THE SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF SOME MONONUCLEAR HYDROCARBYL COMPOUNDS OF IRON.

by

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A thesis submitted in partial fulfillment of the
requirements for the degree of
Master of Science
in the Department of Chemistry,
University of the Western Cape.

Promoter : Dr. S.F. Mapolie (U.W.C.)

1997

DECLARATION

I declare that **THE SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF SOME MONONUCLEAR HYDROCARBYL COMPOUNDS OF IRON** is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

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Genevieve Joorst

ACKNOWLEDGMENTS

I wish to extend my sincere thanks and appreciation to my supervisor, Dr. S.F. Mapolie, for his guidance, patience and encouragement during this project. It was a growing and learning experience.

I am also thankful to my colleagues and friends in our Chemistry Department (U.W.C.) especially Mr. S. Jansen, Mr. G. Smith, Mr. A. Prins, Ms. R. Karlie, Ms. F. Waggie and Mr. K. Darries for all their friendship, motivation and support.

I wish to thank Mr. G.P. Benin-Casa (U.C.T.) for microanalysis and recording the mass spectra. Mr. D. Handfort (U.C.T.) for the ICP analysis. Mr. A. Myburg (SOMCHEM) for performing the GPC analysis.

I would also like to extend my sincere thanks to my family for their support and understanding.

Financial assistance from the University of the Western Cape and SASOL is acknowledged with thanks.

Abstract

Mononuclear hydrocarbyl compounds of the type $L_nM(CH_2)_nCH=CH_2$ (L_nM = $Cp^*Fe(CO)_2$ and $CpFe(CO)_2$, n = 2-4,6), $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ have been synthesized. All these compounds have been fully characterized using analytical techniques such as IR, ^1H and ^{13}C NMR spectroscopy, microanalysis and mass spectrometry.

The results of some reactivity studies on the above hydrocarbyl compounds are reported in this thesis. For example the reactivity of the η^1-alkenyl compounds $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2 and 3) to hydrozirconation was studied. Although the expected binuclear hydrocarbyl compounds $Cp(CO)_2Fe(CH_2)_{n+2}Zr(Cl)Cp_2$ (n = 2 and 3) were not isolated, their presence in solution were detected by carrying out *in-situ* reactions.

The η^1-alkenyl compounds were also subjected to a β-hydride abstraction reaction. This afforded a series of cationic η^2-diene compounds with general formula $\{Cp(CO)_2Fe(C_nH_{2n-2})\}PF_6$.

Some of the reactions of the ω-hydroxyalkyls were also investigated. The bromination of these hydroxy species leads to the formation of ω-bromoalkyls of the

type $Cp(CO)_2Fe(CH_2)_nBr$ (n = 4 and 8). The ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6, 8) were reacted with trifluoroacetic acid which results in iron-carbon cleavage.

Finally the reaction of some ω-hydroxyalkyls with triflic anhydride gives different results depending on the type of solvent employed. In THF a metal containing polyether is isolated as the major product, while in diethyl ether the major species isolated is a ω-chloroalkyl of the type $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5). In the case of the reaction in THF, a small amount of the binuclear hydrocarbyl compound $[CpFe(CO)_2]\{\mu\text{-}(CH_2)_4\}$ can be isolated if $[CpFe(CO)_2]^-$ is added to the reaction mixture.

LIST OF ABBREVIATIONS

IR	Infrared
NMR	Nuclear magnetic resonance
GPC	Gel permeatation chromatography
ICP	Inductive coupled plasma
Cp	η^5-C_5H_5
Cp*	η^5-$C_5(CH_3)_5$
Fp	$CpFe(CO)_2$
Fp*	$Cp^*Fe(CO)_2$
Ph	Phenyl
THF	Tetrahydrofuran
CH_2Cl_2	Dichloromethane
t.l.c.	Thin layer chromatography
d	days
h	hours
min.	minutes

PUBLICATIONS

CONFERENCE CONTRIBUTIONS

Poster Title : "Synthesis of new μ-Hydrocarbyl Transition-metal complexes.",

G. Joorst and S.F. Mapolie, presented at the 33rd Convention of the South-African Chemical Institute, Cape Town, South Africa (1996)

Poster Title : "The synthesis and functionalization of mononuclear hydrocarbyl iron compounds."

