)-P(2)-Ni(1) 112.41 (14)
C(12)-P(2)-Ni(1) 118.16 (10)
C(14)-P(2)-Ni(1) 111.32 (11)
N(2)-N(1)-Ni(1) 132.3 (2)
N(3)-N(2)-N(1) 175.3 (3)
C(5)-N(4)-C(1) 119.7 (2)

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Crystal data	Appendix							
N(4)-C(1)-C(2)	117.1 (2)	1						
N(4)-C(1)-Ni(1)	117.17 (18)							
C(2)-C(1)-Ni(1)	125.73 (25)							
F(4)-C(2)-C(3)	117.2 (2)							
F(4)-C(2)-C(1)	118.6 (2)							
C(3)-C(2)-C(1)	124.2 (2)							
C(2)-C(3)-C(4)	116.0 (2)							
F(5)-C(4)-C(5)	120.4 (2)							
F(5)-C(4)-C(3)	121.3 (2)							
C(5)-C(4)-C(3)	118.3 (2)							
N(4)-C(5)-F(6)	117.2 (2)							
N(4)-C(5)-C(4)	124.6 (2)							
F(6)-C(5)-C(4)	118.2 (2)							
C(7)-C(6)-P(1)	113.2 (2)							
C(9)-C(8)-P(1)	116.2 (2)							
C(11)-C(10)-P(1)	112.1 (2)							
C(13)-C(12)-P(2)	117.2 (2)							
C(15)-C(14)-P(21)	113.7 (2)							
C(17)-C(16)-P(21)	109.7 (3)							

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Appendix

for NiN ₃ (C ₅ F ₃ NH)(PEt ₃) ₂	104.87 (13)	-65.53 (12)	-154.1 (3)	-139.71 (12)	49.88 (12)	-38.7 (3)	-17.73 (14)	171.86 (14)	83.3 (3)	-122.41 (17)	48.01 (16)	136.5 (3)	-1.23 (14)	169.20 (14)	-102.3 (3)	121.84 (14)	-67.73 (14)	20.8 (4)	178.7 (5)	84.9 (3)	-89.4 (3)	176 (4)	-0.9 (3)	178.53 (19)	-4.4 (7)	89.31 (18)	-96.24 (18)	175.0 (5)	-91.3 (2)	83.1 (2)	-179.4 (2)	1.2 (4)	1.5 (4)	-177.8 (2)	179.6 (2)	-1.3 (4)	179.3 (3)	0.5 (4)	-179.9 (2)	0.1(4)	-178.8 (3)	0.1(4)	1.2 (4)	-179.9(2)	-179.7 (2)	70.5 (3)	- 59.1 (3)	55.4 (3)	(c) o.cc-
Table 5: Torsion angles (deg)	C(1)-Ni(1)-P(1)-C(6)	N(1)-Ni(1)-P(1)-C(6)	P(2)-Ni(1)-P(1)-C(6)	C(1)-NI(1)-P(1)-C(10)	N(1)-Ni(1)-P(1)-C(10)	P(2)-Ni(1)-P(1)-C(10)	C(1)-Ni(1)-P(1)-C(8)	N(1)-Ni(1)-P(1)-C(8)	P(2)-Ni(1)-P(1)-C(8)	C(1)-Ni(1)-P(2)-C(16)	N(1)-Ni(1)-P(2)-C(16)	P(1)-Ni(1)-P(2)-C(16)	C(1)-Ni(1)-P(2)-C(12)	N(1)-Ni(1)-P(2)-C(12)	P(1)-Ni(1)-P(2)-C(12)	C(1)-Ni(1)-P(2)-C(14)	N(1)-Ni(1)-P(2)-C(14)	P(1)-Ni(1)-P(2)-C(14)	C(1)-Ni(1)-N(1)-N(2)	P(2)-Ni(1)-N(1)-N(2)	P(1)-Ni(1)-N(2)	Ni(1)-N(1)-N(2)-N(3)	C(5)-N(4)-C(1)-C(2)	C(5)-N(4)-C(1)-C(2)	N(1)-Ni(1)-C(1)-N(4)	$P(2)-Ni(1)-C(1)_N(4)$	P(1)-Ni(1)-C(1)-N(4)	N(1)-Ni(1)-C(1)-C(2)	P(2)-Ni(1)-C(1)-C(2)	P(1)-Ni(1)-C(1)-C(2)	N(4)-C(1)-C(2)-F(4)	NI(1)-C(1)-C(2)-F(4)	N(4)-C(1)-C(2)-C(3)	Ni(1)-C(1)-C(2)-C(3)	F(4)-C(2)-C(3)-C(4)	C(1)-C(2)-C(3)-C(4)	C(2)-C(3)-C(4)-F(5)	C(2)-C(3)-C(4)-C(5)	C(1)-N(4)-C(5)-F(6)	C(1)-N(4)-C(5)-C(4)	F(5)-C(4)-C(5)-N(4)	C(3)-C(4)-C(5)-N(4)	F(5)-C(4)-C(5)-F(6)	C(3)-C(4)-C(5)-F(6)	C(10)-P(1)-C(6)-C(7)	C(8)-P(1)-C(6)-C(7)	$N_1(1) - P(1) - C(6) - C(7)$	C(6)-P(1)-C98)-C(9)	r(10)-r(1)-r(1)-r(2)

Crystal data	Appendix							
Ni(1)-P(1)-C(8)-C(9)	-179.6 (2)							
C(6)-P(1)-C(10)-C(11)	-179.5 (2)							
C(8)-P(1)-C(10)-C(11)	-68.7 (3)							
Ni(1)-P(1)-C(10)-C(11)	60.8 (3)							
C(16)-P(2)-C(12)-C(13)	-52.3 (3)							
C(14)-P(2)-C(12)-C(13)	56.6 (3)							
Ni(1)-P(2)-C(12)-C(13)	-177.7 (3)							
C(16)-P(2)-C(14)-C(15)	175.8 (3)							
C(12)-P(2)-C(14)-C(15)	66.6 (3)							
Ni(1)-P(2)-C(14)-C(15)	-63.2 (3)							
C(12)-P(2)-C(16)-C(17)	-66.4 (4)							
C(14)-P(2)-C(16)-C(17)	-177.1 (3)							
Ni(1)-P(2)-C(16)-C(17)	62.6 (3)							

