THE SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF DIENE AND FUNCTIONALIZED ALKYL COMPLEXES OF IRON

by

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for the degree of Doctor Philosophiae in the Faculty of Science, Department of Chemistry,
University of the Western Cape.

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DECLARATION

I declare that **"THE SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF DIENE AND FUNCTIONALIZED ALKYL COMPLEXES OF IRON"** is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of references.

Dalene Dooling-Mopp

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Thanks for your unconditional love, support and unfailing belief in me. You are an inspiration in my life.

ABSTRACT

This thesis deals with the synthesis, characterisation and reactivity of a number of diene and functionalized alkyl complexes of iron. Iron alkenyl complexes of the type $[(Cp)(CO_2)Fe\{(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6), were used as precursors in the preparation of diene, heterobinuclear μ-alkanediyl and ω-hydroxyalkyl complexes of iron.

Chapter 1 gives an overview of known hydrocarbyl complexes. Chapter 2 deals with the synthesis and characterisation of cationic diene complexes of iron of the type, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$. These complexes were prepared by the reaction of the iron alkenyl complexes, $[(Cp)(CO_2)Fe\{(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6), with trityl salt, (Ph_3CPF_6) (β-hydride elimination) to give a series of cationic diene complexes of iron of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$. The cationic diene complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$, were isolated as yellow air stable solids, which were fully characterized by microcroanalyses, FTIR, ^{1}H NMR, ^{13}C NMR, 2D NMR (COSY) and MALDI-TOF mass spectrometry. Thermal analysis and thermal decomposition studies were also carried out on these compounds.

Chapter 3 details the reactivity studies of these cationic diene complexes. We subjected these complexes to reactions with nucleophiles such as halides, hydrides, phosphines, amines and enolates. These reactions were found to proceed via four generalized pathways i.e.

1) ligand substitution (displacement) of the diene
2) formation of the dimer, $[CpFe(CO)_2]_2$
3) addition to the coordinated diene
4) deprotonation of the diene using tertiary amines i.e. Et_3N

Where possible, the products of these reactions were fully characterized by microanalyses, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

In Chapter 4 we subjected the iron alkenyl complexes, $[(Cp)(CO_2)Fe\{(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6), to hydrozirconation reactions using $Cp_2Zr(H)Cl$ to produce heterobinuclear μ-alkanediyl complexes of the type, $[(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl]$. These complexes were isolated as yellow/brown oils which were found to decompose to the oxo-bridged dimer, $[Cp_2ZrCl]_2O$ and the corresponding iron alkyl compounds, $Cp(CO)_2FeCH_2(CH_2)_nCH_3$. *In situ* reactions of the heterobinuclear μ-alkanediyl complexes with various electrophiles were found to proceed in a similar fashion to those of the known mononuclear iron and zirconium alkyl complexes.

Chapter 5 deals with the reactivity studies of ω-hydroxyalkyl iron complexes of the type $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7) which were prepared by the oxidative hydroboration of the iron alkenyl complexes, $[(Cp)(CO_2)Fe\{(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6). The reactions of the ω-hydroxyalkyl were found to take place at either the metal centre or at the hydroxy group. Where possible the products of these reactions were characterized by microanalyses, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy and FAB mass spectrometry.

ABBREVIATIONS/CHEMICAL FORMULAE

IR = Infrared
NMR = Nuclear Magnetic Resonance
GPC = gel permeation chromatography
Cp = η^5-C_5H_5
Fp = $CpFe(CO)_2$
Ph = Phenyl
PPh_3 = triphenylphosphine
CH_2CI_2 = dichloromethane
THF = tetrahydrofuran
m\e = mass to charge ratio
R = alkyl group
r.t = room temperature
temp = temperature
X = halogen atom
[Zr] = Cp_2ZrC1
NBS = N-bromosuccinimide
h = hour
min = minutes
PPh_3 = triphenylphosphine
CH_2CI_2 = dichloromethane

PUBLICATIONS/CONFERENCE CONTRIBUTIONS

JOURNAL ARTICLES

The synthesis, characterization and some reactions of cationic η^2-(α, ω-diene) complexes of iron.

D. Dooling, G. Joorst and S.F. Mapolie

Polyhedron 20 (2001), 467 – 476

CONFERENCE CONTRIBUTIONS

1. 7th International Chemistry Conference in Africa and 34th convention of the South African Chemical Institute, University of Natal, Durban, South Africa; 6 -10 July 1998; *Synthesis and some reactions of cationic η^2-diene complexes of iron*; D.Dooling and S.F. Mapolie.
2. Inorganic `99, University of Stellenbosch, Stellenbosch, South Africa, 17 – 20 January 1999; *Synthesis, characterization and some reactions of cationic η^2-(α, ω-diene) complexes of iron;* D.Dooling and S.F. Mapolie.
3. ICCC34, 34th International Conference on Coordination Chemistry, University of Edinburgh, Scotland, 9 –14th July 2000; *The preparation, characterization and reactivity of some cationic η^2-(α, ω-diene) complexes of iron;* D.Dooling and S.F. Mapolie.
4. SACI 2000, 35th Convention of the South African Chemical Institute, Potchefstroom, South Africa; 24 – 29 September 2000; *The reactivity*

studies on cationic η^2*-(*α*,* ω*-diene) complexes of iron;* D.Dooling and S.F. Mapolie.

5. SACI/CATSA, South African Chemical Institute and Catalysis Society of South Africa, Bakgatla Resort, Pilanesberg Game Reserve, South Africa, 4 – 8 November 2001, *Synthesis and some reactivity of iron/zirconium heterobimetallic* μ*-hydrocarbyl complexes;* D.Dooling and S.F. Mapolie.

6. SACI 2002, 35th Convention of the South African Chemical Institute, Port Elizabeth, South Africa, 1-5 July 2002, *Early-late* μ*-(*α*,* ω*)alkanediyl complexes of transition metals;* D.Dooling and S.F. Mapolie.

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3. REACTIVITY STUDIES OF CATIONIC η^2-(α,ω-DIENE) COMPLEXES OF THE TYPE $[CpFe(CO)_2(\eta^2\text{-DIENE})]PF_6$

4. SYNTHESIS, CHARACTERIZATION AND SOME REACTIVITY STUDIES OF HETEROBINUCLEAR μ-ALKANEDIYL COMPLEXES OF THE TYPE $[(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl$

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1. OVERVIEW OF HYDROCARBYL COMPLEXES

1.1 Definition of hydrocarbyl Complexes

Hydrocarbyl complexes are by definition compounds which have a hydrocarbon fragment bonded to a transition metal through a direct metal–carbon bond, which could be either a σ **(I, III and IV)** or a π **(II)** bond. These compounds can be classified as either mononuclear (type **I** and **II**), containing a single metal centre ([Figure 1.1], or polynuclear (type **III** and **IV**) [Figure 1.2] containing two or more metal centres. Examples of these hydrocarbyl complexes are shown below:

(I) **(II)**

L_nM = metal and its associated ligands

Figure 1.1: Mononuclear hydrocarbyl compounds

(III) **(IV)**

Figure 1.2: Polynuclear hydrocarbyl compounds

Investigations into the synthesis and characterisation of transition metal hydrocarbyl complexes have become increasingly important [1-6]. These complexes play a crucial role in catalysis [7-11] and have also found broad application in organic synthesis [8, 12-15]. Each of these aspects are discussed below in the following sections.

1.2 Catalytic applications of hydrocarbyl Complexes

Many metal catalyzed reactions are known to involve transition metal hydrocarbyl intermediates. These reactions include a number of industrial processes, which are of commercial importance. Amongst these are the Fischer-Tropsch process (1.2.1), olefin polymerisation (1.2.2), hydroformylation (1.2.3), and the Wacker process (1.2.4). Each of these is briefly discussed below, highlighting the role of transition metal hydrocarbyl compounds in these processes.

1.2.1 Fischer-Tropsch reaction

Hydrocarbyl species have been invoked as intermediates in the Fischer-Tropsch (F-T) process [8, 16 – 22]. The Fischer-Tropsch synthesis is an industrially important process involving the conversion of mixtures of carbon monoxide and hydrogen ('synthesis gas') to long chain hydrocarbons, olefins and oxygenates (Equation 1.1) [17, 18]

$$nCO + H_2 \xrightarrow{\text{catalyst}} \begin{array}{l}\text{alkanes, olefins,}\\ \text{aldehydes, alcohols}\end{array} \qquad (1.1)$$

The reaction proceeds in the presence of heterogeneous metal catalysts based on either Fe, Co, Ni, and Ru, under high temperature and pressure.

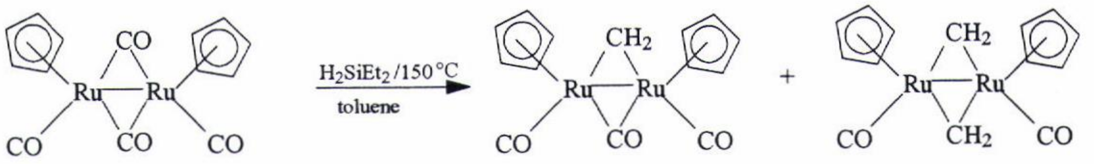
Syngas ($CO + H_2$) is readily available from a variety of fossil fuels. The Fischer-Tropsch synthesis is utilized on a large scale in the South African SASOL plants, due to the large reserves of cheap coal.

Extensive effort and speculation have been focused on the mechanism of the Fischer-Tropsch reaction and a number of catalytic cycles have been proposed. The mechanism originally proposed by Fischer and Tropsch suggests that the reaction occurs as a result of the polymerisation of *methylene (=CH_2)* ("Carbide mechanism"). On the other hand the alkyl mechanism proposes that the reaction is initiated by the formation of a surface *methyl (-CH_3)* species, and that chain growth takes place by insertion of methylene into the metal-alkyl bond. The alkenyl mechanism, proposed by Maitlis [18], suggests that the formation of a surface *vinyl species (-CH=CH_2)* initiates the reaction. The main features of these mechanisms are highlighted below.

1.2.1.1 The Carbide mechanism (formation of methylene species)

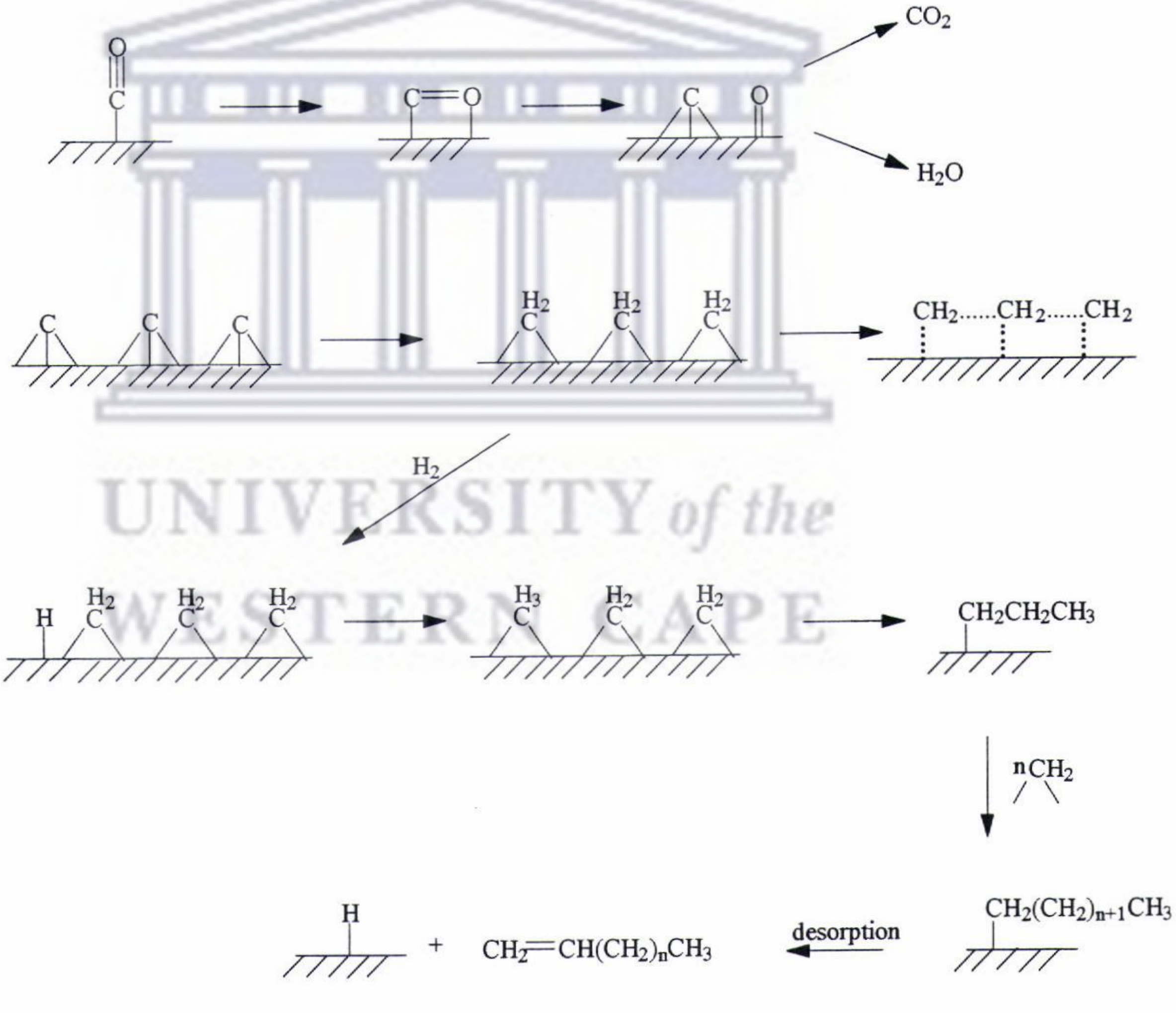
The carbide mechanism depicted in Scheme 1.1 has received fairly general acceptance [8, 22,23]. This mechanism was proposed by Fischer and Tropsch and focuses on the formation of surface carbides (hence, "Carbide Mechanism") which react with hydrogen to give methylenes, which in turn are polymerised. The first step involves the adsorption and subsequent dissocaition of CO into a type of surface carbide. The carbide is then hydrogenated via a surface methyne (CH) to form a surface methylene (CH_2), and finally to methane. The methylene group undergoes oligomerisation with an adsorbed methyl to form a hydrocarbon chain. The repeated insertion of methylene groups results in further chain propagation. The process is terminated by β-hydride elimination, followed by desorption of the alkene products.

A model reaction for the formation of a surface methylene species was reported by Akita and co-workers [24]. The reduction of $[Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2]$ using H_2SiEt_2 as an H_2 substitute resulted in the formation of a mixture of $[Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(CO)_2]$ and $[Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2]$ as shown in Equation 1.2.



(1.2)

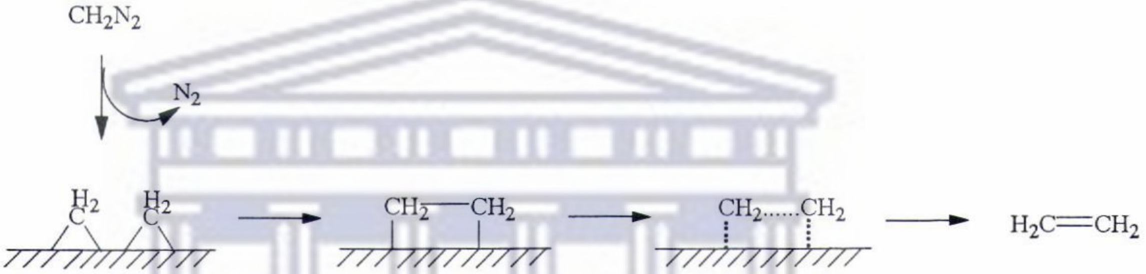
^{13}C and deuterium labelling studies showed that the products were formed from the reduction of μ-CO ligands. This reaction thus models the hydrogenation of CO on the surface of a Fischer-Tropsch catalyst to form a methylene species.



Scheme 1.1: The carbide mechanism for the Fischer-Tropsch reaction

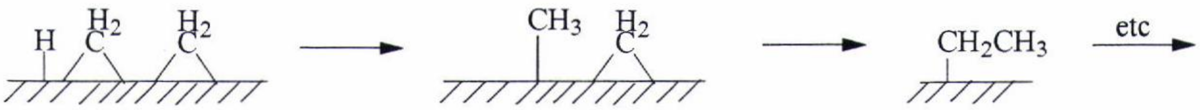
1.2.1.2 The alkyl mechanism

The alkyl mechanism for the Fischer-Tropsch reaction was first proposed by Brady and Petit [19,20]. They found that when diazomethane(CH_2N_2), diluted with an inert gas (He or N_2) was passed over a range of transition metal catalysts, ethylene was the predominant product formed. They concluded that the reaction occured due to the coupling of two methylene species on the surface of the catalyst i.e.



Scheme 1.2. Formation of ethylene by coupling of surface methylene species.

However, when H_2 was mixed with diazomethane, a range of hydrocarbons with similar distribution to that of the Fischer-Tropsch reaction was produced. This suggested that the methylene groups does polymerize on the catalyst surface but that the reaction takes place between the surface methylene and the surface hydrogen to form a surface methyl. Chain growth is propagated by successive insertions of methylene into the metal-alkyl bonds as shown in Scheme 1.3.

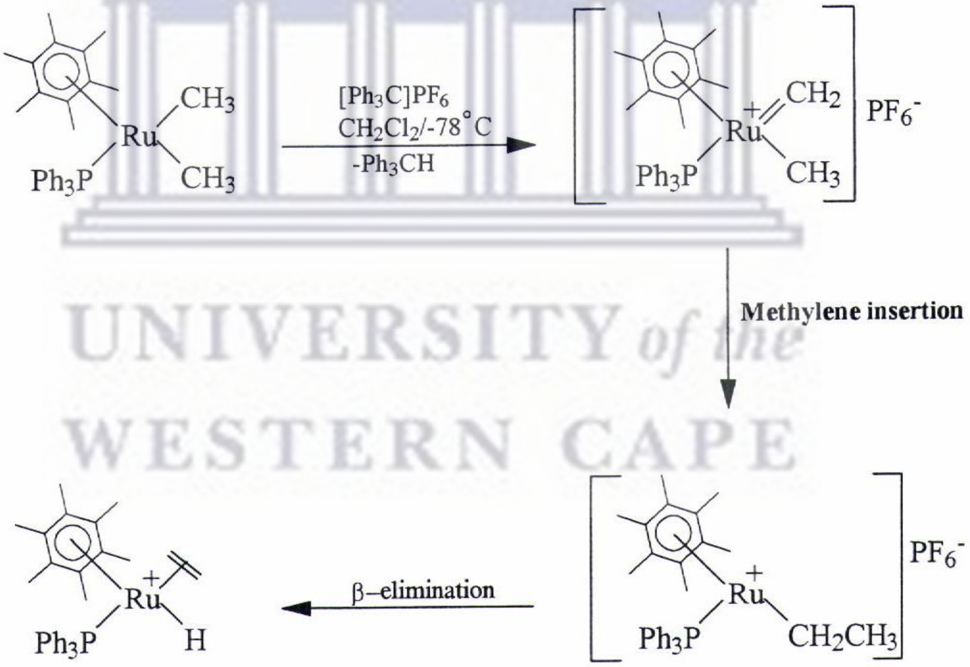


Scheme 1.3. The alkyl mechanism for chain growth in the Fischer-Tropsch reaction.

Termination of chain growth takes place by means of a β-hydride elimination to give α-olefins or by a reduction of the surface alkyls by surface hydrides to give alkanes.

In the Fischer Tropsch reaction, the absorbed methylene species are produced through the reduction of the surface carbide formed by the dissociative chemisorption of CO, as originally suggested by Fischer and Tropsch.

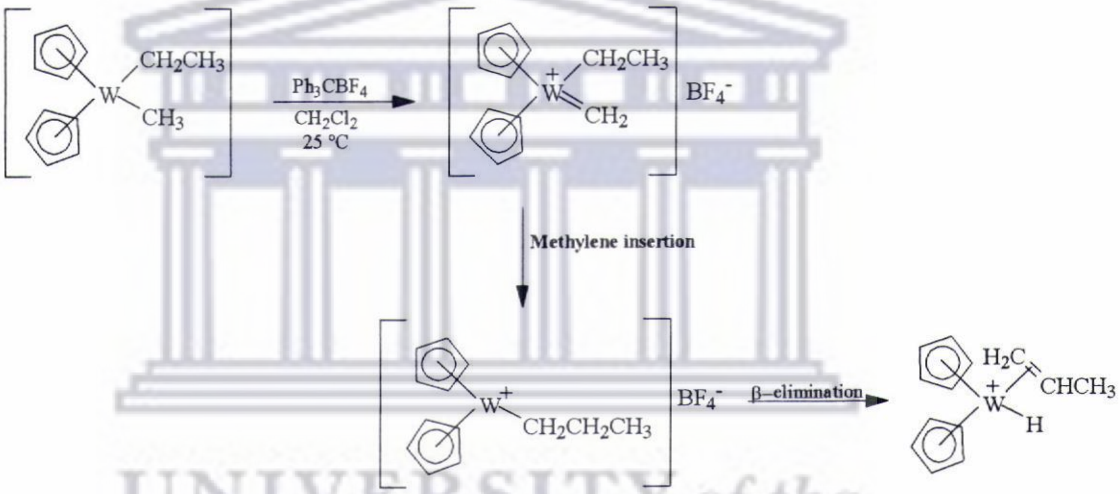
Model reactions illustrating the insertion of a methylene group into an alkyl species have been reported. For example, methylene insertion into a ruthenium-methyl group was suggested for the reaction of [C_6Me_6)Ru(CH_3)$_2$$PPh_3$)] with trityl salt ($Ph_3CPF_6$) [25]. This reaction resulted in the formation of the ethylene(hydrido) complex [C_6Me_6)RuH(C_2H_4)(PPh_3)]. Werner and co-workers postulated that the trityl cation abstracts a hydride ion from the methyl to form a ruthenium-methylidene-methyl complex, which undergoes methylene insertion into the ruthenium-methyl bond and β-hydride elimination to yield the ethylene(hydrido) product as illustrated below:



Scheme 1.4: Model reaction for methylene insertion into a ruthenium-methyl bond

Cooper and Hayes [26] demonstrated the insertion of a methylene group into a metal-ethyl bond. The reaction of $[Cp_2W(CH_3)(C_2H_5)]$ with $[Ph_3C]BF_4$ led to the formation of $[Cp_2W(C_3H_6)H]BF_4$. Methylene insertion into the metal-ethyl bond and subsequent β-hydride elimination results in the formation of the propene(hydrido) product.

This reaction models the insertion of a methylene unit with a surface ethyl in the Fischer-Tropsch reaction.



Scheme 1.5: Model reaction for methylene insertion into a tungsten-ethyl bond.

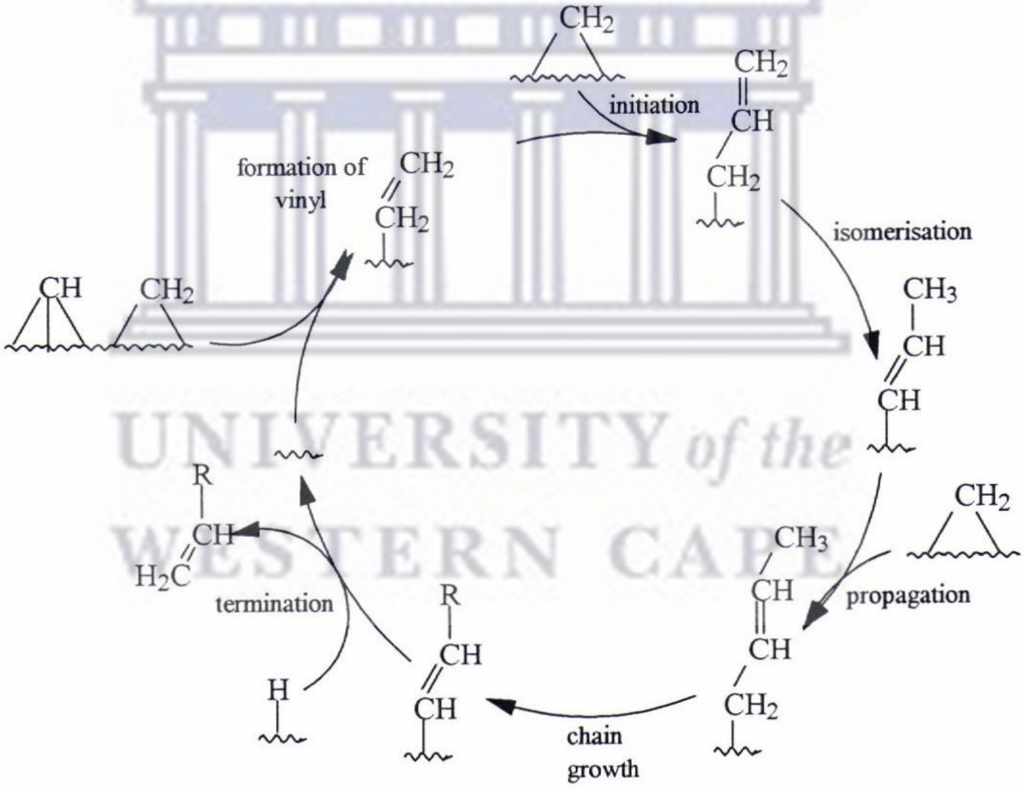
1.2.1.3 The alkenyl mechanism

The alkenyl mechanism was proposed by Maitlis [18, 27]. This mechanism suggests the formation of surface vinyls ($CH{=}CH_2$) by the coupling of surface methynes ($=CH$) and surface methylenes ($=CH_2$). Chain growth takes place via the reaction of the vinyl species with a surface methylene to form an allyl species ($-CH_2CH{=}CH_2$). This isomerises to yield an alkenyl species ($-CH{=}CHCH_3$) which reacts further

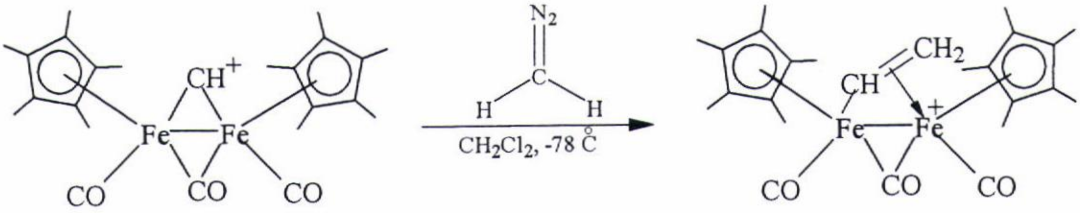
(Scheme 1.6). Termination occurs by the reaction of the alkenyl species with the surface hydride to form the free alkene.

A model reaction for the formation of the vinyl species is the reaction of $[\{Cp^{*}FeCO\}_2(\mu\text{-}CO)(\mu\text{-}CH)]PF_6$ with diazomethane at -78°C in CH_2Cl_2 to form the μ-vinyl complex $[\{Cp^{*}FeCO\}_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)]PF_6$ (Equation 1.3) [28]

The reaction models the proposed coupling of a surface methyne with a surface methylene to form a surface vinyl species.

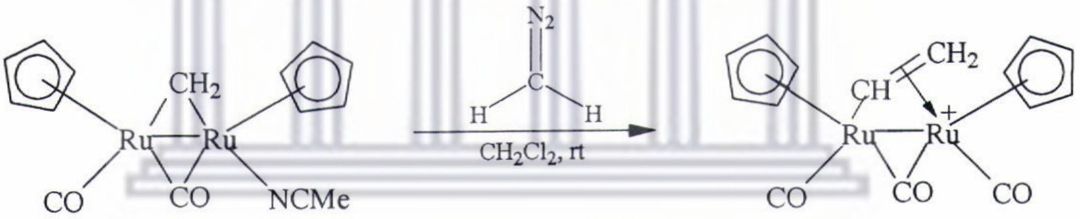


Scheme 1.6: The alkenyl mechanism for the Fischer-Tropsch reaction



(1.3)

Akita and Knox obtained similar results on a diruthenium complex [29]. The reaction of $[Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)]$ with diazomethane in CH_2Cl_2 at room temperature gave the product $[Cp_2Ru_2(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)(\mu\text{-}H)(CO)_2]$ (Equation 1.4). This provides another model reaction for coupling of a surface methyne with a surface methylene to form a surface vinyl species.



(1.4)

In all of the proposed mechanisms, it is evidently clear that metal-hydrocarbyl species play an important role in the Fischer-Tropsch process. The use of transition-metal hydrocarbyl compounds as models for the Fischer-Tropsch reaction has also been illustrated.

1.2.2 Olefin Polymerisation

One of the most commercially important industrial applications involving hydrocarbyl complexes as intermediates is the polymerisation of olefins such as ethylene and propylene.

Two groups of transition metal catalysts are widely used for α-olefin polymerisation and co-polymerisation reactions. The first group are commonly known as "Ziegler-Natta catalysts", while the members of the second group is the so called "metallocene catalysts".

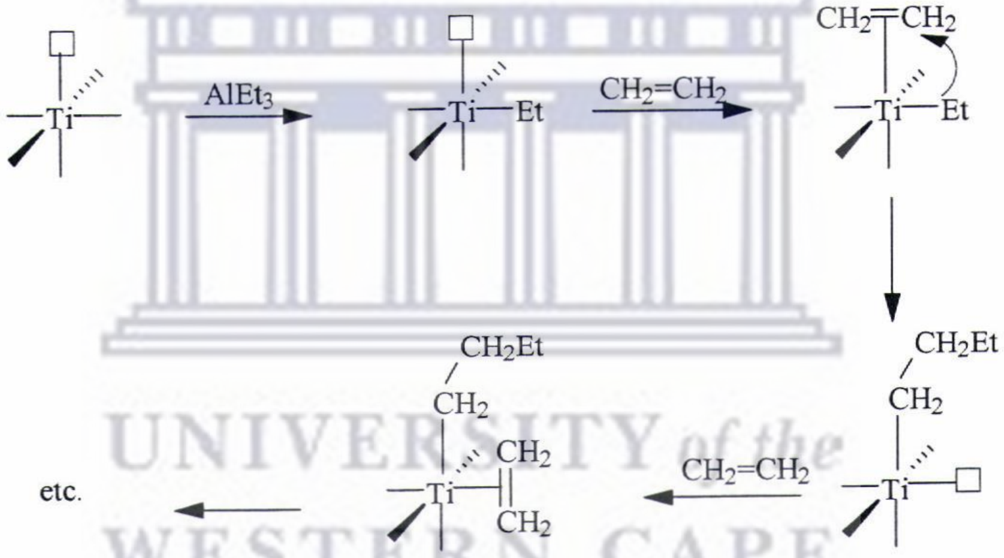
The term "Ziegler-Natta catalysts" were named after Karl Ziegler and Giulio Natta. In late 1952, while studying the reactions between aluminium alkyls and ethylene, Karl Ziegler discovered that $TiCl_4$ together with an aluminium alkyl forms a catalytic system which enables the low-pressure polymerisation of ethylene to give linear polyethylene of high molecular weight [30]. This particular catalyst based on titanium tetrachloride ($TiCl_4$) and triethylaluminium (Et_3Al) as cocatalyst succeeded in polymerizing ethylene into high density polyethylene, (HDPE), at standard pressure and room temperature. Subsequent to this Giulio Natta was able to demonstrate that an appropriate catalyst system was capable of polymerising propene into polypropylene of high molecular weight and with good stereoregularity [31]. Since these early discoveries, Ziegler-Natta catalysts have been used industrially to manufacture polyolefins.

The second type of catalyst is reffered to as "metallocene" catalysts. In 1957, Breslow and Natta [31] reported that $[(C_5H_5)_2TiCl_2]$ could be activated for ethylene polymerisation by a dialkylaluminium chloride cocatalyst. These catalyst systems polymerised ethylene with moderate activity but were inactive to propylene.

The situation changed dramatically in 1976 when Kaminsky and Sinn discovered several new catalyst with high activity [32-36]. These metallocenes are based on two components: a metallocene complex of group IV metals (Ti, Zr, or Hf) and a organoaluminium cocatalyst, methylaluminoxane (MAO), $[Me(AlO)_n]$. These catalyst systems have provided the opportunity to study the mechanisms involving the initiation, propagation and chain termination of Ziegler-Natta polymerisation. In addition, the discovery of chiral metallocene catalysts by Britzinger [37,38] in 1982 has resulted in highly stereospecific polymers. These catalysts have thus become significantly important to both industrial and academic research.

Irrespective of which catalyst is used, in all these systems hydrocarbyl complexes play a central role in the catalytic cycle.

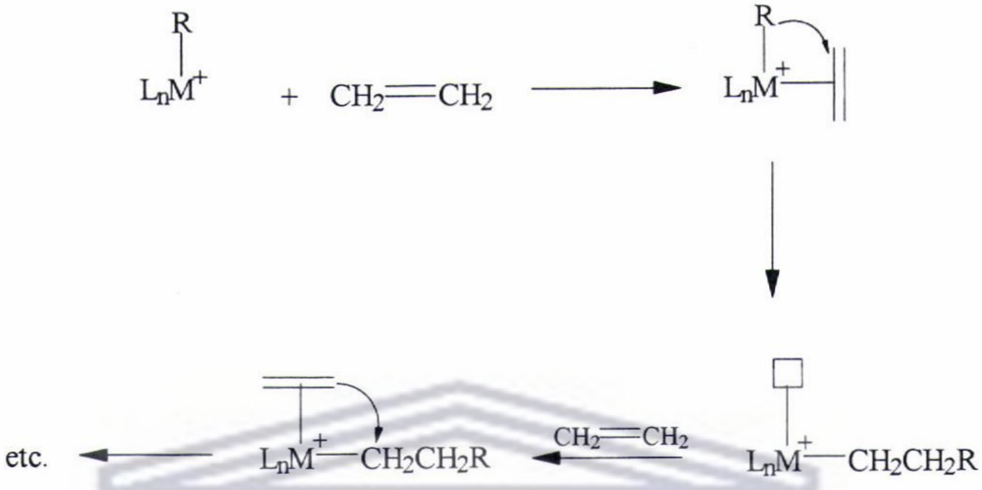
For example, the mechanism proposed by Cossee (Cossee-Arlman mechanism) [7] for the polymerisation of ethylene using a "Ziegler-Natta" catalyst involves a titanium-olefin intermediate as shown in Scheme1.7:



Scheme 1.7: Cossee-Arlman mechanim for polymerisation of ethylene

Transition-metal hydrocarbyl complexes also serve as intermediates in polymerisation of olefins using "metallocene" catalysts, as can be seen from the general catalytic cycle shown Scheme 1.8.

Some examples of metallocene catalysts are summarised in Table 1.1.



L_nM = Metal and associated ligands: for example - Cp_2MX_2, where M = Ti, Zr, Hf, X Cl, Br

Scheme 1.8: General catalytic cycle for polymerisation of α-olefins using metallocene catalyst

Table 1.1: Some examples of metallocene catalysts used in the polymerisation of olefins

METALLOCENE	**COMMENTS**	**REFERENCES**
[Cp_2M-Me_2]	M = Ti, Zr, Hf	40, 41
[Cp_2MPh_2]	M = Ti, Zr, Hf	40
[Ind_2M-Me_2]	M = Ti, Zr, Hf	40, 42

Table 1.1 continued

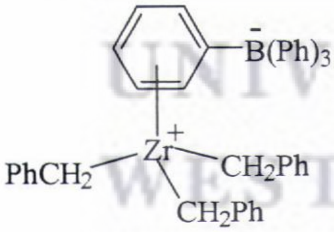
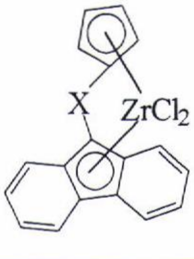
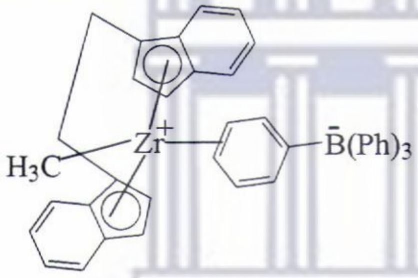
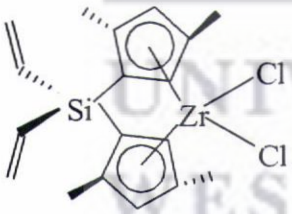
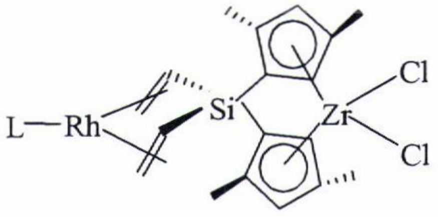
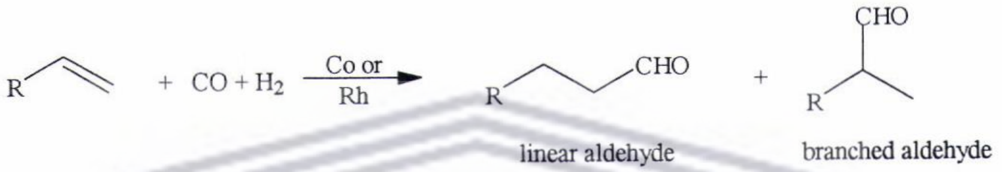
METALLOCENE	COMMENTS	REFERENCES
[Ind_2MPh_2]	M = Ti, Zr Ind = indenyl	40
[$Cp_2Ti(R)Cl$]	R = Me, Et, n-Pr, n-Bu, CH_2Ph, CH_2SiMe_3	42
[$Cp^*{}_2Ti(R)Cl$]	Cp* = C_5Me_5 R = Me, Et, $CH{=}CH_2$	43,44
[$Cp^*{}_2Hf(R)H$]	Cp* = C_5Me_5 R = CH_2CH_3, $CH_2CH_2CH_3$, Ph, CH_2CH_2Ph	45
$Cp_2M(Me)][BPh_4]$	M = Ti, Zr	46
		47
	M = Zr, X = Me_2C M = Hf, X = Me_2C M = Zr, X = Ph_2C	48

Table 1.1 continued

METALLOCENE	**COMMENTS**	**REFERENCES**
		49
		50, 51
		52
	L = indenyl L = Cp L = Cp*	53

1.2.3 Hydroformylation

The oldest and largest homogeneous catalysis reaction involving olefins in industry is hydroformylation [11, 54]. In the hydroformylation process olefins are converted into aldehydes via the reaction with carbon monoxide and hydrogen in the presence of a transition metal catalyst i.e.