G. Joorst and S.F. Mapolie, presented at the Inorganic '97 Symposium, Port Elizabeth, South Africa (1997)

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CHAPTER 1

INTRODUCTION

1.1 Definition of hydrocarbyl compounds and general motivation for the study.

Reactions involving hydrocarbyl compounds involve many processes of fundamental importance which are central to organometallic chemistry.[1,2]

Hydrocarbyl compounds are defined as complexes in which metal centres are bonded to hydrocarbon fragments. These compounds can be classified as either mononuclear, containing a single metal centre [Figure 1.1], or polynuclear, containing two or more metal centres [Figure 1.2]. Examples of the two types of hydrocarbyl compounds are shown below.

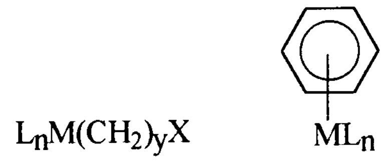


Figure 1.1 Mononuclear hydrocarbyl compounds

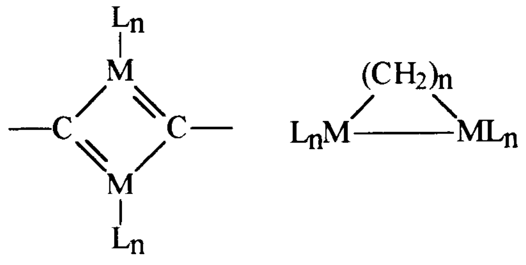
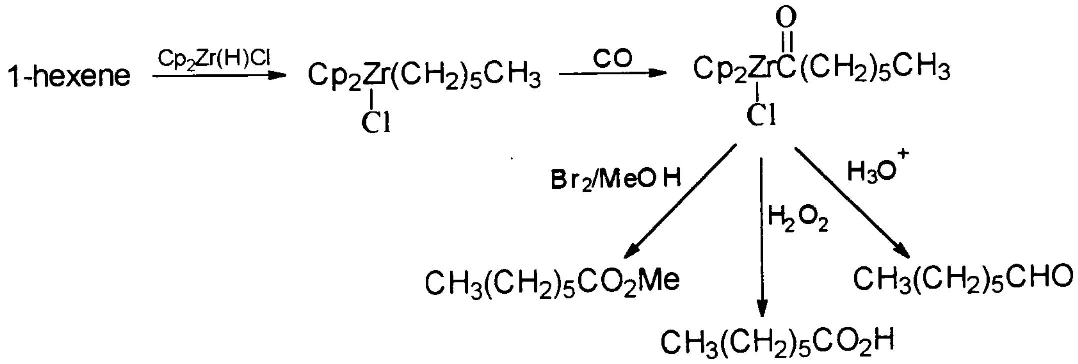


Figure 1.2 Polynuclear hydrocarbyl compounds

L_nM = transition metal and its associated ligands.
X = Br, I, OH *etc.*

Over the years investigations into the synthesis and reactivity of hydrocarbyl compounds have received much attention.[2-6] These studies have reported on a wide variety of hydrocarbyl compounds containing transition metals[2-5] and a few containing main group metals.[6]

The usefulness of hydrocarbyl complexes containing transition metal centres is exemplified by the role they play in organic synthesis.[7-13] Transition metal hydrocarbyl complexes are extensively involved in various synthetic processes leading to the formation of a wide range of organic compounds.[7-11] Here the properties of the organic group coordinated to the transition metal are altered in such a way that it will undergo completely different types of reactions to that of the uncoordinated organic compound. There are numerous examples where hydrocarbyl compounds as intermediates, mediate the conversion of organic compounds. One such example is the carbonylation of olefins via an alkylzirconium intermediate as seen in Scheme 1.1.[7,8]