Symmetry transformations used to generate equivalent atoms:

Appendix

A.2 EXTINCTION COEFFICIENT DETERMINATION

(1) $(\eta^5 - C_5 H_5) Fe(\eta^5 - (CH_3)_2 C_4 H_2 N)$

Concentration (M) Absorbance at 354 nm

0	0
0.0012	0.04004
0.0024	0.08308
0.0036	0.12216
0.0048	0.16434



Therefore the extinction coefficient for $(\eta^5-C_5H_5)Fe(\eta^5-(CH_3)_2C_4H_2N)$ in pentane at 354 nm is 34.2 dm³ mol⁻¹ cm⁻¹

(2) $(\eta^{5}-C_{4}H_{4}Se)Cr(CO)_{3}$

Concentration (M)	Absorbance at 354 nm							
0	0							
0.00156	0.45236							
0.002992	0.94339							
0.003888	1.3042							
0.00468	1.5897							



Therefore the extinction coefficient for $(\eta^5-C_4H_4Se)Cr(CO)_3$ in dichloromethane at 354 nm is 56.4 dm³ mol⁻¹ cm⁻¹

(3) $(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-(CH_{3})_{2}CHC_{6}H_{5})$

Concentration (M)	Absorbance at 354 nm
0	0
0.0018	0.1186
0.0037	0.2516
0.0055	0.3659
0.0074	0.4614



Therefore the extinction coefficient for $(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)$ in dichloromethane at 354 nm is 63.6 dm³ mol⁻¹ cm⁻¹

Appendix

(4) $(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-(CH_{3})_{2}CHC_{6}H_{5})$

Concentration (M) Absorbance at 532 nm

0	0
0.0018	0.0211
0.0037	0.0431
0.0055	0.0651
0.0074	0.0791



Therefore the extinction coefficient for $(\eta^5-C_5H_5)Fe(\eta^6-(CH_3)_2CHC_6H_5)$ in dichloromethane at 532 nm is 10.9 dm³ mol⁻¹ cm⁻¹

Appendix

(5) $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-C_{6}H_{5}Cl)]^{4}PF_{6}^{-1}$

Concentration (M) Absorbance at 354 nm 0 0 0.00196 0.16606 0.00392 0.30254 0.00588 0.46162 0.00784 0.62546



Therefore the extinction coefficient for $[(\eta^5 - C_5H_5)Fe(\eta^6 - C_6H_5Cl)]^+PF_6^-$ in dichloromethane at 354 nm is 78.9 dm³ mol⁻¹ cm⁻¹

Appendix

(6) $[(\eta^{5}-C_{5}H_{5})Fe(\eta^{6}-C_{6}H_{5}Cl)]^{+}PF_{6}^{-1}$

Concentration (M) Absorbance at 532 nm 0 0 0.00196 0.0144 0.00392 0.0277 0.00588 0.0395 0.00784 0.0492



Therefore the extinction coefficient for $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_5Cl)]^+PF_6^-$ in dichloromethane at 532 nm is 6.3 dm³ mol⁻¹ cm⁻¹

Appendix

(7) $[(\eta^5 - C_5 H_5)Fe(\eta^6 - C_6 H_4 Cl_2)]^+ PF_6^-$

Concentration (M) Absorbance at 354 nm 0 0 0.00176 0.11528 0.00352 0.27412 0.00528 0.39146 0.00704 0.55695



Therefore the extinction coefficient for $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_4Cl_2)]^+PF_6^-$ in dichloromethane at 354 nm is 80.1 dm³ mol⁻¹ cm⁻¹

Appendix

(8) $[(\eta^5 - C_5 H_5)Fe(\eta^6 - C_6 H_4 Cl_2)]^+ PF_6^-$

Concentration (M) Absorbance at 532 nm000.001760.015050.003520.03270.005280.04680.007040.0660



Therefore the extinction coefficient for $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_4Cl_2)]^+PF_6^-$ in dichloromethane at 532 nm is 9.3 dm³ mol⁻¹ cm⁻¹

A.3 HARTREE-FOCK CALCULATIONS

The purpose of this study is to estimate the wavefunction stability of the electronic wavefunction of a 16-electron intermediate species formed by the photolysis of dimethylazaferrocene, $(\eta^{5}-C_{5}H_{5})(\eta^{5}-(CH_{3})_{2}C_{4}H_{2}N)$ Fe, in low-temperature matrixes containing carbon monoxide. The initially produced carbonyl containing species exhibited a carbonyl stretching absorption at 1999 cm⁻¹. Similar experiments with the unsubstituted azaferrocene species produced a feature at 1974 cm⁻¹, which was assigned to $(\eta^{5}-C_{5}H_{5})(\eta^{1}-C_{4}H_{4}N)$ Fe(CO). The calculations presented here are designed to determine if alternative high-spin wavefunctions are energetically close to the ground wavefunction, which could explain the difference in spectroscopic parameters observed in these two experiments. Previous studies on carbonyl systems have provided evidence for the formation of intermediates with triplet as well as singlet multiplicity, which has been used to explain the observed kinetic and spectroscopic properties of these intermediates.

Starting geometry of $(\eta^5-C_5H_5)(\eta^1-(CH_3)_2C_4H_2N)Fe(CO)$

The initial geometry of this intermediate was estimated using semi-empirical molecular mechanic MM2 routine in the Chem 3D programme suite.