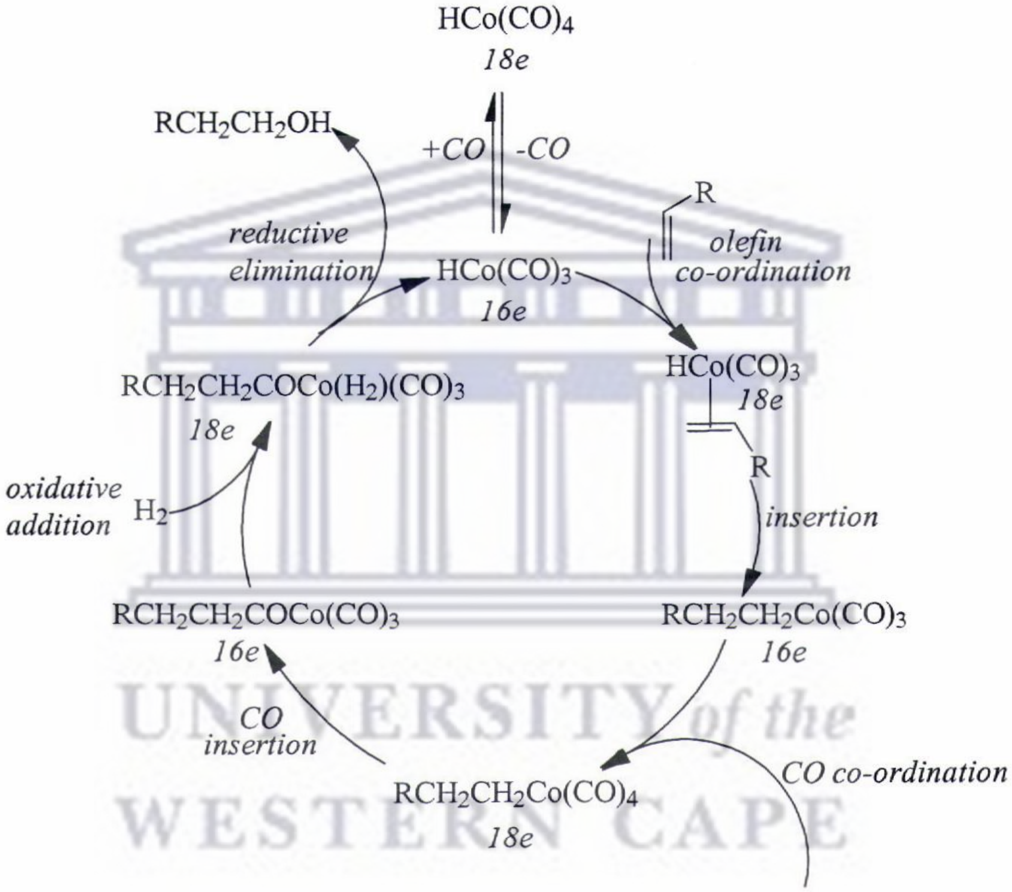


(1.5)

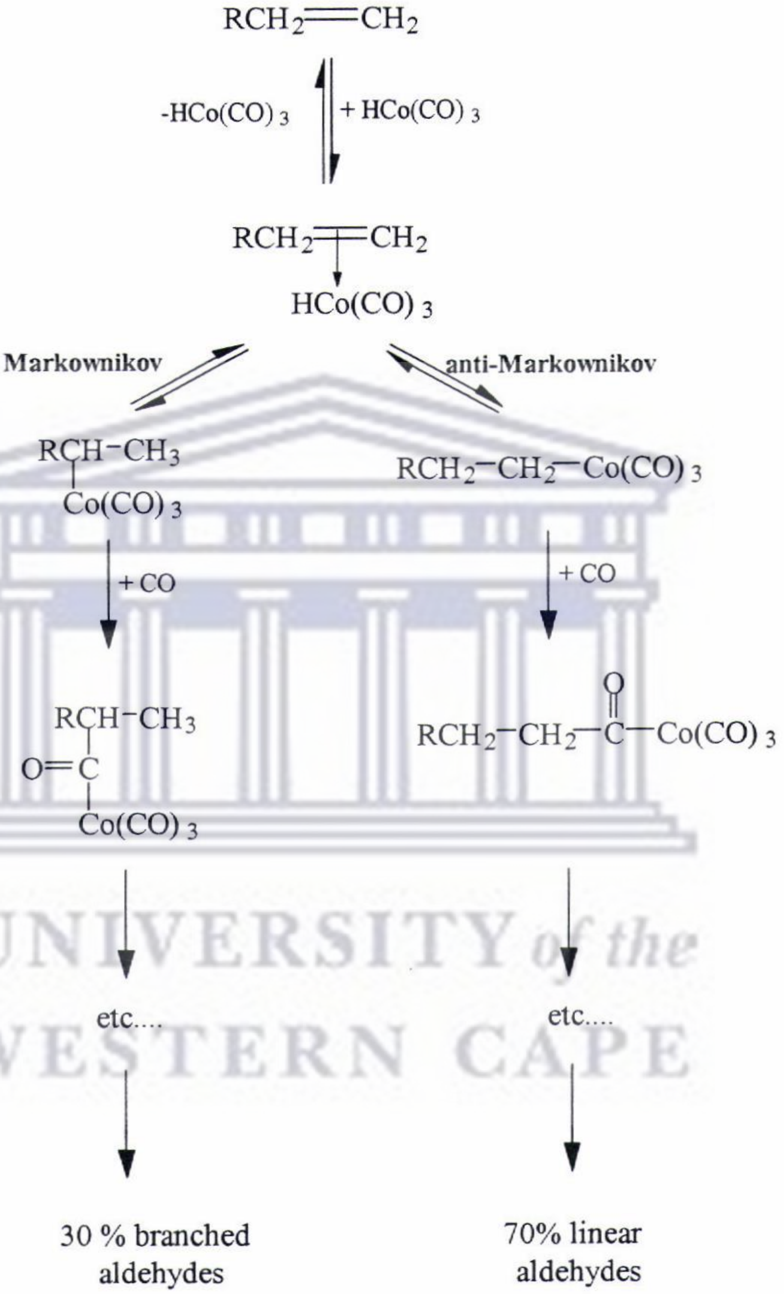
The process was originally developed by Otto Roelen (BASF) in 1938 using a cobalt catalyst and referred to as the 'oxo process'. The process operates at elevated temperatures and high CO/H_2 pressures. The active catalyst is $HCo(CO)_3$ which is formed in situ from $Co_2(CO)_8$. The catalytic cycle is shown in Scheme 1.9.

When starting with an olefin other than ethylene the addition of $HCo(CO)_3$ in the catalytic cycle can follow a Markownikov or anti-Markownikov pathway as shown in Scheme 1.10. This leads to the formation of branched and linear products in a ratio of 30:70. Since the aldehydes are reduced to detergent alcohols, which are linear, the branched isomer is undesirable. The addition of R_3P allows for regio control optimizing towards linearity in detergent alcohols, one of the biggest applications of hydroformylation.

More efficient catalysts are obtained by replacing cobalt with rhodium. The addition of phosphines or amine ligands to the Co and Rh compounds optimizes the activity and selectivity of the catalyst. The catalytic cycle for the rhodium based catalyst is closely analogous to that outlined for cobalt and is facilitated by the dissociation of phosphine ligand to give the 16 valence electron species. The hydroformylation process illustrates the use of cobalt and rhodium hydrocarbyl complexes as important intermediates in the catalytic cycle.



Scheme 1.9: Conventional mechanism for hydroformylation by an unmodified cobalt carbonyl catalyst



Scheme 1.10: $HCo(CO)_3$ addition to an olefin

1.2.4 The Wacker process

The Wacker process is a palladium-catalyzed process for the oxidation of ethylene to acetaldehyde [11,54]. Conversion of ethylene to acetaldehyde differs from hydroformylation in that a C_n olefin is converted to a C_n aldehyde, not a C_{n+1} aldehyde as in hydroformylation. This process is based on the combination of three well known reactions demonstrated in the equations below.

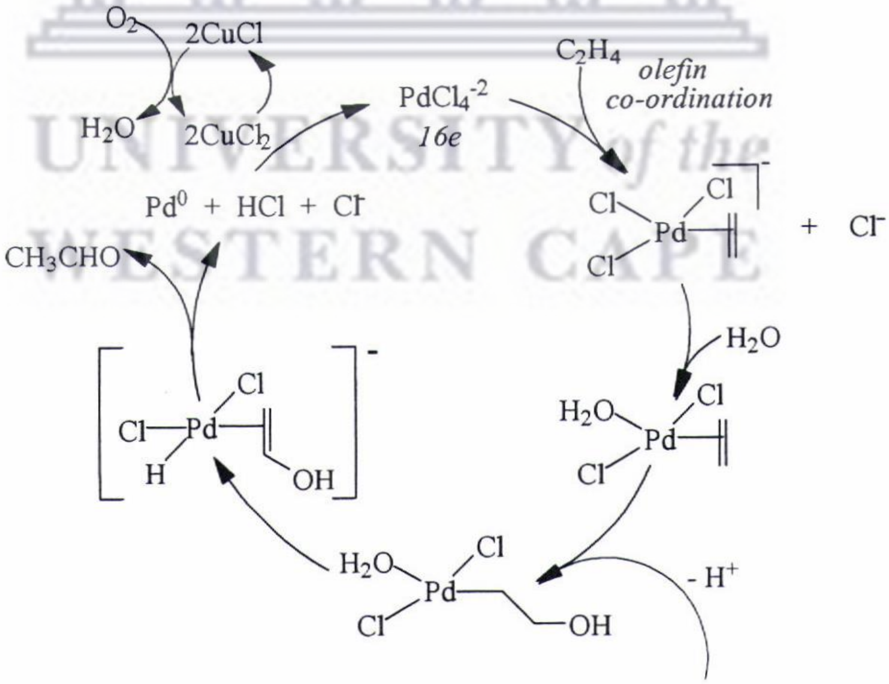
$$PdCl_4^{-2} + C_2H_4 + H_2O \longrightarrow CH_3CHO + Pd^0 + 2HCl + 2Cl^- \quad (1.5)$$

$$Pd^0 + 2CuCl_2 + 2Cl^- \longrightarrow PdCl_4^{-2} + 2CuCl \quad (1.6)$$

$$2CuCl + 1/2\,O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O \quad (1.7)$$

$$C_2H_4 + 1/2O_2 \longrightarrow CH_3CHO \quad (1.8)$$

The formation of a palladium olefin complex is an important step in the catalytic cycle, as shown in Scheme 1.11.



Scheme 1.11: The oxidation of ethylene to acetaldehyde by palladium(II)

A key step in the oxidation reaction involves the nucleophillic attack of water on a palladium-ethylene complex, which illustrates the importance of the role of hydrocarbyl complexes in the industrially important Wacker process.

1.3 Applications of hydrocarbyl complexes to Organic Synthesis

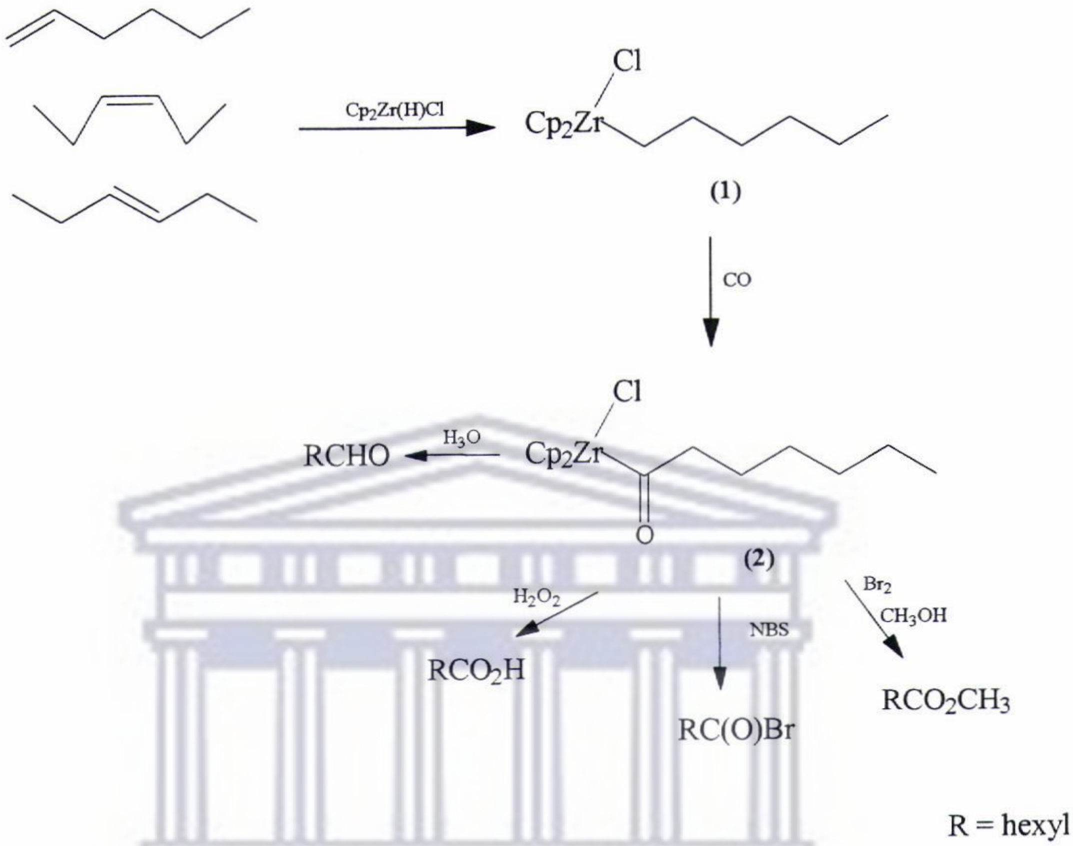
Transition metal hydrocarbyl complexes are involved in various synthetic processes leading to a wide range of organic compounds [8, 12-15]. Complexation of the hydrocarbon to the metal changes the reactivity of the organic group. The complexed hydrocarbon is able to undergo reactions under conditions where the corresponding free organic group is usually inert. Alternatively it could cause the co-ordinated hydrocarbon to be inert towards reagents with which the free hydrocarbon normally reacts. There are numerous examples where hydrocarbyl complexes play a role in metal-mediated organic synthesis. Some of these are illustrated below:

1.3.1 Zirconium alkyls as intermediates in organic synthesis

One example is the carbonylation of olefins of via an alkylzirconium intermediate [8, 55 – 58]. The reaction of the alkylzircononium species **(1)** with carbon monoxide leads to the formation of the mononuclear zirconium-acyl complex **(2)**. The latter can be converted, depending on subsequent procedures, into an aldehyde, carboxylic acid, ester, or an acyl halide as shown in Scheme 1.12.

1.3.2 Iron complexes in organic syntheses

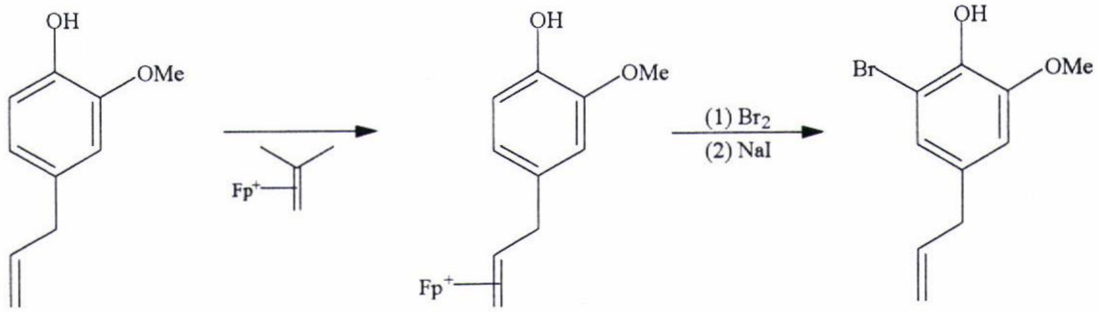
Iron complexes bearing the cyclopentadienyl(dicarbonyl)iron moiety have found numerous applications in organic synthesis [15, 59-63]. They could serve as protecting groups as well as intermediates in organic syntheses.



Scheme 1.12: Carbonylation of hexenes mediated by $Cp_2Zr(H)Cl$

1.3.2 a) Iron complexes as protecting groups in organic synthesis

Hydrocarbons coordinated to the $[CpFe(CO)_2]^+$ cation becomes more susceptible to nucleophiles and more resistant to electrophiles [64,65]. These complexes can thus be used as protecting groups against electrophillic attack. This is illustrated in Scheme 1.13. In these reactions the complexation of the cationic iron centre occurs quite readily for unsubstituted alkenes. Reactions for substituted alkenes and alkynes are quite sluggish, so selective protection is possible. Decomplexation of the iron is achieved by treatment with sodium iodide.

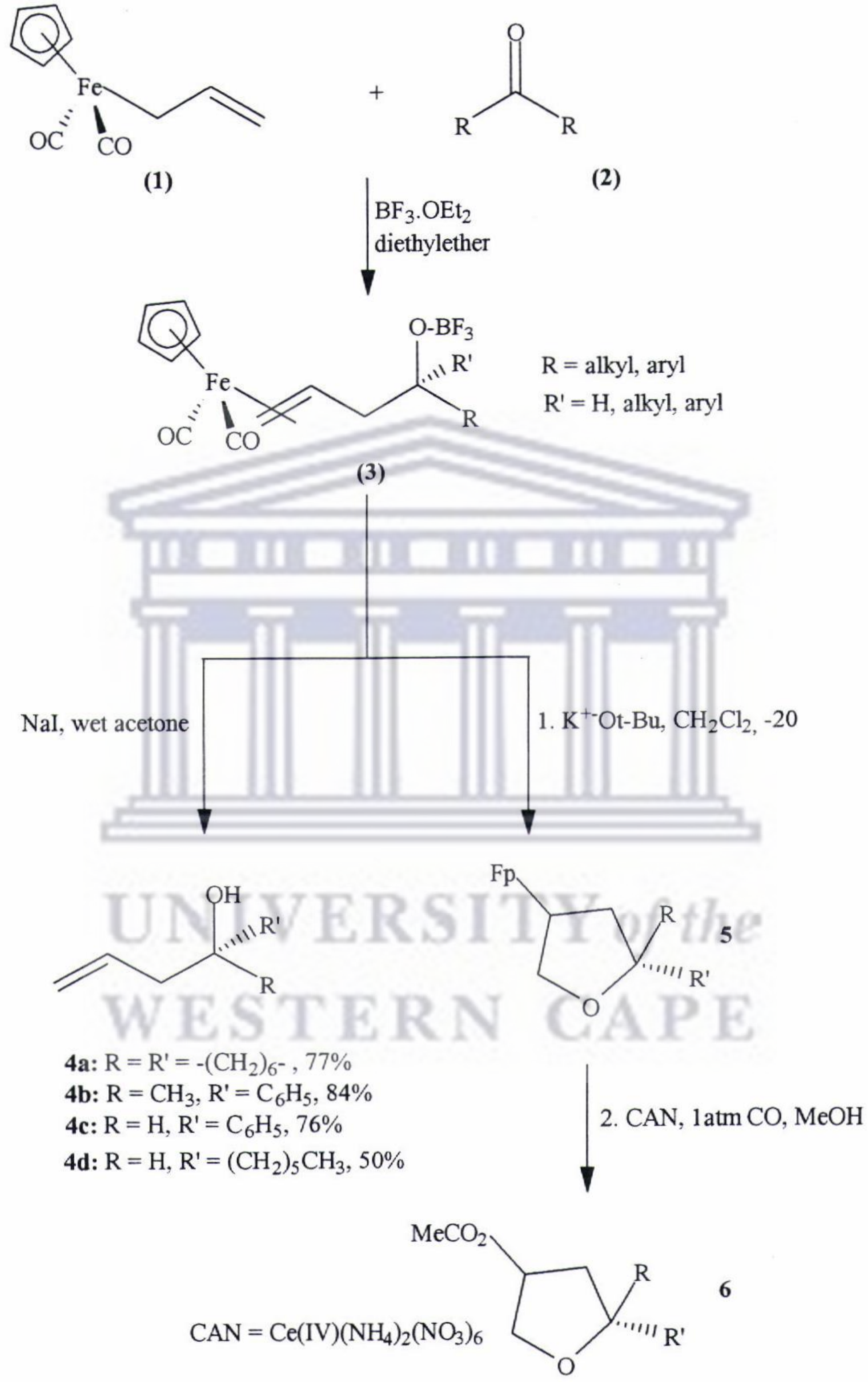


Scheme 1.13: Example of iron-hydrocarbyl complex as protecting group in organic synthesis

1.3.2 b) Iron complexes as intermediates in organic synthesis

An example where these iron containing hydrocarbyl complexes serves as intermediates in organic synthesis is the Lewis acid-catalyzed addition reactions of allyliron(II) reagents to aldehydes and ketones reported by Turos and co-workers [66-69].

These addition reactions lead to the formation of stable zwitteronic iron-alkene complexes of the type **3**. Treatment of **3** with NaI in wet acetone lead to the formation of the alcohols **(4a - 4d)** in 50-84% yields. **3** was also found to readily undergo cyclization upon treatment with K^+O^t-Bu in dichloromethane at -20°C, producing iron-substituted furans **5** as a intermediate [67-69]. The latter can subsequently be transformed to furan esters **(6)** with ceric ammonium nitrate under a CO atmosphere. The products derived from the iron-alkene complexes prepared from the aldehyde were isolated in 40-45% yield, whereas those obtained from the analogous ketones only gave yields of 20%. Some of these transformations are summarised in Scheme 1.14.

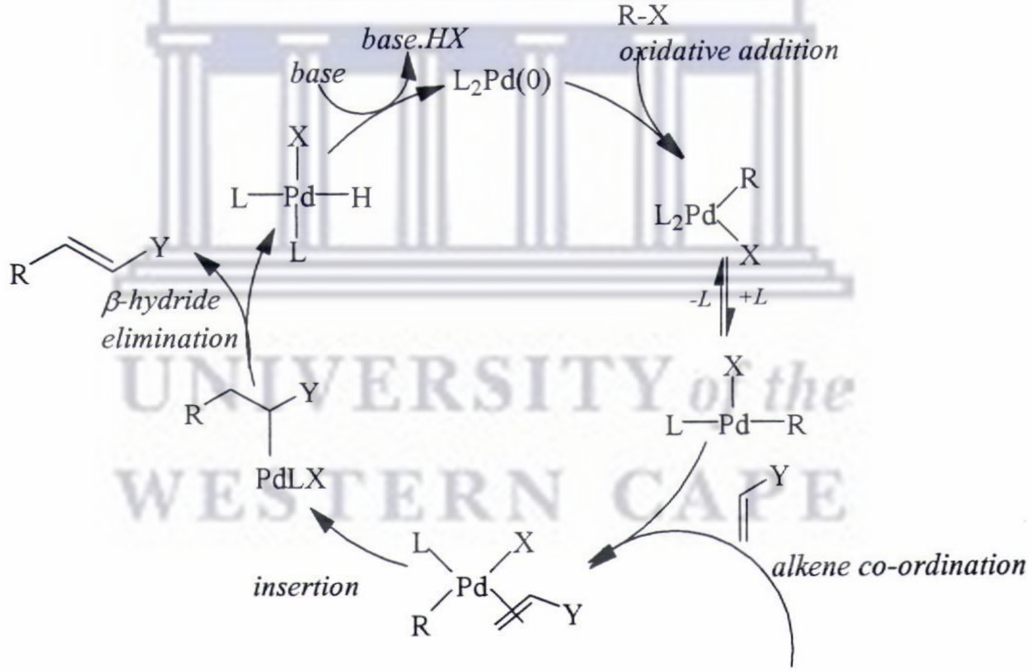


Scheme 1.14 Example of an iron hydrocarbyl complex as an intermediate in organic synthesis

1.3.3 Palladium complexes in organic synthesis

The Heck reaction is one of the most important C-C coupling reactions in organic synthesis[70-73]. This involves the reaction between aryl or vinyl halides and alkenes in the presence of a base and a palladium catalyst.

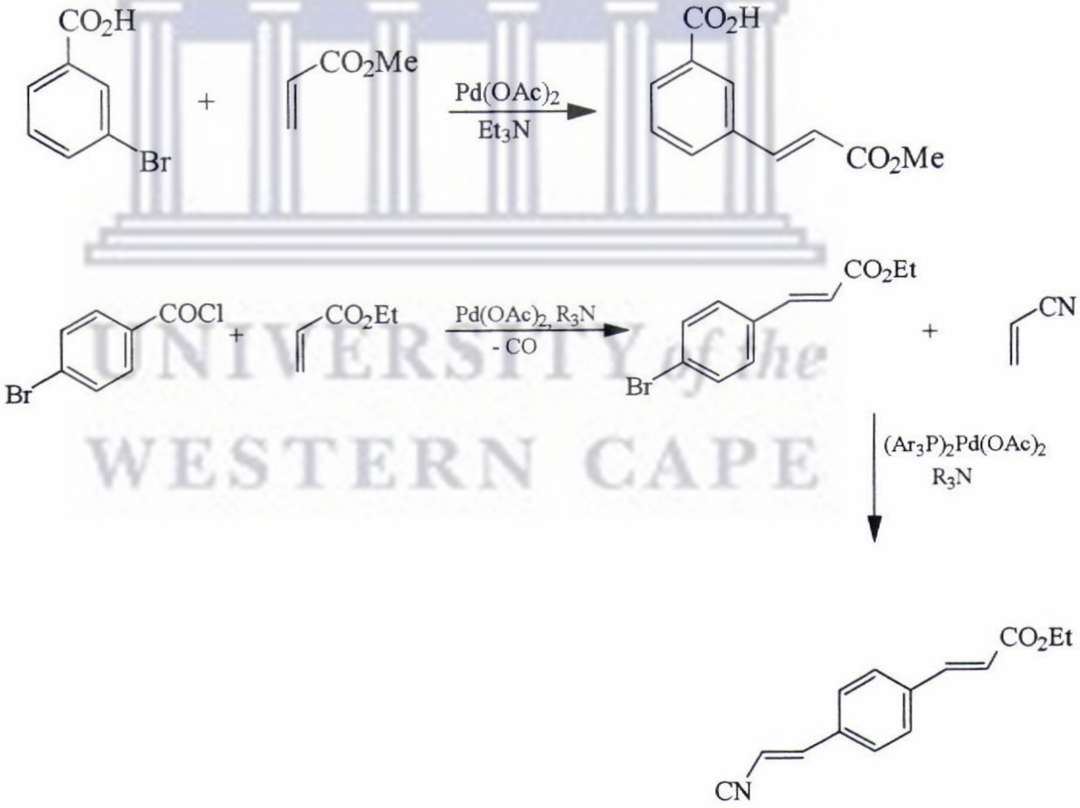
The mechanism for this reaction involves the initial oxidative addition of the vinyl or aryl halide to the palladium centre, coordination of the alkene, insertion of the alkene into the metal-carbon bond and finally β-hydride elimination to give the product. Loss of HX from the palladium is neutralised by the base added during the reaction.



Scheme 1.15: Mechanism for the Heck reaction

The reaction is catalyzed by palladium(0) complexes generated from either Pd(0) compounds, such as [Pd(PPh_3)$_4$] and [Pd_2(dba)$_3$] (dba = dibenzylidene acetone), or from Pd(II) salts, such as the acetate and the chloride. Palladium acetate is used more often because of its higher insolubility in organic solvents. The Pd(II) salts are reduced in situ to Pd(0), by the base or the phosphine. Phosphines are almost always added, either seperately or already complexed to palladium. Some of the common bases used includes tertiary amines, alkali acetates, carbonates and phosphates.

The aryl halides employed are usually bromides and iodides, the latter being more reactive. Aryl acid chlorides, although rarely used, are more reactive than the aryl bromides. At high temperatures the aryl acid chloride undergoes decarbonylation prior to the insertion of the alkene resulting the product being an aryl alkene and not a acyl alkene. Acylated aryl alkenes can be isolated at lower temperatures. Some examples of the Heck reaction is illustrated below:



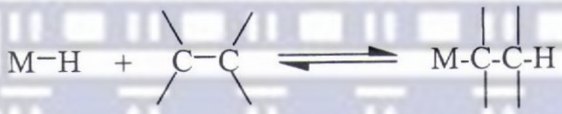
Scheme 1.16 Examples of the Heck reaction ilustrating the use of palladium complexes in organic synthesis.

1.4 A brief summary of known examples of hydrocarbyl complexes

1.4.1 Mononuclear transition-metal alkyl complexes

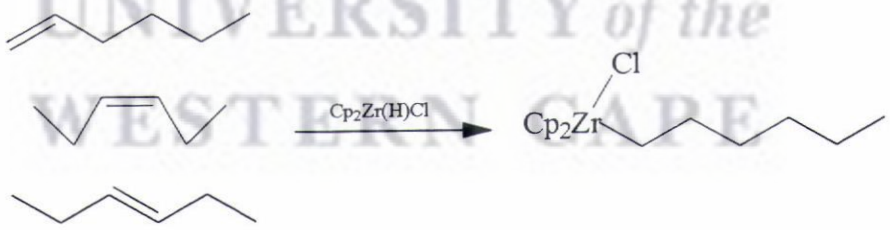
Transition metal alkyls were amongst the first organometallic compounds known and have been extensively studied [74,75]. There are several general methods for the synthesis of transition-metal alkyl complexes. The section which follows discusses these methods very briefly, listing some examples of these compounds.

1.4.1.1 Addition of a transition metal hydride to an olefin



(1.6)

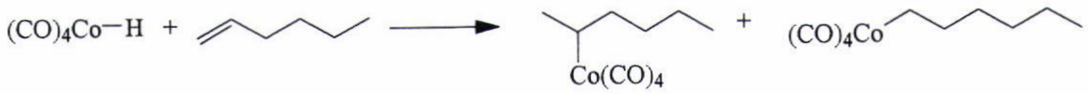
Alkenes and alkynes insert readily into a M-H bonds. This is the so-called hydrometallation reaction. An example of this reaction is hydrozirconation which involves the insertion of a Zr-H bond into an alkene/alkyne as shown below [56-58].



(1.7)

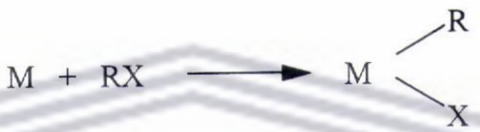
A similar type of reaction is also observed for some main group elements e.g. hydroboration, hydroalumination and hydrostannation.

Reactions of this type are important steps in catalytic reactions. For example, the reaction below serves as an important step in the hydroformylation process (discussed in section 1.2.3).



(1.8)

1.4.1.2 Oxidative addition reactions



(1.9)

Oxidative addition is the term used to describe the addition of a substrate R-X to a coordinatively unsaturated metal complex M. This leads to an increase in the coordination number as well as the oxidation state of the complex. The oxidative addition reaction plays an important role in stoichiometric and catalytic reactions.

Low valent metal complexes, particularly those of Ir^I, Ni^0, Pd^0 and Pt^0, undergoes oxidative addition reactions with alkyl, alkenyl, benzyl and aryl halides.

The reaction proceeds most readily with coordinatively unsaturated complexes (e.g. square planar) and those containing labile ligands e.g. [76].

$$\underset{\text{Vaska's complex}}{[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}]} + \mathrm{MeI} \longrightarrow [\mathrm{Ir^{\,III}Me(I)(Cl)(CO)(PPh_3)_2}]$$

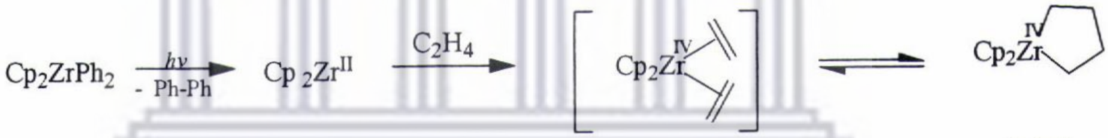
(1.10)

The oxidative addition reactions of organic halides with platinum compounds proceeds readily. The first well-defined σ-alkyl complex of platinum(II), *trans*-[PtIMe($P^nPr_3)_2$], was first prepared by Foss in collaboration with Chatt and Shaw in 1952 [77]. Foss studied the reaction of *trans*-[PtIMe($P^nPr_3)_2$] with methyl iodide i.e.

$$trans\text{-}[PtIMe(P^nPr_3)_2] + MeI \longrightarrow trans\text{-}[PtI_2Me_2(P^nPr_3)_2] \qquad (1.11)$$

This work was continued by Chatt and Shaw in 1959. Since then the oxidative addition reactions of 16-electron organoplatinum(II) complexes have been studied extensively [78 – 80].

Another example of an oxidative addition type reaction is that of low valent early transition metals with alkenes and alkynes resulting in the formation of metallocycles e.g.



(1.12)

1.4.1.3 Reactions of metal anions with organic halides

$$L_nM^- + RX \longrightarrow L_nMR + X^- \qquad (1.13)$$

A large number of anionic transition metal complexes are easily prepared by reduction of the corresponding metal halide or bimetallic complexes or by treatment of a transition metal hydride with a base. These anions react with a variety of alkyl halides to give the corresponding neutral transition metal alkyl complexes.

This reaction is most useful for reactions involving anionic transition metal complexes containing π ligands such as CO, C_5H_5 or PR_3. Some examples of these complexes are discussed below.

In 1957 the first reported manganese-containing hydrocarbyl complex, $[(CO)_5MnCH_3]$, was synthesised using this method [81]. This was the first transition metal carbonyl alkyl compound to be prepared. It was synthesized by the reaction of sodium manganesepentacarbonyl and methyl iodide (Equation 1.14)

$$Na[Mn(CO)_5] \quad + \quad CH_3I \longrightarrow [(CO)_5MnCH_3] \quad + \quad NaI \tag{1.14}$$

The analogous ethyl and n-propyl manganesepentacarbonyl complexes have also been synthesised [82], but were reported to be extremely unstable, decomposing under vacuum at - 10°C [83].
Similarly, complexes of the type $Re(CO)_5$ (where $R = CH_3$ [84], CH_2CH_3 [85]) have been prepared using the same methodology. A prevoius review of manganesepentacarbonyl and rheniumpentacarbonyl alkyls as well as the synthesis of the longer chain analogues has been reported by Moss and Anderson [86].

The iron and ruthenium-alkyl compounds were synthesised using this method.

$$Na[Cp(CO)_2M] \quad + \quad RX \longrightarrow Cp(CO)_2FeR + NaX$$

$M = Fe, Ru$
$X = Cl, Br$
$R = alkyl$

(1.15)

The preparation of the complexes where R = Me or Et and M = Fe, were the first iron-alkyl compounds reported [87]. Shortly thereafter, King reported the synthesis of the compound of the type where $R = {}^{n}Bu$ [88]. A complete series of these complexes has since been synthesised. [89–93]. The ruthenium analogues were prepared using the same synthetic method [92–96].

1.4.1.4 Reactions of transition metal halides MX, with alkylating agents

$$MX + M'R \longrightarrow MR + M'X$$

(1.16)

Treatment of transition metal halides with primary alkyl derivatives of lithium, magnesium, zinc, and mercury generally results in the formation of transition metal alkyls. This is the most widely applicable synthetic method, both for homoleptic metal alkyls and for complexes stabilzed by donor ligands .

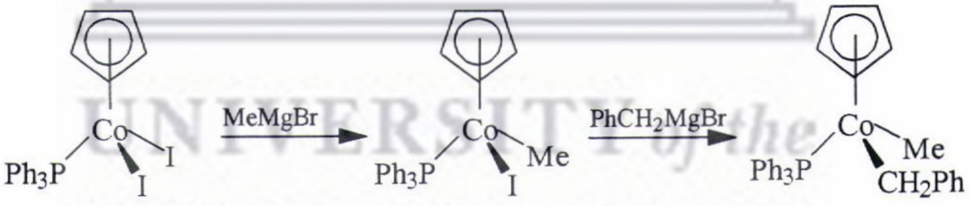
Some examples of these reactions are shown in Equations 1.17 – 1.19

$$RMgX + MnCl_2 \longrightarrow R_2Mn$$

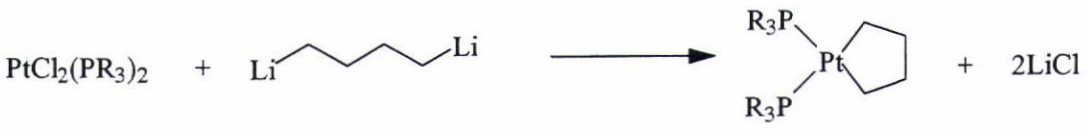
R = Me, Et, n-Pr, ^{t}Bu, ^{i}Pr

X = Br,Cl

(1.17)



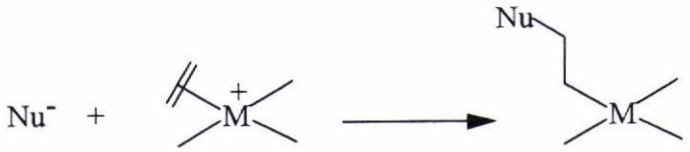
(1.18)



(1.19)

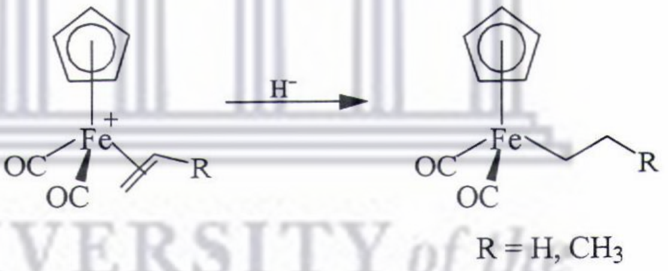
1.4.1.5 Via nucleophillic attack on coordinated ligands

A characteristic reaction of a number of metal-olefin complexes, particularly those of Pd(II), Pt(II), and Fe(II), is nucleophillic attack on the complexed olefin as illustrated below :

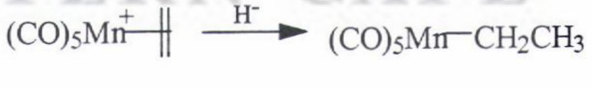


(1.20)

Examples of these reactions includes the addition of $NaBH_4$ to the cationic olefin complexes of iron and manganese [83].



(1.21)



(1.22)

1.4.2 Functionalised transition-metal alkyls

1.4.2.1 Halogenoalkyl complexes of transition metals

Halogenoalkyl transition metal complexes are functionalized alkyl complexes of the general formula $[L_yM(CH_2)_nX]$ (L_yM = metal and its associated ligands, X = Br, Cl, I or F, $n \geq 1$). The first known halogenoalkyl transition metal complexes were reported independently by Petit [97] in 1966 and Green in 1967 [98]. They reported on the synthesis of [CpFe(CO)$_2$CH$_2$Cl] by the reaction of the methoxymethyl complex (A) with gaseous HCl. The methoxymethyl complex **(A)** was prepared by the reaction of chloromethyl methyl ether with the Fp anion.

$$\begin{tikzcd} \mathrm{Na[CpFe(CO)_2]} + \mathrm{ClCH_2OCH_3} \arrow[r] & \underset{\mathbf{(A)}}{\mathrm{[Cp(CO)_2Fe\text{-}CH_2OCH_3]}} + \mathrm{NaCl} \arrow[d, "\mathrm{HCl}"] \\ & \mathrm{[Cp(CO)_2Fe\text{-}CH_2Cl]} \end{tikzcd} \quad (1.23)$$

Green also reported the synthesis of the bromo analogue, [CpFe(CO)$_2$CH$_2$Br], using HBr instead of HCl.