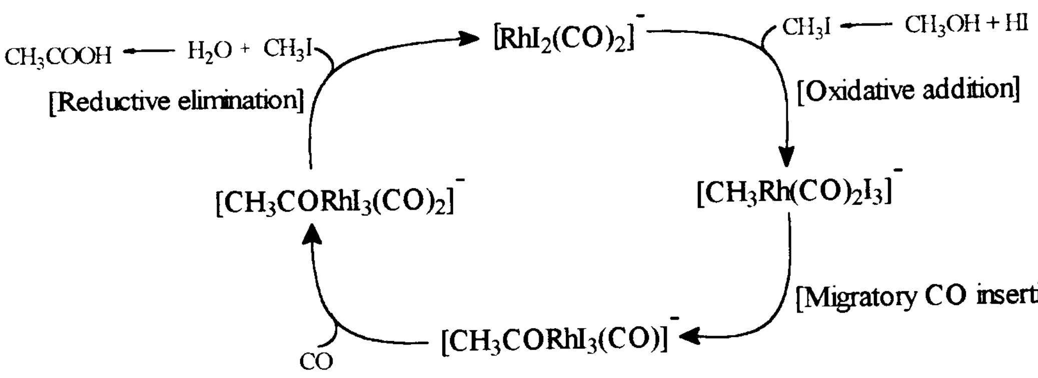
Scheme 1.1 Carbonylation of 1-hexene mediated by $Cp_2Zr(H)Cl$.

Transition metal complexes can also behave as catalysts or catalyst precursors in the transformation of organic compounds. An example is the Monsanto-acetic acid process in which a rhodium complex catalyses the carbonylation of methanol.[12]

Another example is the hydroformylation process where olefins in the presence of synthesis gas, ($CO + H_2$) are transformed into aldehydes and alcohols using a cobalt or rhodium catalyst.[13]

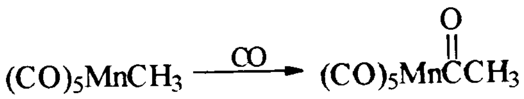
Hydrocarbyl complexes undergo a wide variety of chemical reactions which are common to many catalytic cycles.[14] They may for example act as model compounds for intermediates in catalytic processes, thus giving insight into a number of key reactions.

Some examples of reactions which involve hydrocarbyl compounds and which play an important role in catalytic cycles are exemplified in the Monsanto-acetic acid process [Scheme 1.2].[12]



Scheme 1.2 The mechanism for the Monsanto-acetic acid synthesis.

The Monsanto-acetic acid process is initiated by the oxidative addition of CH_3I to the rhodium centre to afford the hydrocarbyl complex, $[CH_3Rh(CO)_2I_3]^-$. Oxidative addition is the reaction of neutral molecules, such as H_2 or alkyl halides, with a coordinatively unsaturated transition metal complex. The oxidatively added ligands normally undergo further transformation. In the Monsanto-acetic acid process, the intermediate undergoes alkyl migration to give the corresponding acetyl species. Alkyl migration takes place when a σ-bonded organic ligand, the alkyl group, migrates to a dative covalently bonded carbon monoxide ligand, on the same metal centre to form an acetyl ligand. An example of a reaction which models the migratory insertion is shown below.[15]



$$(CO)_5MnCH_3 \xrightarrow{CO} (CO)_5Mn\overset{\overset{O}{\|}}{C}CH_3 \qquad (1.1)$$

The organic products of the afore-mentioned catalytic cycle are formed via reductive elimination, where the organic fragments are eliminated from the intermediate organometallic species to regenerate the active catalyst system. The reductive elimination reaction can be modeled by a known reaction such as the one below. Here a platinum containing hydrocarbyl species eliminates methane.[14]

$$cis\text{-}PtH(CH_3)(PPh_3)_2 \longrightarrow Pt(PPh_3)_2 + CH_4 \qquad (1.2)$$

Some key reactions in the Fischer-Tropsch process have also been modeled using hydrocarbyl complexes.[16,17,19] The Fischer-Tropsch reaction involves the catalytic conversion of synthesis gas ($CO + H_2$), to hydrocarbons and oxygenated compounds

[Eq. 1.3].[16,17] This reaction has been widely utilized in the production of synthetic fuels, waxes and lubricants (Table 1.1).[18]

$$CO + H_2 \xrightarrow{[cat.]} \begin{array}{c}\text{alkanes, olefins,}\\ \text{aldehydes and alcohols}\end{array} \qquad (1.3)$$