These starting coordinated were used as the input file to Gaussian 98W programme and these parameters were optimised at the restricted Hartree-Fock level using the limited 3G basis set.

Appendix

Starting coordinates

		Z-Matrix	orientation:		
Center	Atomic	Atomic	Coordinates	(Angstroms)	
Number	Number	Туре	X	Y	Z
1	26	0	0.000000	0.000000	0.000000
2	-1	0	0.000000	0.000000	1.710000
3	7	0	1.645472	0.000000	-1.068582
4	6	0	1.180000	0.000000	1.710000
5	1	0	2.179848	0.000000	1.692548
6	6	0	0.364640	1.122247	1.710000
7	1	0	0.673610	2.073158	1.692548
8	6	0	-0.954640	0.693587	1.710000
9	1	0	-1.763534	1.281282	1.692548
10	6	0	0954640	-0.693587	1.710000
11	1	0	-1.763534	-1.281282	1.692548
12	6	0	0.364640	-1.122247	1.710000
13	1	0	0.673610	-2.073158	1.692548
14	-1	0	2.611034	0.000000	-1.693232
15	6	0	2.906737	0.000000	-0.581900
16	6	0	3.138803	0.000000	0.900040
17	1	0	2.184336	0.000000	1.405404
18	1	0	3.697634	-0.884351	1.168428
19	1	0	3.697634	0.884351	1.168428
20	6	0	3.759352	0.000000	-1.631042
21	1	0	4.757888	0.000000	-1.576963
22	6	0	3.025031	0.000000	-2.766129
23	1	0	3.385028	0.000000	-3.699083
24	6	0	1.718581	0.000000	-2.418510
25	6	0	0.659774	0.000000	-3.481019
26	1	0	1.134908	0.000000	-4.450889
27	1	0	0.049916	-0.884351	-3.369677
28	1	0	0.049916	0.884351	-3,369677
29	6	0	-1.677341	0.000000	-1.089278
30	8	0	-2.589282	0.000000	-1.704390

Appendix

After Optimisation	of the struc	ctural parameters a	a stationary point	was reached.
Ite	m '	Value '	Threshold	Converged?

	nem	value	Inresnold	Converged
Maximum	Force	0.000090	0.000450	YES
RMS	Force	0.000018	0.000300	YES
Maximum	Displacement	0.001335	0.001800	YES
RMS	Displacement	0.000204	0.001200	YES
Predicted	change in Energy=	-2.683707D-07		

Opimization completed -- Stationary point found.

Distance matrix (angstroms):

		1	2	3	4	5
1	Fe	0.000000				
2	Ν	1.890803	0.000000			
3	С	2.214415	3.294087	0.000000		
4	Н	2.99557	3.550924	1.071713	0.000000	
5	С	2.170163	3.540916	1.409984	2.215488	0.000000
6	Н	2.938214	3.972845	2.221411	2.671675	1.077254
7	С	2.248416	4.060192	2.291882	3.323548	1.426939
8	Н	3.006010	4.771741	3.332263	4.328548	2.236790
9	С	2.248416	4.060192	2.291882	3.323548	2.292434
10	Н	3.006010	4.771741	3.332263	4.328548	3.337549
11	С	2.170163	3.540916	1.409984	2.125488	2.283959
12	Н	2.938214	3.972845	2.221411	2.671675	3.324723
13	С	3.064680	1.422803	3.693240	3.520140	4.202190
14	С	3.708557	2.653983	3.370588	2.771029	4.147777
15	Н	3.314915	2.853702	2.435005	1.714199	3.344605
16	Н	4.440307	3.345097	4.012609	3.327541	4.999038
17	Н	4.440307	3.345097	4.012609	3.327541	4.581450
18	С	4.151826	2.282328	5.036168	4.853179	5.466468
19	H	5.153571	3.319776	5.790453	5.442111	6.300288
20	С	4.082383	2.286103	5.530210	5.606719	5.751943
21	Н	5.046427	3.324632	6.595064	6.683126	6.768071
22	С	2.910596	1.425907	4.672197	4.976818	4.761638
23	С	3.360821	2.633517	5.475595	6.006883	5.329786
24	H	4.427039	3.471416	6.499670	6.964315	6.372289
25	Н	3.337385	3.005343	5.478888	6.102693	5.437840
26	Н	3.337385	3.005343	5.478888	6.102693	5.054123
27	С	1.663544	2.867890	3.713298	4.612769	3.316915
28	Ο	2.813920	3.960713	4.734426	5.692852	4.207158
		6	7	8	9	10
6	H	0.000000				
7	С	2.231956	0.000000			
8	Н	2.685265	1.078730	0.000000		
9	С	3.329689	1.409441	2.224907	0.000000	
10	Н	4.341417	20224907	2.686565	1.078730	0.000000
11	С	3.324723	2.292434	3.337549	1.426936	2.236790
12	Н	4.331648	3.329689	4.341417	2.231956	2.685265