Since then many halogenoalkyl complexes have been synthesized. These complexes have been comprehensively reviewed by Moss and Friedrich [99, 100]. Longer chain halogenoakyl complexes, which have been studied in some detail are those of Mo [101-105], Fe [106, 107], Ru [108], W [101, 109, 110] and Pt [111-113].

Halogenoalkyl complexes could serve as precursors to a large variety of compounds that have been implicated as models in several catalytic processes. Amongst these are acyclic and cyclic carbene complexes [102, 103], as well as bimetallic hydrocarbon-bridged complexes [101, 106, 107, 114]. Thus for example, the reaction of [Cp(CO)$_2$Fe(CH$_2$)$_n$X] (n = 3-5, X = Cl, Br) with Na[CpFe(CO)$_2$] gives the binuclear complex [CpFe(CO)$_2$]{μ-(CH$_2$)$_n$} which could serve as a models for hydrocarbons on a catalyst surface i.e) the Fischer-Tropsch reaction discussed in section 1.2.
Some examples of halogenoalkyl transition metal complexes are listed in Table 1.3.

1.4.2.2 ω-Hydroxyalkyl complexes of transition metals

ω-Hydroxyalkyl transition metal complexes are functionalized transition metal alkyls in which the alkyl chain contains a hydroxy group at the terminal end [Figure 1.3].

$$L_nM(CH_2)_yOH$$

L_nM = metal and its associated ligands

Figure 1.3. ω-Hydroxyalkyl transition metal complex

These complexes have been proposed as model compounds for intermediates in a number of catalytic processes [11, 17, 54, 128]. For example, it has been shown in Scheme 1.10 that the oxidation of ethylene to acetaldehyde by palladium(II) choride (the Wacker process) goes via a β-hydroxyethyl complex.

Hydroxymethyl complexes have been extensively studied in literature [129-136] . There are however fewer examples of longer chain ω-hydroxyalkyl transition metal complexes [137-143].

Some examples of these complexes are summarized in Table 1.4

Table 1.3: Some examples of halogenoalkyl transition metal complexes

Compound	Synthesis	Comments	Ref:
[L_nMCH_2X[	[$L_nMCH_2OCH_3$] + HX(gas)	L_nM = $CpMo(CO)_3$ $CpW(CO)_3$ $Mn(CO)_3$ $CpFe(CO)_2$ $CpRu(CO)_2$, $Cp^*Ru(CO)_2$ X= Cl, Br, I	97, 98, 115-119
[L_nMCH_2Cl]	[$L_nM\{CH_2OC(O)Me\}$] + HCl	L_nM = $CpMo(CO)_3$ $CpFe(CO)_2$	120
(η^5-C_5R_5)$M(CO)_3(CH_2)_nX$	Na[(η^5-C_5R_5)$M(CO)_3$] + $X(CH_2)_nX$	X = Br, I; R = H; n =3,4; M = Mo X = Br,R = H; n = 3 –7; M =W X = I; R = H, n = 3,4, M =W R = CH_3; n = 3; M= Mo R = CH_3; n = 3, 4; M= W	101, 102, 109
[L_nMCH_2X]	$NaML_n$ + XCH_2X'	LnM = $CpMo(CO)_3$ $CpW(CO)_3$ $CpFe(CO)_2$ $Mn(CO)_5$ XCH_2X' = $ClCH_2I$	121

Table 1.3 continued ......

COMPOUND	**SYNTHESIS**	**COMMENTS**	**REF:**
$[(\eta^5\text{-}C_5R_5)M(CO)_3(CH_2)_nI]$	$[(\eta^5\text{-}C_5R_5)M(CO)_3(CH_2)_nBr]$ + NaI	R= H; n = 3 – 7; M = W R = CH_3 ; n = 3,4; M = W	109
trans-$[CpMo\{P(OPh)_3\}(CO)_2CH_2X]$	$[CpMo\{P(OPh)_3\}(CO)_2CHO]$ + E	E = H, CH_3 X = Cl, Br, I	122
$[Cp(CO)_2(PPh_iMe_{3-i})Mo\{(CH_2)_nBr\}]$	$Na[Cp(CO)_2(PPh_iMe_{3-i})Mo]$ + $Br(CH_2)_nBr$	n = 3,4; *i* = 0 –3,	105
$[Cp(CO)_2(PPh_iMe_{3-i})Mo\{(CH_2)_nI\}]$	$[Cp(CO)_2(PPh_iMe_{3-i})Mo\{(CH_2)_nBr\}]$ + NaI	n = 3,4; *i* = 0 –3,	105
$[L_nMCH_2I]$	$[L_nMCH_2Br]$ + NaI	$CpW(CO)_3$ $L_nM = CpFe(CO)_2$	115, 119
$[CpFe(PPh_3)(CO)CH_2Cl]$	$[CpFe(PPh_3)(CO)CH_2OCH_3]$+ HCl		123, 124
$[CpFe(CO)_2CH_2Cl]$	$[CpFe(CO)_2CH_2NMe_2]$ + CH_3COCl		125
$[CpFe(PPh_3)(CO)CH_2X]$	$[CpFe(PPh_3)(CO)CH_2OMen]$ + HX	X = Br, Cl, I	124

Table 1.3 continued ......

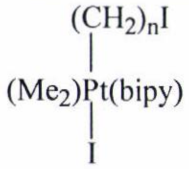
Compound	Synthesis	Comments	Ref:
$[(\eta^5\text{-}C_5R_5)M\{(CH_2)_nX\}]$	$Na[(\eta^5\text{-}C_5R_5)M(CO)_2]$ $+ X(CH_2)_nX$	where R = H X = Br; n = 3 –7 X = Br; n = 3 – 10; M = Fe X = Br; n = 3-5; M = Ru X = Cl; n = 3; M = Fe, Ru X = I; n = 3; M = Fe where R = CH_3 X = Br; n = 3- 5; M = Fe	106 - 108
$[(\eta^5\text{-}C_5R_5)M(CO)_2\{(CH_2)_nI\}]$	$[(\eta^5\text{-}C_5R_5)M(CO)_2\{(CH_2)_nBr\}]$ $+ NaI$	where R= H n = 3 – 10; M = Fe n = 3, 5; M =Ru where R = CH_3 n = 3- 5; M = Fe	106, 108
$[Ir(PMe_2Ph)_2(CO)(Br)_2(CH_2CH_2Br)]$	$[Ir(PMe_2Ph)_2(CO)(C_2H_4)]BPh_4$ $+ Br_2$		126
 $(Me_2)Pt(bipy)((CH_2)_nI)(I)$	$[Pt(Me)_2(bipy)] + I(CH_2)_nI$	bipy = 2,2'-bipyridine n = 1 - 5	113

Table 1.3 continued ......

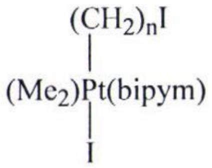
Compound	**Synthesis**	**Comments**	**Ref:**
 $\overset{(CH_2)_nI}{\underset{I}{(Me_2)Pt(bipym)}}$	$[Pt(Me)_2(bipym)]$ + $I(CH_2)_nI$	bipym = 2,2'-bipyrimidine n = 3 - 6	112
$[Co(DH)_2py\{(CH_2)_nX\}]$	$[Co(DH)_2pyCl]$ + $X(CH_2)_nX$	X = Br, n = 3 – 7 X = I, n = 3 reaction carried out in the presence of $NaBH_4$ DH = monoanion of dimethylglyoxime	127

Table 1.4: Some examples of ω-hydroxyalkyl transition metal complexes

Compound	**Synthesis**	**Comments**	**Ref**
$Cp(CO)_2MCH_2OH$	$[CpM(CO)_3]^+$ + $NaBH_3CN$	M = Fe, Ru	130
$Cp^*(CO)_2MCH_2OH$	$Cp^*M(CO)_3]^+$ + $NaBH_4$	M = Fe, Ru, Os	131 - 133
$(\eta^5\text{-}C_5R_5)(CO)_2Fe(CH_2)_nCH_2OH$	$Cp(CO)_2Fe(CH_2)_{n-1}CH{=}CH_2$ + BH_3 + OH^- + H_2O_2	R = H, Me n = 3-5, 7	137, 138
$CpRe(CO)(NO)CH_2OH$	$[CpRe(NO)(CO)_2][BF_4]$ + $NaBH_4$		135
$(CO)_5MCH(C_6H_5)OH$	$(CO)_5MCH(C_6H_5)OSi(CH_3)_3$ + HX/H_2O	M = Mn, Re X= Cl, F	128
$K_2[Cl_5Pt(CH_2CH_2OH)]$	$K_2[Cl_4Pt]$ + ICH_2CH_2OH		140
$XHgCH_2CH_2OH$	$HgX_2 + CH_2CH_2 \longrightarrow HgCH_2CH_2X \xrightarrow{H_2O}$	X = Cl, Br	139
$(CO)_2[P(OCH_3)_3]_2FeCH_2OH$	$(CO)_2[P(OCH_3)_3]_2FeCH_2O$ + HCl/Et_2O		134

1.4.3 Binuclear compounds

Binuclear complexes have long been recognized to have different reactivities from that of their mononuclear analogues and have thus attracted particular interest. A number of in-depth reviews on these complexes have been published [144-148]. Thus, we will give only a brief overview of μ-(α,ω)-alkanediyl binuclear complexes which are pertinent to our study.

1.4.3.1.1. μ-(α,ω)-Alkanediyl complexes

μ-(α,ω)-alkanediyl complexes are binuclear metal compounds of the general formula $L_xM\text{-}(CH_2)_n\text{-}M'L_y$, in which two metal centres are bonded to the two terminal carbon atoms of the bridging alkyl chain. These compounds are also referred to as polymethylene bridged compounds. Two types of μ-(α,ω)-alkanediyl compounds are known, *viz* those without a metal-metal bond (I) and those with a metal-metal bond (II) [Figure 1.4] [145,146]

L_nM = metal and associated ligands

Figure 1.4: Two types of μ-(α,ω)-alkanediyl complexes

The section which follows discusses some examples of μ-(α,ω)-alkanediyl complexes, highlighting type I complexes of iron and zirconium respectively, which is pertinent to our study. A summary of some of the known μ-(α,ω)-alkanediyl complexes are listed in Table 1.4.

1.4.3.1a) *Iron containing μ-(α,ω)-alkanediyl complexes*

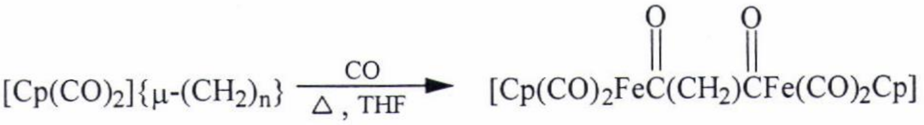
The compounds $[CpFe(CO)_2]_2\{(\mu\text{-}CH_2)_n\}$, where n = 3-6, reported by King in 1963 [88, 149], were the first μ-(α,ω)-alkanediyl complexes prepared. These were synthesised using the method in Equation 1.24.

$$2[NaCp(CO)_2Fe] + X(CH_2)_nX \longrightarrow [Cp(CO)_2Fe]_2\{(\mu\text{-}CH_2)_n\} + 2NaX \qquad X = Br \tag{1.24}$$

Moss and Scott later extended this series to include the compounds where n = 3 – 12 [150]. These complexes have also been prepared by other routes. For example, the photochemical decarbonylation of the diacyl species $[Cp(CO)_2\{CO(CH_2)_4CO\}Fe(CO)_2Cp]$ also leads to the formation of the complex, $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_4\}$ [151]. The addition of $[Cp(CO)_2Fe]^-$ to the monohaloalkyl compounds $[Cp(CO)_2M(CH_2)_nBr]$ (M = Mo or W, n = 3,4) [101] or $[Cp(CO)_2Fe(CH_2)Br]$ (n = 3-5) [107] also lead to the formation of the diiron complexes. In these cases the iron anion displaces both the bromide as well as the Mo or W units.

Attempts to prepare the μ-(1,2)-ethanediyl complex, $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_2\}$, have resulted only in the formation of the iron dimer, $[CpFe(CO)_2]_2$ [151].

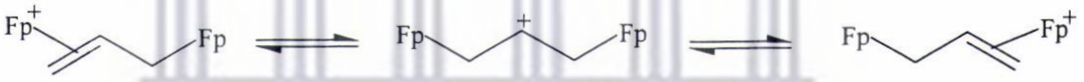
The alkanediyl diiron compounds were reported to undergo various reactions similar to those of the monoalkyl complexes. For example, the thermally induced CO reaction leads to "CO insertion" into the Fe-C bond, forming the diacyl species [151, 152] i.e.



$$[Cp(CO)_2]\{\mu\text{-}(CH_2)_n\} \xrightarrow[\Delta\text{, THF}]{CO} [Cp(CO)_2Fe\overset{O}{\overset{\|}{C}}(CH_2)\overset{O}{\overset{\|}{C}}Fe(CO)_2Cp] \qquad (1.25)$$

The reaction is reversible and photolysis of the diacyl species produces $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3,4).

As observed with mononuclear iron alkyl complexes, these complexes undergo β-hydride abstraction with trityl salt. β-Hydride abstraction from the alkanediyl bridged iron compounds $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ leads to the formation of a cationic olefin species in which one iron atom is π-bonded and the other σ-bonded to the alkenyl chain. The first example of this reaction was reported by King and Bisnette [101]. The β-hydride abstraction reaction of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_3\}$ leads to the formation of a symmetrical cationic complex as shown below :

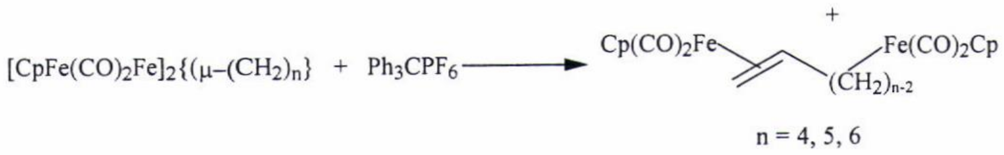


1 **2** **3**

(1.26)

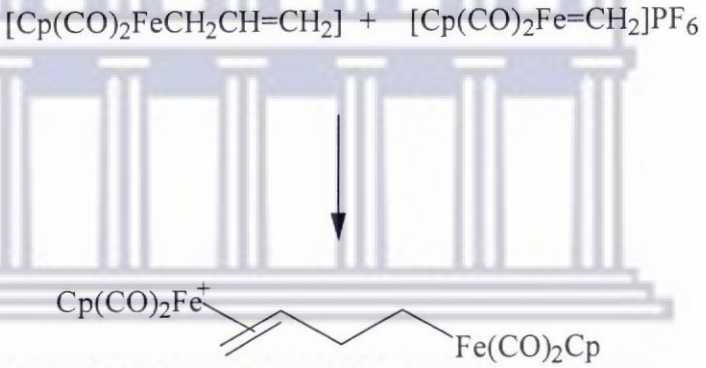
The complex was initially thought to be the carbonium ion (complex **2**) which exists in dynamic equilibrium with complexes **1** and **3**. Later it was reported that that the compound is fluxional rather than dynamic in equilibrium [153].

Moss carried out the β-hydride abstraction the alkanediyl bridged iron compounds $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$, where n = 4-6], yielding the cationic complexes as depicted in equation 1.27:



(1.27)

The complex where n = 4 was also reported by Cutler *et.al* [154]. This complex was prepared by the alkylation of $Cp(CO)_2FeCH_2CH{=}CH_2$ with the $Cp(CO)_2Fe$-methylidene cation, producing the cationic μ-η^1,η^2-butenediyl complex as shown below :



(1.28)

The synthesis of mixed metal μ-(α,ω)-alkanediyl complexes were reported by Moss. These complexes were prepared by the reaction of $Na[Cp(CO)_2Fe]$ with α,ω-dibromalkanes to produce the monoalkyl iron compound [107]. The latter compound is reacted further to produce mixed-metal complexes as shown below:

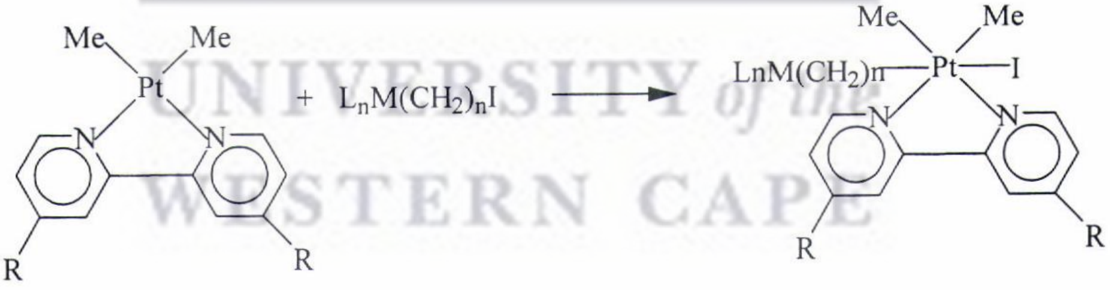
$$\begin{tikzcd}
2[NaCp(CO)_2Fe] + X(CH_2)_nX \arrow[r] & {[Cp(CO)_2Fe(CH_2)_nX] + NaX} \arrow[dl] \\
{[Cp(CO)_2Fe(CH_2)_nML_n]} &
\end{tikzcd}$$

$X = Cl, Br$
$ML_n = Cp(Mo)CO_3$

(1.29)

The mixed metal alkanediyl complex of the type $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ n = 3, 4, was prepared by the addition of $[CpRu(CO)_2]^-$ to $[Cp(CO)_2Fe(CH_2)_nI]$ [155].

Moss prepared a series of mixed metal μ-(α,ω)-alkanediyl complexes by the oxidative addition reaction of the metal iodoalkyl complexes $[L_nM(CH_2)_nI]$ with the square planar Pt(II) complexes [114] as illustrated in Equation 1.30.



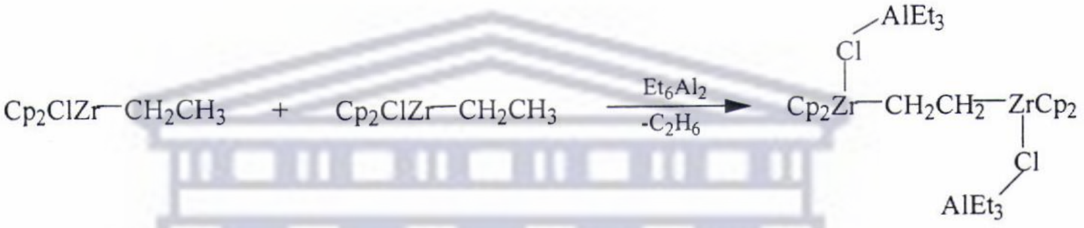
$R = H, CH_3$

(1.30)

where $R = H$, $ML_n = CpW(CO)_3, Cp^*W(CO)_3$, $n = 3\text{-}5$
where $R = CH_3$, $ML_n = CpFe(CO)_2, Cp^*Fe(CO)_2$, $n = 4$
$ML_n = CpRu(CO)_2, Cp^*Ru(CO)_2$, $n = 4$
$ML_n = Re(CO)_5$, $n = 4$

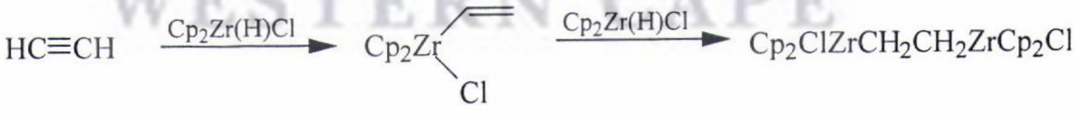
1.4.3.1b) Zirconium containing μ-(α, ω)-alkanediyl complexes

Kaminsky and Sinn isolated the μ-(1,2)ethanediyl di-zirconium compound from the reaction of [Cp_2ZrCl_2] with triethylalane. [$Cp_2ClZrEt$] is the initial product formed, which combines by intermolecular β-hydrogen transfer to form the μ-(1,2)ethanediyl di-zirconium complex as shown in Equation 1.31. Ethane is eliminated during the reaction [156].



(1.31)

The μ-(1,2)ethanediyl di-zirconium complex of the type $[Cp_2ZrCl]_2\{(\mu\text{-}CH_2)_2\}$ was prepared by the hydrozirconation of the vinylzirconium compound using $Cp_2Zr(H)Cl$ as shown in Equation 1.32. The latter compound was obtained from the hydrozirconation of acetylene, which amounts to an overall-double hydrozirconation of an alkyne.



(1.32)

Bullock reported on the synthesis of Ru-Zr complex by the hydrozirconation of the vinylruthenium complex [157, 158].

$$[Cp(Me_3P)_2RuCH{=}CH_2] \xrightarrow{Cp_2Zr(H)Cl} [Cp(Me_3P)_2RuCH_2CH_2ZrCp_2Cl] \qquad (1.33)$$

Examples of other μ-(α,ω)-alkanediyl complexes are listed in Table 1.5.

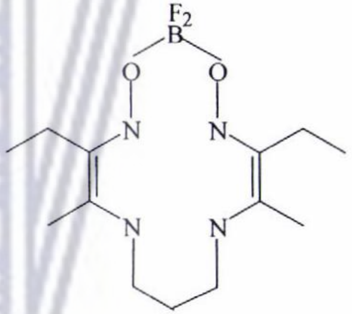
Table 1.5: Examples of μ-(α,ω)-alkanediyl complexes

Compound	Synthesis	Comments	REF
$[Et_3Al\{\mu\text{-}Cl)Ti(\eta^5\text{-}Cp)]_2\{\mu\text{-}(CH_2)_2\}$	$(\eta^5\text{-}Cp)_2TiCl_2$ + $AlEt_3$		35
$[Cp(CO)_3M(CH_2)_2M'(CO_3)Cp]$	$[Cp(CO)_3M(C_2H_4)]^+$ + $[Cp(CO)_3M']^-$	M = M' = Mo M = M' = W M = Mo, M' = W	159,160
$[CpMo(CO)_3]_2\{\mu\text{-}(CH_2)_n\}$	$[CpMo(CO)_3]^-$ + $X(CH_2)X$	X = Br, I n = 4 and 10	32,161
$[CpW(CO)_3]_2\{\mu\text{-}(CH_2)_n\}$	$[CpW(CO)_3]^-$ + $I(CH_2)_nI$	n = 3 – 5	103, 162
$[CpW(CO)_2(PPh_3)_2]_2\{\mu\text{-}(CH_2)_2\}$	$[CpW(CO)_2PPh_3]^-$ + $[CpW(CO)_2(PPh_3)(C_2H_4)]^+$		160
$[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_2\}$	$[Mn(CO)_5]^-$ + $Mn(CO)_5(C_2H_4)^+$		163

Table 1.5 continued .....

Compound	**Synthesis**	**Comments**	**Ref**
$[LnM(CH_2)_2Re(CO)_5]$	$[(CO)_5ReC_2H_4)]^+$ + $[LnM]^-$	$Cp(CO)_3W$ LnM = $Cp(CO)_3Mo$ $Mn(CO)_5$ $Re(CO)_5$	160, 163
$FpCH(Me)CH_2CH_2Fp$	$2[CpFe(CO)_2]-$ + $ICH(Me)CH_2CH_2I$	Fp = $CpFe(CO)_2$	155
$[Cp(CO)_2Ru]_2\{(\mu\text{-}CH_2)\}$	$[CpRu(CO)_2]^-$ + CH_2Cl_2		164
$[Cp(CO)_2Ru]_2\{(\mu\text{-}CH_2)_n\}$	$2[CpRu(CO)_2]^-$ + $X(CH_2)_nX$	X =Cl. n= 2 X = I , n = 3- 10	155,164, 165
$(CO)_4Os(CH_2)_nOs(CO)_4$	$[Os_2(CO)_8]^{-2}$ + $I(CH_2)_nI$	n = 2, 3	166

Table 1.5 continued .....

Compound	**Synthesis**	**Comments**	**Ref**
$[Co(DH)_2py]_2\{(\mu\text{-}CH_2)_n\}$	$2[Co(DH)_2pyCl]$ + $Br(CH_2)_nBr$	reaction carried out in the presence of $NaBH_4$ DH = monoanion of dimethylglyoxime $n = 4 - 8$	127, 167
$CpCo(CO)(CH_2)_n(CO)Cp$	$[Cp_2(CO)_2Co_2]^{-2}$ + $I(CH_2)_nI$	$n = 3$ and 4 the CO ligands bridge the two metal centres	168, 169
$[Rh(L)X]_2\{(\mu\text{-}CH_2)_n\}$	$LRh + X(CH_2)_nX$	L = 	170
$[Rh(L)]_2\{(\mu\text{-}CH_2CH_2)\}]$	$[RhL]_2 + C_2H_4$	L = dibenzotetramethyl aza(14) annulene	171
$[PtIMe_2(L)]_2\{(\mu\text{-}CH_2)_n\}]$	$PtMe_2(L) + I(CH_2)_nI$	L = 1,10 phenanthroline, $n = 2–5$ L = bipyridine, $n = 3-5$	112, 172, 173

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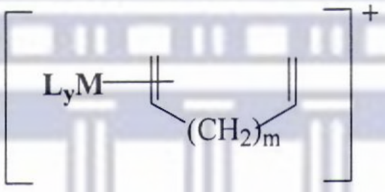
2. SYNTHESIS AND CHARACTERIZATION OF CATIONIC η^2-(α,ω-DIENE) COMPLEXES, OF THE TYPE $[CpFe(CO)_2(\eta^2\text{-DIENE})]PF_6$

2.1 Introduction

Cationic η^2-(α, ω-diene) complexes are compounds which have a diene ligand π bonded to a cationic metal centre *via* only one of the C-C double bonds. The general structure for such cationic diene complexes is shown below:



L_yM = Metal and its associated ligands

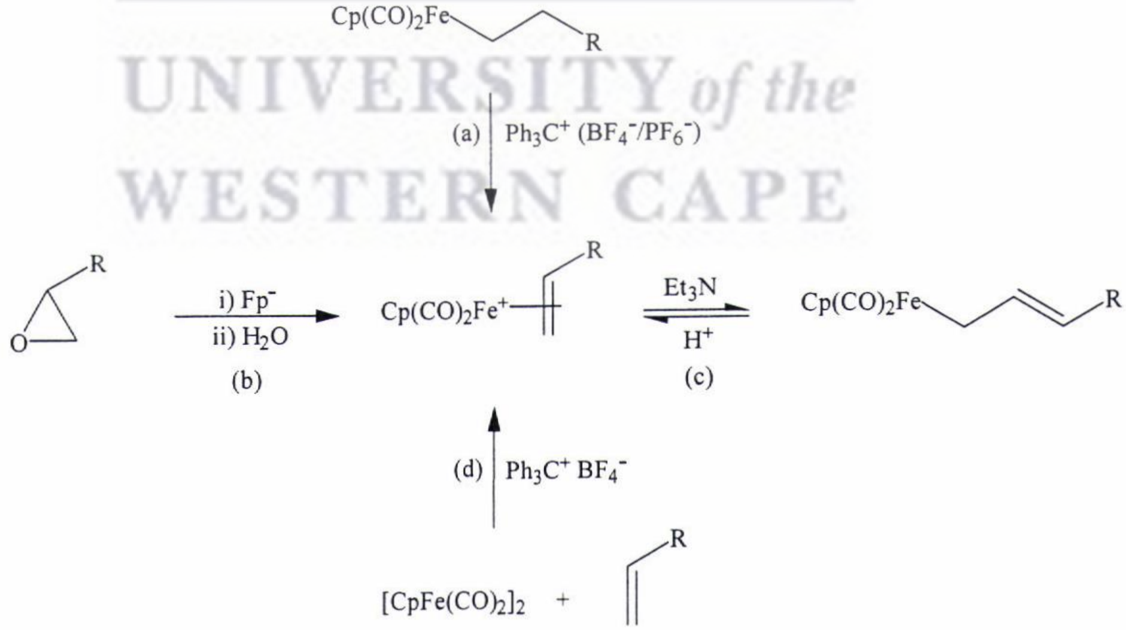
Figure 2.1: General structure of a cationic diene complex

Although cationic η^2-alkene complexes of iron [1-6] have been extensively studied, reports on the diene analogues are sparse. Only a few examples of these types of complexes are known and very little has been reported on the reactivity of these species. The reactivity of the monosubstituted η^2-alkene iron complexes of the type, $[(Cp)Fe(CO)_2(\eta^2\text{-}CH_2\text{=}CHR)]^+$, (R = H, CH_3, Ph), has been extensively studied and reported in the literature [2,5]. Some reactions of the cationic $[(Cp)Fe(CO)_2(\text{butadiene})]^+$ complex with nucleophiles have been briefly reported by Rosenblum and co-workers [7]. However, no reports on the reactivity of other acyclic $[(Cp)Fe(CO)_2(\eta^2\text{-diene})]^+$ complexes have been encountered. These compounds could be implicated in organic synthesis and could also serve as potential model compounds for intermediates in some catalytic reactions. They could for example play a role in the polymerization and dimerization of dienes. It is in light of this that we have embarked on a preliminary study of some of these complexes. Consequently we have prepared a series of compounds with the general formula $[(Cp)Fe(CO)_2(C_mH_{2m-2})](PF_6)$ and we have investigated the reactivity of these with nucleophiles.

Monosubstituted η^2-alkene iron complexes of the type, $[(Cp)Fe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$, (R = H, alkyl) are readily accessible via a number of different routes. Some of these transformations are discussed below.

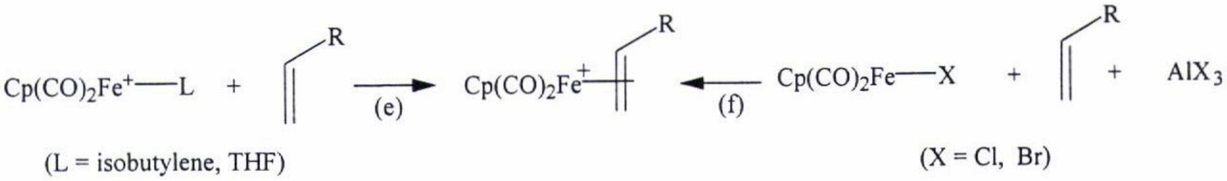
2.2 General methods of preparation of cationic $[CpFe(CO)_2(\eta^2\text{-alkene})]$ complexes

These complexes are available either through the conversion of a co-ordinated allyl or alkyl, or epoxide into an olefin ligand or directly from the iron dimer $[CpFe(CO)_2]_2$, **(Scheme 2.1):**



Scheme 2.1

or through a ligand exchange reaction **(Scheme 2.2),**



Scheme 2.2

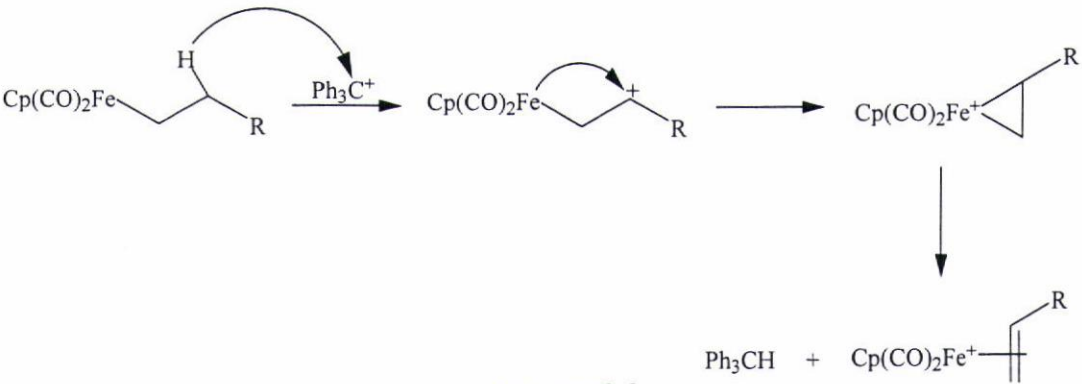
2.2.1 β - Hydride elimination from metal-alkyl complexes

This method is based on the ability of the trityl carbonium ion (Ph_3CBF_4/PF_6) to abstract a hydride ion from the β carbon atom of metal alkyl complexes **(Scheme 2.1, reaction a).**

In the case of main group metals, the main metal-alkyls fragment to form the alkene, metal cation, and triphenylmethane as the by product [8-10].

Transition-metal alkyls on the other hand rearrange to cationic π-complexes as illustrated in Scheme 2.3. Green and Nagy were the first to report on the β - hydride elimination reaction with a series of iron alkyl complexes of the type [$Cp(CO)_2FeR$] (R =Et, n-Pr, iso-Pr) [11]. A number of alkyliron complexes of the type $Cp(CO)_2R$ (R = H, alkyl), have since been reported to react with trityl salt, giving triphenylmethane and a cationic iron olefin complex [4, 6, 12-16].

These reactions can readily be monitored by the replacement of the νCO) of the alkyliron complexes (~ 2000, 1950 cm^{-1}) with the ν(CO) of the cationic iron olefin complexes (~ 2080, 2040 cm^{-1}). The latter complexes are isolated as yellow powders or crystalline compounds.



Scheme 2.3

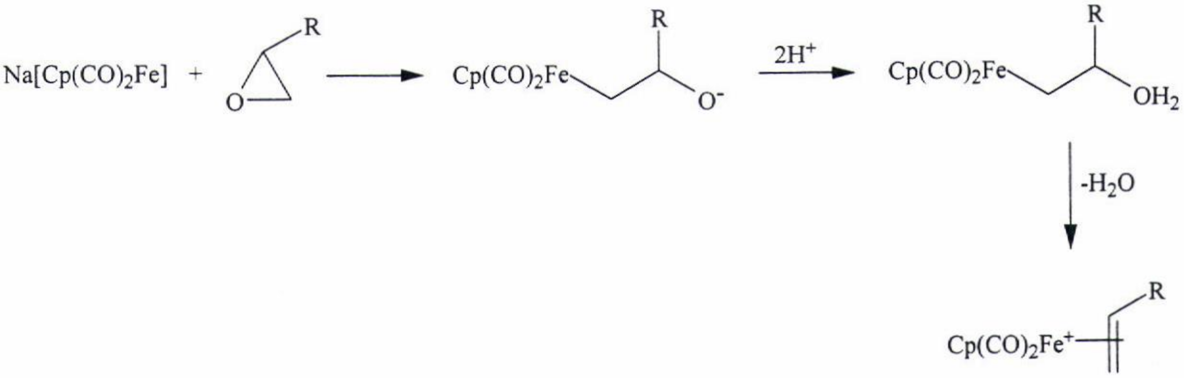
2.2.2 The reaction of $Na^+[CpFe(CO_2)]^-$ with epoxides

This reaction involves the conversion of epoxides to the corresponding alkoxide by the Fp anion at or below room temperature **(Scheme 2.1, reaction b)** [4, 6, and 17]. The resulting alkoxide is protonated *in situ* with 2 equiv of flouroboric acid (HBF_4) or hexaflourophosponic acid (HPF_6) to the corresponding Fp-(η^2-olefin) complexes. The overall stereochemistry of the reaction sequence is best accounted for in two successive processes: epoxide ring opening and elimination of H_2O. This is shown in **Scheme 2.4**.

The reaction occurs stereospecifically with complete retention of configuration. Further more epoxides possessing other functional groups such as aldehydes and ester groups are not affected by the reaction.

The epoxide sequence is well suited to the synthesis of relatively unstable olefin complexes, since the intermediate alkoxides may be converted to the cation at very low temperatures.

It has previously been reported that the abstraction of the β hydride involves the direct interaction between the bulky carbonium ion and the hydrogen undergoing attack [14]. The reaction is highly stereo selective, proceeding *via* removal of the trans-hydride.



Scheme 2.4

2.2.3 Protonation of iron–allyl complexes

Reaction c (Scheme 2.1) is based on the early work of Green [18] and provides a general route to (η^1-allyl)Fp complexes from allyl halides or tosylates. On protonation of the (η^1-allyl)Fp complexes with hydrogen chloride or aqueous acids, the cationic olefin complex is formed. This reaction is reversible and deprotonation may generally be achieved by a tertiary amine base [4, 19]. The deprotonation is highly stereoselective, proceeding by loss of an allylic proton *trans* to the metal olefin bond.

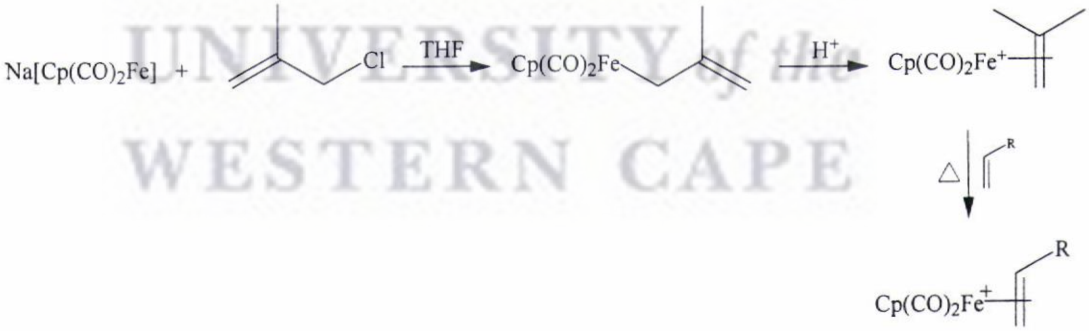
2.2.4 By direct oxidation of the iron dimer [CpFe(CO$_2$)]$_2$ in the presence of an olefin

The reaction of $[CpFe(CO)_2]_2$ with triphenylmethyl tetraflouroborate in the presence of alkenes leads to the formation of cationic iron-olefin complexes of the type $[CpFe(CO)_2(\eta^2\text{-alkene})]^+BF_4^-$ **(reaction d, scheme 2.1)** [20].

A limitation with these reactions is that some substrates reacts with the trityl cation, thus limiting the reaction to certain olefins. For these substrates, preoxidation of the dimer, Fp_2, has to be carried out . The dimer is pre-treated with the trityl cation, which serves as an oxidizing agent. The reaction is carried out in CH_2Cl_2 solution, in the absence of the alkene. The excess of the Ph_3CPF_6 is quenched from the reaction mixture using cycloheptatriene which converts it to triphenylmethane. The tropylium salt formed is removed by trituration with water. The intermediate Fp-L (L = CH_2Cl_2) undergoes displacement to the Fp-olefin after the addition of the alkene.