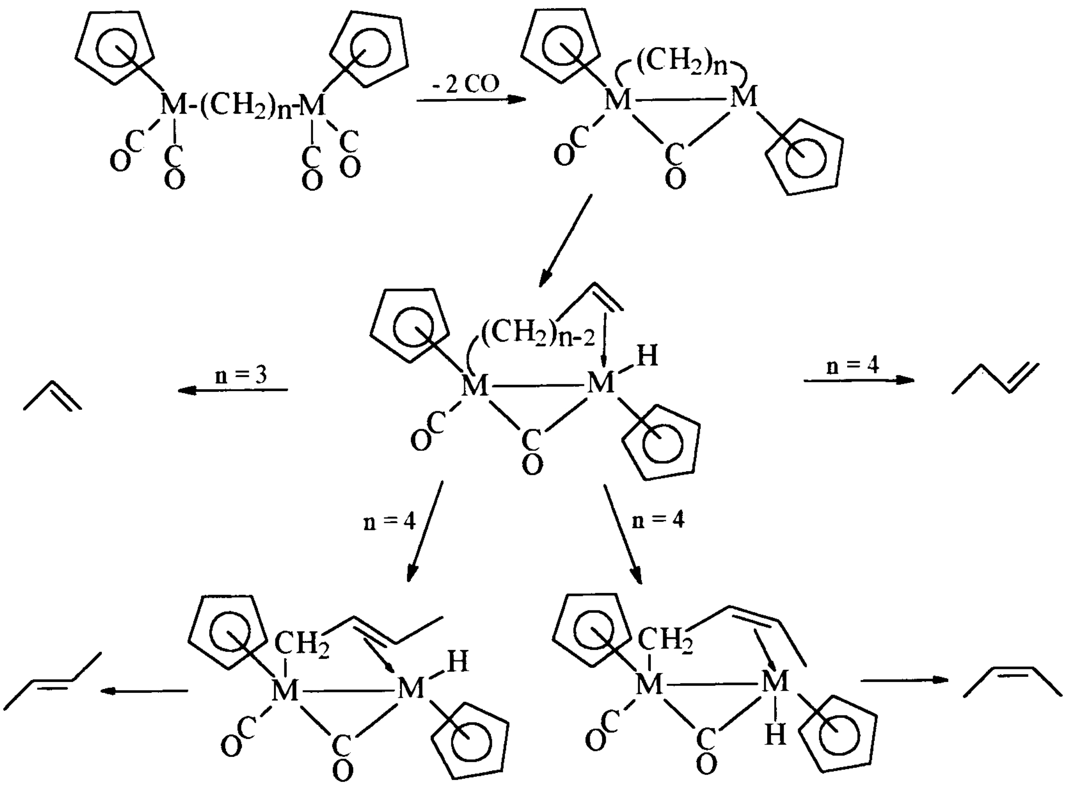
Table 1.1 Some typical products formed via the Fischer-Tropsch process.[18]

Catalyst	**Promoter**	**Temperature (°C)**	**Pressure (atm)**	**Products**
Fe, Co, Ni	ThO_2, MgO, Al_2O_3, K_2O	150-350	1-30	Paraffinic and olefinic hydrocarbons varying from methane to waxes, plus small quantities of oxygenated products
Ru		150-250	100-1,000	High molecular-weight paraffinic hydrocarbons

There has been a fair amount of controversy regarding the exact mechanism of the Fischer-Tropsch reaction and a number of catalytic cycles have been proposed.[16,17,19-21] The debates about the mechanism are a result of the numerous products obtained which vary in the carbon length and the type of functional groups present. The fact that a mixture of products is obtained, necessitates the use of elaborate separation and purification techniques which adds to the overall cost of the process.[17] Because of these problems, there has been great research activity geared to the optimization of the Fischer-Tropsch process. Many of the steps in the Fischer-