Appendix

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	0					
13	С	4.469118	5.046839	5.850549	5.046839	5.850549
14	С	4.327284	5.254871	6.167328	5.254871	6.167328
15	Н	3,590231	4.503423	5.464643	4.503423	5.464643
16	H	5.281064	6.031712	7 002916	5 823461	6 658447
17	Н	4 50575	5 823461	6 6 5 8 4 4 7	6.031712	7.002916
18	C	5 662641	6 243292	6 968331	6 243292	9.968331
10	н	6 421444	7 184405	7 937440	7 184405	7 937440
20	C	6 01013/	6 257314	6 840630	6 257314	6 8/0630
20	н Ц	6 998425	7 207544	7 72225	7 207544	7 722325
21	C	5 121261	5 071672	5 606212	5.071672	5 606212
22	C	5 750075	5 250608	5 562683	5 250608	5.562683
23	с u	6 734030	6 226010	5.502085	5.259008	5.502085
24	11 11	6.734030	5 147047	5 467706	4 200761	5.016001
25	п	5.260525	J.14/04/	5.407790	4.099/01	5.010091
20	п	3.300323	4.899/01	2.054628	3.14/04/	2.407790
27	Č	4.000279	2.700401	2.934038	2.700401	2.934038
28	0	4.480128	3.305167	3.216384	3.305167	3.210384
11	C		12	13	14	15
11		0.000000	0.000000			
12	H	1.077254	0.000000	0.000000		
13	C	4.202190	4.469118	0.000000	0.000000	
14	C	4.147777	4.327284	1.521993	0.000000	0.000000
15	H	3.344605	3.590231	2.192852	1.072740	0.000000
16	H	4.581450	4.505785	2.152078	1.087455	1.742166
17	Н	4.999038	5.281064	2.152078	1.087455	1.742166
18	C	5.466468	5.662641	1.349170	2.495078	3.405084
19	H	6.300288	3.421444	2.160587	2.782931	3.828176
20	С	5.751943	6.010134	2.234997	3.689046	4.424800
21	H	6.768071	6.998425	3.275601	4.673501	5.467933
22	С	4.761638	5.131361	2.231051	3.730174	4.165276
23	С	5.329786	5.750075	3.720554	5.183923	5.487134
24	Η	6.372289	6.734030	4.318083	5.834045	6.280161
25	Н	5.054123	5.360525	4.193050	5.574460	5.765104
26	Η	5.437840	6.030808	4.193050	5.574460	5.765104
27	С	3.316915	4.000279	4.271322	5.218467	4.948224
28	0	4.207158	4.846128	5.380411	6.383162	6.115466
		16	17	18	19	20
16	Η	0.000000				
17	Н	1.751651	0.000000			
18	С	2.797849	2.797849	0.000000		
19	Η	2.825965	2.825965	1.076875	0.000000	
20	С	4.070984	4.070984	1.418256	2.236073	0.000000
21	Η	4.968118	4.968118	2.236058	2.707843	1.076796
22	С	4.286175	4.286175	2.229245	3.270442	1.347622
23	С	5.751198	5.751198	3.692402	4.682760	2.512762
24	Н	6.325863	6.325863	3.950807	4.804652	2.573948
25	Н	6.041273	6.291631	4.312637	5.314263	3.235562
26	Η	6.291631	6.041273	4.312637	5.314263	3.235562
27	С	5.919271	5.919271	5.057076	6.128083	4.513524
28	Ο	7.070783	7.070783	6.057147	7.134011	5.336707
		21	22	23	24	25

21	Н	0.000000				
22	С	2.162071	0.000000			
23	С	2.819942	1.519927	0.000000		
24	H	2.435584	2.120748	1.085220	0.000000	
25	Н	3.566279	2.184962	1.086738	1.749543	0.000000
26	Н	3.566279	2.184962	1.086738	1.749843	1.762705
27	С	5.255464	3.168449	2.795847	3.845823	2.522570
28	0	5.934671	4.001687	3.207555	4.112338	2.768383
		26	27	28		
26	Н	0.000000				
27	С	2.522570	0.000000			

Appendix

Final coordinates:

		Standard	Orientation		
Center	Atomic	Atomic		Coordinates	(Angstroms)
Number	Number	Туре	Х	Y	Z
1	26	0	0.000000	0.688582	0.000000
2	. 7	0	0.143266	-1.196785	0.000000
3	6	0	-2.165130	1.153176	0.000000
4	. 1	0	-2.991652	0.470952	0.000000
5	6	0	-1.544040	1.699240	1.141980
6	5 1	0	-1.812602	1.499005	2.165824
7	6	0	-0.650461	2.722210	0.704721
8	1	0	-0.078069	3.376629	1.343282
9	6	0	-0.650461	2.722210	-0.704721
10) 1	0	-0.078069	3.376629	-1.343282
11	6	0	-1.544040	1.699240	-1.141980
12	. 1	0	-1.812602	1.499005	-2.165824
13	6	0	-0.787028	-2.273318	0.000000
14	. 6	0	-2.307879	-2.214388	0.000000
15	1	0	-2.710341	-1.220007	0.000000
16	1	0	-2.700000	-2.725983	-0.875826
17	' 1	0	-2.700000	-2.725983	0.875826
18	6	0	-0.146349	-3.460664	0.00000
19) 1	0	-0.620601	-4.427485	0.000000
20	6	0	1.247472	-3.198533	0.000000
21	1	0	2.040566	-3.926883	0.000000
22	6	0	1.405442	-1.8660202	0.000000
23	6	0	2.776771	-1.204738	0.000000
24	. 1	0	3.521988	-1.993633	0.000000
25	1	0	2.952468	-0.593716	-0.881352
26	1	0	2.952468	-0.593716	0-881352
27	6	0	1.545056	1.305170	0.000000
28	8	0	2.494684	1.990389	0.000000