2.2.5 Displacement of isobutylene from $[CpFe(CO_2(\eta^2\text{-isobutylene})]^+$

The exchange reaction has proven to be a very convenient method for the preparation of cationic Fp(olefin) complexes [21, 22]. $Fp(\eta^2\text{-isobutylene})BF_4$ (A), prepared by the metallation of isobutenyl chloride, followed by protonation, is isolated as air stable yellow-orange crystalline solids, which can be stored indefinitely at 0°C. This complex is however thermodynamically unstable and carrying out thermal decomposition of it in the presence of an acceptor olefin leads to the formation of the cationic Fp-(olefin) **(Scheme 2.5).**



Scheme 2.5

The reaction is confined to compounds which are more stable than the isobutylene complex since thermal conditions are required for the exchange. Monosubstituted cyclic and acyclic olefins are thus well suited for the exchange, since thermodynamic stability decreases with increasing alkyl substitution of the olefin.

Steric factors also play an important role in the exchange reaction. A good example is the exchange reactions of cyclopentene and cyclohexene which gives 100% and 2% yields of the cationic Fp-(olefin) complexes respectively, under identical reaction conditions. It has been reported that a serious steric compression exists in the case of the cyclohexene complex, involving an axial ring proton at C_4 of the cyclohexene ring with the Fp group [20]. These interactions are absent in the cyclopentene complex accounting for the difference in yields of the reactions.

2.2.6 Displacement of THF from $[CpFe(CO)_2(THF)]^+$

$[CpFe(CO)_2(THF)]BF_4$, prepared from the reaction of $CpFe(CO)_2I$ and $AgBF_4$ in THF reacts with olefins in dichloromethane to yield $[CpFe(CO)_2(\eta^2\text{-olefin})]BF_4$ complexes (reaction e, Scheme 2.1, L = THF) [22, 23]. The $AgBF_4$ serves as a Lewis acid to remove the iodide from $CpFe(CO)_2I$, generating the $[CpFe(CO)_2]^+$ intermediate. When the reaction is carried out in THF, the $[CpFe(CO)_2(THF)]BF_4$ complex is isolated as red hygroscopic crystals, which can be recrystallised in over 90% yield using CH_2Cl_2/hexane.

With the exception of cyclohexene, reported yields for these reactions were generally fairly high. The yields can however be improved if the mixture of $[CpFe(CO)_2(THF)]BF_4$ and the olefin is treated with BF_3. The BF_3 complexes with the displaced THF ligand forming a BF_3-THF adduct. For cyclohexene, an increase in the yield from 17% to 92% was reported, when BF_3 was added to the reaction mixture.

2.2.7 Displacement of a halide from CpFe(CO$_2$X (X = Cl, Br, I) in the presence of Lewis acid

The reaction of $CpFe(CO_2)X$ (X = Cl, Br, I) with an olefin in the presence of a Lewis acid leads to the formation of cationic $Fp(\eta^2\text{-olefin})$ complexes [24, 25].

$$\mathrm{CpFe(CO)_2X} + \mathrm{CH_2{=}CHR} + \mathrm{AlX_3} \longrightarrow [\mathrm{CpFe(CO)_2(\eta^2\text{-}CH_2{=}CH_2R)}]^+\mathrm{AlX_4}^-$$

$X = Br,Cl$

(2.1)

Exchange reactions using $CpFe(CO_2)I$ as the starting material were reported by Reger and Coleman [26]. The reaction involves the use of $AgBF_4$ to abstract the iodide ion from $CpFe(CO_2)I$, generating the co-ordinatively unsaturated $[CpFe(CO)_2]^+$ which reacts with the olefin producing the Fp(η^2-olefin) complex.

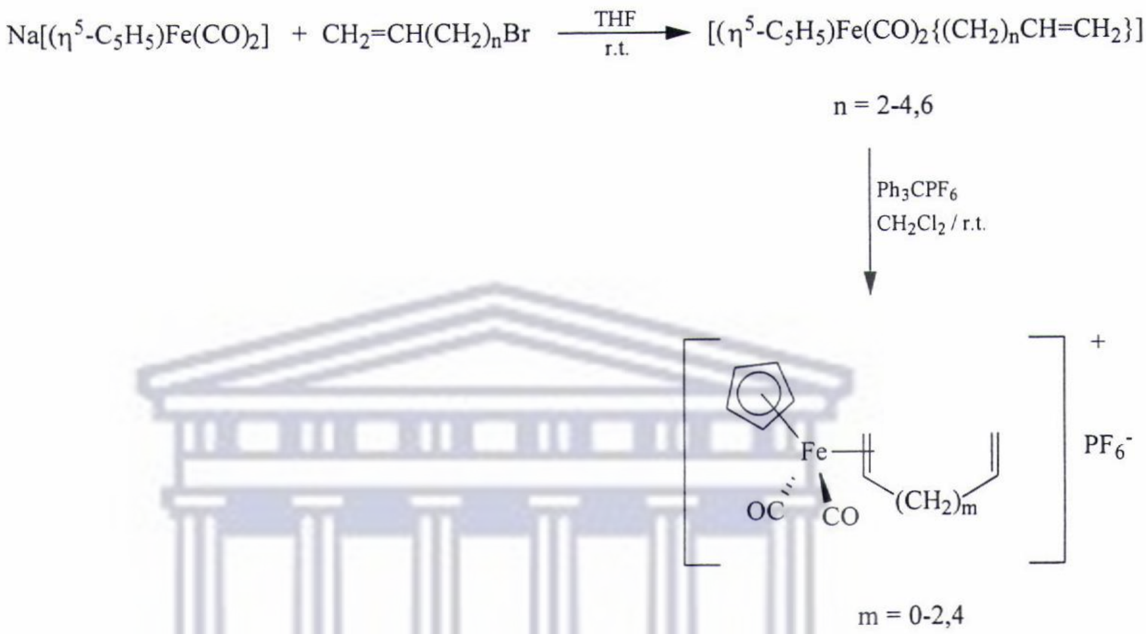
All of the methods discussed above are related to the preparation of cationic η^2-alkene complexes of iron. There are very few examples of the diene analogues cited in literature. The preparation of $[Cp(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)]PF_6$ (compound **1**) using the method of β-hydride abstraction, was however reported by Green and Nagy [18]. Longer chain analogues have not been reported. Consequently we have prepared a series of compounds with the general formula $[(Cp)Fe(CO)_2(C_mH_{2m-2})](PF_6)$ using the method of β-hydride abstraction from η^1-alkenyl complexes.

2.3 Results and Discussion

2.3.1 Synthesis of cationic η^2- (α,ω-diene) complexes, $[CpFe(CO)_2(\eta^2\text{-diene})]PF_6$,

The preparation of the complexes, $[(Cp)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$, was carried out by the reaction of the appropriate $[(Cp)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ [27, 28] with triphenylcarbenium–hexaflourophosphate, (Ph_3CPF_6). The overall reaction scheme for the preparation of the η^2-diene complexes is outlined in **Scheme 2.6.**

All the compounds were isolated as yellow air stable solids, which show thermal decomposition in the range 150-160 °C. They are insoluble in most organic solvents, with the exception of acetone and acetonitrile. They are however partially soluble in dichloromethane.



Compound	m	Diene
1	0	1, 3-butadiene
2	1	1, 4-pentadiene
3	2	1, 5-hexadiene
4	4	1, 7-octadiene

Scheme 2.6

2.3.2 Characterization of cationic η^2-(α,ω-diene) complexes, [CpFe(CO)$_2$(η^2-diene)]PF$_6$

2.3.2 a) IR spectra

The infrared spectral data for compounds **1 - 4** are summarized in **Table 2.1.** All the compounds show two strong ν(CO) bands at 2077 cm^{-1} and 2040 cm^{-1} for the terminal carbonyls. The ν(CO) bands for compounds **1-4** appear at higher frequencies, relative to those of the corresponding η^1-alkenyl compounds, $[(Cp)Fe(CO)_2\{(CH_2)_nCH=CH_2\}]$, (n = 2 - 4, 6). The latter compounds have two strong ν(CO) bands at 2000 cm^{-1} and 1940 cm^{-1} . This significant increase of the ν(CO) values in going from the neutral alkenyl compound to the cationic diene species is due to the decrease in electron density on the metal centre. This results in less back-donation of electrons to the π-antibonding orbitals of the CO, therefore leading to stronger CO bonds and thus higher ν(CO) frequencies in the IR spectrum.

All the spectra also exhibit two bands of medium intensity at 1518 and 1625 cm^{-1}. This can be assigned to ν(C=C) of the coordinated and uncoordinated C-C double bonds of the diene respectively. The band assigned to ν(C=C) at 1518 cm^{-1} is absent in the IR spectra of the parent alkenyl complexes. It can thus be concluded that this must then be due to the double bond of the diene ligand, which is bonded to the metal in a η^2–fashion. The position of this band is indicative of a π-coordinated alkene as opposed to the ν(C=C) band of the uncoordinated pendant alkene functionality, which has been reported to appear about 100 cm^{-1} higher [29]. The IR spectroscopy results thus indicate that only one of the double bonds of the diene moiety is coordinated to the iron centre i.e. we have η^2 coordination and not η^4 coordination.

In the case of compound **1** the corresponding bands are observed at 1517 and 1624 cm^{-1} . The distinctive difference in the ν(C=C) of the uncoordinated C-C double bond for compound **1** can be ascribed to the fact that the two double bonds are conjugated. This is unlike the other complexes in which the double bonds of the diene system are isolated.

2.3.2 b) ^{1}H NMR spectra

The ^{1}H NMR spectra for all the compounds show signals, which are characteristic of species containing a vinylic functionality. The assignments of the vinylic protons for compounds **1-4** are based on the structure in **Figure 2.2** and are listed in **Table 2.2.**

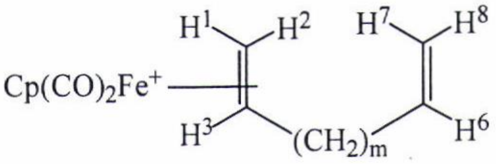


Figure 2.2: Labelling of protons to assist ^{1}H NMR assignments for the complexes **1-4**

The spectra of all the compounds show two doublets in the region δ 3.6-3.9 ppm and δ 4.0-4.2 ppm. These signals were assigned to the coordinated vinylic protons, H^1 and H^2 respectively. These protons have *trans* $(J_{3,2})$ and *cis* $(J_{3,1})$ coupling constants of ~ 14 Hz and 8 Hz respectively. The chemical shift difference between protons H^1 and H^2 are ~ 0.4 ppm in all the compounds except compound **1**. The butadiene compound shows a lower chemical shift difference of 0.2 ppm for the coordinated vinylic protons. Similar results for other π-coordinated α-olefins were reported previously. Rosenblum *et al* ascribed the large chemical shift differences to the anisotropic effects associated with the cyclopentadienyl ring currents. However effects of the CO ligands may also be significant [30]. The signals in the region δ 4.9-6.0 ppm, with the exception of the sharp broad peak around δ 5.9 ppm, were assigned to the protons H^5 and H^6 of the uncoordinated vinylic protons. The sharp broad peak around δ 5.9 ppm observed in all the spectra were assigned to the cyclopentadienyl protons. The corresponding peak for the cyclopentadienyl protons of the [(Cp)Fe(CO)$_2${η^1-alkenyl}] compounds appears around δ 4.7 ppm. This downfield chemical shift is again due to the influence of the cationic metal centre, which draws electrons from the neighbouring Cp ring, hence leading to the deshielding of the Cp protons.

Table 2.1: Yields, micro-analytical and infrared spectral data for compounds, $[(Cp)Fe(CO)_2\{\eta^2\text{-}CH{=}CH(CH_2)_mCH{=}CH_2\}]PF_6$, m = 0 - 2, 4

			Analysis %				IR Data [a]			
			Found		Calculated		$\nu(CO)cm^{-1}$		$\nu(C{=}C)cm^{-1}$	
Compound	**m**	**Yield%**	**C**	**H**	**(C)**	**(H)**				
1	0	49	35.12	2.93	35.14	2.95	2080(s)	2049(s)	1624(m)	1517(m)
2	1	46	36.94	3.34	36.95	3.36	2080(s)	2048(s)	1639(m)	1518(m)
3	2	40	38.63	3.72	38.64	3.74	2075(s)	2043(s)	1639(m)	1519(m)
4	4	50	41.69	4.46	41.69	4.43	2077(s)	2045(s)	1640(m)	1521(m)

[a] Measured as DRIFTS in a KBr matrix, s =strong, m = medium.

Table 2.2: ^{1}H NMR spectral data for the compounds **1-4**

Compound	**Chemical Shift** (**δ-ppm**)^a	**Assignment**
1	(3.85, d, 1H, $J_{3,2,TRANS}$ = 14 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(4.04, d, 1H, $J_{3,1,CIS}$ = 7.2 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(5.54, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}C\underline{H}{=}CH_2}$
	(5.90, m, 8H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}C\underline{H})\text{-}CH{=}C\underline{H}_2}$, $\mathrm{C_5\underline{H}_5}$
2	(2.50, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}C\underline{H}_2CH{=}CH_2}$
	(3.18, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}C\underline{H}_2CH{=}CH_2}$
	(3.68, d, 1H, $J_{3,2,TRANS}$ = 14.6 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(4.15, d, 1H, $J_{3,1,CIS}$ = 8.4 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(5.19, m, 3H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}C\underline{H})\text{-}CH_2CH{=}C\underline{H}_2}$
	(5.85, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}CH_2C\underline{H}{=}CH_2}$
	(5.91, s, 5H)	$\mathrm{C_5\underline{H}_5}$
3	(1.65 - 2.62, 4 x m, 4H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(C\underline{H}_2)_2CH{=}CH_2}$
	(3.64, d, 1H, $J_{3,2,TRANS}$ = 14.4 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(4.07, d, 1H, $J_{3,1,CIS}$ = 8.4 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(5.04, m, 2H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(CH_2)_2CH{=}C\underline{H}_2}$
	(5.24, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}C\underline{H})\text{-}(CH_2)_2CH{=}CH_2}$
	(5.81, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(CH_2)_2C\underline{H}{=}CH_2}$
	(5.91, s, 5H)	$\mathrm{C_5\underline{H}_5}$
4	(1.50 - 2.70, 3 x m, 8H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(C\underline{H}_2)_4CH{=}CH_2}$
	(3.64, d, 1H, $J_{3,2,TRANS}$ = 14.6 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(4.06, d, 1H, $J_{3,1,CIS}$ = 8.2 Hz)	$\mathrm{Fe(\eta^2\text{-}C\underline{H}_2{=}CH)}$
	(4.95, m, 2H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(CH_2)_4CH{=}C\underline{H}_2}$
	(5.31, m, 1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}C\underline{H})\text{-}(CH_2)_4CH{=}CH_2}$
	(5.81, m,1H)	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\text{-}(CH_2)_4C\underline{H}{=}CH_2}$
	(5.90, s, 5H)	$\mathrm{C_5\underline{H}_5}$

^{a}acetone d$_6$ as solvent

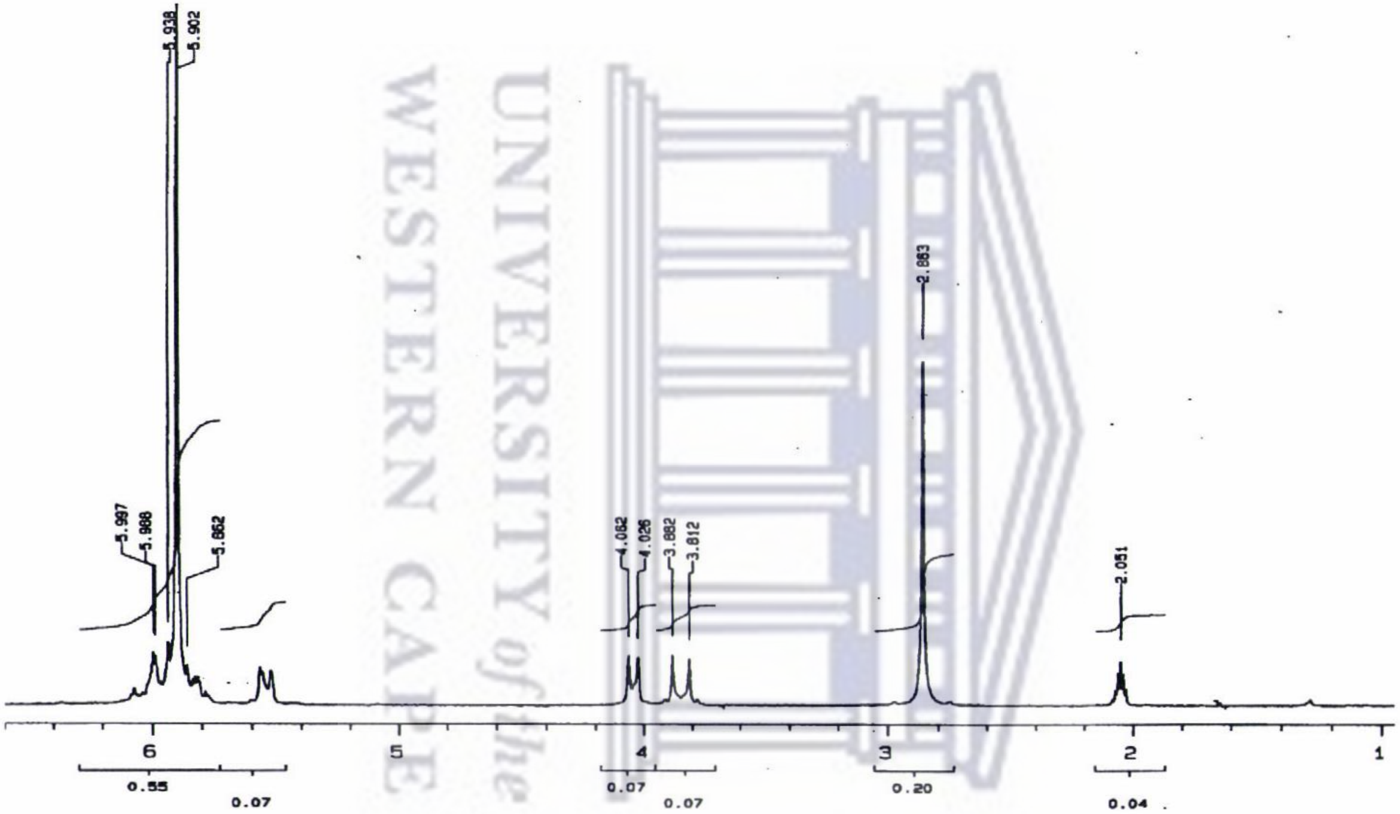


Figure 2.3 ^{1}H NMR spectrum of compound **1**

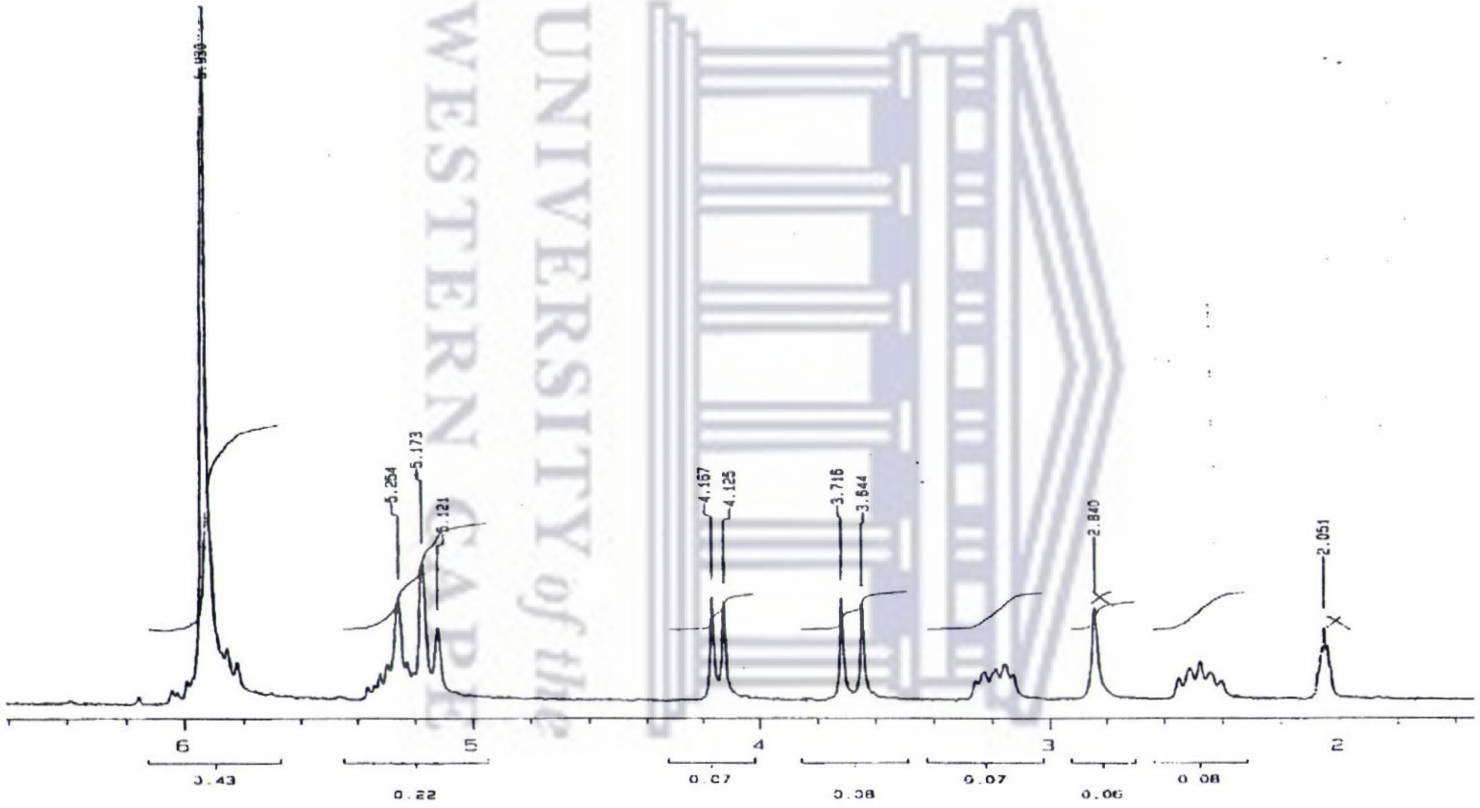


Figure 2.4 ^{1}H NMR spectrum of compound **2**

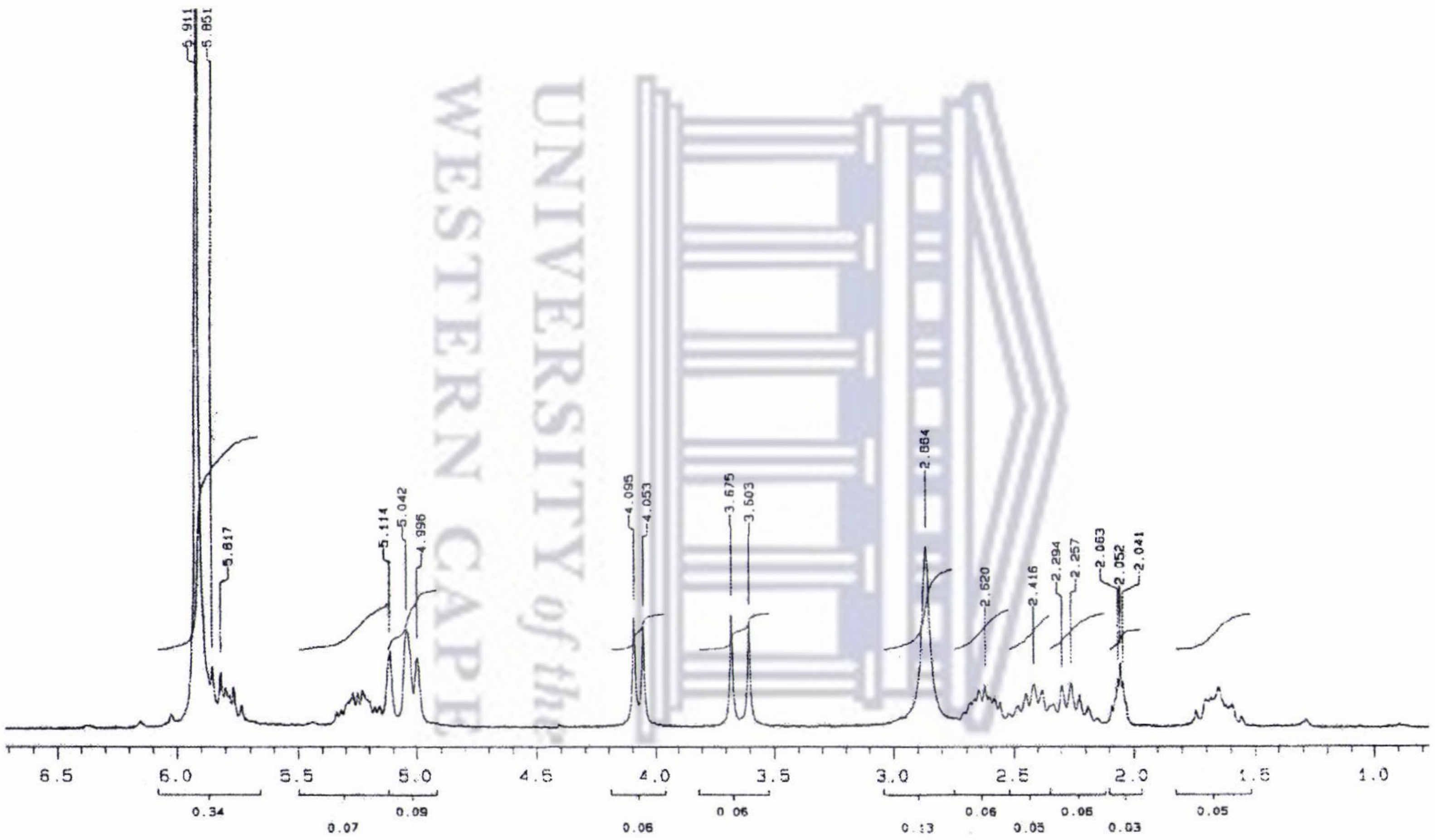


Figure 2.5 ^{1}H NMR spectrum of compound **3**

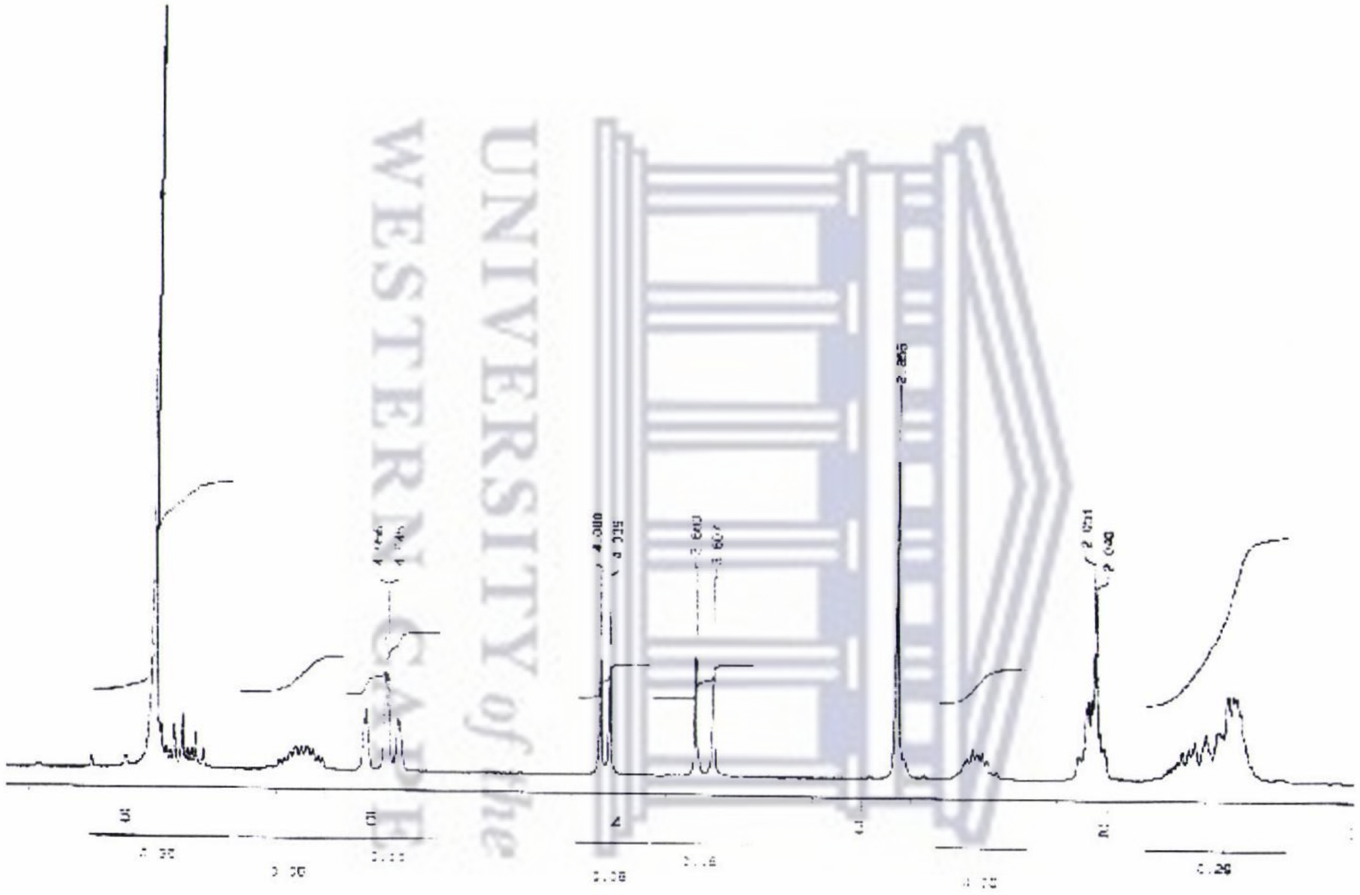


Figure 2.6 ^{1}H NMR spectrum of compound **4**

2.3.2 c) ^{13}C NMR spectra

The ^{13}C NMR spectra for the series of $[(Cp)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$ complexes **(1- 4)** were all recorded in acetone-d_6 and are briefly discussed here. The assignment of the carbonyls and vinylic carbons are based on the structure in **Figure 2.7.**

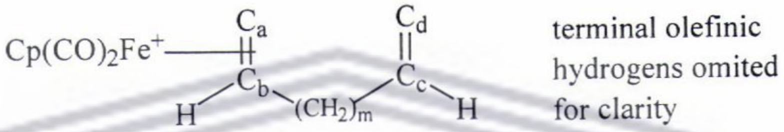


Figure 2.7: Labelling of carbon atoms to assist ^{13}C NMR assignments for the complexes **1-4**

Two carbonyl resonances are observed at δ 209 ppm and 201 ppm. It has previously been reported that monosubstituted olefin complexes exhibit two CO resonances due to steric interactions between the carbonyl group and the olefin ligand resulting from a conformation in which the olefin is near the $CpFe(CO)_2$ moiety. This causes the CO to have different chemical environments [30].

The π- coordinated vinylic carbons C_a and C_b were assigned to the peaks in the region δ 52-56 ppm and δ 85-89 ppm respectively. The uncoordinated vinylic carbons were assigned to the peaks in the region of δ 114-125 ppm and δ 137-139 ppm. The intense peak at δ ~ 90 ppm observed in all the spectra is due to the cyclopentadienyl resonance.

Table 2.3: ^{13}C NMR spectral data for the compounds **1-4**

Compound	**Chemical Shift (δ-ppm)**[a]	**Assignment**
1	52.71 88.05 90.22 124.66 137.71 208.89 211.22	$Fe(\eta^2-\underline{C}H_2=CH)$ $Fe(\eta^2-CH_2=\underline{C}H)$ $\underline{C}_5H_5$ $Fe(\eta^2-CH_2=CH)CH=\underline{C}H_2$ $Fe(\eta^2-CH_2=CH)\underline{C}H=CH_2$ $\underline{C}O$ $\underline{C}O$
2	40.15 54.72 85.82 90.26 118.06 137.07 209.33 211.22	$Fe(\eta^2-CH_2=CH)\underline{C}H_2CH=CH_2$ $Fe(\eta^2-\underline{C}H_2=CH)$ $Fe(\eta^2-CH_2=\underline{C}H)$ $\underline{C}_5H_5$ $Fe(\eta^2-CH_2=CH)CH_2CH=\underline{C}H_2$ $Fe(\eta^2-CH_2=CH)CH_2\underline{C}H=CH_2$ $\underline{C}O$ $\underline{C}O$
3	36.39 ; 36.93 55.26 87.61 90.09 116.40 137.39 209.21 211.42	$Fe(\eta^2-CH_2=CH)(\underline{C}H_2)_2CH=CH_2$ $Fe(\eta^2-\underline{C}H_2=CH)$ $Fe(\eta^2-CH_2=\underline{C}H)$ $\underline{C}_5H_5$ $Fe(\eta^2-CH_2=CH)(CH_2)_2CH=\underline{C}H_2$ $Fe(\eta^2-CH_2=CH)(CH_2)_2\underline{C}H=CH_2$ $\underline{C}O$ $\underline{C}O$
4	30.75, 32.09, 33.27, 36.28, 54.88 88.88 90.07 114.95 139.18 209.27 211.50	$Fe(\eta^2-CH_2=CH)(\underline{C}H_2)_4CH=CH_2$ $Fe(\eta^2-CH_2=CH)(\underline{C}H_2)_4CH=CH_2$ $Fe(\eta^2-\underline{C}H_2=CH)$ $Fe(\eta^2-CH_2=\underline{C}H)$ $\underline{C}_5H_5$ $Fe(\eta^2-CH_2=CH)(CH_2)_4CH=\underline{C}H_2$ $Fe(\eta^2-CH_2=CH)(CH_2)_4\underline{C}H=CH_2$ $\underline{C}O$ $\underline{C}O$