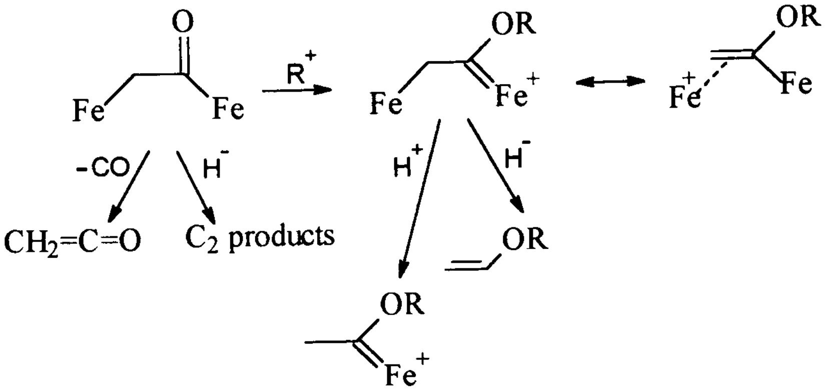
Tropsch process can be modeled using reactions involving hydrocarbyl complexes. This has provided more insight into the overall process.[16,17,19-24]

Below are some examples of how the study of hydrocarbyl complexes can give insight into the Fischer-Tropsch process. Knox *et al.*[23] accounted for the hydrocarbon formation in the Fischer-Tropsch reaction by evaluating the hydrocarbon evolution during the thermal decomposition of hydrocarbyl compounds such as $[CpM(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$, where M = Fe and Ru [Scheme 1.3]. They found that hydrocarbons are eliminated from intermediate dimetallocycles in which the metal atoms are linked. These intermediates strongly favour the loss of alkenes via β-elimination and reductive elimination processes.



Scheme 1.3 Decomposition of some binuclear hydrocarbyl compounds.

Akita *et al.*[24] synthesized homo and heterobimetallic hydrocarbyl complexes of the type, $Cp(CO)_2FeCH_2COML_n$, ML_n = $Mn(CO)_5$, $CpFe(CO)_2$, CpNi(CO) and $CpMo(CO)_2(PPh_3)$. They proposed that these compounds may act as model complexes for intermediates in the Fischer-Tropsch synthesis of oxygenated products. The compound $Cp(CO)_2FeCH_2COFe(CO)_2Cp$, was subjected to reduction, carbonylation and decarbonylation, conditions which are relevant to CO hydrogenation,. It was found that this compound is not susceptible to carbonylation, while decarbonylation results in the liberation of a ketene species. Reduction with $LiAlH_4$ resulted in organic products such as propane and n-propyl alcohol. Reactions with electrophiles proceeded at the acyl oxygen which produced binuclear oxycarbene species, which in turn exhibited reactivity towards electrophiles and nucleophiles [Scheme 1.4].[24]



Scheme 1.4 Fragmentation of the iron-acyl binuclear complex.

1.2 Summary of known hydrocarbyl complexes of transition metals.

A vast number of hydrocarbyl compounds have been synthesized over the last few years.[2-5,22] An in-depth overview of these complexes have appeared in a number of excellent reviews.[2-5,22] Consequently, only iron-containing alkyl, alkenyl and acyl hydrocarbyl compounds and their transformations are discussed in this section. In addition, hydrocarbyl compounds containing ruthenium and manganese metal centres in general, are also examined.

1.2.1 Iron-containing hydrocarbyl compounds

Cp(CO)$_2$Fe-alkyl compounds

The first iron-containing alkyl compounds were reported by King in 1963.[25] In the formation of these compounds King utilized the high nucleophilicity of the iron anion, $[CpFe(CO)_2]^-$, in displacement reactions with organohalides. Ever since then, this type of reaction has been one of the most widely used synthetic routes to hydrocarbyl compounds.[26-30] Mono- and binuclear compounds have been prepared via multiple or single displacement reactions, depending on the nature of the halogen derivatives used [Eqs. 1.4 and 1.5].[26,28-32]

$$Na[Cp(CO)_2Fe] + X(CH_2)_nCH_3 \longrightarrow Cp(CO)_2Fe(CH_2)_nCH_3 + NaX \qquad (1.4)$$

$$2\,Na[Cp(CO)_2Fe] + X(CH_2)_nX \longrightarrow Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp + 2\,NaX \qquad (1.5)$$