Electronic structure at Optimised Geometry

Appendix

			Pop	ulation	analys	sis usir	ig the	SCF d	ensity				
Orbita	l symn	netries:											
Occup	ied	(A') (A')	(A') (A')	(A') (A'')	(A') (A')	(A") (A')	(A' (A') (A') (A') (A) (A	') (4 ') (4	A") A')	(A') (A')	
		(A') (A') (A')	(A') (A') (A")	(A") (A') (A")	(A') (A") (A')	(A') (A') (A')	(A' (A' (A'') (A') (A') (A') (A) (A) (A	") (A ') (A ") (A	4') 4') A")	(A') (A') (A')	
Virtual	1	(A') (A") (A")	(A') (A") (A')	(A') (A") (A')	(A") (A")	(A') (A'')	(A' (A') (A') (A') (A' ') (A	') (/ ') (/	4") 4")	(A') (A")	
		(A') (A') (A")	(A') (A") (A')	(A') (A') (A")	(A') (A") (A')	(A") (A") (A')	(A' (A' (A') (A') (A') (A') (A) (A) (A	") (, ') (, ') (,	A') A') A')	(A') (A') (A")	
The ele	ectroni	(A") ic state	(A') is 1-A'	(A')									
Alpha	occ. e	igenval	lues	-285.7	3300	-31.4	3485	-27.38	8440	-27.37	7692	-27.37	536
Alpha	occ. e	igenval	lues	-20.3	4968	-15.2	8292	-11.08	8480	-11.08	\$429	-11.07	932
Alpha	occ. e	igenval	lues	-11.0	1/399	-11.0	1369	-11.0	1369	-11.04	2888	-11.02	526
Alpha	occ. e	igenval	ues	-10.9	19996	-10.9	4400	-10.94	4397	1 26	1432	-4.13	040
Alpha	occ. e	igenval	lues	-2./	4010	-2.14	4490 7710	-2.73	5511	-1.30	500	-1.20	120
Alpha	occ e	igenval	ues	-1.1	4443	-0.9	1/12	-0.90	0/44 1701	-0.90	1227	-0.93	120
Alpha	occ. e	igenval	ues	-0.9	10014 10155	-0.7	700/ 5100	-0.74	t/04 1201	-0.74	1337	-0.72	911 076
Alpha	occ. e	igenval	ues	-0.7	2133	-0.0	5700 5700	-0.04	+291 1611	-0.5	1161	-0.57	020 500
Alpha		igenval	ues	-0.5	20210	-0.5	2002 2002	-0.54	1044	-0.54	0101	-0.55	802
Alpha		igenval	ues	-0.5	8500	-0.5	4175	0.52	2758	-0.52	2043	-0.30	836
Alpha	000,0	igenval	1105	-0.3	0000	-0.3	8733	-0.34	1682	-0.32	\$715	-0.42	734
Alpha		igenval	ues	-0.2	4279	-0.19	9433	-0.19	9015	0.52	,,15	0.51	151
Alpha	virt e	igenval	ues	0.2	2931	0.2	6530	0.28	8827	0.2	9184	033	941
Alpha	virt e	igenval	ues	0.2	8037	0.4	2194	0.42	2837	0.4	4669	0.52	993
Alpha	virt e	igenval	nes	0.5	4567	0.5	9608	0.61	764	0.6	3308	0.63	807
Alpha	virt e	ioenval	ues	0.5	4617	0.6	4929	0.64	1945	0.6	8697	0.71	826
Alpha	virt e	igenval	ues	0.7	3404	0.7	3822	0.74	4143	0.7	4185	0.74	951
Alpha	virt	igenval	ues	0.7	5252	0.7	6300	0.79	8008	0.7	9965	0.85	329
Alpha	virt e	igenval	ues	0.8	9464	0.9	4037	1.00)524	1.0	2207	1.02	821
Alpha	virt e	igenval	ues	1.0	3158	1.0	4717	1.20)722	3.9	3483	3.96	641
Alpha	virt e	igenval	ues	3.9	9665	4.0	1135	4.28	3676				

The stability of the wavefunction was tested using the Stable=Opt routine, which looks for unrestricted wavefunctions which are close in energy to the restricted solution obtained in these calculations. In this case such an instability was found.

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Appendix

Stability analysis using <AA,BB:AA,BB> singles matrix:

Eigenvectors of the stability matrix:

Eigenvector 1:	Triplet-A'	Eigenvalue=-0.2425419
61 -> 64	0.17161	
62 -> 64	0.61985	
62 -> 67	0.24912	
63 -> 64	-0.12548	
Eigenvectro 2:	Triplet-A"	Eigenvalue= 0.0973028
61 -> 65	0.16657	
62 -> 65	0.65980	
63 -> 65	-0.13756	
Eigenvector 3:	Singlet-A"	Eigenvalue= 0.1299263
61 -> 65	0.16241	
62 -> 65	0.66447	
63 -> 65	-0.13874	
Eigenvector 4:	Triplet-A'	Eigenvalue= 0.2186020
61 -> 64	0.10251	
62 -> 64	-0.27671	
62 -> 67	0.60462	
62 -> 73	0.11624	
63 -> 66	-0.12253	
Eigenvector 5:	Triplet-A"	Eigenvalue= 0.2223757
62 -> 65	-0.10142	
62 -> 66	0.65430	
62 -> 69	0.10338	
62 -> 71	0.14366	

63 -> 66 -0.13379

Eigenvector 6:	Singlet-A'	Eigenvalue= 0.2361212
62-> 64	-0.36523	
62 -> 67	0.56351	
62 -> 73	0.11470	
63 -> 67d	-0.10939	

The wavefunction has an RHF -> UHF instability.

An alternative unrestricted wavefunction was then calculated at this opitmised geometry. The electronic structure calculated is as follows

Orbital symmetries:

Alpha orbitals:

Occupied	(A')	(A')	(A')	(A')	(A')	(A')	(A')	(A')	(?A)	(?A)
	(?A)	(?A)	(A')	(A')	(A')	(A')	(A')	(A')	(A')	(A')
	(A')	(A')	(A')	(A')	(?B)	(A')	(A')	(?C)	(?C)	(?C)
	(A')	(A')	(?D)	(?D)	(?D)	(?D)	(?C)	(?D)	(?D)	(?C)
	(?C)	(?C)	(?C)	(?D)	(?D)	(?C)	(?D)	(?D)	(?C)	(?C)
	(?C)	(?C)	(?D)	(?D)	(?C)	(?D)	(?C)	(?C)	(?D)	(?D)
	(?C)	(?D)	(?D)							
Virtual	(?D)	(?D)	(?C)	(?D)	(?D)	(?D)	(?D)	(?C)	(?C)	(?B)
	(?D)	(?D)	(?C)	(?C)	(?C)	(?C)	(?C)	(?D)	(?C)	(?C)
	(?C)	(?C)	(?C)	(?C)	(A'')	(?C)	(?C)	(A')	(?C)	(A')
	(A'')	(A')	(?A)	(?A)	(?B)	(Λ')	(?C)	(A')	(?D)	(?B)
	(?B)	(?C)	(?D)							