[a] acetone d_6 as solvent

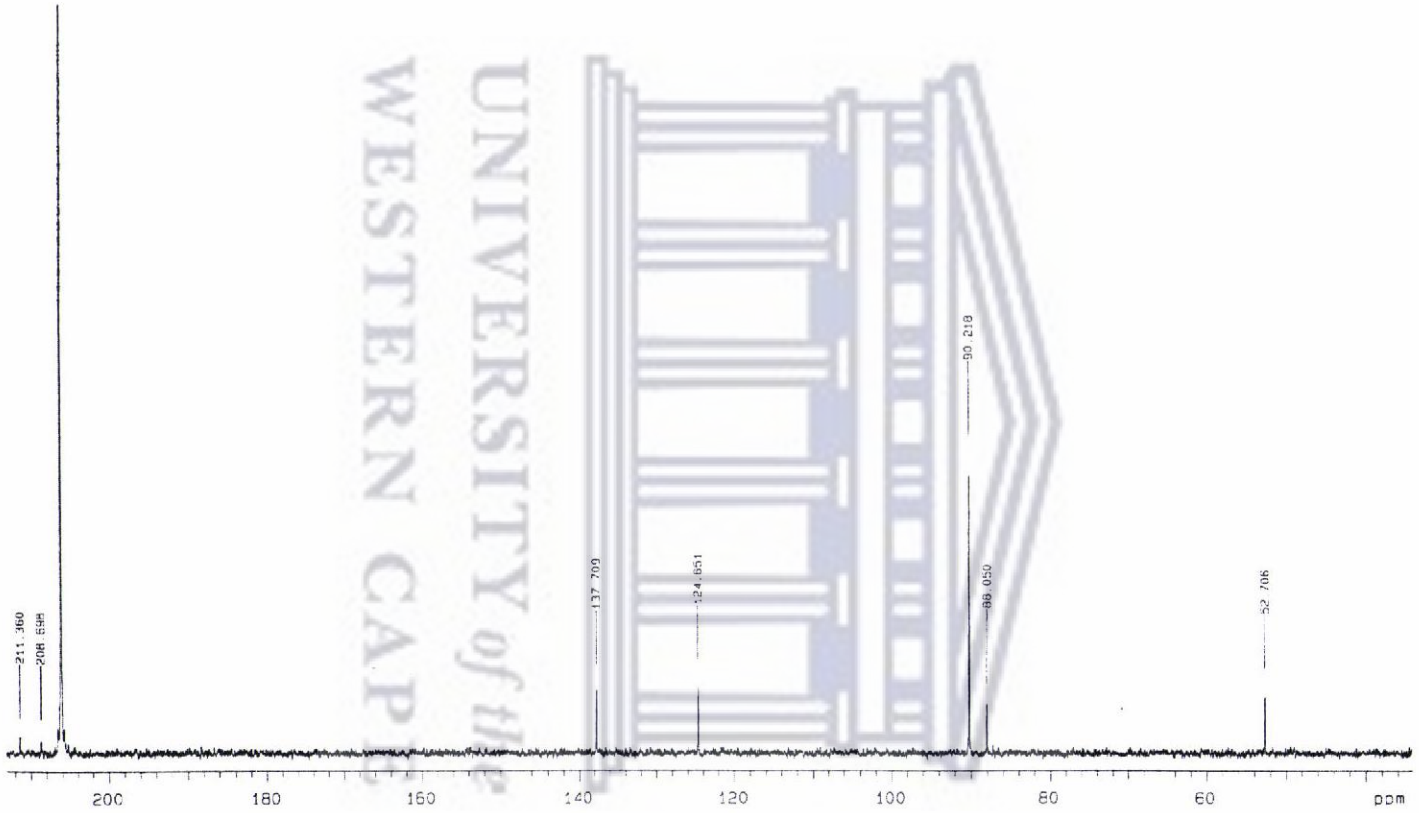


Figure 2.8 ^{13}C NMR spectrum of compound **1**

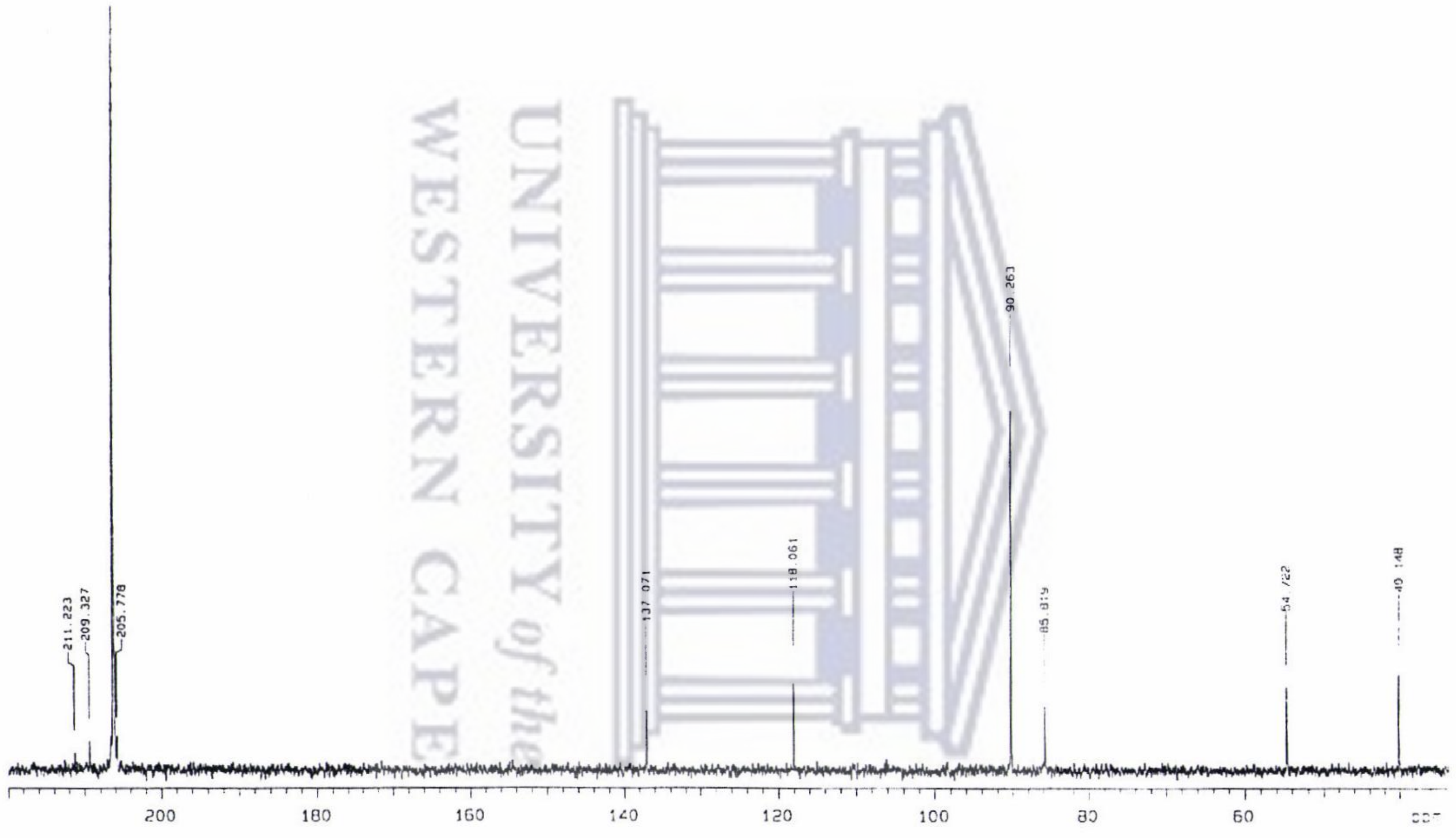


Figure 2.9 ^{13}C NMR spectrum of compound **2**

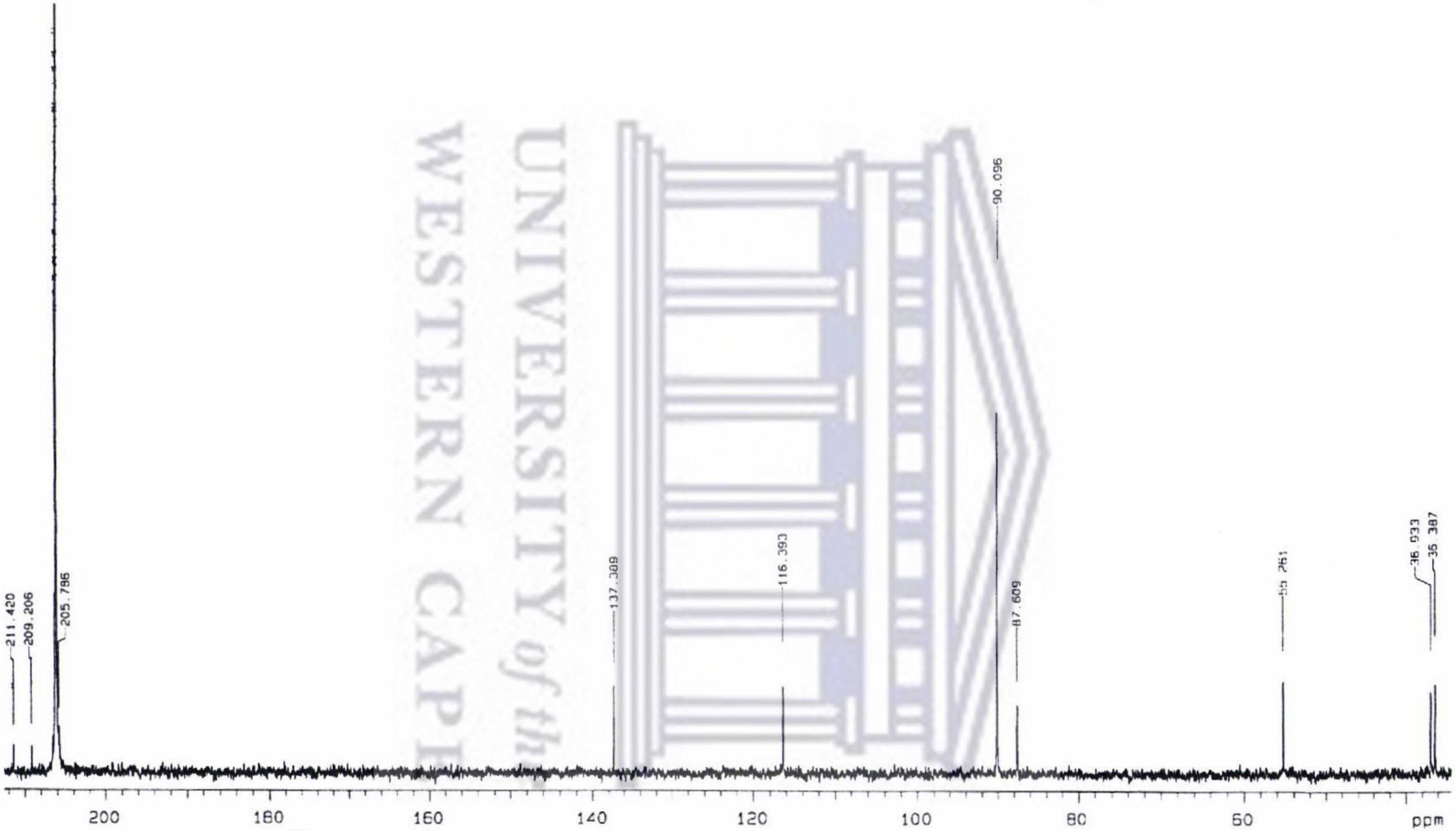


Figure 2.10 ^{13}C NMR of compound **3**

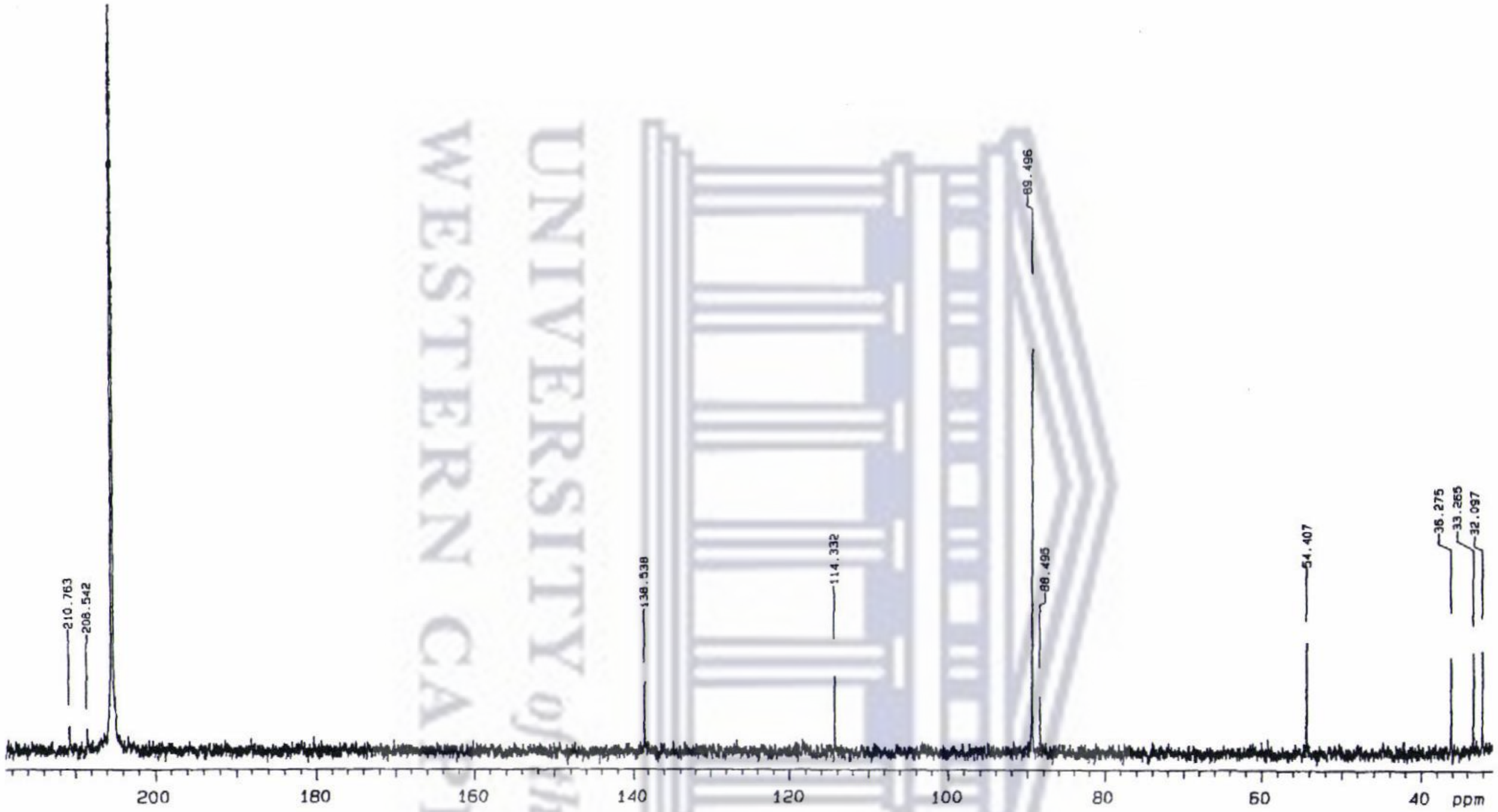


Figure 2.11 ^{13}C NMR of compound **4**

2.3.2 d) Mass Spectrometry

The complexes were analysed using Matrix-Assisted Laser Desorption Ionization Time of Flight mass spectrometry (MALDI-TOF, MS). The investigation was carried out on the neat complexes without using a matrix and operating in the reflector mode. It was found that there was no need to add a cationization agent, as the complexes themselves are cationic. Relatively low laser power was employed since operating at high laser power resulted in extensive fragmentation of the sample in the ion-source. All the compounds investigated with the exception of the Fp-butadiene species show parent ions corresponding to the cationic complexes (i.e. species without the PF_6^- counter ion). In the case of the butadiene complex only fragment ions of the molecular species are observed in the mass spectrum. The spectra of all four compounds show an extremely strong peak (base peak in all cases) at m/e 186. This can be assigned to the ion $[Cp_2Fe]^+$, ferrocenium ion. In addition many of the lower mass peaks (< m/e 150) can be assigned to fragments, which are derived directly from $[Cp_2Fe]^+$. This is not unusual as the ferrocenium ion has previously been observed in the mass spectra of some hydrocarbyl complexes containing the $CpFe(CO)_2$ unit. The ferrocene is presumably a decomposition product of the iron hydrocarbyl species. Decomposition of the parent compound to ferrocene most likely occurs within the ion source of the MALDI-TOF instrument.

Table 2.4: m/e values corresponding to parent ions for compounds **1-4**

Compound	M^+ (m/e values)
1	-
2	245
3	259
4	287

2.3.2 e) Thermal analysis

The thermal properties of compounds **1-4** were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC Analysis of compounds 1-4

The DSC traces for compounds **1-4** were recorded in the range 30-200 °C, using a heating rate of 10 °C/ min. The DSC data are summarized in Table 2.5. The DSC trace for the butadiene complex, **1**, exhibits strong endothermic peaks, which occur at 150.41 °C, 156.6 °C and 165 °C, which correlates to the range in which these compounds were found to decompose on the hotstage melting point apparatus (150 – 160 °C). There is also a weak endothermic peak at 127.41°C. Compounds **2-4**, unlike compound **1**, show only two endothermic peaks occurring in the region 125-135 °C. This is around the same temperature at which ligand dissociation occurs as evidenced by the loss of CO in the TGA plots (see discussion below). An analogous endothermic peak is also observed in the DSC of the butadiene species, albeit much weaker. The second endothermic peak observed in the DSC of compounds **2-4**, occurs in the temperature range of 120-200 °C. This second peak is thought to correspond to the temperature at which major compound decomposition commences. As mentioned previously compound **1**, has three peaks in this region at 150.41, 156.6 and 165 °C. It is not clear why the butadiene species shows different thermal behaviour to the other Fp-diene species. It could be related to the fact that in the case of compound **1**, the coordinated diene is conjugated; while in the case of the other compounds the diene functionalities are isolated. It would also appear that this structural difference somehow affects the thermal behaviour of compound **1**. It is apparent that its mode of decomposition is different to that of the other compounds.

Table 2.5: DSC data for compounds **1-4**

Compound	**Endothermic peaks (°C)**			
1	150.41	156.6	165	127.41 (w)
2	135.25	190		
3	126.08	200[a]		
4	128.50	175.75		

[a] approximate values – peaks not very distinguished
w = weak

TGA Analysis of Compound 1-4

Compounds **1-4** were also subjected to thermogravimetric analysis (TGA). For all the compounds with the exception of compound **1**, decomposition appears to be a two-step process. The initial phase apparently involves the loss of the carbonyl ligands. This assessment is based on the % mass loss observed during the first phase. The weight loss roughly corresponds to that of the CO ligands. The second phase of the decomposition of compounds **2-4,** commences around 160 °C and represents the total decomposition of the compound. The % mass loss during this phase corresponds with the loss of the organic ligands from the complex. For compound **1**, only a single decomposition step is observed, commencing at 150 °C. The % weight loss in this case corresponds to the loss of the carbonyl ligands simultaneously with the organic ligands. The various decomposition points for the complexes are listed in **Table 2.6.** These decomposition points were estimated from the peak maxima of the TGA curves.

Table 2.6: TGA decomposition points for compounds **1-4**

Compounds	**Decomposition points (°C)**^{a}	
1	150	
2	150	158
3	94	153
4	97	152

^{a}Peaks refers to the onset of decomposition

2.3.2 f) Thermal decomposition studies of compounds 1-4 in the solid state

We also investigated the thermal decomposition of the compounds **1-4** in the solid state by heating the complexes above their decomposition points until the compounds had visibly decomposed. The volatile decomposition products were trapped at low temperature (-196°C) and analysed by GC-MS. The apparatus employed to conduct the thermal decomposition studies is shown in **Figure 2.2.**

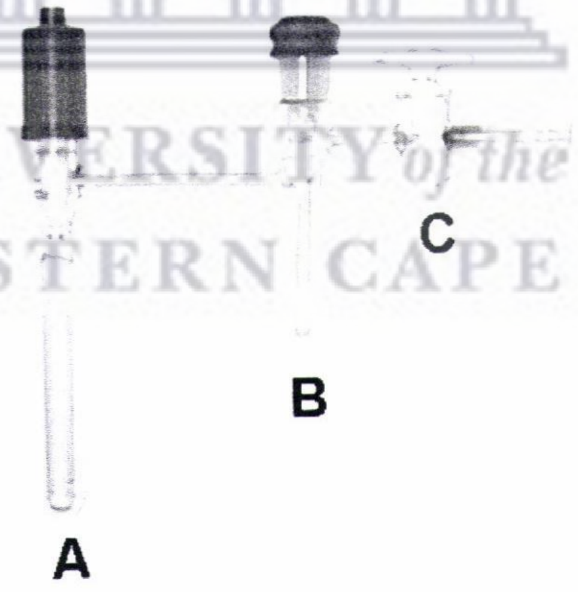


Figure 2.2: Apparatus employed for thermal decomposition studies

About 50 mg of the $[Cp(CO)_2Fe\text{-}(diene)]^+$ complex was placed in tube **A**. The whole apparatus was then evacuated for 20 min. The apparatus was then disconnected form the vacuum by closing tap **C**. The tap connecting the sample tube (**A**) and the cold tube (**B**) were left open. Tube **A** was immersed in an oil bath set at 150 °C while the cold finger (tube **B**) was placed in a liquid nitrogen bath. The sample was heated until visible decomposition was complete. The volatile products trapped in the liquid nitrogen-cooled tube were analysed by removing a sample using a gas tight syringe and injecting it into the GC-MS. In all cases the only volatile organic materials we could detect were the [1, (n-1)] dienes. These dienes are formed as a direct result of dissociation from the metal centre. No other organic decomposition products were detected. The observed products are similar to those, which were observed for these compounds when solutions of the samples were heated. Thus for example heating the Fp-butadiene in deuterated acetone to about 50°C results in free butadiene being detected in the NMR spectrum. The dissociation is fairly facile for the Fp-butadiene species but occurs less readily in solution for the higher homologues, although traces of the free diene can be observed even at such relatively low temperatures as 50°C. The solid-state decomposition seems to proceed via the initial dissociation of the coordinated diene. There are no signs of any diene rearrangement occuring during the thermal decomposition process.

2.4 Conclusion

The reactions of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ complexes, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\{(CH_2)_nCH{=}CH_2\}]$ (n = 2-4, 6), with trityl salt lead (Ph_3CPF_6) lead to the formation of the cationic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$ complexes. These compounds were isolated as yellow air stable solids, which show thermal decomposition in the range 150-160 °C. They were found to be insoluble in most organic solvents, with the exception of acetone and acetonitrile. They are however partially soluble in dichloromethane. Microanalyses, FTIR, ^{1}H NMR, ^{13}C NMR and MALDI-TOF mass spectroscopy were employed to characterize these compounds. Thermal analysis and thermal decomposition studies were also carried out on these compounds. This revealed that initial decomposition occurs via simple ligand dissociation processes.

2.5 Experimental

General Procedures

All experiments, unless otherwise stated, were carried out under nitrogen using typical Schlenk line techniques. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, the n-bromo-1-alkenes, and triphenylcarbenium hexaflourophosphate were used as purchased without further purification. Dichloromethane was dried by refluxing over P_2O_5 and distilling under nitrogen. All solvents were maintained over molecular sieves, and degassed prior to use. All column chromatography was performed using deactivated alumina 90 (70 - 230 mesh) purchased from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using either NaCl solution cells or as DRIFTS spectra in a KBr matrix. NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^{1}H NMR and 50.30 MHz for ^{13}C NMR, using tetramethylsilane as an internal standard. Elemental analyses and thermal decomposition studies were performed at the micro-analytical laboratory of the University of Western Cape. Thermal analysis was performed at the University of the Western Cape. Matrix-Assisted Laser Desorption Ionization Time of Flight mass spectrometry (MALDI-TOF, MS) was carried out at Howard University.

The $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ compounds were prepared from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ using literature methods [10]. The η^1-alkenyl products were isolated as yellow oils and were used immediately after purification by column chromatography to prepare the η^2-(α,ω-diene) complexes.

2.5.1 General method for the preparation of the diene complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_mH_{2m-2})]PF_6$; where m = 4-6, 8 (1 – 4)

The preparation of the η^2-butadiene complex **1** is described below to illustrate the general procedure employed.

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CH_2CH{=}CH_2\}]$ (0.21g, 1.03 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a solution of Ph_3CPF_6 (0.45g, 1.59 mmol) dissolved in CH_2Cl_2 (10 ml). The initial orange/yellow solution turned black with a yellow tint. The mixture was allowed to stand for 18h at room temperature. During this time a yellow crystalline material precipitated out of solution. Acetone (10 ml) was added to the mixture upon which the solid dissolved. The slow addition of diethyl ether (40 ml) afforded a yellow solid, which was collected on a Hirsch funnel and allowed to dry in air. The product was recrystallized by dissolving in a minimum amount of acetone, followed by the addition of diethyl ether. The resulting yellow solid was obtained in 49% yield.

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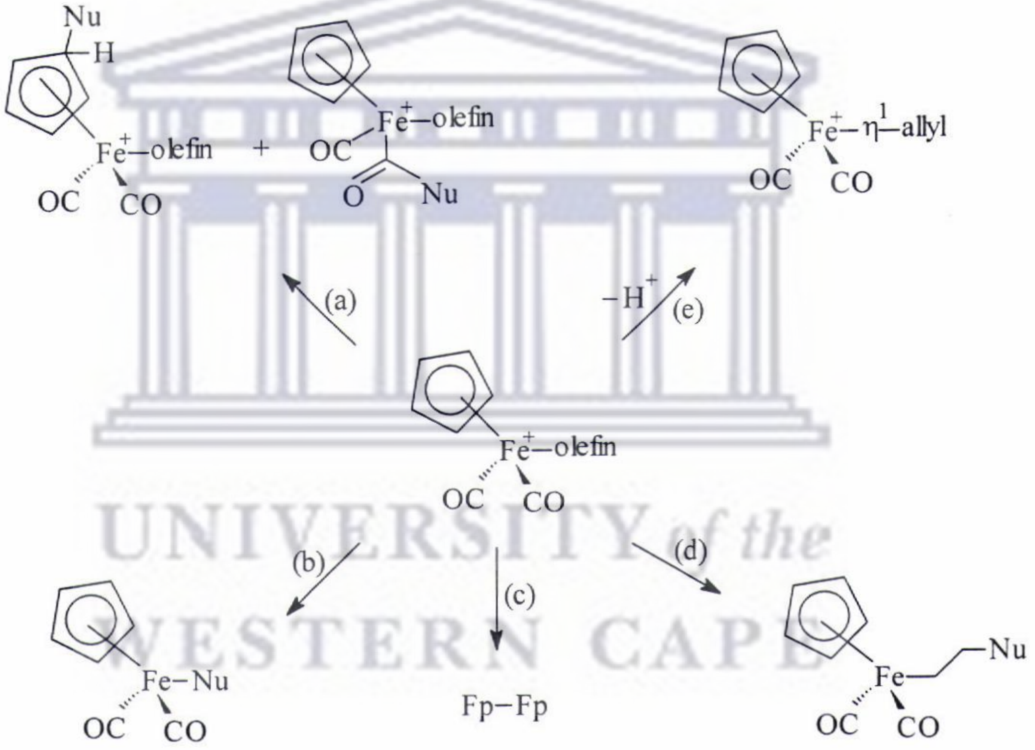
3. REACTIVITY STUDIES OF CATIONIC η^2-(α,ω-DIENE) COMPLEXES, OF THE TYPE [CpFe(CO)$_2$(η^2-DIENE)]PF$_6$

3.1 Introduction

The reactions of cationic dicarbonyl η^5-cyclopentadienyl(olefin) complexes have previously been reported to proceed via a number of generalized pathways [1]. These are summarized in **Scheme 3.1**.



Scheme 3.1

Of these, nucleophillic addition to either the cyclopentadienyl ring or to a carbonyl ligand (path a), which has been observed for [Fp-(allene)]$^+$ [2] or [FpL]$^+$ cations [3-6]. (L = CO, CS, PPh$_3$), is not observed for simple olefin complexes. The displacement of the ligating olefin (path b) and the formation of the dimer (path c) can compete effectively with the desired addition reaction (path d). Another pathway, allylic deprotonation (path e) leads to the formation of η^1-allyl complexes [7 – 9].

The reactivity of the monosubstituted η^2-alkene iron complexes of the type, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$, (R = H, CH_3, Ph), has been studied extensively and reported in the literature [8, 10 11]. Some reactions of the cationic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{butadiene})]^+$ complex with nucleophiles have been briefly reported by Rosenblum and co-workers [12]. However, no reports on the reactivity of other acyclic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-diene})]^+$ complexes have been encountered.

We have thus examined the reactions of nucleophiles with the cationic complexes of the type $[Fp\text{-}\eta^2\text{-}(\alpha,\ \omega\text{-dienes})]^+$, **1**- **4**. These reactions were found to proceed via four general routes:

1. ligand substitution (displacement) of the diene (path b, Scheme 3.1)
2. formation of the dimer (path c, Scheme 3.1)
3. addition to the coordinated diene (path d, Scheme 3.1)
4. deprotonation of the diene using tertiary amines i.e. Et_3N (path e, Scheme 3.1)

The analytical and spectral data of the products of these reactions are summarized in Tables **3.1** – **3.6** and are discussed below.

3.2 Results and discussion

3.2.1 Reactions with halides

Reactions of 1 and 2 with NaCl and NaI

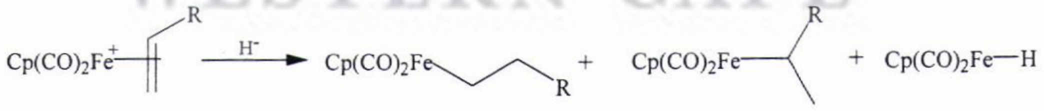
The reactions of **1** and **2** with NaCl in an acetone solution lead to the exclusive formation of $CpFe(CO)_2Cl$ (**5**). The product was isolated as a red, air stable crystalline solid. The reaction was easily monitored by IR spectroscopy by following the replacement of the carbonyl bands for the $Fp\text{-}\eta^2\text{-}(\alpha,\ \omega\text{-diene})$ complexes, **1** and **2** at 2045 and 2080cm^{-1}, with two strong carbonyl stretching frequencies at 2040 and

2000 cm^{-1} for the product. Using this method, it was found that the reaction was complete after 3 days. The ^1H NMR of the product exhibits a single strong peak at δ 5.25 ppm which is assigned to the cyclopentadienyl protons. This correlates well with data obtained from an authentic sample of $CpFe(CO)_2Cl$. Analogous results were obtained when using sodium iodide in place of the chloride, with $CpFe(CO)_2I$ being formed in good yields.

3.2.2 Reactions with hydrides

Reaction of 1 and 2 with $NaBH_4$ and $LiAlH_4$

The reactions of various hydrides with olefin complexes $[CpFe(CO)_2(CH_2{=}CHR)]^+$ (R = H, CH_3, $(CH_2)_3CH_3$) has been extensively studied by Baird and co-workers [13, 14]. It was reported that at room temperature these reactions generally yielded the expected iron-alkyl products. The reactions were shown to proceed via *exo* attack of the hydride on the co-ordinated olefin, without any recognizable pattern of regioselectivity. Under certain conditions attack of the hydride initially occurred at the carbonyl carbon atom, apparently yielding $[CpFe(CO)(CH_2{=}CHR)(CHO)]^+$, which subsequently rearranges to $[CpFe(CO)_2H]$ and the olefin. Depending on the reaction conditions, a number of products can be obtained from this reaction :



(3.1)

In our case, similar reaction patterns were observed for the reactions of **1** and **2** with $NaBH_4$ and $LiAlH_4$. These reactions were carried out at room temperature resulting in a complex mixture of η^1-alkenyl species, evident by the appearance of a number of Cp resonances (σ 4.7 - 5.1ppm) in the ^1H NMR spectra of the reaction products. The region of these Cp resonances suggests that the reactions proceed via the addition of the nucleophile to the coordinated diene. Literature reports for products of addition reactions shows NMR spectra in which the Cp signals appear in the range between δ 4.9 - 5.1 ppm [8]. Due to the complex nature of the ^{1}H NMR spectra, it was not possible to unequivocally identify any of the products. We were also not able to effectively separate the various products due to similarities in their chemical and physical natures.

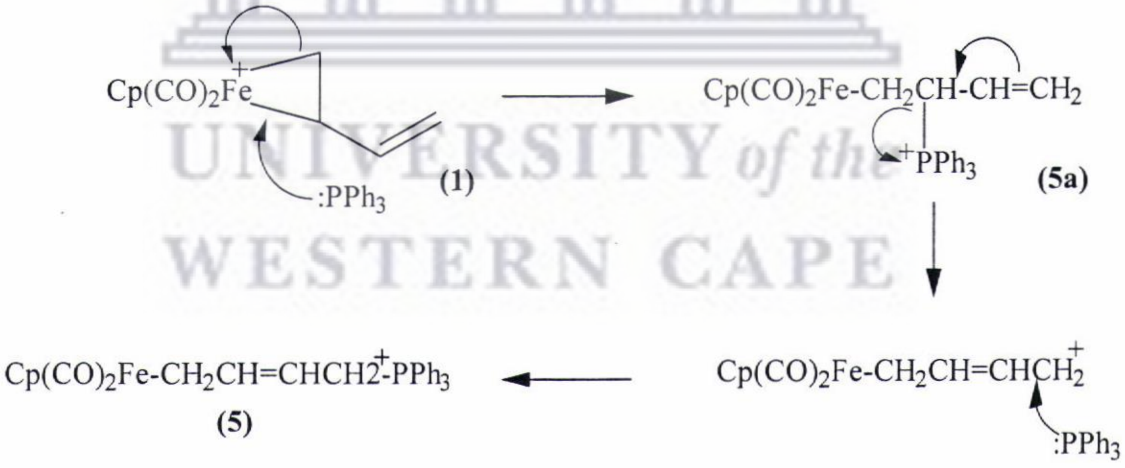
3.2.3 Reactions with phosphines

Reaction of **1 –4** *with triphenylphosphine*

The reactivity of iron complexes of the type $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$ (R = H, CH_3, Ph) with heteroatomic nucleophiles has previously been investigated by Rosenblum and co-workers [8]. For example, the reaction of the ethylene complex (R = H) with triphenylphoshine was found to proceed via the addition of PPh_3, giving a yellow air-stable crystalline phosphosphonium adduct, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2CH_2PPh_3)]^+$. In contrast, the addition product obtained from the reaction with the propylene complex (R = CH_3) was found to be unstable, decomposing to give the cation $[CpFe(CO)_2PPh_3)]^+$ and the free olefin. With the styrene complex (R = Ph), no phosphonium adduct was isolated. However, the formation and rapid decomposition of the addition product was observed in a NMR experiment. For the reaction of $[CpFe(CO)_2(\eta^2\text{-acenaphthylene})]^+$ with PPh_3, a NMR reaction revealed the formation of the addition product, followed by conversion to $[CpFe(CO)_2(PPh_3)]^+$ and free acenaphthylene [15].

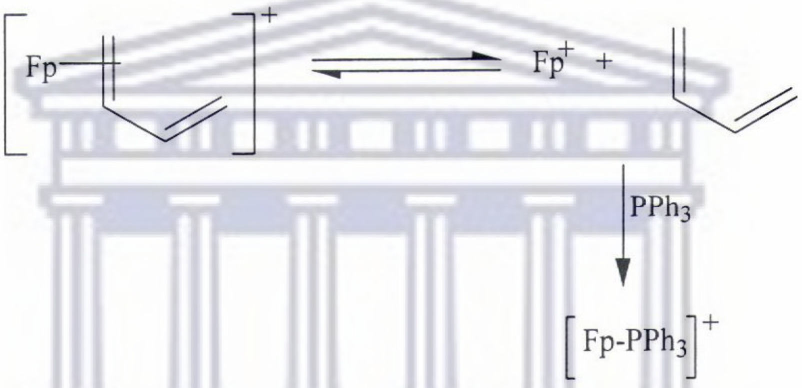
For the reactions of compounds **1 – 4** with PPh_3 in an inert atmosphere under a constant flow of nitrogen, the displacement product, $[CpFe(CO)_2(PPh_3)][PF_6]$, was isolated in each case. These reactions took place rapidly at room temperature and the product was isolated as a pale yellow, air stable crystalline solid after a reaction time of around 2 h.

Repeating these reactions using a sealed system, gave a different result for compound **1**, while the reactions of compounds **2** – **4** gave the same results as obtained previously. In the case of compound **1**, the reaction proceeds via an addition mechanism resulting in the formation of the cationic species, $Fp\text{-}CH_2CH{=}CHCH_2\text{-}{}^{+}PPh_3$, (compound **5**), which was isolated as an unstable yellow/brown oil. The ^1H NMR spectrum of this yellow brown oil shows two distinct signals in the vinylic region, at 5.0 ppm and 6.2 ppm respectively. The signals resonate for one proton each. Of the possible products of addition of triphenylphosphine to compound **1**, compound **5** is the only one which has an internal C=C functionality with each carbon having a single proton. The above reaction was also followed in a sealed NMR tube and this yielded similar results. Monitoring the reaction via ^1H NMR revealed that the addition product was most likely formed via a rearrangement process as shown in Scheme 3.2. Unfortunately compound **5** was found to be highly unstable with the result that we were unable to isolate it in a pure state. We were thus not able to fully characterise it.



Scheme 3.2

We are also not entirely sure why a different reaction product is obtained when the reaction is carried out in a sealed system as opposed to doing the reaction under a constant flow of nitrogen. It is however speculated that the butadiene complex undergoes some dissociation in solution to produce the free diene ligand (some NMR evidence for this). Butadiene being volatile is then removed in the nitrogen stream aiding further dissociation of the starting diene complex. This leads to a lowering of the possibility of the addition product being formed. In the sealed system the equilibrium in Scheme 3.3 is more to the left which means that the cationic diene complex is the more prevalent species present in solution. This would thus ensure that the addition reaction takes place.



Scheme 3.3

Reactions of 1 and 2 with PMe_3

The reactions of **1** and **2** with PMe_3 take place rapidly at room temperature resulting in a complex mixture of η^1-alkenyl species, evident by the appearance of a number of Cp resonances (σ 4.7-5.1ppm) in the ^1H NMR spectra of the reaction products. The appearance of vinylic protons suggests that the reactions proceed via the addition of the nucleophile to the coordinated diene. Our observations are in agreement with reports in the literature, where it was found that the Cp signals for the products of addition reactions appear in the range between δ 4.9 - 5.1 ppm [8]. Due to the complex nature of the ^1H NMR spectra, it was not possible to identify unequivocally any of the products. Once again it was also not possible to separate the various components of the mixture.

Table 3.1 Yields, melting points and IR data for products obtained from reactions of η^2 – diene compounds with halides and triphenylphosphine

Starting Complex	**Reagent**	**Product**	**Yield (%)**	**Melting point (°C)**	**$^a\nu(CO)cm^{-1}$**	
1, 2	Cl^-	$Cp(CO)_2Fe\text{-}Cl$	86 - 89	110 - 112	2040(s)	2000(s)
1, 2	I^-	$Cp(CO)_2Fe\text{-}I$	56 - 60	117 - 121	2037(s)	1991(s)
1 – 4	$:PPh_3$	$[CpFe(CO)_2PPh_3)]^+PF_6^-$	90 - 95	115 - 117	2057(s)	2013(s)
1	$:PPh_3{}^b$	$[CpFe(CO)_2\text{-}CH_2CH{=}CHCH_2PPh_3{}^+]\ PF_6^-$	71	OIL	2007(s)	1950(s)

[a] CH_2Cl_2 as solvent in NaCl solution cells (s = strong)

[b] reaction in sealed tube

Table 3.2: ^{1}H NMR spectral data compounds **5 - 8.**

Compound	**Chemical shift** **(δ-ppm)**	**Assignment**
$Cp(CO)_2Fe$-Cl	5.25	(s, 5H, $C_5\underline{H}_5$)
$Cp(CO)_2Fe$-I	5.28	(s, 5H, $C_5\underline{H}_5$)
$[CpFe(CO)_2PPh_3)]^+PF_6^-$	5.65 7.0 – 7.8	(s, 5H, $C_5\underline{H}_5$) (m, 15) $P\underline{Ph}_3$
$[CpFe(CO)_2$-$CH_2CH=CHCH_2PPh_3^+]\ PF_6^-$	0 – 2.0 (m, 2H) 4.7 5.0 6.2 7.0 – 7.8	$FpC\underline{H}_2CH=CHCH_2PPh_3^+$ $C_5\underline{H}_5$ (m, 1H) $FpCH_2CH=C\underline{H}CH_2PPh_3^+$ (m, 1H)$FpCH_2C\underline{H}=CHCH_2PPh_3^+$ (m, 15) $P\underline{Ph}_3$

3.2.4 Reactions with triethylamine

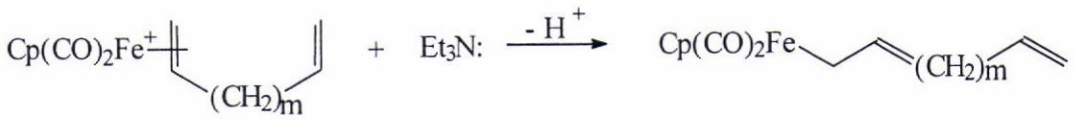
The reactivity of amines with iron complexes of the type $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$ (R = H, CH_3, Ph) was studied by Rosenblum and co-workers [8]. With the exception of the styrene complex (R = Ph) the addition of amines such as methylamine, dimethylamine, trimethylamine and benzylamine to these cations were reported to take place with high regioselectivity, attack occuring at the most highly substituted carbon centre.

Tertiary amines are commonly used to deprotonate Fp-(olefin) cations with allylic protons [7]. The ease with which deprotonation is achieved attests to the powerful acidifying effect complexation has on the allylic protons in these complexes. The deprotonation reaction is highly stereospecific and requires a C-H bond trans to the metal-olefin bond. Thus, for example, the cationic Fp-(cycloheptene) complex is inert to deprotonation, since it lacks allylic protons trans to the Fp-olefin bond. This is in sharp contrast to the other cycloalkene complexes, all of which possess allylic protons with the trans stereochemistry, hence undergoing deprotonation with ease.

Another factor, which plays an important role in these reactions are steric factors. This is best illustrated by the reaction of $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHCPh_3)]^+$ with triethylamine, which was reported to resist deprotonation decomposing to the dimer, (Fp_2).

The treatment of the diene compounds **(2-4)** with triethylamine results in the deprotonation of the diene ligand producing Fp-(η^1-dienyl) complexes as shown in Equation 1. The reactions proceed fairly rapidly at room temperature in dichloromethane and are complete within 45 minutes. Its progress was easily monitored by following the replacement of the carbonyl bands of the Fp-η^2-(α, ω-dienes) **(2-4)** at ~2045 and 2080 cm^{-1}

with those of the neutral Fp-η^1-(α, ω-1-dienyl) products at ~1950 and 2005 cm^{-1}. The products were isolated as relatively unstable yellow/brown oils.