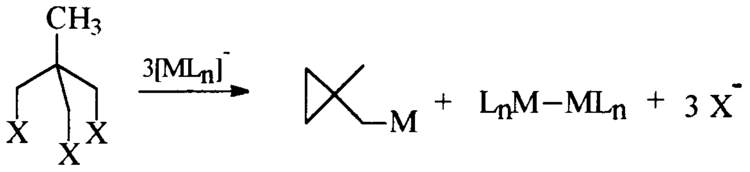
$$X = Cl, Br, I;\ n = 3\text{-}12$$

King[26] made the di-iron hydrocarbyl compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3-6), while Moss *et al.*[31] extended this series to include the compounds n = 3-12. Moss *et al.*[28,29,32] also prepared a number of heterobinuclear hydrocarbyl complexes. They reacted the iron anion, $[CpFe(CO)_2]^-$ with dihaloalkanes in single displacement reactions to produce a range of ω-haloalkyl complexes of the type, $Cp(CO)_2Fe(CH_2)_nX$ (X = Br, n = 3-5)[28] and (X = Br, I, n = 6-10)[29]. In subsequent reactions with transition metal anions, the ω-haloalkyl compounds were transformed to new heteronuclear hydrocarbyl compounds, an example of which is shown below.[28]

$$Cp(CO)_2Fe(CH_2)_3Br + Na[ML_n]^- \longrightarrow Cp(CO)_2Fe(CH_2)_3ML_n + NaBr$$

$$ML_n = CpMo(CO)_3$$

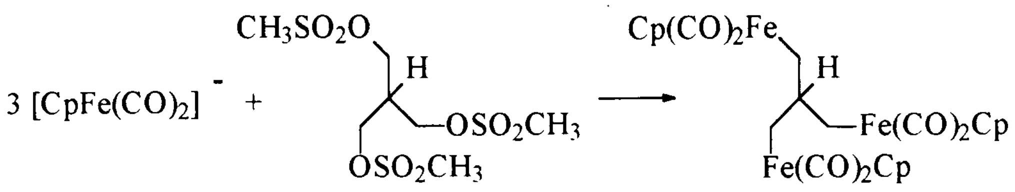
Reactions of transition metal anions with organic polyhalogen substrates containing more than two halogens have also been reported. Wilkinson *et al.*[33] reacted the transition metal anions $[CpFe(CO)_2]^-$, $[CpMo(CO)_3]^-$ and $[CpW(CO)_3]^-$ with $MeC(CH_2X)_3$ (X = Br and I). They, however, did not isolate the expected polynuclear compounds $MeC(CH_2ML_n)_3$ (ML_n = $[CpFe(CO)_2]$, $[CpMo(CO)_3]$, $[CpW(CO)_3]$). Instead the reactions afforded mononuclear hydrocarbyl compounds containing a substituted cyclopropane ring as shown below.



(1.7)

X = Br and I, L_nM = $[CpFe(CO)_2]$, $[CpMo(CO)_3]$ and $[CpW(CO)_3]$

Wuest and Kabayashi[34] subsequently reported the successful substitution of trimesylate groups with $[CpFe(CO)_2]^-$ anion which resulted in the formation of a polynuclear hydrocarbyl compound [Eq. 1.8].



(1.8)

$[Cp(CO)_2Fe(\eta^1$-alkenyl)] compounds

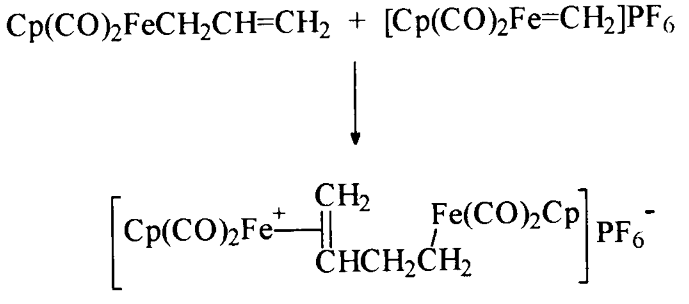
Green *et al.*[35,36] utilized substitution reactions to synthesize the first $[Cp(CO)_2Fe(\eta^1$-alkenyl)] complexes of the type $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 1 and 2). $[Cp(CO)_2Fe(\eta^1$-alkenyl)] compounds are complexes containing σ-bonded alkene groups. Green prepared his series of alkenyl compounds by reacting the iron anion with appropriate organohalogens as illustrated in Eq. 1.9.

$$[CpFe(CO)_2]^- + Br(CH_2)_nCH{=}CH_2 \longrightarrow Cp(CO)_2Fe(CH_2)_nCH{=}CH_2 + Br^- \qquad (1.9)$$

$$n = 1 \text{ and } 2$$

Using Green's method, King *et al.*[37] prepared $Cp(CO)_2FeCH{=}CH_2$ while Mapolie *et al.*[30] prepared $Cp(CO)_2Fe(CH_2)_3CH{=}CH_2$. To date no reported synthesis for $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$, (n>3) has been documented.