Beta orbitals:

Occupied	(A')	(A')	(A')	(A')	(A')	A')	(A')	(A')	(?A)	(?A)
	(?A)	(?A)	(A')	(A')	(A')	(A')	(A')	(A')	(A')	(A')
	(A')	(A')	(A')	(A')	(A')	(A')	(?A)	(?A)	(?A)	(?A)
	(A')	(A')	(?B)	(?B)	(?B)	(?B)	(?B)	(?B)	(?C)	(?C)
	(?C)	(?C)	(?B)	(?C)	(?C)	(?C)	(?B)	(?C)	(?C)	(?B)
	(?A)	(?C)	(?B)	(?C)	(?C)	(?A)	(?C)	(?C)	(?B)	(?C)
	(?B)	(?B)	(?C)							

Appendix

Molecular modelling calculations Append									pendix	
Virtual	(?B)	(?C)	(?B)	(?A)						
	(?A)	(?C)	(?B)	(?A)	(?B)	(?A)	(?B)	(?B)	(?A)	(?A)
	(?B)	(?A)	(?A)	(?B)	(?B)	(?A)	(?A)	(?A)	(A')	(A')
	(A'')	(A')	(?A)	(?A)	(?A)	(A')	(?A)	(A')	(?B)	(?B)
	(?A)	(?A)	(?B)							

Unable to determine electronic state: an orbital has unidentified symmetry.

Alnha	occ eigenvalues	-258 78478	-31 50314	-27 45147	-27 44712	-27 44241
Alpha	occ eigenvalues	-20 30298	-15 27696	-11 09012	11 08204	_11.08154
Alpha	occ. cigenvalues	-20,30296	-13.27090	-11.09012	.11.00204	-11.00134
Alpha	occ. eigenvalues	-11.07276	-11.07080	-11.03481	-11.02317	-11.00679
Alpha	occ. eigenvalues	-10.99702	-10.97401	-10.96203	-10.95051	-4.25567
Alpha	occ. eigenvalues	-2.89448	-2.86304	-2.85160	-1.31758	-1.20402
Alpha	occ eigenvalues	-1.14906	-0.98203	-0.96775	-0.96745	-0.93791
Alpha	occ. eigenvalues	-0.91244	-0.80326	-0.74734	-0.74350	-0.72384
Alpha	occ. eigenvalues	-0.68151	-0.65679	-0.64670	-0.59424	-0.59036
Alpha	occ. eigenvalues	-0.58498	-0.57056	-0.56323	-0.55474	-0.54468
Alpha	occ. eigenvalues	-0.53767	-0.53044	-0.52578	-0.52464	-2.51663
Alpha	occ. eigenvalues	-0.50867	-0.49065	-0.45158	-0.44166	-0.43716
Alpha	occ. eigenvalues	-0.43030	-0.41894	-0.40697	-0.38597	-0.32046
Alpha	occ. eigenvalues	-0.31342	-0.25635	-0.20042		
Alpha	virt eigenvalues	0.23262	0.25703	0.29612	0.30952	0.34230
Alpha	virt eigenvalues	0.36962	0.37498	0.44829	0.48431	0.51252
Alpha	virt eigenvalues	0.54278	0.60106	0.61982	0.63469	0.63941
Alpha	virt eigenvalues	0.64488	0.64711	0.64983	0.68931	0.71622
Alpha	virt eigenvalues	0.73441	0.73722	0.73940	0.74083	0.74875
Alpha	virt eigenvalues	0.75107	0.76115	0.79255	0.79509	0.84864
Alpha	virt eigenvalues	0.89381	0.93451	10619	1.02023	1.02527
Alpha	virt eigenvalues	1.04090	1.09180	1.19798	3.81776	3.83256
Alpha	virt eigenvalues	3.88670	3.99404	4.26655		

Beta	occ. eigenvalues	-258.78480	-31.47852	-27.42663	-27.42332	-27.41675
Beta	occ. eigenvalues	-20.31167	-15.27860	-11.08657	-11.08236	-11.08140
Beta	occ. eigenvalues	-11.07613	-11.07431	-11.03314	-11.02488	-11.01009
Beta	occ. eigenvalues	-10.99409	-10.98617	-10.96256	-10.94981	-4.14503
Beta	occ. eigenvalues	-2.75702	-2.74126	-2.70753	-1.35190	-1.20598
Beta	occ. eigenvalues	-1.15126	-0.97867	-0.97463	-0.96771	-0.94010
Beta	occ. eigenvalues	-0.91134	-0.80497	-0.75518	-0.74449	-0.73873
Beta	occ. eigenvalues	-0.72452	065920	-0.65108	-0.59339	-0.58003
Beta	occ. eigenvalues	-0.57503	-0.57406	-0.56345	-0.55855	-0.54532
Beta	occ. eigenvalues	-0.53321	-0.52707	-0.52501	-0.52091	-0.51355
Beta	occ. eigenvalues	-0.50928	-0.45338	-0.44492	-0.44053	-0.43743
Beta	occ. eigenvalues	-0.42810	-0.40100	-0.39275	-0.35722	-0.28170
Beta	occ. eigenvalues	-0.26417	-0.20495	-0.17627		
Molecular modelling calculations						Appendix
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Beta	virt eigenvalues	0.26953	0.27586	0.28469	0.32297	0.34774
Beta	virt eigenvalues	0.39409	0.44985	0.52360	0.53327	0.54393
Beta	virt eigenvalues	0.54851	0.57073	0.61035	0.62086	0.63945
Beta	virt eigenvalues	0.63988	0.64586	0.64793	0.67825	0.71698
Beta	virt eigenvalues	0.72395	0.73245	0.73554	0.73764	0.74352
Beta	virt eigenvalues	0.75468	0. 7579 7	0.78698	0.79456	0.84705
Beta	virt eigenvalues	0.89274	0.93414	1.00481	1.01977	1.02511
Beta	virt eigenvalues	1.03821	1.04832	1.19773	3.84941	3.98036
Beta	virt eigenvalues	3.99647	4.03903	4.18177		

This wavefunction exhibited considerable spin contaminatin with a S^2 value of 3.0354.