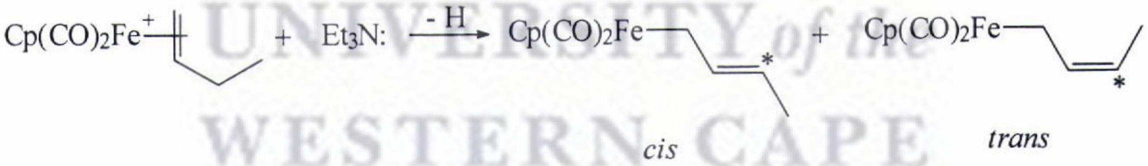
6, m=1

7, m=2

8, m=4

(3.2)

The reactions of the Fp-η^2-(α, ω-dienes) **(2-4)** with triethylamine are in agreement with those reported for the related alkene complexes. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-alkene})]^+$ complexes were reported to undergo deprotonation in the presence of a tertiary amine base, yielding *cis* and *trans* (η^1-allyl) complexes. The deprotonation reaction is highly regiospecific and proceeds by preferential removal of an allylic proton *trans* to the metal-olefin bond to give mixtures of *cis* and *trans* isomers [7, 9, 11, 16]. This is best illustrated by the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-butene})]$ with triethylamine as shown below:



(3.3)

The cyclopentadienyl signals for the *cis* and *trans* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-butenyl})]$ isomers in the above reaction were reported to appear at δ 4.65 and δ 4.58 ppm respectively. Also, two protons in the region δ 4.8 – 5.9 ppm were observed for the *cis* and *trans* methylene protons at C* [9]. A similar pattern was found in the ^{1}H NMR spectra of compounds **6 – 8**. The two distinct singlets in the region at δ 4.65 ppm – 4.75 ppm, assigned to the cyclopentadienyl protons for the η^1-(α, ω-dienyl)iron complexes **6 - 8** are suspected to be due to the *cis* and *trans* isomers. The two resonances at δ 5.0 ppm and δ 5.3 ppm could possibly be assigned to the *cis* and *trans* methylene protons. A single multiplet at ~δ 2.12 ppm was observed for the $FpCH_2$ protons in the Fp-η^1-(α, ω-dienyl) complexes. A multiplet at ~δ 5.7 ppm, obscured by the proton for C_d, was assigned to the proton at C_b. The terminal vinylic protons at C_d and C_e remain unefftected, as expected.

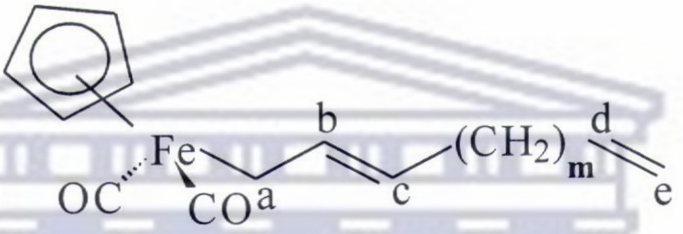


Figure 3.1: Labelling of proton atoms to assist ^1H NMR assignments for the η^1-(α, ω-diene)iron complexes **6 - 8**

Table 3.3: Yields, melting points and IR data for products obtained from reactions of η^2 – diene compounds with triethylamine

Starting Complex	**Product**	**Yield (%)**	**$^a\nu(CO)cm^{-1}$**	
2	Fp-$CH_2CH=CHCH=CH_2$ 6	40	2005(s)	1950(s)
3	Fp-$CH_2CH=CHCH_2CH=CH_2$ 7	47	2005(s)	1950(s)
4	Fp- $CH_2CH=CH(CH_2)_3CH=CH_2$ 8	43	2005(s)	1950(s)

[a] Neat film between NaCl plates (s = strong)

Table 3.4: ^{1}H NMR spectral data compounds **6 - 8.**

Compound	**Chemical^a Shift (δ-ppm)**	**Assignment**
6	2.12	(m, 2H) Fp-C$\underline{H_2}$CH=CHCH=CH$_2$
	4.97	(m, 1H) Fp-CH$_2$CH=C$\underline{H}$CH=CH$_2$
	4.97	(m, 2H) Fp-CH$_2$CH=CHCH=C$\underline{H_2}$
	5.30	(m, 1H) Fp-CH$_2$CH=C$\underline{H}$CH=CH$_2$
	5.70	(m, 1H) Fp-CH$_2$C$\underline{H}$=CHCH=CH$_2$
	5.70	(m, 1H) Fp-CH$_2$CH=CHC$\underline{H}$=CH$_2$
	4.67	(s, 5H, C$_5\underline{H}_5$)
	4.73	(s, 5H, C$_5\underline{H}_5$)
7	2.12	(m, 2H) Fp-C$\underline{H_2}$CH=CHCH$_2$CH=CH$_2$
	2.67	(t, 1H) Fp-CH$_2$CH=CHC$\underline{H_2}$CH=CH$_2$
	2.80	(t, 1H) Fp-CH$_2$CH=CHC$\underline{H_2}$CH=CH$_2$
	4.97	(m, 1H) Fp-CH$_2$CH=C$\underline{H}$CH$_2$CH=CH$_2$
	4.97	(m, 2H) Fp-CH$_2$CH=CHCH$_2$CH=C$\underline{H_2}$
	5.30	(m, 1H) Fp-CH$_2$CH=C$\underline{H}$CH$_2$CH=CH$_2$
	5.70	(m, 1H) Fp-CH$_2$C$\underline{H}$=CHCH$_2$CH=CH$_2$
	5.70	(m, 1H) Fp-CH$_2$CH=CHCH$_2$C$\underline{H}$=CH$_2$
	4.67	(s, 5H, C$_5\underline{H}_5$)
	4.73	(s, 5H, C$_5\underline{H}_5$)

Table 3.4 continued

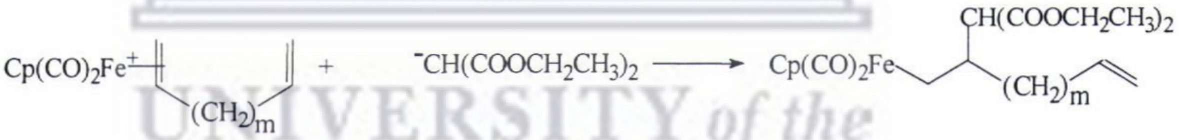
Compound	**Chemical[a] Shift (δ-ppm)**	**Assignment**
8	1. –2.4	(2 x m, 6H) $Fp\text{-}CH_2CH=CH(C\underline{H_2})_3CH=CH_2$
	2.12	(m, 2H) $Fp\text{-}C\underline{H_2}CH=CH(CH_2)_3CH=CH_2$
	4.97	(m, 1H) $Fp\text{-}CH_2CH=C\underline{H}(CH_2)_3CH=CH_2$
	4.97	(m, 2H) $Fp\text{-}CH_2CH=CH(CH_2)_3CH=C\underline{H_2}$
	5.30	(m, 1H) $Fp\text{-}CH_2CH=C\underline{H}(CH_2)_3CH=CH_2$
	5.70	(m, 1H) $Fp\text{-}CH_2C\underline{H}=CH(CH_2)_3CH=CH_2$
	5.70	(m, 1H) $Fp\text{-}CH_2CH=CH(CH_2)_3C\underline{H}=CH_2$
	4.67	(s, 5H) $C_5\underline{H}_5$
	4.73	(s, 5H) $C_5\underline{H}_5$

[a] $CDCl_3$ as solvent

3.2.5 Reactions with lithium diethylmalonate

Enolate anions, generated in a THF solution with bis(trimethylsilyl)amide $Li[N(SiMe_3)_2]$, were reported to react readily with a suspension of Fp-olefin salts at temperatures below 0°C. The products were isolated as yellow, air stable oils or yellow solids [12].

Nucleophillic addition to the butadiene complex **1** was previously reported to take place either by direct or conjugate addition to the coordinated double bond. With lithium dimethylmalonate, a single product was formed in 86% yield derived from direct addition at C_2 [12]. In our hands similar results were obtained for the reactions of the cationic diene complexes **1 – 4** with diethylmalonate. The products were isolated in high yields as amber oils and identified as products **9 – 12**. The compounds are obtained from direct addition at C_b as shown in Equation 3.4. They exhibit two strong ν(CO) bands for the terminal carbonyls at 2004 and 1944 cm $^{-1}$.



m = 0, 1, 2, 4

(3.4)

The assignments of the signals in the NMR spectra of compounds **9-12** are based on the structure in Figure 3.2.

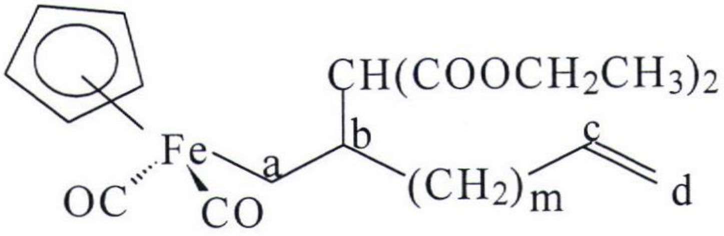


Figure 3.2: Labelling of proton atoms to assist ^{1}H NMR assignments for complexes **9-12**

The ^{1}H NMR spectra of all the products exhibit signals for the three vinylic protons of C_c and C_d in the region between δ 5.0 - 6.0 ppm. These are typical of what is observed for the η^1-alkenyl compounds and also correspond to the position of the uncoordinated vinylic protons for the cationic Fp-η^2-(α, ω-diene) compounds **1 - 4**. The two single proton multiplets at δ 1.0 and δ 1.7 ppm are due to the to Fp-CH_2 protons at C_a. The intense peak at δ 4.7 ppm, observed in all the spectra was assigned to the cyclopentadienyl protons.

Table 3.5: Yields and IR data for products obtained from reactions of η^2 – diene compounds with diethylmalonate *i.e.* compounds **9 - 12**

Starting Complex	**Product**	**Yield (%)**	**$^a\nu(CO)cm^{-1}$**	
1	$Fp\text{-}CH_2CH\{(CH(COOEt)_2)\}CH{=}CH_2$ **9**	81	2004(s)	1944(s)
2	$Fp\text{-}CH_2CH\{(CH(COOEt)_2)\}CH_2CH{=}CH_2$ **10**	87	2004(s)	1944(s)
3	$Fp\text{-}CH_2CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$ **11**	81	2004(s)	1944(s)
4	$Fp\text{-}CH_2CH\{(CH(COOEt)_2)\}(CH_2)_4CH{=}CH_2$ **12**	85	2004(s)	1944(s)

[a] Neat film between NaCl plates (s = strong)

Table 3.6: ^1H NMR spectral data for compounds **9 - 12.**

Compound	Chemical Shift (δ-ppm)	Assignment
9	0.98	(t, 1H) $FpC\underline{H}_2CH\{(CH(COOEt)_2)\}CH=CH_2$
	1.25	(m, 6) $CH(COOCH_2C\underline{H}_3)_2$
	1.74	(dd, 1H) $FpC\underline{H}_2CH\{(CH(COOEt)_2)\}CH=CH_2$
	2.71	(m, 1H) $FpCH_2C\underline{H}\{(CH(COOEt)_2)\}CH=CH_2$
	3.32	(d, 1H) $C\underline{H}(COOCH_2CH_3)_2$
	4.15	(m, 4) $CH(COOC\underline{H}_2CH_3)_2$
	4.79	(s, 5H) $C_5\underline{H}_5$
	5.05	(m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH=C\underline{H}_2$
	5.60	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{H}=CH_2$
10	1.1	(t, 1H) $FpC\underline{H}_2CH\{(CH(COOEt)_2)\}CH_2CH=CH_2$
	1.26	(m, 6) $CH(COOCH_2C\underline{H}_3)_2$
	1.65	(dd, 1H) $FpC\underline{H}_2CH\{(CH(COOEt)_2)\}CH_2CH=CH_2$
	2.20	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{H}_2CH=CH_2$
	2.30	(m, 1H) $FpCH_2C\underline{H}\{(CH(COOEt)_2)\}CH_2CH=CH_2$
	3.0	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{H}_2CH=CH_2$
	3.50	(d, 1H) $C\underline{H}(COOCH_2CH_3)_2$
	4.19	(m, 4) $CH(COOC\underline{H}_2CH_3)_2$
	4.83	(s, 5H) $C_5\underline{H}_5$
	5.05	(m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2CH=C\underline{H}_2$
	5.80	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2C\underline{H}=CH_2$

Table 3.6 continued

Compound	**Chemical Shift (δ-ppm)**	**Assignment**
11	1.1	(t, 1H) $FpC\underline{H_2}CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$
	1.27	(m, 6) $CH(COOCH_2C\underline{H_3})_2$
	1.60	(dd, 1H) $FpC\underline{H_2}CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$
	1.4 –2.4	(m, 4H) $FpCH_2CH\{(CH(COOEt)_2)\}(C\underline{H_2})_2CH{=}CH_2$
	2.10	(m, 1H) $FpCH_2C\underline{H}\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$
	3.50	(d, 1H) $C\underline{H}(COOCH_2CH_3)_2$
	4.19	(m, 4) $CH(COOC\underline{H_2}CH_3)_{\underline{2}}$
	4.79	(s, 5H) $C_5\underline{H_5}$
	4.82	(s, 5H) $C_5\underline{H_5}$
	5.0	(m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}C\underline{H_2}$
	5.80	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}(CH_2)_2C\underline{H}{=}CH_2$
12	1.1	(t, 1H) $FpC\underline{H_2}CH\{(CH(COOEt)_2)\}(CH_2)_4CH{=}CH_2$
	1.27	(m, 6) $CH(COOCH_2C\underline{H_3})_2$
	1.50	(dd, 1H) $FpC\underline{H_2}CH\{(CH(COOEt)_2)\}(CH_2)_4CH{=}CH_2$
	1.4 –2.4	(m, 8H) $FpCH_2CH\{(CH(COOEt)_2)\}(C\underline{H_2})_4CH{=}CH_2$
	2.0 (m, 1H)	(m, 1H) $FpCH_2C\underline{H}\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$
	3.50 (d, 1H)	(d, 1H) $C\underline{H}(COOCH_2CH_3)_2$
	4.20 (m, 4)	(m, 4) $CH(COOC\underline{H_2}CH_3)_2$
	4.77	(s, 5H) $C_5\underline{H_5}$
	4.81	(s, 5H) $C_5\underline{H_5}$
	5.0	(m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2CH{=}C\underline{H_2}$
	5.80	(m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2C\underline{H}{=}CH_2$

3.3 Conclusion

The reactivity studies of the cationic η^2-(α,ω-diene) complexes of the type, [(η^5-C_5H_5)Fe$(CO)_2${η^2-(α,ω-diene)}]PF_6 have shown that the reactions proceeds via four generalized pathways i.e.

1) ligand substitution (displacement) of the diene
2) formation of the dimer
3) addition to the coordinated diene
4) deprotonation of the diene using tertiary amines i.e.) Et_3N

Where possible, the products of these reactions were fully characterized by microanalyses, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

3.4 Experimental

General Procedures

All experiments, unless otherwise stated, were carried out under nitrogen using typical Schlenk line techniques. Triphenylphoshine, trimethylphospine, triethylamine and diethylmalonate were used as purchased without further purification. Tetrahydrofuran was distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane was dried by refluxing over P_2O_5 and distilling under nitrogen. All solvents were maintained over molecular sieves, and degassed prior to use. All column chromatography was performed using deactivated alumina 90 (70 - 230 mesh) purchased from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using either NaCl solution cells or as DRIFTS spectra in a KBr matrix. NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^1H NMR and 50.30 MHz for ^{13}C NMR, using tetramethylsilane as an internal standard. Elemental analyses were performed at the micro-analytical laboratory of the University of Western Cape.

3.4.1 Reactions of 1 and 2 with NaCl and NaI

A solution of compound **1** (0.20 g, 0.53 mmol) in dry acetone (5 ml) was added dropwise to a mixture of sodium chloride (0.03 g, 0.53 mmol) suspended in dry acetone (5 ml). The reaction mixture was allowed to stir at room temperature for 3 days. The yellow reaction mixture turned an intense orange colour during this period. The solvent was removed on a rotatory evaporator leaving an orange solid. The solid was dissolved in a minimum amount of dichloromethane and the solution was chromatographed over an alumina column using CH_2Cl_2 as eluent. An orange band was collected, which on removal of the solvent gave an orange-red solid, identified by its IR and ^1H NMR spectra as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$ (86 % yield). The corresponding iron-pentadiene compound **2** undergoes a similar reaction, yielding the same product in 89 % yield. Analogous results were obtained using NaI in the place of NaCl.

3.4.2 Reactions of 1 and 2 with $NaBH_4$ and $LiAlH_4$

The reaction of compound **1** with $NaBH_4$ is described below. The procedure was also extended to compound **2**.

A solution of compound **1** (0.20 g, 0.53 mmol) in dry acetone (5 ml) was treated dropwise with a solution of $NaBH_4$ (0.02g, 0.53 mmol) dissolved in dry acetone (5 ml). The reaction mixture was allowed to stir at room temperature for approximately 2 days. The yellow reaction mixture goes darker in color almost immediately. The solvent was removed on a rotatory evaporator leaving a yellow/brown oil. The ^{1}H NMR of the crude reaction mixture revealed that the reaction resulted in the formation of a complex mixture of η^1-alkenyl species, evident by the appearance of a number of Cp resonances (σ 4.7 - 5.1ppm). Attempts to separate these products were unsuccessful. Analogous results were obtained using $LiAlH_4$ in place of $NaBH_4$.

3.4.3 Reactions of 1–4 with tertiary phosphines

A solution of compound **1** (0.20 g, 0.53 mmol) in dry acetone (5 ml) was added dropwise to a solution of triphenylphosphine (0.14 g, 0.53 mmol) dissolved in dry acetone (5 ml). The resulting pale yellow solution was stirred under a constant flow of nitrogen for 1 h at room temperature after which the solvent was removed by rotatory evaporation. The resulting pale yellow crystalline solid obtained was recrystallized by dissolving in a minimum amount of acetone (6 ml) followed by the dropwise addition of diethyl ether (20 ml). The product was collected on a Hirsch funnel as fine pale yellow crystals and identified as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)][PF_6]$ in 92 % yield. Similar reactions were carried out using compounds **2-4** as the starting material resulting in the same product in 90 - 95 % yields. The above reactions were repeated in a sealed Schlenk tube previously flushed with nitrogen and the reaction time extended to 1 day. The Schlenk tube was sealed off during the reaction with no nitrogen flowing through. Compounds **2** - **4** yielded the same product *viz.* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)][PF_6]$. Compound **1** however yielded a brown oil identified as $[(\eta^5\text{-}C_5H_5)\{CH_2CH{=}CHCH_2PPh_3\}]^+$, compound **5.** With PMe_3 a complex mixture of η^1-alkenyl complexeswere formed on reaction with **1**, evident by the appearance of a number of Cp resonances (σ 4.7 - 5.1) in the ^1H NMR spectrum of the reaction product.

The corresponding iron-pentadiene compound **2** undergoes a similar reaction with PMe_3, also yielding a complex mixture of products.

3.4.4 Reactions of 2-4 with triethylamine

The reaction of compound **2** with triethylamine is described here but the procedure has also been applied to compounds **3** and **4**, which gave similar results.

A suspension of compound **2** (0.20 g, 0.51 mmol) in 10 ml CH_2Cl_2 was treated dropwise with triethylamine (0.07 ml, 0.51 mmol). The yellow solution turns brown immediately and the iron-diene complex goes into solution upon addition of Et_3N. The mixture was allowed to stir at room temperature for 45 min. The solvent was removed from the reaction mixture by rotatory evaporation, leaving a brown residue. The residue was extracted with ether, filtered and the solvent removed from the filtrate. The remaining brown oil was dissolved in a minimum amount of hexane and chromatographed on an alumina column using hexane as eluent. Only one yellow band was observed, which upon removal of the solvent yielded a yellow-brown oil identified as the product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CH{=}CHCH{=}CH_2)]$, (compound **6**). In a similar manner compounds **7** and **8** were isolated in 40 and 45% yield respectively, using compounds **3** and **4** as starting materials.

3.4.5 Reactions of 1-4 with diethylmalonate

The reaction of compound **1** with diethylmalonate is described below. Again the procedure was also extended to compounds **2** – **4**.

To a solution of Li[N(SiMe$_3$)$_2$] in THF at -78°C was added diethylmalonate (0.08 ml, 0.51 mmol). After 15 min, the resultant clear solution of the diethylmalonate anion was added to a suspension of compound **1** (0.20 g, 0.51 mmol) in THF (10 ml) at -78°C. The reaction mixture was stirred at this temperature and then allowed to warm to room temperature over a period of 3 h. The solution remains orange/yellow throughout the reaction. The solvent was removed by rotatory evaporation leaving a yellow/brown oil. The oil was dissolved in a minimum amount of CH$_2$Cl$_2$ and the solution chromatographed on a neutral alumina column. Elution with CH$_2$Cl$_2$ gave a yellow band, which on the removal of the solvent, yielded the product as a yellow/brown oil. This was identified as an η^1-alkenyl compound, with a malonate substituent at the β position of the chain (compound **9**, 84% yield).

Products **10** – **12** were isolated in 80 – 86% yields starting from the corresponding compounds **2-4** and using a similar procedure.

3.5 References

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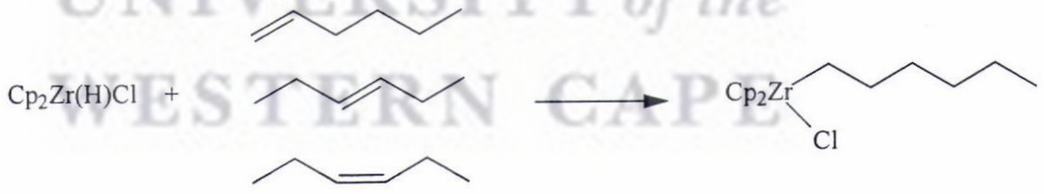
4. SYNTHESIS, CHARACTERIZATION AND SOME REACTIVITY STUDIES OF HETEROBINUCLEAR μ-ALKANEDIYL COMPLEXES, OF THE TYPE $[(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl$

4.4 Introduction

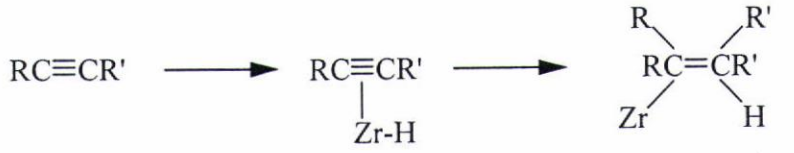
The hydrozirconation reaction involves the reaction of an unsaturated hydrocarbon with the zirconium hydride, $Cp_2Zr(H)Cl$. [1]. The reaction involves the insertion of the unsaturated hydrocarbon into the Zr-H bond producing an alkylzirconium complex. The bulky nature of the Cp_2ZrCl-group ensures that it becomes attached to the to the least sterically hindered position of the olefin either by regiospecific addition of Zr-H to a terminal olefin or addition to an internal olefin followed by isomerization to the least hindered position of the alkyl chain. This isomerization occurs through a series of insertion and beta-hydride elimination reactions. These reactions are quite fast and the olefin is rapidly isomerized to the terminal alkyl form. The regiospecificity of the hydrozirconation reaction is illustrated in Scheme 4.1 below.



Scheme 4.1: Hydrozirconation of isomeric olefins illustrating regiospecificity

The relative rates for hydrozirconation of alkenes with $Cp_2Zr(H)Cl$ at room temperature are α-olefin > *cis* internal olefin ≈ *trans* internal olefin > exocyclically functionalized olefin > cyclic olefin > disubstituted olefin > trisubstituted olefin [2]. Tetrasubstituted olefins such as tetramethylethylene fail to react with the hydride after many hours at room temperature, as do trisubstituted cyclic olefins such as 1-methylcyclohexene.

With alkynes, the less hindered *cis*-alkenylzirconinonium species is formed:



R' more bulky than R

(4.1)

When there is only a slight difference in the steric influence of the two groups, (e.g. R = Me, R' = Et), a mixture of the two possible products is obtained.

$Cp_2Zr(H)Cl$, commonly known as "Schwartz reagent", is a white solid with low solubility in commonly used organic solvents. The zirconium hydride was first prepared by Wailes *et al.* by the partial reduction of Cp_2ZrHCl with $LiAlH_4$ in THF as well by reduction of Cp_2ZrCl_2 using magnesium metal [3]. The use of $LiAlH_4$ as reducing agent can lead to the overreduction of Cp_2ZrCl_2 leading to the formation of the undesirable and insoluble Cp_2ZrH_2. The more hindered hydride $LiAl(O\text{-}t\text{-}Bu)_3H$ has thus been used as a more selective reagent [4].

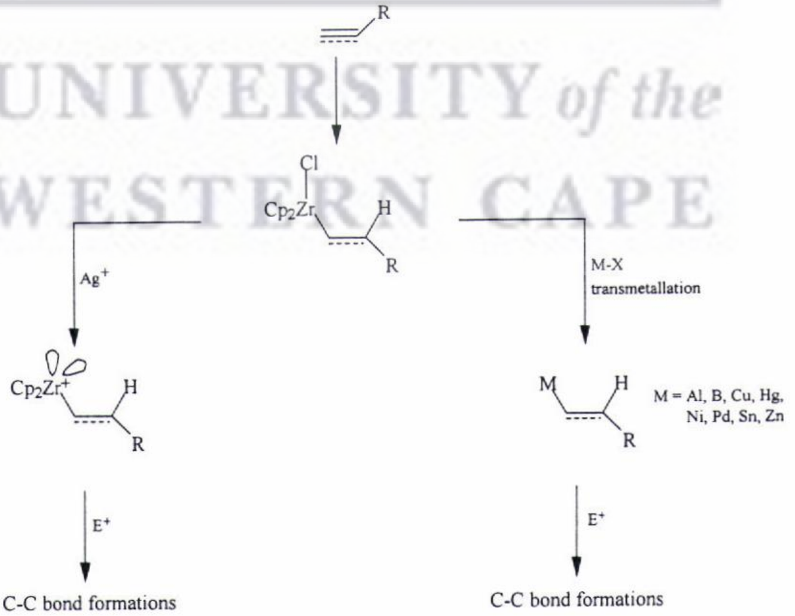
In 1974 Shwartz and co-workers reported on the preparation of $Cp_2Zr(H)Cl$ using a different reductant i.e. $Na[AlH_2(OCH_2CH_2OMe)_2]$, commercially known as Red-Al [5]. This protocol leads to contamination of the reagent with 30% NaCl. An improved procedure for the preparation of Schwartz's reagent involving the reaction of the dihydride Cp_2ZrH_2 with CH_2Cl_2 was reported by Buchwald *et.al.* [6, 7]. Cp_2ZrCl_2 is reduced to the dihydride Cp_2ZrH_2, which is washed with CH_2Cl_2 to form the desired monohydride $Cp_2Zr(H)Cl$..

Transformation of the monohydride to Cp_2ZrCl_2 was reported to occur very slowly [3].

4.4.3 Importance of hydrozirconation

The hydrozirconation reaction has been found to be of great importance in organic synthesis [2, 8 - 12]. The relative ease of preparation of the alkenyl- and alkylzircononcenes by hydrozirconation of alkynes and alkenes with $Cp_2Zr(H)Cl$ has made these organozirconocenes important in the formation of carbon-carbon bonds and carbon-heteroatom bond formation. Some examples of these transformations are highlighted in section 4.3. However, the bulky cyclopentadienyl groups around the zirconium atom prevent the attack of many organic electrophiles, thus limiting the reactions of these organozirconocenes to those with CO, isonitriles and halogen sources.

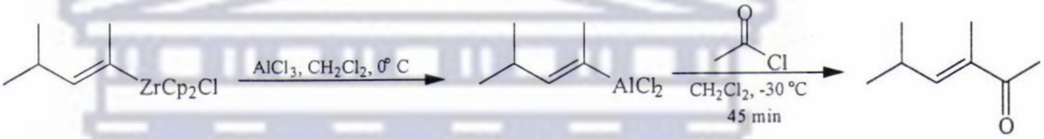
Much of the chemistry of organozirconocenes has been focused on indirect reaction pathways involving transmetallation or activation of the organozirconocene by ligand abstraction [12 - 19].



Scheme 4.2: Indirect reaction pathways for the reactions of organozirconocenes

Transmetallations, mostly to Al [5, 20], Zn [21 - 27], Pd [28 - 34], B [35 – 41], Cu and Ni [42 - 48] are synthetically useful in carbon-carbon bond forming reactions.

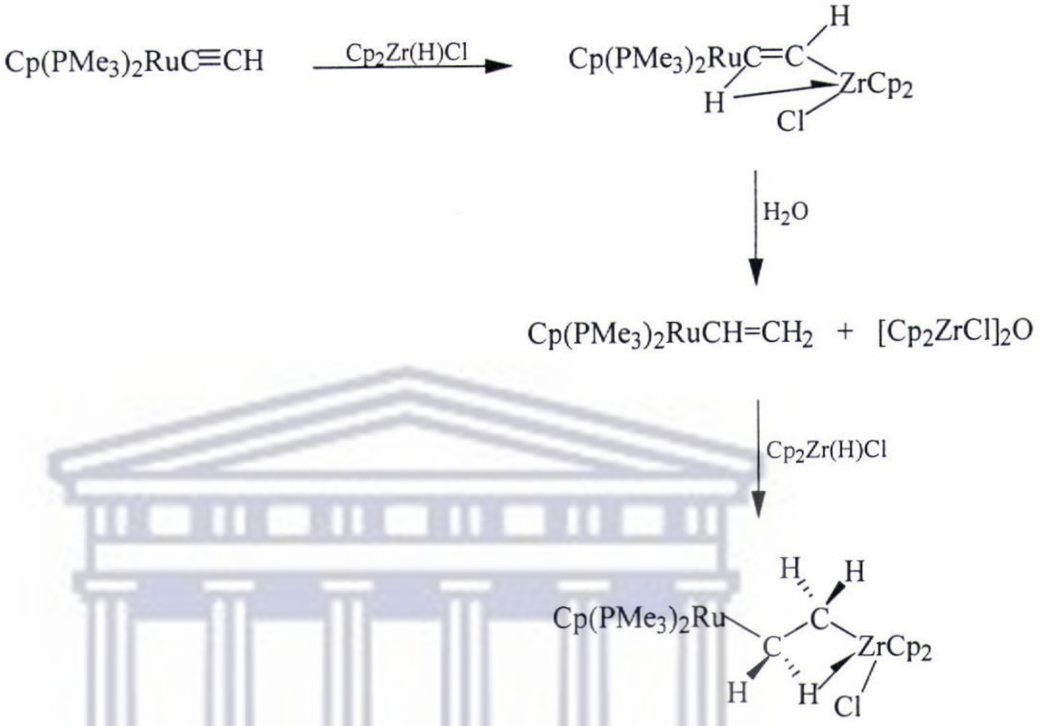
Transmetallation reactions from zirconium to aluminium were first reported by Schwartz and Carr in 1977 [20]. They reported the reaction of Cp_2ZrRCl with $AlCl_3$ yielding the corresponding organoaluminium dichlorides. Subsequent acylation with acetyl chloride provided the α,β-unsaturated ketone in high yield. Without transmetallation to aluminium, alkenylzirconocenes cannot be acylated with acid chlorides [5].



(4.2)

Hydrozirconation also plays an important role in the formation of early/late heterobimetallic complexes. These early-late heterobimetallic complexes combine the hard electrophillic and oxophillic early metal centre with the soft nucleophillic late transition metal centre. These complexes have thus ignited great interest as models in important catalytic reactions. Also, these complexes could give rise to reactivity patterns which are vastly different from that of their mononuclear analogues. For example, a binuclear complex of rhodium has been reported to show outstanding catalytic activity in hydroformylation [49, 50] and in methanol carbonylation [51].

Bullock reported the hydrozirconation of the complexes $Cp(PMe_3)_2RuCH=CH_2$ and $Cp(PMe_3)_2RuC=CH$ which leads to the formation of C_2-bridged Ru/Zr complexes [52] as shown in Scheme 4.3.



Scheme 4.3: Hydrozirconation in the formation of early/late heterobimetallic complexes.

There are a few examples in the literature of early/late heterobimetallic complexes containing two or more -CH_2- bridges. Consequently, we have prepared a series of early/late heterobinuclear μ-alkanediyl Fe-Zr complexes of the type $[(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl]$, n = 2-4, 6 and studied their reactivity. Further more, the zirconocene unit of these complexes make them potential catalysts in the polymerisation of olefins.

4.5 Results and discussion

4.2.1 Synthesis of the heterobinuclear μ-alkanediyl Fe-Zr complexes

These complexes were prepared by the hydrozirconation of the η^1-alkenyl iron species with the general formula $[(Cp)(CO_2)Fe(CH_2)_nCH=CH_2]$ (n = 2-4, 6) [53, 54]. Preliminary reactions were carried out on an NMR scale in a nitrogen-purged glove box. The expected Fe-Zr binuclear complexes were detected via ^{1}H NMR spectroscopy and subsequently isolated from the NMR sample as unstable yellow oils. This prompted us to carry out the reaction on a large scale. These preparative-scale hydrozirconation reactions were also carried out in a glovebox using equimolar amounts of $Cp_2Zr(H)Cl$ and the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ complexes. In some instances we managed to isolate the heterobinuclear μ-alkanediyl complexes of the type $[(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl]$ as illustrated below:

Scheme 4.4

These complexes were isolated as unstable yellow oils which could be handled only in the glovebox. The μ-alkanediyl compounds **13-16** (where n = 2-4, 6 respectively) prepared were characterized by ^{1}H NMR and IR spectroscopy. Due to the highly sensitive nature of the compounds , we were unable to further characterize these compounds. In most cases these compounds decomposed to the corresponding iron alkyl complexes, $Cp(CO)_2FeCH_2(CH_2)_nCH_3$ (n =2-4, 6), and $[Cp_2ZrCl]_2O$ as illustrated below:

$$[(Cp)Fe(CO)_2\text{-}CH_2(CH_2)_nCH_2\text{-}Zr(Cp)_2Cl]$$

$$\downarrow$$

$$[(Cp)Fe(CO)_2\{CH_2(CH_2)_nCH_3\}] \quad + \quad [Cp_2ZrCl]_2O$$

$$n = 2\text{-}4,\ 6$$

Scheme 4.5

The $[Cp_2ZrCl]_2O$ by-product was filtered off from the reaction mixture yielding a pale yellow solid which was further purified by recrystallisation from dichloromethane and hexane. The identity of the $[Cp_2ZrCl]_2O$ complex was confirmed by ^1H NMR and microanalysis.

The iron alkyl complexes were isolated as yellow brown oils which were purified by column chromotography. These complexes were characterized by ^1H, ^{13}C and IR spectroscopy. The spectroscopic data were compared with that of authentic samples of the iron alkyl complexes.

Following the reactions via ^1H NMR indicates that the heterobinuclear complexes are formed, but that they decompose to the iron alkyl complexes and $[Cp_2ZrCl]_2O$. This could be due to small traces of H_2O in the solvent. However, all attempts to exclude all traces of water by using ultra-dry solvents and doing most of the manipulation in the glovebox, could not prevent the decomposition of the heterobinuclear complexes.

4.2.2 Characterization of the heterobinuclear μ-alkanediyl Fe-Zr complexes

^{1}H NMR spectra

The ^{1}H NMR spectra for compounds **13-16** exhibit similar characteristics. The spectra of all the compounds exhibit a distinct triplet in the region δ 0.8-1.0 ppm which was assigned to the protons of the Zr-CH_2 group. The intense singlet at δ 6.22 ppm integrating for 10 protons was assigned to the protons of the cyclopentadienyl groups attached to the zirconium centre. Small traces of unreacted $Cp_2Zr(H)Cl$ was observed in most of the spectra evident by a small singlet at δ 6.49 ppm. The positions of these peaks were further confirmed by carrying out a model hydrozirconation reaction using 1-hexene. The mononuclear zirconium-hexyl complex isolated exhibits a Zr-Cp peak at δ 6.22 ppm and an intense triplet in the region δ 0.8 – 1.0 ppm assigned to the Zr-CH_2 unit. The ^{1}H NMR spectrum for compound **15** (where n = 4) together with the corresponding mononuclear zirconium complex, $Cp_2(Cl)Zr(CH_2)_5CH_3$ are shown in Figure 4.1 and 4.2 respectively to illustrate these characteristic peaks.

In the spectra of the Fe-Zr complexes the intense singlet at δ 4.72 ppm integrating for five protons was assigned to the cyclopentadienyl peak attached to the iron centre. Further more, the disappearance of olefinic protons of the parent $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ complexes indicates that addition of the Zr-H across the double bond had in fact occurred.