The geometry optimisation was repeated using unrestricted Hartree-Fock level with the STO-3G basis set. The results of this optimisation is as follows.

Center	Atomic	Atomic		Coordinates	(Angstroms)
Number	Number	Туре	X	Y	Ζ
1	26	0	-0.608346	0.000000	0.322585
2	7	0	0.990214	0.000000	-0.687238
3	6	0	-0.004490	0.000000	2.453076
4	1	0	0.985445	0.000000	2.863682
5	6	0	-0.777890	1.141980	2.160177
6	1	0	-0.475173	2.165824	2.303639
7	6	0	-2.100281	0.704721	1.849959
8	1	0	-2.946596	1.343282	1.650845
9	6	0	-2.100281	-0.704721	1.849959
10	1	0	-2.946596	-1.343282	1.650845
11	6	0	-0.777890	-1.141980	2.160177
12	1	0	-0.475173	-2.165824	2.303639
13	6	0	2.377125	0.000000	-0.369677
14	6	0	3.037546	0.000000	1.001565
15	1	0	2.347579	0.000000	1.822976
16	1	0	3.673227	-0.875826	1.108324
17	1	0	3.673227	0.875826	1.108324
18	6	0	3.125974	0.000000	-1.491945
19	1	0	4.202313	0.000000	-1.525889
20	6	0	2.241414	0.000000	-2.600550
21	1	0	2.513348	0.000000	-3.642444
22	6	0	0.985026	0.000000	-2.113135
23	6	0	-0.236496	0.000000	-3.017602
24	1	0	0.111356	0.000000	-4.045562
25	1	0	-0.858629	-0.881352	-2.886576
26	1	0	-0.858629	0.881352	-2.886576
27	6	0	-1.876909	0.000000	-0.753578
28	8	0	-2.927162	0.000000	-1.271542

Input orientation:

Appendix

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	Distance matrix (angstroms):					
		1	2	3	4	5
1	Fe	0.000000				
2	Ν	1.890803	0.000000			
3	С	2.214415	3.294087	0.000000		
4	Н	2.999557	3.550924	1.071713	0.000000	
5	С	2.170163	3.540916	1.409984	2.215488	0.000000
6	Н	2.938214	3.972845	2.221411	2.671675	1.077524
7	С	2.248416	4.060192	2.291882	3.323548	1.426936
8	Η	3.006010	4.771741	3.332263	4.328548	2.236790
9	С	2.248416	4.060192	2.291882	3.323548	2.292434
10	Н	3.006010	4.771741	3.332263	4.328548	3.337549
11	С	2.170163	3.540916	1.409984	2.215488	2.283959
12	Н	2.938214	3.972845	2.221411	2.671675	3.324723
13	С	3.064680	1.422803	3.693240	3.520140	4.202191
14	С	3.708577	2.653983	3.370588	2.771029	4.147777
15	Н	3.314915	2.853702	2.435006	1.714199	3.344605
16	Н	4.440307	3.345098	4.012609	3.327541	4.999038
17	Н	4.440307	3.345098	4.012609	3.327541	4.581450
18	С	4.151826	2.282328	5.036168	4.853180	5.466468
19	Н	5.153571	3.319776	50790453	5.442111	6.300288
20	С	4.082383	2.286103	5.530210	5.606719	5.751943
21	Н	5.046427	3.324632	6.595064	6.683126	6.768071
22	С	2.910596	1.425907	4.672197	4.976818	4.761638
23	С	3.360822	2.633517	5.475595	6.006883	5.329786
24	Н	4.427039	3.471416	6.499670	6.964315	6.372289
25	Н	3.337385	3.005343	5.478888	6.102693	5.437840
26	Н	3.337385	3.005343	5,478888	6.102693	5.054123
27	С	1.663544	2.867890	3.713298	4.612769	3.316915
28	0	2.813920	3.960712	4.734426	5.692852	4.207158
		6	7	8	9	10
6	Н	0.000000				
7	С	2.231956	0.000000			
8	Н	2.685265	1.078730	0.000000		
9	С	3.329689	1.409441	2.224907	0.000000	
10	Н	4.341417	2.224907	2.686565	1.078730	0.000000
11	С	3.324723	2.292434	3.337549	1.426936	2.236790
12	Н	4.331648	3.329689	4.341417	2.231956	2.685265
13	С	4.469118	5.046839	5.850550	5.046839	5.850550
14	С	4.327284	5.254871	6.167328	5.254871	6.167328
15	Н	3.590231	4.503423	5.464643	4.503423	5.464643
16	Н	5.281064	6.031712	7.002916	5.823461	6.658447
17	Н	4.505785	5.823461	6.658447	6.031712	7.002916
18	С	5.662641	6.243292	6.968331	6.243292	6.968331
19	Н	6.421444	7.184405	7.937440	7.184405	7.937440
20	С	6.010134	6.257315	6.840630	6.257315	6.840630
21	Н	6.998425	7.207544	7.722325	7.207544	7.722325
22	С	5.131362	5.071674	5.606212	5.071674	5.606212
23	С	5.750075	5.259608	5.562683	5.259608	5.562683
24	Η	6.734030	6.336019	6.603372	6.336019	6.603372