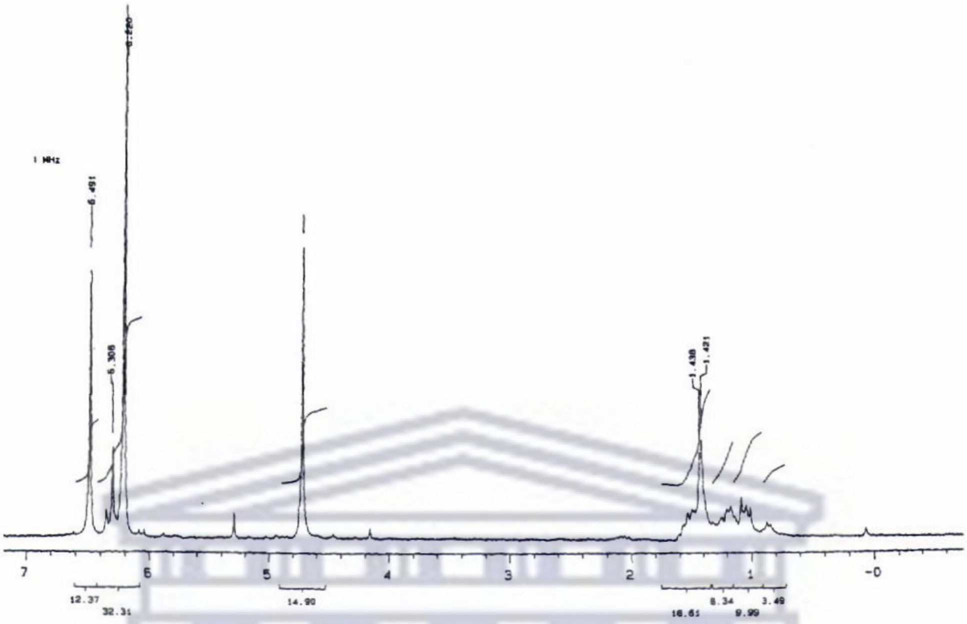


Figure 4.1: ^{1}H nmr spectrum of compound **15**

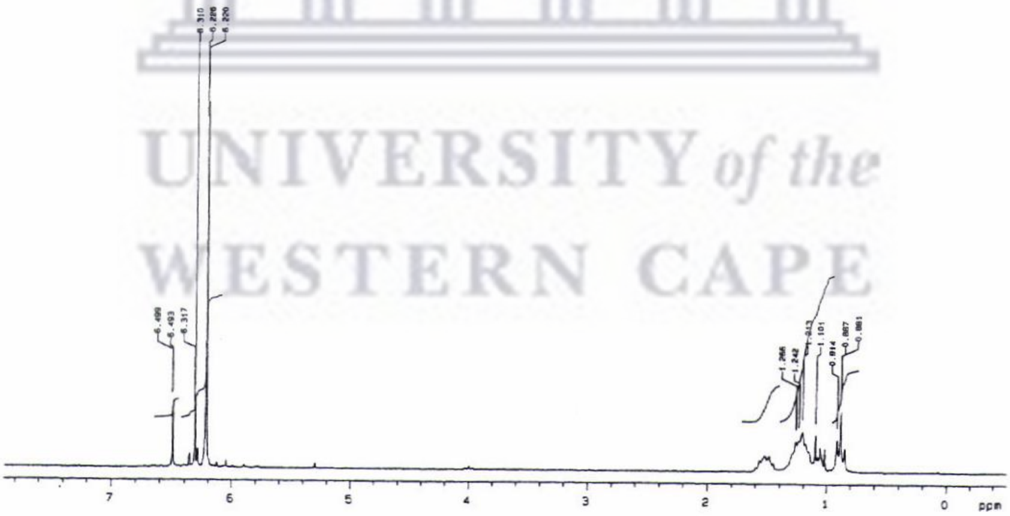
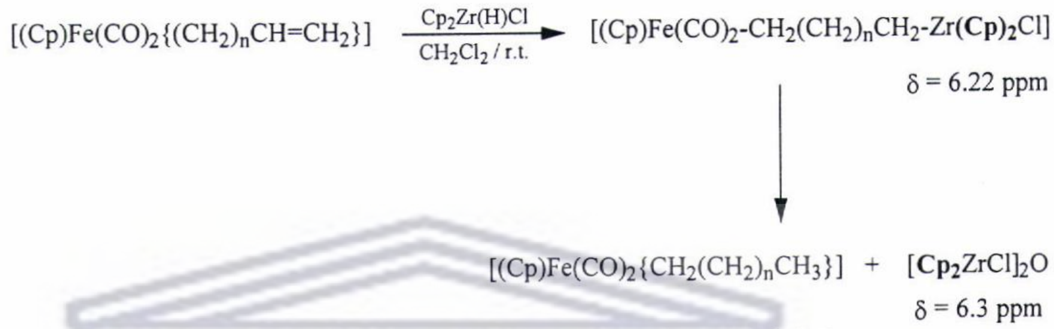


Figure 4.2: ^{1}H nmr spectrum for $Cp_2(Cl)Zr(CH_2)_5CH_3$

For the reactions in which the μ-alkanediyl heterobinuclear complexes decompose to the iron alkyl complexes, $Cp(CO)_2FeCH_2(CH_2)_nCH_3$, (n = 2-4, 6), and $[Cp_2ZrCl]_2O$, an intense cyclopentadienyl peak at 6.3 ppm due to the formation oxo-bridged dimer, $[Cp_2ZrCl]_2O$, is observed. The singlet observed at δ 4.72 was assigned to the cyclopentadienyl peak attached to the iron centre of the iron alkyl complex, $Cp(CO)_2FeCH_2(CH_2)_nCH_3$ (n =2-4, 6).

Figure 4.3: ^1H NMR spectrum for a mixture $Cp(CO)_2FeCH_2(CH_2)_4CH_3$ and $Cp_2ZrCl]_2O$

Monitoring the reaction using ^1H NMR spectroscopy revealed that the heterobinuclear μ-alkanediyl complexes are formed and subsequently decompose *in situ* to a mixture of the iron alkyl complexes and the oxo-bridged dimer, $[Cp_2ZrCl]_2O$. As alluded to previously a cyclopentadienyl peak at δ 6.22 ppm is observed initially in the ^1H NMR spectra. This can be attributed to the Cp group attached to the zirconium centre of the heterobinuclear μ-alkanediyl complexes, $(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl$ (n = 2-4, 6). With time this peak disappears and is replaced with a cyclopentadienyl resonance at δ 6.3 ppm which is due to the formation of the $[Cp_2ZrCl]_2O$. These transformations are summarized in Scheme 4.6.

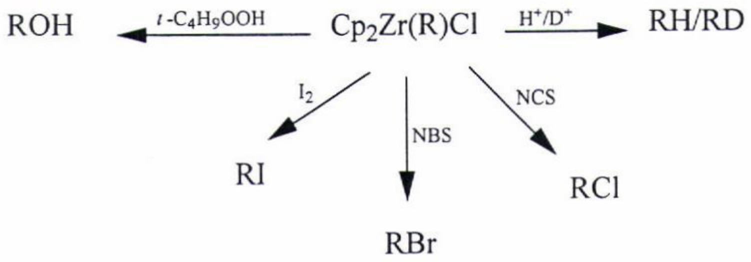


Scheme 4.6

The IR spectral data for the heterobinuclear μ-alkanediyl Fe-Zr complexes, **13–16,** and the iron alkyl complexes resembles those of the analogous parent iron-alkenyl complexes, $[(Cp)(CO_2)Fe(CH_2)_nCH=CH_2]$ (n = 2-4, 6) , in the ν(CO) region. Two strong ν(CO) bands in the region of 2000 cm^{-1} and 1940 cm^{-1} are observed in the spectra for all the compounds. However the ν(C=C) at ~1625cm^{-1} observed in the spectra of the iron alkenyl complex is absent in both the heterobinuclear μ-alkanediyl Fe-Zr complexes and the iron alkyl complexes.

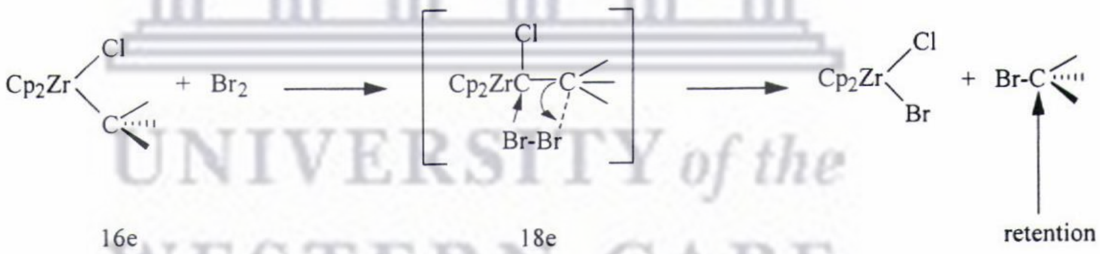
4.2.3 Reactivity of the heterobinuclear μ-alkanediyl Fe-Zr complexes

It has previously been found that mononuclear organozirconium complexes, produced by the hydrozirconation of unsaturated hydrocarbons are of high value as intermediates in organic synthesis. A variety of products may be obtained from them stereospecifically by electrophillic cleavage of the C-Zr bond. For example, these organozirconum compounds can react with Br_2, N-bromo- or N-chlorosuccinimide to give the corresponding organic halides (Scheme 4.7)



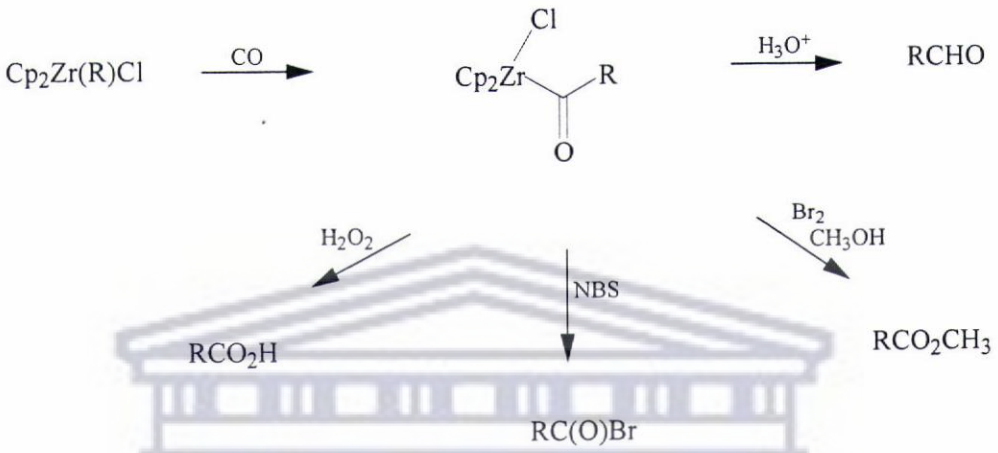
Scheme 4.7

It has previously been shown that electrophillic cleavage of the Zr-C bond proceeds through a concerted mechanism, with retention of configuration at the carbon atom [5, 11]. The electrophillic reagent coordinates to the zirconium atom by donation of a pair of electrons to the vacant low lying d-orbital of the metal atom. For example with Br_2, the reaction Scheme in 4.8 prevails.



Scheme 4.8

Organozirconium complexes can also be used to a lesser extent in the formation of direct C-C bond formation. One such example is the reaction with carbon monoxide which results in the corresponding acyl complex via CO insertion. These mononuclear zirconium-acyl complexes can be converted, depending on subsequent procedures, into aldehydes, carboxylic acid, esters, or acyl halides (Scheme 4.9). For example, an aldehyde is produced by hydrolysis of the RC(O)Zr bond with dilute aqueous acid. Treatment of the zirconium acyl with NBS gives the acyl bromide. The acyl-zirconium bond can be cleaved by other oxidative procedures as well. Reaction with Br_2 in methanol yields the methyl ester. While reactions with aqueous H_2O_2 followed by acidification gives the carboxylic acid.



Scheme 4.9

We subjected the heterobinuclear μ-alkanediyl compounds **13-16** to similar reactions. Each of these is discussed below:

4.2.3.1. Reaction with H_2O

It has been reported previously that zirconiumalkyl compounds react with water, according Equation 4.3 below [55]:

$$Cp_2Zr(Cl)CH_3 + H_2O \longrightarrow [Cp_2ZrCl_2]O + CH_4 \qquad (4.3)$$

Complexes **13-16** were reacted *in situ* in a CH_2Cl_2 solution with H_2O. The formation of the heterobinuclear μ-alkanediyl complexes (**13-16**) were carried out in the glovebox using equimolar ratio's of the $[(Cp)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ complexes and $Cp_2Zr(H)Cl$. The sealed Schlenk tube was removed from the glovebox and *in situ* reactions with water were conducted outside of the glovebox on a nitrogen Schlenk-line. The expected iron alkyls of the type $Cp(CO)_2FeCH_2(CH_2)_nCH_3$ (n = 2-4, 6) and $[Cp_2ZrCl]_2O$ were obtained after work up of the reaction.

$$[(Cp)Fe(CO)_2\{(CH_2)_nCH{=}CH_2\}] \ + \ Cp_2Zr(H)Cl$$

$$\Big\downarrow \ CH_2Cl_2 \,/\, \text{r.t.}$$

$$[(Cp)Fe(CO)_2\text{-}CH_2(CH_2)_nCH_2\text{-}Zr(Cp)_2Cl]$$

$$\Big\downarrow \ H_2O$$

$$[(Cp)Fe(CO)_2\{CH_2(CH_2)_nCH_3\}] \ + \ [Cp_2ZrCl]_2O$$

$$n = 2\text{-}4,\ 6$$

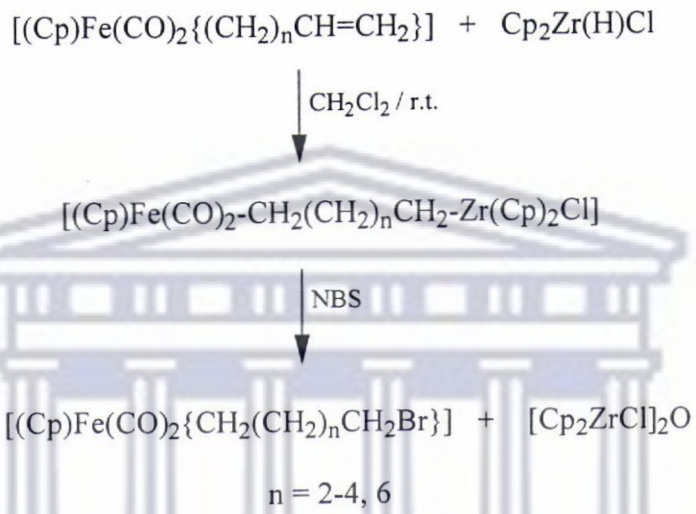
Scheme 4.10

$[Cp_2ZrCl]_2O$ was isolated as an off-white solid which was filtered off. The iron alkyls were isolated as yellow oils and further purified by column chromatogaraphy. The latter was isolated in 70 – 80 % yields. The NMR as well as the IR spectra of the iron alkyls correlates to that of the known compounds as reported in literature [56 –60].

4.2.3.2 Reaction with N-bromosuccinimide

The reactions of zirconium alkyls with N-bromosuccinide (NBS) are known to produce alkylbromides [5,11].

We subjected complexes **13-14** to the *in situ* reaction with NBS. Solutions of compounds in dichloromethane were treated with N-bromosuccinimide inside a glovebox. The reaction mixture was allowed to stir for a few minutes after which the work up was done outside of the glovebox. The expected ω-bromoalkyl complexes of the type $[Cp(CO)_2Fe(CH_2)_nBr]$ (n = 4-5) were obtained by electrophillic cleavage of the C-Zr bond.



Scheme 4.11

The ω-bromoalkyl complexes were isolated in yields 65-70 % as yellow brown oils which were purified by column chromotography. The identity of these complexes were confirmed by comparing it's ^1H NMR, ^{13}C NMR and IR spectra with those previously reported.

Previous reports for the preparation of ω-bromoalkyl complexes, $[Cp(CO)_2Fe(CH_2)_nBr]$, involves the reaction of $Na[CpFe(CO)_2]$ with $Br(CH_2)_nBr$ (n = 3–5) [61]. This leads to the formation of the undesired $[CpFe(CO)_2]_2$ and $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$. These reactions are temperature dependant and the reaction has to be carried out -20°C for the formation of the desired $[Cp(CO)_2Fe(CH_2)_nBr]$, making the work-up procedure for the reaction more difficult. Preparation of these ω-bromoalkyl complexes *via* the heterobinuclear μ-alkanediyl compounds thus seems to be the more viable route and the yields of the ω-bromoalkyl complexes products obtained are slightly higher.

4.2.3.3 Reactions with I_2

The reactions of μ(α,ω)-alkanediyl complexes of iron of the type $[(Cp)(CO_2)Fe(CH_2)_nFe(CO)_2Cp]$, n =3, 4, with iodine ($I_2$) were previously reported to produce $[CpFe(CO)_2I]$ and $I(CH_2)I$ [62].

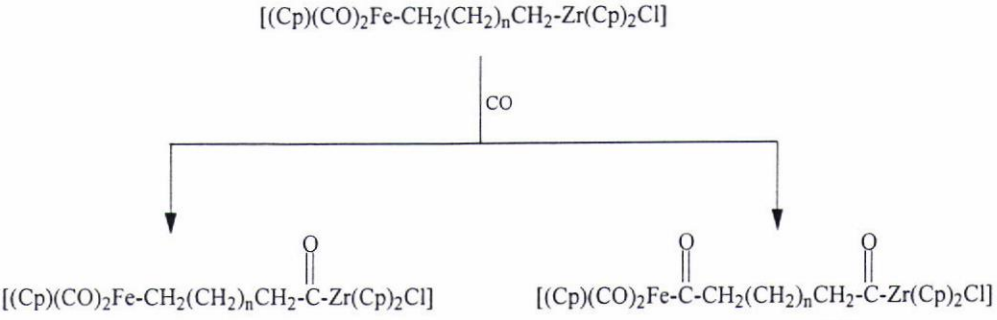
We subjected complexes **13-14** to the *in situ* reaction with iodine. Similar reaction patterns were observed for these reactions. Solutions of compounds **13-14** in dichloromethane were treated with iodine inside a glovebox. The reaction mixture was allowed to stir for a few minutes after which the work up was done outside of the glovebox. The expected cleavage products $[CpFe(CO)_2I]$ and $I(CH_2)_nI$ (n= 4,5) were isolated from the reaction mixture. $[CpFe(CO)_2I]$ was isolated as a purple-black, air stable crystalline solid in 70 – 75% yields whilst $I(CH_2)_nI$ (n= 4,5) was isolated as a pale yellow oil in 40 – 45% yields. $[Cp_2ZrClI]$ was formed as a by-product evident by the appearance of cyclopentadienyl peak at 6.3 ppm in the ^1H NMR of the crude reaction mixture. The latter was not isolated as it could not be separated from the column material.

The identity of $[CpFe(CO)_2I]$ and $I(CH_2)_nI$ (n= 4,5) were confirmed by comparing their ^1H NMR and IR spectra to authentic samples and previously reported spectral data [62].

4.4.3.1 Reactions with CO

Both zirconium alkyls and zirconium alkenyl chlorides have been reported to readily undergo clean and high yield CO insertion into the C-Zr bond to produce the zirconium acyl complexes. These reactions were reported to take place rapidly at room temperature and at 1.5 atm pressure, yielding stable acylzirconium(IV) species, which do not lose CO, even under vacuum [8]. Iron alkyl compounds on the other hand are known to undergo CO insertion into the Fe-C bond under more forcing reaction conditions. For example, the CO insertion of $CpFe(CO)_2Me$ was reported to take place at 125 °C and 200 atm of CO pressure affording the stable acyl complex, $CpFe(CO)_2COMe$ [63]. Very few iron acyls have been prepared by this method, due to the more convenient synthesis from $Na[CpFe(CO)_2]$ with RCOCl.

Given the above we were prompted to evaluate the reactivity of the Fe-Zr binuclear complexes with CO under various reactions conditions. The reactions were carried out in dry CH_2Cl_2 in a 300 ml stainless steel autoclave. The heterobinuclear μ-alkanediyl compounds dissolved in CH_2Cl_2 were transferred to the autoclave in a glovebox. The autoclave was sealed off and removed from the glovebox and the reaction with CO was conducted outside glovebox. The reaction mixture was pressurized with CO at various pressures and the reactions were performed at room temperature. Different products were obtained depending on the reaction conditions. These are discussed below. For example, either the monoacyl compounds or the diacyl compounds may be isolated as illustrated below.



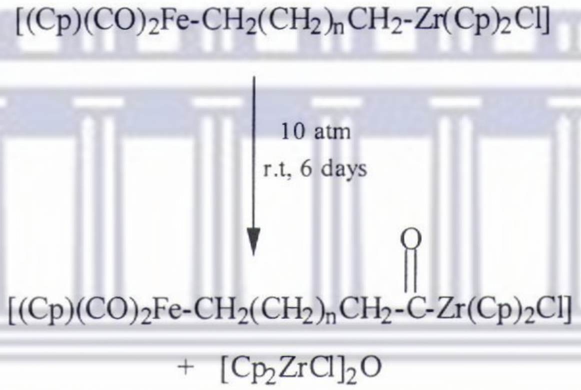
(17) **(18)**

Scheme 4.12

4.2.3.4 (a) Reactions with CO at 10 atm and room temperature

The reactions at 10 atm were carried out at room temperature for 6 days. Preliminary reactions at short reaction times revealed that the CO reactions were fairly sluggish. It was thus decided to use extensive reaction times. The results are discussed below.

At 10 atm, CO insertion into the C-Zr bond was observed resulting in the formation of the binuclear and monoacyl complex, $[Cp_2(Cl)ZrC(O)CH_2(CH_2)_nCH_2Fe(CO)_2(Cp)]$, n = 3,4 (Equation 4.4).



$$[(Cp)(CO)_2Fe\text{-}CH_2(CH_2)_nCH_2\text{-}Zr(Cp)_2Cl] \xrightarrow[\text{r.t, 6 days}]{\text{10 atm}} [(Cp)(CO)_2Fe\text{-}CH_2(CH_2)_nCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Zr(Cp)_2Cl] + [Cp_2ZrCl]_2O$$

n = 3 **17a**
n = 4 **17b**

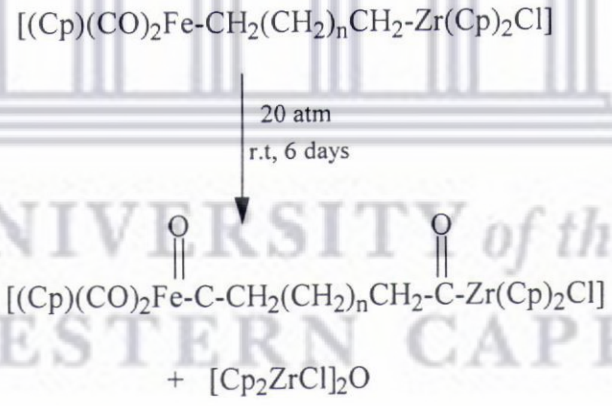
(4.4)

This was evident by the appearance of the peak for the CH_2 group adjacent to the acyl at δ 3.2 ppm and a shift in the Zr-Cp resonance from δ 6.2 ppm to 5.89 ppm in the ^1H NMR spectra. The corresponding peaks for the analogous mononuclear zirconium complex were reported to appear at δ 2.8 ppm and δ 5.8 ppm respectively. The peak for the cyclopentadienyl group attached to the iron centre remained unaffected, further suggesting that CO insertion occurs only into the Zr-C bond. If the reaction is conducted for shorter reaction times, then unreacted starting material is detected.

The oxo-bridged dimer, $[Cp_2ZrCl]_2O$, was formed as a by product of the reaction evident by the appearance of a cyclopentadienyl resonance at δ 6.3 ppm in the ^1H nmr spectra. This is due to gradual decomposition of the starting material with time. Due to the sensitive nature of the Zr-C bond attempts to separate the products were unsuccessful.

4.2.3.4 (b) Reactions with CO at 20 atm and room temperature

The reactions with CO at 20 atm and room temperature were carried out for 6 days. In these reactions two distinct triplets at δ 2.8 ppm and δ 3.2 ppm were observed in the ^1H nmr spectra. These two peaks suggest the formation of two acyl species ($C(O)\text{-}CH_2$) indicating that CO insertion occurs at both the Fe-C and the Zr-C bond i.e.



$$[(Cp)(CO)_2Fe\text{-}CH_2(CH_2)_nCH_2\text{-}Zr(Cp)_2Cl] \xrightarrow[\text{r.t, 6 days}]{\text{20 atm}} [(Cp)(CO)_2Fe\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2(CH_2)_nCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Zr(Cp)_2Cl] + [Cp_2ZrCl]_2O$$

n = 4 **18**

(4.5)

Further more the cyclopentadienyl resonances of both the Zr-Cp and the Fe-Cp show dramatic shifts. The singlet at δ 5.89 ppm was assigned to the cyclopentadienyl peak attached to the zirconium centre and the singlet at δ 4.85 ppm was assigned to the cyclopentadienyl peak attached to the iron centre. The corresponding peaks for the analogous heterobinuclear μ-alkanediyl starting material appears at δ 6.22 ppm and and δ 4.72 ppm for the Zr-Cp and the Fe-Cp respectively. Again, $[Cp_2ZrCl]_2O$, was observed in the reaction mixture. The latter is formed as a result of the decomposition of the intermediate μ-alkanediyl complexes.

4.5 Conclusion

The hydrozirconation reactions of the iron alkenyl complexes, $[(Cp)(CO_2)Fe\{(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6), leads to the formation of the heterobinuclear μ-alkanediyl complexes, $(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cp)_2Cl]$, **13-16.** These complexes were isolated as yellow/brown unstable oils. However, due to the oxophillic nature of the zirconium centre, these complexes were shown to readily decompose to the oxo-bridged dimer, $[Cp_2ZrCl]_2O$ and the corresponding iron alkyl compounds, $Cp(CO)_2FeCH_2(CH_2)_nCH_3$. *In situ* reactions of the heterobinuclear μ-alkanediyl complexes with various electrophiles were found to proceed in a similar fashion to those of the known mononuclear iron and zirconium alkyl complexes.

4.4 Experimental

General procedures

All manipulations of air-sensitive materials were conducted under nitrogen using standard Schlenk tube techniques or working in a nitrogen purged glove box. Zirconocene hydrogen chloride was obtained from Fluka or Sigma Aldrich. Iodine was purchased from Sigma-Aldrich. Reagent grade tetrahydrofuran was distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane was dried by refluxing over P_2O_5 and distilled under nitrogen. All solvents were maintained over molecular sieves, and stored in a glovebox. All column chromatography was performed using deactivated alumina 90 (70 - 230 mesh) purchased from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using NaCl solution cells. NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^1H NMR and 50.30 MHz for ^{13}C NMR, using $CDCl_3$ as an internal standard. These complexes $[(Cp)(CO_2)Fe(CH_2)_nCH{=}CH_2]$ (n = 2-4, 6) were prepared using literature methods [53, 54].

4.4.1 General method for the preparation of the heterobinuclear μ-alkanediyl, $(Cp)(CO_2)FeCH_2(CH_2)_nCH_2Zr(Cl)(Cp)_2$, where n = 2-4, 6

The preparation of complex **1** is described below to illustrate the general procedure employed.

A solution of $[(Cp)Fe(CO)_2\{CH_2CH_2CH{=}CH_2\}]$ (0.18g, 0.78 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a suspension of $Cp_2Zr(H)Cl$ (0.2g, 0.78 mmol) in CH_2Cl_2 (5 ml) in a glovebox. The resulting orange/yellow solution was allowed to stir at room temperature for 3 hrs. The Schlenk tube was then sealed off and removed from the glovebox. The solvent was removed from the reaction mixture under vacuum by attaching the sidearm of the Schlenk tube to the vacuum line. The resulting yellow/brown oil was transferred back to the glovebox. The reaction mixture was then transferred to a NMR tube. In some instances the heterobinuclear μ-alkanediyl complexes were isolated as yellow/brown oils in almost 100% yields, while in other cases a mixture of the heterobinuclear μ-alkanediyl complexes and the iron alkyl complex, $Cp(CO)_2Fe(CH_2)_3CH_3$, together with $[Cp_2ZrCl]_2O$ were isolated. In the latter case a yellow/brown semi-solid was isolated. The semi-solid was extracted several times with hexane. The pale yellow solid was filtered off and further purified by recrystallisation with CH_2Cl_2/ hexane at room temperature. The white crystalline solid formed was identified as $[Cp_2ZrCl]_2O$. Removal of the solvent from the yellow filtrate resulted in a yellow/brown oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution was chromatographed on an alumina column made up in hexane. Elution with hexane gave a yellow band which on removal of the solvent resulted in a yellow/brown oil remaining which was identified as the iron alkyl complexes, $Cp(CO)_2Fe(CH_2)_3CH_3$ (80 – 85 % yield).

4.4.2 Reaction of $[CpFe(CO)_2\{CH_2CH_2CH{=}CH_2\}]$ with $Cp_2Zr(H)Cl$ followed by reaction with H_2O: preparation of $Cp(CO)_2Fe(CH_2)_3CH_3$

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CH_2CH{=}CH_2\}]$ (0.18g, 0.78 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a suspension of $Cp_2Zr(H)Cl$ (0.2g, 0.78 mmol) dissolved in CH_2Cl_2 (5 ml) in a glovebox. The solution was stirred at room temperature for 10 minutes. The reaction mixture was removed from the glovebox and treated with H_2O (~1 ml). The yellow/brown solution goes lighter in colour and a white precipitate was formed almost immediately. The white precipitate was filtered off. The water was separated from the reaction mixture using a separatory funnel. The organic layer was collected and dried over $MgSO_4$. The $MgSO_4$ was filtered off and the solvent was removed from the filtrate upon which a yellow brown oil was obtained. This was identified as the iron alkyl compound, $Cp(CO)_2Fe(CH_2)_3CH_3$ which was isolated in 77 % yield.

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{(CH_2)_nCH=CH_2\}]$ (n = 3) with $Cp_2Zr(H)Cl$ followed by the reaction with H_2O was carried out in a similar manner yielding $Cp(CO)_2Fe(CH_2)_4CH_3$ (71 %) as the product.

4.4.3 Reaction of $[CpFe(CO)_2\{(CH_2)_nCH=CH_2\}]$, n = 2, 3, with $Cp_2Zr(H)Cl$ followed by reaction with N-bromosuccinimide: preparation of $[Cp(CO)_2Fe\{(CH_2)_nCH_2CH_2Br\}]$.

The *in situ* reaction of compound **13** with N-bromosuccinimide is described below but the procedure was also extended to compound **14.**

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CH_2CH=CH_2\}]$ (0.18g, 0.78 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a suspension of $Cp_2Zr(H)Cl$ (0.2g, 0.78 mmol) dissolved in CH_2Cl_2 (5 ml) in a glovebox. The resultant yellow solution was stirred at room temperature for approximately 30 minutes. The reaction mixture was treated with N-bromosuccinimide (0.78 mmol) (inside glovebox). The yellow/brown solution goes darker in color almost immediately. The solvent was removed from the reaction mixture resulting in a yellow/brown semi-solid remaining. The semi-solid was extracted several times with hexane. The pale yellow solid was filtered off and further purified by recrystallisation with CH_2Cl_2/ hexane at room temperature. The white crystalline solid formed was identified as $[Cp_2ZrCl]_2O$. Removal of the solvent from the yellow filtrate resulted in a yellow/brown oil remaining. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution was chromatographed on an alumina column made up in hexane. Elution with hexane gave a yellow band which on removal of the solvent resulted in a yellow/brown oil remaining. The oil was identified as $[Cp(CO)_2Fe(CH_2)_4Br]$ (67 %) by comparing its IR and ^1H NMR to previously reported spectral data.

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{(CH_2)_nCH{=}CH_2\}]$ (n = 3) with $Cp_2Zr(H)Cl$ followed by the reaction with N-bromosuccimide was carried out in a similar manner yielding $[Cp(CO)_2Fe(CH_2)_5Br]$ (69 % yield).

4.4.4 Reaction of $[CpFe(CO)_2\{(CH_2)_nCH{=}CH_2\}]$, n = 2, 3, with $Cp_2Zr(H)Cl$ followed by reaction with I_2: preparation of $Cp(CO)_2FeI$

The *in situ* reaction of compound **13** with iodine is described below but the procedure was also extended to compound **14.**

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CH_2CH{=}CH_2\}]$ (0.18g, 0.78 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a suspension of $Cp_2Zr(H)Cl$ (0.2g, 0.78 mmol) dissolved in CH_2Cl_2 (5 ml) in a glovebox. The resultant yellow solution was stirred at room temperature for approximately 30 minutes. The reaction mixture was treated with iodine (0.2g, 0.78 mmol) inside the glovebox. The yellow/brown solution goes dark brown in color almost immediately. The solvent was removed from the reaction mixture resulting in a dark brown solid remaining. The solid was dissolved in a minimum amount of CH_2Cl_2 and the solution was chromatographed on a neutral alumina column. A pale yellow band was eluted with hexane, giving a pale-yellow oil on removal of the solvent. The product was identified as $I(CH_2)_4I$ (40 %) by comparing its IR and ^1H NMR spectra to previously reported spectral data. Elution with CH_2Cl_2 gave a dark brown band, which on the removal of the solvent, yielded a dark purple-black crystalline solid, of which the IR and ^{1}H NMR spectra were identical to those of the authentic sample for [Cp(CO)$_2$FeI] (74 %).

The reaction of [(η^5-C$_5$H$_5$)Fe(CO)$_2${(CH$_2$)$_n$CH=CH$_2$}] (n = 3) with Cp$_2$Zr(H)Cl followed by the reaction with I$_2$ was carried out in a similar manner yielding the same results. I(CH$_2$)$_5$I was isolated in 43% and Cp(CO)$_2$FeI in 72 % yield.

4.4.5 Reaction of [CpFe(CO)$_2${(CH$_2$)$_n$CH=CH$_2$}], n = 3, 4, with Cp$_2$Zr(H)Cl followed by reaction with CO

A solution of [(η^5-C$_5$H$_5$)Fe(CO)$_2${(CH$_2$)$_n$CH=CH$_2$}] (n = 3, 4) (0.18g, 0.78 mmol) in CH$_2$Cl$_2$ (5 ml) was added drop-wise to a suspension of Cp$_2$Zr(H)Cl (0.2g, 0.78 mmol) dissolved in CH$_2$Cl$_2$ (5 ml) in a glovebox. The solution was stirred at room temperature for approximately 30 minutes. The reaction mixture was transferred to a 300 ml stainless steel autoclave inside a glovebox. An additional 30 ml CH$_2$Cl$_2$ was added to the reaction mixture inside of the autoclave. The autoclave was sealed off and removed from the glovebox and the reaction with CO was conducted outside the glovebox. The reaction mixture was pressurised with CO at various pressures and the reactions were performed at room temperature. Each of these reactions is described below.

4.4.5 (a) Reactions with CO at 10 atm and room temperature

The reaction at 10 atm was carried out at room temperature for 6 days. The reaction mixture was stirred at under this pressure for 6 days at room temperature. The pressure was released from the autoclave. The autoclave was re-sealed off and returned to a nitrogen purged glovebox for the work up of the reaction. The reaction mixture was filtered into a Schlenk tube inside of a glovebox. The Schlenk tube was then sealed off and removed from the glovebox. The solvent was removed from the reaction mixture under vacuum by attaching the sidearm of the Schlenk tube to the vacuum line. The resulting yellow semi-solid was transferred back to the glovebox. The reaction product was then transferred to a NMR tube. The product was identified by ^{1}H NMR and IR as a mixture of the binuclear monoacyl complex, $[Cp_2(Cl)ZrC(O)CH_2(CH_2)_nCH_2Fe(CO)_2(Cp)]$, n = 3,4, and the oxo-bridged dimer, $[Cp_2Z(rCl)]_2O$.

4.4.5 (b) Reactions with CO at 20 atm and room temperature

The reactions at 20 atm were carried out at room temperature for 6 days in a similar manner to the reaction with CO at 10atm discussed above. The product was isolated as an orange semi-solid. The solid was identified by ^{1}H NMR and IR spectroscopy as a mixture of the binuclear monoacyl complex, $[Cp_2(Cl)ZrC(O)CH_2(CH_2)_nCH_2C(O)Fe(CO)_2(Cp)]$, n = 4, and the oxo-bridged dimer, $[Cp_2Zr(Cl)]_2O$.

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5. REACTIVITY STUDIES OF ω-HYDROXYALKYL IRON COMPLEXES, OF THE TYPE $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$

5.1 Introduction

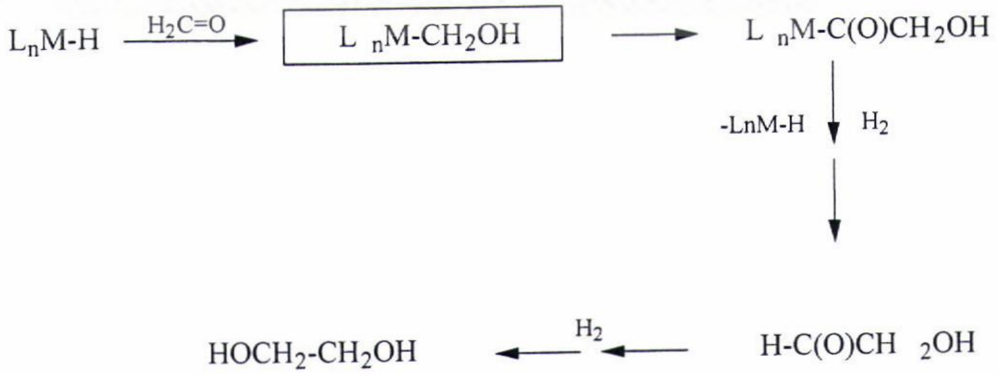
As stated in Chapter 1, ω-hydroxyalkyl complexes can be regarded as a sub-division of the group of compounds generally known as functionalized transition metal alkyls. ω-Hydroxyalkyl transition metal complexes are compounds in which the alkyl chain contains a hydroxy group at the terminal end of the carbon chain [Figure 5.1].

$L_nM(CH_2)_yOH$

L_nM = metal and its associated ligands

Figure 5.1 ω-Hydroxyalkyl transition metal complex

These compounds have been known since 1967 and several examples have been highlighted in Chapter 1. These complexes have been proposed as key intermediates or model compounds in a number of catalytic processes of industrial importance. One such example is the Wacker process (Scheme 1.11, Chapter 1) which illustrates the role of β-hyroxyethyl complexes in the oxidation of ethylene to acetaldehyde. Another example is the hydroformylation of formaldehyde depicted in Scheme 5.1 [1-2].



Scheme 5.1 Formaldehyde hydroformylation

In view of this, many hydroxymethyl complexes have been studied [3 - 10]. However, very few long chain hydroxy-alkyl compounds are known and very little is known of their reactivity. In this chapter we report on various reactions of the previously reported ω-hydroxyalkyl iron complexes of the type $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7) [11, 12]. These compounds were prepared by the oxidative hydroboration reaction of the corresponding η^1-alkenyl complexes, $[(Cp)(CO)_2Fe\{(CH_2)_{n-1}CH{=}CH_2\}]$.

$$[(Cp)Fe(CO)_2\{(CH_2)_nCH{=}CH_2\}] \xrightarrow[\text{ii) NaOH/ }H_2O_2]{\text{i) }BH_3\text{/THF}} [(Cp)Fe(CO)_2\{(CH_2)_nCH_2CH_2OH\}] \quad n = 2\text{-}4,6 \qquad (5.1)$$

Some reactivity studies on these compounds have been studied previously [13]. In this section we report on other reactions of some of these compounds.

5.2 Results and discussion

5.2.1 Reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4, 6) with PPh_3

Mononuclear alkyliron compounds of the type $[CpFe(CO)_2R]$ (R = alkyl) are known to undergo carbonyl insertion reactions with tertiary phosphines under thermal conditions to yield phosphine-susbtituted acyl compounds [14] as depicted in equation 5.2.

$$[(Cp)Fe(CO)_2R] \xrightarrow{PPh_3\text{, reflux}} [(Cp)(PPh_3)(CO)FeC(O)R] \qquad (5.2)$$

Another established route to the formation of mononuclear alkyliron compounds is *via* the photochemical decarbonylation of the corresponding acyl species [15,16].

These compounds have also been prepared by the reaction of $[CpFe(CO)_2R$ (R = alkyl) with PPh_3 under UV irradiation [15].

Davies *et al.* reported on a similar reaction for the β–hydroxyethyl iron complex, $[(CpFe)(CO)_2\{(CH_2)_2OH\}]$, yielding an iron acyl complex as illustrated below [17]:

$$[(Cp)Fe(CO)_2\{CH_2CH_2OH\}] + PPh_3 \xrightarrow{\text{THF, reflux}} [(Cp)(PPh_3)(CO)FeC(O)CH_2CH_2OH] \qquad (5.3)$$

The reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4,6) with triphenylphosphine followed a similar trend resulting in the formation of $[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_nCH_2OH]$ (compounds **19 – 22**).

$$\begin{gathered}[(Cp)Fe(CO)_2\{CH_2(CH_2)_nCH_2OH\}] + PPh_3 \\ \Big\downarrow \text{THF, reflux} \\ [(Cp)(PPh_3)(CO)FeC(O)CH_2(CH_2)_nCH_2OH] \\ n = 2\text{-}4,\ 6\end{gathered} \qquad (5.4)$$

These reactions were carried out under reflux in a THF solution and were easily monitored by IR spectroscopy by following the replacement of the carbonyl bands of ω-hydroxyalkyl complexes at ν(CO) 2001 and 1940 cm^{-1}, with that of the carbonyl bands for the iron acyl complexes at ν(CO) 1914 and 1604 cm^{-1}. The reaction was found to be complete within 24 hours. The products were isolated as stable orange-yellow oils. In some instances it was possible to recrystallise the products to yield very low melting point solids. Compounds **20** and **21** were thus isolated as orange crystalline solids which melts at room temperature.

5.2.1 a) IR spectra

The infrared spectral data for compounds **19 – 22** are summarized in Table 5.1. The IR spectrum of all the compounds shows a single terminal ν(CO) band at 1914 cm^{-1}. This position reflects the π-acceptor properties of the tertiary phosphine ligand. A broad band at 1604 cm^{-1} for the acyl carbonyl is also observed in all the spectra. A strong broad band in the region 2900 cm^{-1} was assigned to the ν(OH) frequency of the hydroxy functionality.

5.2.1 b) ^{1}H NMR spectra

The ^{1}H nmr spectral data for compounds **19-22** are summarized in Tables **5.2.** The ^{1}H nmr spectra of all the products exhibit similar trends. From the ^{1}H NMR spectra of compounds **19–22** it appears that the compounds exists as diastereo isomers. Splitting of the signal for the CH_2CO protons gives rise to two resonances at 2.5ppm and 2.8 ppm. In addition two cyclopentadienyl resonances at 4.40 and 4.41 ppm are also observed in all the spectra. The extent of splitting of the CH_2CO protons does not vary noticeably with increasing length of the alkyl chain. The splitting of the CH_2CO proton signals could arise from the diastereomeric shielding of these protons by the asymmetric [CpFe(CO)(L)] groups. In this case, the two protons in each CH_2CO group would be non-equivalent and coupling between these protons could give rise to the observed splitting. Such shielding effects have been reported for the compounds $[(Cp)(CO)(PPh_3)Fe\{COC_2H_5\}]$ [18] and $[(Cp)(CO)(PPh_3)Fe\{COCH_2Ph\}]$ [19]. Detailed studies on the preferred conformations of alkyl groups attached to the chiral auxillary $Fe(Cp)(CO)(PPh_3)$ in mononuclear compounds have also been reported [20, 21].

All the compounds exhibit a distinct triplet at 3.58 ppm for the protons attached to the carbon adjacent to the hydroxyl group. The aromatic protons attached to the triphenylphosphine moiety resonates in the region 7.3 - 7.6 ppm. The remaining aliphatic protons were assigned to the signals in the region in the region 0.8 – 1.5 ppm.

5.2.1 c) ^{13}C NMR spectra

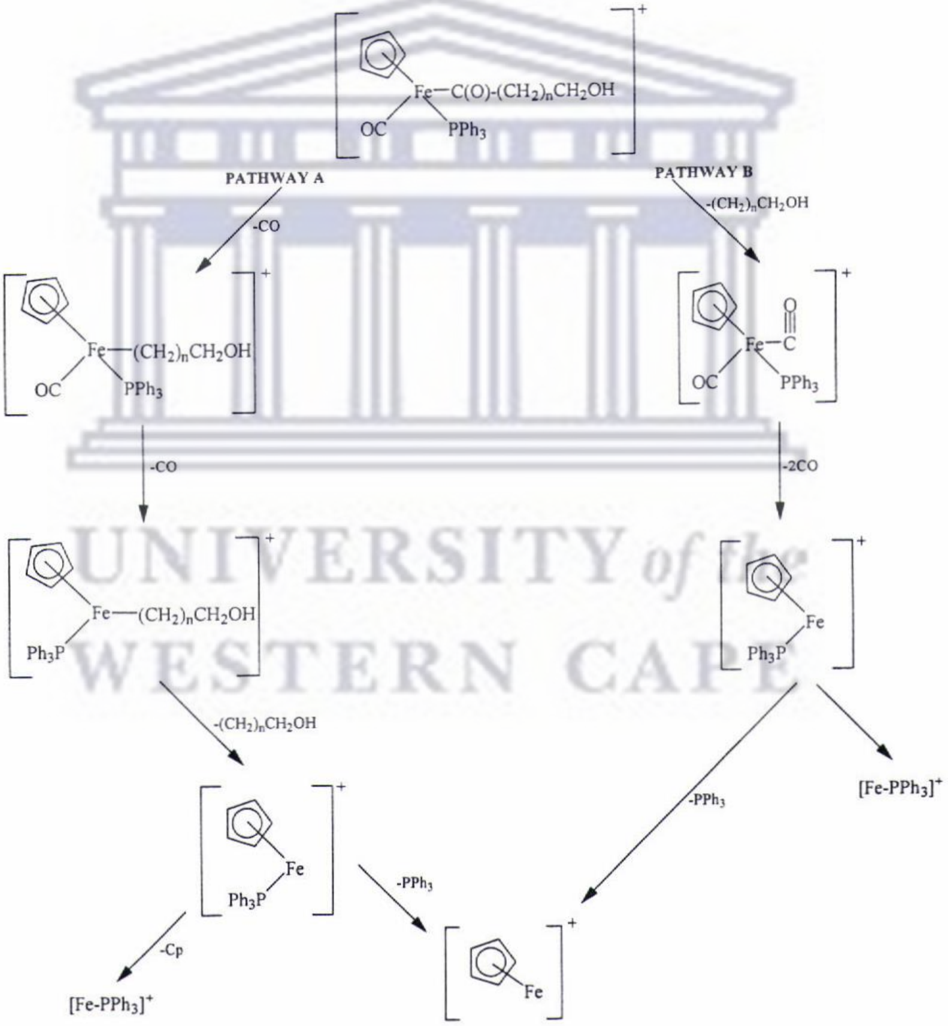
The ^{13}C NMR spectra for the series of $[(Cp)(PPh_3)(CO)Fe\{C(O)CH_2(CH_2)_nCH_2OH\}]$ $(n = 2 - 4, 6)$, complexes **(19- 22)** show a carbonyl resonance at δ 220 ppm. The variation of the hydrocarbon chain length had no significant effect on the chemical shift of these peaks. The carbon atom adjacent to the acyl carbonyl ($Fe\text{-}C(O)\underline{C}H_2\sim$) was assigned to the peak in the region 65 - 66 ppm . The carbon atoms adjacent to the hydroxy group for complexes **19-22**, were assigned to the peaks in the region 62-63 ppm. The intense peak at δ ~ 85 ppm observed in all the spectra is due to the cyclopentadienyl carbons. The remaining aliphatic carbons were assigned to the peaks in the region 20-40 ppm. The ^{13}C NMR spectral data for compounds **19-22** are summarized Tables **5.2.**

5.2.1 d) Mass spectra

The complexes were analyzed using Fast Atom Bombardment mass spectrometry (FAB-MS). (M+H) ion peaks are observed in the mass spectra of all the compounds **19–22**. All the spectra show several peaks which are characteristic of compounds containing the $[(Cp)Fe(CO)_2]$ group.

Two fragmentation pathways are discernible for all the compounds. The first pathway, (pathway A, Scheme 5.2), involves initial loss of the carbonyl ligands (either sequentially or simultaneously) to ultimately give $[(Cp)(PPh_3)Fe(C_nH_{2n}OH)]^+$. This is followed by loss of the hydroxy functionalised alkyl chain resulting in the $[(Cp)(PPh_3)Fe]^+$ ion (m/e 383). The cyclopentadienyl or triphenylphosphine ligand is then eliminated to give the ions $[(Cp)Fe]^+$ (m/e 121) or $[(PPh_3)Fe]^+$ (m/e 318).

The second pathway, (pathway B, Scheme 5.2), involves the loss of the hydroxyalkyl ligand from the acyl moiety resulting in $[(Cp)(CO)_2(PPh_3)Fe)]^+$ (m/e 439), followed by the loss of the carbonyl ligands resulting in $[(Cp)(PPh_3)Fe]^+$ (m/e 383). Loss of either the cyclopentadienyl or triphenylphosphine ligand once again gives the ions $[(C_5H_5)Fe]^+$ (m/e 121) and $[(PPh_3)Fe]^+$ (m/e 318). The possible fragmentation pathway summarised in Scheme 5.2 resemble similar fragmentation routes for iron alkyls, $[CpFe(CO)_2R]$. The assignments of the major peaks in the mass spectra of compounds **19-22** are summarised in Table 5.4.



Scheme 5.2: Possible fragmentation patterns for the ω-hydroxyalkyl iron complexes, $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7), i.e. compounds **19-22.**

Table 5.1 Yields, micro-analytical and infrared spectral data for the products obtained from reactions $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7) with triphenylphosphine

Compound	**Yield**	**[a]Analysis**		**[b]ν(CO)cm^{-1}**	**[b]ν(OH)cm^{-1}**
	(%)	**C**	**H**		
$[(Cp)(CO)(PPh_3)Fe\{C(O)(CH_2)_3CH_2OH\}]$ **19**	31	67.92 (67.58)	6.32 (6.26)	1914(s) 1601(m)	2934 (br)
$[(Cp)(CO)(PPh_3)Fe\{C(O)(CH_2)_4CH_2OH\}]$ **20**	49	68.21 (68.06)	6.23 (6.47)	1913(s) 1604(m)	2934 (br)
$[(Cp)(CO)(PPh_3)Fe\{C(O)(CH_2)_5CH_2OH\}]$ **21**	78	67.92 (67.58)	6.47 (6.26)	1913(s) 1604(m)	2930 (br)
$[(Cp)(CO)(PPh_3)Fe\{C(O)(CH_2)_7CH_2OH\}]$ **22**	38	70.37 (69.36)	6.51 (6.47)	1913(s) 1604(m)	2931 (br)

[a] Calculated values in parentheses.

[b] CH_2Cl_2 solution in NaCl solution cells, s = strong, m = medium, br = broad.

Table 5.2: ^1H NMR spectral data compounds **19-22**

Compound no	**Chemical shift (δ-ppm)[a]**	**Assignment**
19	0.80-1.6	(2 xm, 4H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(C\underline{H_2})_2CH_2OH]$
	2.56	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_2CH_2OH]^b$
	2.87	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_2CH_2OH]^b$
	3.50	(t, 2H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_2C\underline{H_2}OH]$
	4.40, 4.41	(2xs, 5H, $C_5\underline{H}_5)^b$
	7.30-7.60	(m, 15H) $[(Cp)(P\underline{Ph_3})(CO)Fe\text{-}C(O)CH_2(CH_2)_2CH_2OH]$
20	0.80-1.6	(3xm, 6H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2C\underline{H_2})_3CH_2OH]$
	2.54	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_3CH_2OH]^b$
	2.80	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}CH_2)_3CH_2OH]^b$
	3.53	(t, 2H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_3C\underline{H_2}OH]$
	4.40, 4.41	(2xs, 5H, $C_5\underline{H}_5)^b$
	7.30-7.60	(m, 15H) $[(Cp)(P\underline{Ph_3})(CO)Fe\text{-}C(O)CH_2(CH_2)_3CH_2OH]$

[a] $CDCl_3$ as solvent

[b] compounds were isolated as diastereo isomers

Table 5.2 continued

Compound no	Chemical shift (δ-ppm)[a]	Assignment
21	0.80-1.6	(4xm, 8H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2C\underline{H_2})_{\underline{4}}CH_2OH]$
	2.56	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_4CH_2OH]^b$
	2.83	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_{\underline{4}}CH_2OH]^b$
	3.54	(t, 2H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_{\underline{2}}(CH_2)_4C\underline{H_2}OH]$
	4.40, 4.41	$(2xs, 5H, C_5\underline{H_5})^b$
	7.20-7.60	(m, 15H) $[(Cp)(P\underline{Ph_3})(CO)Fe\text{-}C(O)CH_2(CH_2)_4CH_2OH]$
22	0.80-1.6	(m, 12H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(C\underline{H_2})_{\underline{6}}CH_2OH]$
	2.54	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}(CH_2)_6CH_2OH]^b$
	2.80	(m, 1H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)C\underline{H_2}CH_2)_6CH_2OH]^b$
	3.61	(t, 2H) $[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_{\underline{2}}(CH_2)_6C\underline{H_2}OH]$
	4.40, 4.41	$(2xs, 5H, C_5\underline{H_5})^b$
	7.20-7.60	(m, 15H) $[(Cp)(P\underline{Ph_3})(CO)Fe\text{-}C(O)CH_2(CH_2)_6CH_2OH$

[a] $CDCl_3$ as solvent

[b] compounds were isolated as diastereo isomers

Table 5.3: ^{13}C NMR spectral data compounds **19-22**

Compound No	Chemical shift (δ-ppm)[a]	Assignment
19	20.63, 32.35	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(\underline{C}H_2)_2CH_2OH}]$
	62.24	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_2\underline{C}H_2OH}]$
	65.50	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)\underline{C}H_2(CH_2)_2CH_2OH}]$
	85.27	$\mathrm{\underline{C}_5H_5}$
	127.94 – 136.84	$[\mathrm{(Cp)((P\underline{Ph}_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_2CH_2OH}]$
	219	CO
20	25.07, 25.60, 32.54, 62.31	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(\underline{C}H_2)_3CH_2OH}]$
	66.10	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2CH_2)_3\underline{C}H_2OH}]$
	85.22	$[\mathrm{(Cp)(PPh_3)(CO)Fe\text{-}C(O)\underline{C}H_2(CH_2)_3CH_2OH}]$
	127.90 – 136.91	$\mathrm{\underline{C}_5H_5}$
	219	$[\mathrm{(Cp)(P\underline{Ph}_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_3CH_2OH}]$
		CO

[a] $\mathrm{CDCl_3}$ as solvent

Table 5.3 continued

Compound No	**Chemical shift (δ-ppm)^a**	**Assignment**
21	25.04, 25.58, 28.89, 32.67	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(\underline{C}H_2)_4CH_2OH]$
	63.07	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2CH_2)_4\underline{C}H_2OH]$
	66.12	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)\underline{C}H_2(CH_2)_4CH_2OH]$
	85.25	$\underline{C}_5H_5$
	127.91 – 136.97	$[(Cp)(P\underline{Ph}_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_4CH_2OH]$
	219	CO
22	25.01, 25.62, 29.00, 29.19, 29.39, 32.75	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2(\underline{C}H_2)_6CH_2OH]$
	62.87	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)CH_2CH_2)_6\underline{C}H_2OH]$
	66.35	$[(Cp)(PPh_3)(CO)Fe\text{-}C(O)\underline{C}H_2(CH_2)_6CH_2OH]$
	85.16	$\underline{C}_5H_5$
	127.82 – 136.93	$[(Cp)(P\underline{Ph}_3)(CO)Fe\text{-}C(O)CH_2(CH_2)_6CH_2OH$
	220	CO

^{a}CDCl$_3$ as solvent

Table 5.4: Mass spectral data for the complexes $[(Cp)(PPh_3)(CO)Fe\{C(O)CH_2(CH_2)_nCH_2OH\}]$ (n = 2–4, 6), compounds **19-22**

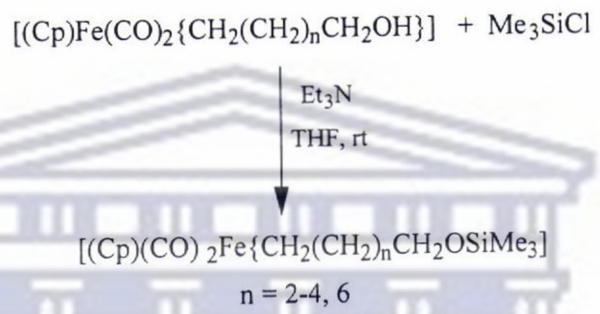
Ion[a]	Relative Intensities			
	19[b]	**20**[b]	**21**[b]	**22**[b]
M+H	4.84	6.79	15.71	14.47
M-CO	-	2.82	8.11	9.03
M-2CO	4.87	4.96	6.48	4.81
M-2CO-OH-C_nH_{2n}	100	100	100	100
M-2CO-OH-C_nH_{2n}-PPh_3	9.00	11.74	14.97	15.04
M-2CO-OH-C_nH_{2n}-Cp	10.81	14.94	16.54	34.01
M-2CO-Cp	2.02	3.19	5.87	7.74
M-2CO-Cp-C_nH_{2n}	5.42	4.89	7.59	14.43
M-2CO-PPh_3	2.28	2.79	3.52	-
M-2CO-PPh_3-Cp	1.41	-	3.34	18.40
M-2CO-PPh_3-C_nH_{2n}	-	9.52	10.87	-
M-OH-C_nH_{2n}	30.24	38.90	65.12	66.54

[a] All the ions have a single positive charge, M = $[(Cp)(PPh_3)(CO)Fe\{C(O)CH_2(CH_2)_nCH_2OH\}]$, (n = 2–4, 6).

[b] Peak intensities relative to base peak at m/e 383.

5.2.2 Reactions of $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7) with $ClSiMe_3$

The ω-hydroxyalkyl iron complexes, $[(C_5H_5)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 2-5, 7), reacts with trimethylchlorsilane under basic conditions to give the corresponding silylether derivatives $[(C_5H_5)(CO)_2Fe\{(CH_2)_nCH_2OSiMe_3]$, compounds **23 - 26**.



$$[(Cp)Fe(CO)_2\{CH_2(CH_2)_nCH_2OH\}] + Me_3SiCl \xrightarrow[\text{THF, rt}]{Et_3N} [(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OSiMe_3]$$

n = 2-4, 6

(5.5)

These reactions were carried out at room temperature and were found to be complete within 1 hour. The products were isolated as yellow/brown oils. The reaction conditions used in this study are very similar to those reported for the conversion of primary alcohols to silylether derivatives [22]. These complexes are however thermally less stable and the yields are much lower in comparison to the silylether derivatives derived from primary alcohols. This could be due to the influence of the metal centre which affects the thermal stability. In solution and even under nitrogen, these complexes appears to decompose relatively rapidly evident by the appearance of a fine brown solid which forms in solution.

The IR spectra of the compounds show two sharp bands in the ν(CO) region at 2001 cm^{-1} and 1940 cm^{-1}, similar to those of the starting ω-hydroxyalkyl compounds.

The ^1H NMR of all the compounds shows a characteristic triplet at ~3.56 ppm for the protons attached to the carbon adjacent to the oxygen (CH_2O) and an intense singlet at ~ 0.1 ppm for the methyl moeity of the trimethylsilyl group. Varying the length of the alkyl chain had no significant effect on the position of the CH_2O resonances. The remaining aliphatic protons were assigned to the signals in the region 0.8 – 1.6 ppm. The IR, ^{1}H and ^{13}C NMR data for compounds **23–26** are summarized in Tables **5.5 – 5.7**.

Table 5.5: Yields, and infrared spectral data for products obtained from reactions $[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OH\}]$ (n = 3-5, 7) with trimethylchlorosilane

Compound	**Compound**	**Yield (%)**	**$^a\nu(CO)cm^{-1}$**
$[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OSiMe_3]$	**23**	56	2001(s) 1940(s)
$[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OSiMe_3]$	**24**	58	2001(s) 1940(s)
$[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OSiMe_3]$	**25**	65	2001(s) 1940(s)
$[(Cp)(CO)_2Fe\{(CH_2)_nCH_2OSiMe_3]$	**26**	54	2001(s) 1940(s)

$^a CH_2Cl_2$ solution in NaCl solution cells, s = strong

Table 5.6: ^{1}H NMR spectral data compounds **23-26.**

Compound	Chemical shift (δ-ppm)[a]	Assignment
23	0.10	(s, 9H) $Fp-CH_2(CH_2)_2CH_2-OSi(C\underline{H_3})_3$
	0.84	(t, 2H) $Fp-C\underline{H_2}(CH_2)_2CH_2-OSi(CH_3)_3$
	1.2-1.6	(m, 4H) $Fp-CH_2(C\underline{H_2})_{\underline{2}}CH_2-OSi(CH_3)_3$
	3.57	(t, 2H) $Fp-CH_2(CH_2)_2C\underline{H_2}-OSi(CH_3)_3$
	4.72	(s, 5H) $C_5\underline{H_5}$
24	0.10	(s, 9H) $Fp-CH_2(CH_2)_3CH_2-OSi(C\underline{H_3})_3$
	0.85	(t, 2H) $Fp-C\underline{H_2}(CH_2)_3CH_2-OSi(CH_3)_3$
	1.2-1.6	(m, 6H) $Fp-CH_2(C\underline{H_2})_{\underline{3}}CH_2-OSi(CH_3)_3$
	3.55	(t, 2H) $Fp-CH_2(CH_2)_3C\underline{H_2}-OSi(CH_3)_3$
	4.75	(s, 5H) $C_5\underline{H_5}$
25	0.10	(s, 9H) $Fp-CH_2(CH_2)_4CH_2-OSi(C\underline{H_3})_3$
	0.82	(t, 2H) $Fp-C\underline{H_2}(CH_2)_4CH_2-OSi(CH_3)_3$
	1.2-1.6	(m, 8H) $Fp-CH_2(C\underline{H_2})_{\underline{4}}CH_2-OSi(CH_3)_3$
	3.56	(t, 2H) $Fp-CH_2(CH_2)_4C\underline{H_2}-OSi(CH_3)_3$
	4.72	(s, 5H) $C_5\underline{H_5}$
26	0.10	(s, 9H) $Fp-CH_2(CH_2)_6CH_2-OSi(C\underline{H_3})_3$
	0.87	(t, 2H) $Fp-C\underline{H_2}(CH_2)_6CH_2-OSi(CH_3)_3$
	1.2-1.6	(m, 12H) $Fp-CH_2(C\underline{H_2})_{\underline{6}}CH_2-OSi(CH_3)_3$
	3.58	(t, 2H) $Fp-CH_2(CH_2)_6C\underline{H_2}-OSi(CH_3)_3$
	4.74	(s, 5H) $C_5\underline{H_5}$

[a] $CDCl_3$ as solvent

Table 5.7: ^{13}C NMR spectral data compounds **23-26.**

Compound	**Chemical shift** (δ-ppm)[a]	**Assignment**
23	0.43	$Fp\text{-}CH_2(CH_2)_2CH_2\text{-}OSi(\underline{C}H_3)_3$
	3.17	$Fp\text{-}\underline{C}H_2(CH_2)_2CH_2\text{-}OSi(CH_3)_3$
	34.22, 37.69	$Fp\text{-}CH_2(\underline{C}H_2)_2CH_2\text{-}OSi(CH_3)_3$
	62.36	$Fp\text{-}CH_2(CH_2)_2\underline{C}H_2\text{-}OSi(CH_3)_3$
	85.27	C_5H_5
	217.57	CO
24	0.46	$Fp\text{-}CH_2(CH_2)_3CH_2\text{-}OSi(\underline{C}H_3)_3$
	3.42	$Fp\text{-}\underline{C}H_2(CH_2)_3CH_2\text{-}OSi(CH_3)_3$
	30.87, 32.42, 36.00	$Fp\text{-}CH_2(\underline{C}H_2)_3CH_2\text{-}OSi(CH_3)_3$
	62.80	$Fp\text{-}CH_2(CH_2)_3\underline{C}H_2\text{-}OSi(CH_3)_3$
	85.28	C_5H_5
	217.58	CO

[a] $CDCl_3$ as solvent

Table 5.7 continued

Compound	**Chemical shift** **(δ-ppm)**[a]	**Assignment**
25	0.46	$Fp-CH_2(CH_2)_4CH_2-OSi(\underline{C}H_3)_3$
	3.55	$Fp-\underline{C}H_2(CH_2)_4CH_2-OSi(CH_3)_3$
	25.54, 32.81, 34.58, 38.22	$Fp-CH_2(\underline{C}H_2)_4CH_2-OSi(CH_3)_3$
	62.78	$Fp-CH_2(CH_2)_4\underline{C}H_2-OSi(CH_3)_3$
	85.27	$\underline{C}_5H_5$
	217.64	CO
26	0.43	$Fp-CH_2(CH_2)_6CH_2-OSi(\underline{C}H_3)_3$
	3.75	$Fp-\underline{C}H_2(CH_2)_6CH_2-OSi(CH_3)_3$
	25.75, 29.32, 29.55, 32.78, 34.83, 38.33	$Fp-CH_2(\underline{C}H_2)_6CH_2-OSi(CH_3)_3$
	62.81	$Fp-CH_2(CH_2)_6\underline{C}H_2-OSi(CH_3)_3$
	85.33	$\underline{C}_5H_5$
	217.74	CO

[a] $CDCl_3$ as solvent

5.2.3 Reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ ($n = 2\text{-}4, 6$) with acryloyl chloride

Acrylic esters can be formed by reacting alcohols with acryloyl chloride. Acrylic esters are useful building blocks for macromolecular materials acting as monomers in addition polymerization. Our aim was to carry out similar esterification reactions using the ω-hydroxyalkyl iron complexes to produce iron containing acrylic esters. These new materials could potentially be employed in free radical polymerization to produce organometallic polymers. The ω-hydroxyalkyl iron complexes, $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ ($n = 2\text{-}4, 6$) was found to react with acryloyl chloride under basic conditions resulting in the corresponding esters **27 - 30** (Equation 5.6).

$$\begin{array}{c} [(Cp)Fe(CO)_2\{CH_2(CH_2)_nCH_2OH\}] \ + \ CH_2{=}CHC(O)Cl \\ \Big\downarrow \begin{array}{l} \text{THF, rt} \\ Et_3N \end{array} \\ [(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2O\text{-}C(O)CH{=}CH_2] \\ n = 2 - 4, 6 \end{array} \qquad (5.6)$$

These reactions were carried out at room temperature and were found to be complete within 2 hours . The products were isolated as yellow/brown oils in 39-51 % yields . The nature of these products are similar to those of the ω-hydroxyalkyl compounds in that they are unstable and decompose in solution and in the presence of air or light. Complexes **27 – 30** were characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy. The analytical data are summarized in Tables **5.8 – 5.10**.

The IR spectra of the compounds shows two sharp bands in the ν(CO) region at 2001 cm^{-1} and 1940 cm^{-1}, similar to those of the starting ω-hydroxyalkyl compounds. Two bands of medium intensity was at 1636 cm^{-1} and 1620 cm^{-1} was assigned to the ν(CO) of the acyl group and the ν(C=C) of the vinylic group respectively.

The ^{1}H NMR of all the compounds shows signals which are characteristic of a species containing a vinylic functionality. The spectra of all the compounds shows two doublets and an unresolved multiplet in the region δ 5.8 – 6.4 ppm. Each of these signals integrates for 1 proton and were assigned to the vinylic protons ($CH=CH_2$). The spectra of all the compounds shows a distinct triplet at δ ~ 4.1 ppm for the CH_2O protons. These protons exhibit a downfield shift of ~ 0.4 ppm in comparison to the starting ω-hydroxyalkyl compounds. This downnfield chemical shift is due to the presence of the neighbouring carbonyl and vinylic protons.

The intense singlet at δ~ 4.7 ppm observed in all the spectra were assigned to the protons attached to the cyclopentadienyl ring. The remaining aliphatic protons were assigned to the signals in the region δ 0.8 – 1.7 ppm.

Table 5.8 Yields, melting points and IR data for [(Cp) $(CO)_2Fe\{CH_2(CH_2)_nCH_2O\text{-}C(O)\text{-}CH{=}CH_2\}$] (n = 2-4, 6), compounds **27** - **30**.

Compound	**Yield (%)**	**$^a\nu(CO)/cm^{-1}$**	**$^a\nu(C(O)R)cm^{-1}$**	**$^a\nu(C{=}C)cm^{-1}$**
$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$ **27**	51	1998(s) 1940(s)	1636(m)	1619(m)
$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$ **28**	39	2000(s) 1937(s)	1637(m)	1620(m)
$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$ **29**	45	2001(s) 1940(s)	1636(m)	1617(m)
$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$ **30**	30	1997(s) 1939(s)	1632(m)	1615(m)

[a] Neat oil between NaCl plates, s = strong, m = medium.

Table 5.9: ^{1}H NMR spectral data compounds **27-30.**

Compound	Chemical shift (δ-ppm)[a]	Assignment
27	0.86	(t, 2H) $[(Cp)(CO)_2Fe\{C\underline{H}_2(CH_2)_2CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	1.21 – 1.60	(m, 4H) $[(Cp)(CO)_2Fe\{CH_2(C\underline{H}_2)_2CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.16	(t, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2C\underline{H}_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.72	(s, 5H) $C_5\underline{H}_5$
	5.80	(m, 1H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}C(O)\text{-}C\underline{H}{=}CH_2\}]$
	6.13, 6.36	(2xm, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}C(O)\text{-}CH{=}C\underline{H}_2\}]$
28	0.87	(t, 2H) $[(Cp)(CO)_2Fe\{C\underline{H}_2(CH_2)_3CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	1.20 – 1.71	(m, 6H) $[(Cp)(CO)_2Fe\{CH_2(C\underline{H}_2)_3CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.12	(t, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3C\underline{H}_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.71	(s, 5H) $C_5\underline{H}_5$
	5.81	(m, 1H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}C(O)\text{-}C\underline{H}{=}CH_2\}]$
	6.13, 6.35	(2xm, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}C(O)\text{-}CH{=}C\underline{H}_2\}]$
29	0.85	(t, 2H) $[(Cp)(CO)_2Fe\{C\underline{H}_2(CH_2)_4CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	1.22 – 1.73	(m, 8H) $[(Cp)(CO)_2Fe\{CH_2(C\underline{H}_2)_{\underline{4}}CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.14	(t, 2H $[(Cp)(CO)_2Fe\{CH_2(CH_2)_4C\underline{H}_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.72	(s, 5H) $C_5\underline{H}_5$
	5.84	(m, 1H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}C(O)\text{-}C\underline{H}{=}CH_2\}]$
	6.13, 6.35	(2xm, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}C(O)\text{-}CH{=}C\underline{H}_2\}]$
30	0.86	$[(Cp)(CO)_2Fe\{C\underline{H}_2(CH_2)_6CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	1.23 – 1.69	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_{\underline{6}}CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.16	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6C\underline{H}_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	4.72	(s, 5H) $C_5\underline{H}_5$
	5.80	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}C(O)\text{-}C\underline{H}{=}CH_2\}]$
	6.13, 6.36	(2xm, 2H)$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}C(O)\text{-}CH{=}C\underline{H}_2\}]$

[a] $CDCl_3$ as solvent

Table 5.10: ^{13}C NMR spectral data compounds **27-30.**

Compound	Chemical shift (δ-ppm)[a]	Assignment
27	1.88	$[(Cp)(CO)_2Fe\{\underline{C}H_2(CH_2)_2CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	32.86, 33.56	$[(Cp)(CO)_2Fe\{CH_2(\underline{C}H_2)_2CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	63.79	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2\underline{C}H_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	84.79	$\underline{C}_5H_5$
	128.32	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}C(O)\text{-}CH{=}\underline{C}H_2\}]$
	129.77	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}C(O)\text{-}\underline{C}H{=}CH_2\}]$
	166.30	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2O\text{-}\underline{C}(O)\text{-}\underline{C}H{=}CH_2\}]$
	217.65	CO
28	2.97	$[(Cp)(CO)_2Fe\{\underline{C}H_2(CH_2)_3CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	28.24, 30.83, 37.68	$[(Cp)(CO)_2Fe\{CH_2(\underline{C}H_2)_3CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	64.77	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3\underline{C}H_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	85.24	$\underline{C}_5H_5$
	128.64	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}(O)\text{-}CH{=}\underline{C}H_2\}]$
	130.27	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}C(O)\text{-}\underline{C}H{=}CH_2\}]$
	166.2	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_3CH_2O\text{-}\underline{C}(O)\text{-}CH{=}CH_2$
	217.63	$\underline{C}O$

[a] $CDCl_3$ as solvent

Table 5.10 continued

Compound No	Chemical shift(δ-ppm)[a]	Assignment
29	3.32	$[(Cp)(CO)_2Fe\{\underline{C}H_2(CH_2)_4CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	25.63, 28.69, 34.35, 38.05	$[(Cp)(CO)_2Fe\{CH_2(\underline{C}H_2)_4CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	64.75	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4\underline{C}H_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	85.30	$\underline{C}_5H_5$
	128.71	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}C(O)\text{-}CH{=}\underline{C}H_2\}]$
	130.29	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}C(O)\text{-}\underline{C}H{=}CH_2\}]$
	166.33	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_4CH_2O\text{-}\underline{C}(O)\text{-}CH{=}CH_2\}]$
	217.64	$\underline{C}O$
30	3.59	$[(Cp)(CO)_2Fe\{\underline{C}H_2(CH_2)_6CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	25.93, 28.61, 29.23, 29.31, 34.73, 38.24	$[(Cp)(CO)_2Fe\{CH_2(\underline{C}H_2)_6CH_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	64.75	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6\underline{C}H_2O\text{-}C(O)\text{-}CH{=}CH_2\}]$
	85.30	$\underline{C}_5H_5$
	128.71	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}C(O)\text{-}CH{=}\underline{C}H_2\}]$
	130.29	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}C(O)\text{-}\underline{C}H{=}CH_2\}]$
	166.33	$[(Cp)(CO)_2Fe\{CH_2(CH_2)_6CH_2O\text{-}\underline{C}(O)\text{-}CH{=}CH_2\}]$
	217.64	$\underline{C}O$

[a] $CDCl_3$ as solvent

5.3 Conclusion

The reactions of the ω-hydroxyalkyl iron complexes, $[(C_5H_5)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4, 6) were found to take place at either the metal centre or at the hydroxy group. For the reactions of ω-hydroxyalkyl iron complexes with triphenylphosphine the reactions was found to take place at the metal centre *via* a "carbonyl insertion" reaction resulting in the corresponding acyl iron complexes. The reactions of with silyl and acryloyl chloride on the other hand was found to take place at the hydroxy group and proceed in a similar manner to those for primary alcohols.

5.4 Experimental

General Procedures

All experiments, unless otherwise stated, were carried out under nitrogen using typical Schlenk line techniques. Triphenylphoshine was purchased from Merck. Trichloromethylsilane and acryloyl chloride was purchased from Sigma-Aldrich. All these reagents were used as purchased without further purification. Tetrahydrofuran was distilled from sodium/benzophenone ketyl under nitrogen. All solvents were maintained over molecular sieves, and degassed prior to use. All column chromatography was performed using deactivated alumina 90 (70 - 230 mesh) purchased from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using NaCl solution cells. NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^{1}H NMR and 50.30 MHz for ^{13}C NMR, using tetramethylsilane as an internal standard. Elemental analyses were performed at the micro-analytical laboratory of the University of Western Cape.

5.4.1 Reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4, 7) with PPh_3

The reaction of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2OH\}]$ with PPh_3 is outlined below to illustrate the general procedure used.

A solution of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2OH\}]$ (0.1g, 0.39 mmol) in dry THF (10 ml) was treated with PPh_3 (0.1g, 0.39 mmol). The reaction mixture was allowed to reflux under an inert atmosphere for approximately 1 day. The resulting yellow-orange reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered into a round bottom flask and the solvent was removed by rotatory evaporation leaving a orange-yellow oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution chromatographed on a neutral alumina column made up in ether. Elution with ether gave a orange band, which on the removal of the solvent, yielded the product as an orange-yellow oil (30-80 % yield).

For compounds **20 and 21** recrystallisation with hexane/ether afforded the product as a orange-yellow crystalline solid which melts at room temperature.

5.4.2 Reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4, 6) with $ClSiMe_3$

A solution of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2OH\}]$ (0.1g, 0.39 mmol) in dry THF (10 ml) was treated with $ClSiMe_3$ (0.05 ml, 0.39 mmol). Et_3N (0.05ml, 0.38 mmol) was added to the reaction mixture. The reaction goes pale yellow and a white precipitate forms almost immediately. The reaction mixture was allowed to stir at room temperature for approximately 2 hours.

The reaction mixture was filtered into a round bottom flask and the solvent was removed by rotatory evaporation leaving a yellow oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution chromatographed on a neutral alumina column made up in hexane. Elution with hexane gave a yellow band, which on removal of the solvent, yielded the product as a unstable yellow/brown oil, identified as $[(Cp)(CO)_2Fe\{(CH_2)_3CH_2OSiMe_3]$ (compound **24**).

In a similar manner compounds **23 – 26** were iolated as yellow/brown oils in 50-65% yields using $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ where n = 3-4, 6 respectively.

5.4.3 Reactions of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_nCH_2OH\}]$ (n = 2-4, 6) with acryloyl chloride

A solution of $[(Cp)(CO)_2Fe\{CH_2(CH_2)_2CH_2OH\}]$ (0.1g, 0.39 mmol) in dry THF (10 ml) was treated with $CH_2{=}CHCOCl$ (0.04 ml, 0.39 mmol). To the stirred solution, Et_3N (0.23 ml, 1.68 mmol) was added. The reaction goes pale yellow and a white precipitate forms almost immediately. The reaction mixture was allowed to stir at room temperature for 2 hours.

The white preciptate was filtered off from the reaction mixture and washed thoroughly with THF. The solvent was removed from the filtrate resulting in a yellow brown oil remaining. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution was chromatographed on a neutral alumina column made up in hexane. Elution with hexane yielded the product as a yellow/brown oil. This was identied as $[(Cp)(CO)_2Fe\{(CH_2)_3CH_2O\text{-}C(O)CH{=}CH_2]$ (compound **27**, 51% yield).

The reactions of $[(Cp)(CO)_2Fe\{CH_2CH_2(CH_2)_nCH_2OH\}]$ (n = 4-5, 7) with $CH_2{=}CHCOCl$ were carried out under the same reaction conditions as the above reaction. The expected products, $[(Cp)(CO)_2Fe\{CH_2\ (CH_2)_3CH_2O\text{-}C(O)CH{=}CH_2]$, compounds **28-30**, were isolated as unstable yellow/brown oils in 39-51% yields.

5.5 References

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