Molec	ular model	ling calculation	ons			Appendix
25	Н	6.030809	5.147047	5.467796	4.899762	5.016091
26	H	5.360526	4.899762	5.016091	5.147047	5.467796
27	С	4.000279	2.706461	2.954638	2.706461	2.954638
28	0	4.846128	3.305167	3.216384	3.305167	3.216384
		11	12	13	14	15
11	С	0.000000				
12	H	1.077254	0.000000			
13	С	4.202191	4.469118	0.000000		
14	С	4.147777	4.327284	1.521993	0.000000	
15	H	3.344605	43.590231	2.192852	1.072740	0.000000
16	I-I	4.581450	4.505785	2.152078	1.087455	1.742166
17	H	4.999038	5.281064	2.152078	1.087455	1.742166
18	С	5.466468	5.662641	1.349170	2.495078	3.405084
19	I-I	6.300288	6.421444	2.160587	2.782931	3.828176
20	С	5.751943	6.010134	2.234997	3.689046	4.424800
21	Н	6.768071	6.998425	3.275601	4.676501	5.467933
22	С	4.761638	5.131362	2.231051	3.730174	4.165276
23	С	5.329786	5.750075	3.720554	5.183923	5.487134
24	H	6.372289	6.734030	4.318083	5.834045	6.280161
25	H	5.054123	5.360526	4.193050	5.574460	5.765104
26	IH	5.437840	6.030809	4.193050	5.574460	5.765104
27	С	3.316915	4.000279	4.271322	5.218467	4.948224
28	0	4.207158	4.846128	5.380411	6.383162	6.115466
		16	17	18	19	20
16	H	0.000000	0.000000			
17	Н	1.751651	0.000000	0.000000		
18	C	2.797849	2.797849	0.000000	0.000000	
19	H	2.825965	2.825965	1.076875	0.000000	0.000000
20		4.070984	4.070984	1.418256	2.236073	0.000000
21	FI C	4.908118	4.908118	2.230038	2.707843	1.0/0/90
22	C	4.2001/3	4.200173	2.229243	3.270442	1.34/022
23		6 225862	6 2 2 5 9 6 2	3.092402	4.082700	2.515702
24		6.041273	6 201631	3.930607	4.004032	2.373940
25	LI	6 201631	6.041273	4.312037	5 314203	3.235562
20	C	5 010271	5 919273	5.057076	6 128083	A 513524
28	0	7 070783	7 070783	6.057147	7 134010	5 336707
20	U	21	22	23	7.154010	25
21	н	0.000000		23	∠-r	23
22	C	2 162071	0.000000			
23	č	2.819942	1.519927	0.000000		
24	H	2.435584	2.120748	1.085220	0.000000	
25	H	3.566279	2.184962	1.086738	1.749543	0.000000
26	H	3.566279	2.184962	1.086738	1.749543	1.762705
27	C	5.255464	3.168449	2.795847	3.845823	2.522570
28	0	5.934671	4.001687	3.207555	4.114388	2.768383
	-					
		26	27	28		
26	H	0.000000				
27	C	2.522570	0.000000			

0

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2.768383 1.171033 0.000000

Stoichiometry	C12H13FeNO		
Framework group	CS[SG(C8H5FeNO), X(C4H8)]		
Deg. of freedom	47		
Full point group	CS NOp 2		
Largest Abelian subgroup	CS NOp 2		
Largest concise Abelian subgroup	CS NOp 2		
	Standard orientation :		

Center	Atomic	Atomic		Coordinates	(Angstroms)
Number	Number	Туре	Х	Y	Z
1	26	0	0.000000	0.688582	0.000000
2	7	0	0.143266	-1.196785	0.000000
3	6	0	-2.165130	1.153176	0.000000
4	1	0	-2.991652	0.470953	0.000000
5	6	0	-1.544040	1.699241	1.141980
6	1	0	-1.812601	1.499005	2.165824
7	6	0	-0.650461	2.722211	0.704721
8	1	0	-0.078068	3.376629	1.343282
9	6	0	-0.650461	2.722211	-0.704721
10	1	0	-0.078068	3.376629	-1.343282
11	6	0	-1.544040	1.699241	-1.141980
12	1	0	-1.812601	1.499005	-2.165824
13	6	0	-0.787028	-2.273318	0.000000
14	6	0	-2.307879	-2.214388	0.000000
15	1	0	-2.710342	-1.220006	0.000000
16	1	0	-2.700000	-2.725983	-0.875826
17	1	0	-2.700000	-2.725983	0.875826
18	6	0	-0.146350	-3.460664	0.000000
19	1	0	-0.620602	-4.427485	0.000000
20	6	0	1.247472	-3.198533	0.000000
21	1	0	2.040565	-3.926883	0.000000
22	6	0	1.405442	-1.860202	0.000000
23	6	0	2.776771	-1.204739	0.000000
24	1	0	3.521987	-1.993633	0.000000
25	1	0	2.952467	-0.593717	-0.881352
26	1	0	2.952467	-0.593717	-0.881352
27	6	0	1.545056	1.305170	0.000000
28	8	0	2.494684	1.990388	0.000000

These results confirmed that at this model chemistry the optimised geometry produces a wavefunction which is singlet in character, as both restricted and unrestricted Hartree-Fock calculations resulted in relaxed to the same geometry. In the case of the unrestricted calculation the S^2 value was 0.000. However, the presence of solutions of higher multiplicity with similar energies to the ground state solution would suggest that slight perturbations to this geometry will have significant effect on the electronic structure of the intermediate.

Appendix

Consequently variations of this optimised gas-phase geometry, as are likely in the condensed matrix, can provide a reasonable explanation for the observed variation in the infrared spectroscopic parameters.

Unfortunately the rather small basis set used in these calculations could not provide reliable estimates of the normal vibrational modes for the intermediate.