The chemical reactivity of these [$Cp(CO)_2Fe(\eta^1$-alkenyl)] species has also generated interest from other workers.[38-42] Rosenblum *et al.*[38-41] reported numerous investigations on the synthesis and transformation of the η^1-allyl compound, $Cp(CO)_2FeCH_2CH{=}CH_2$. In his studies he utilized the concept that neutral [$Cp(CO)_2Fe(\eta^1$-alkenyl)] compounds are susceptible to electrophilic attack at the unsaturated end. Cutler *et al.*[42] have also used this synthetic route to prepare binuclear hydrocarbyl compounds. They alkylated $Cp(CO)_2FeCH_2CH{=}CH_2$ with the $Cp(CO)_2Fe$-methylidene to afford a cationic μ-η^1,η^2-butenediyl complex as shown in Eq. 1.10.



$$Cp(CO)_2FeCH_2CH{=}CH_2 + [Cp(CO)_2Fe{=}CH_2]PF_6 \longrightarrow \left[Cp(CO)_2Fe^{+}\!\!-\!\!\begin{array}{c} CH_2 \\ \| \\ CHCH_2CH_2 \end{array}\!\!\!-\!Fe(CO)_2Cp \right] PF_6^-$$

(1.10)

Iron-acyl compounds

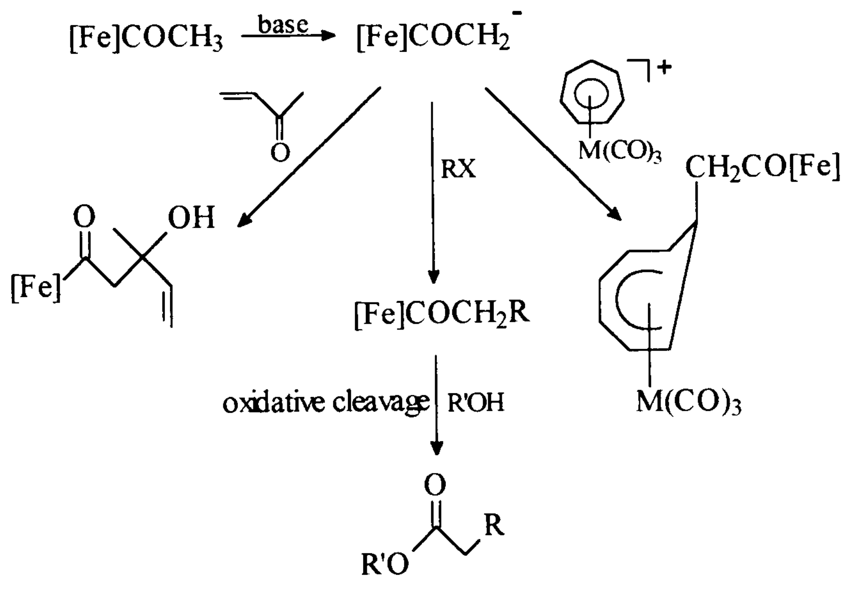
The class of iron-acyl compounds discussed below contains a σ-bonded acyl group adjacent to the iron centre. Mono and binuclear hydrocarbyl iron-acyl compounds of this type have been prepared by the reaction between acyl chloride derivatives and the iron anion, $[CpFe(CO)_2]^-$ in displacement reactions [Eqs. 1.11 and 1.12].[25]

$$[CpFe(CO)_2]^- + ClCOCH_3 \longrightarrow Cp(CO)_2FeCOCH_3 \qquad (1.11)$$

$$2\,[CpFe(CO)_2]^- + ClCO(CH_2)_4COCl \longrightarrow Cp(CO)_2FeCO(CH_2)_4COFe(CO)_2Cp \qquad (1.12)$$

The most extensively studied iron-acyl formation reaction involves the "insertion" of CO into the Fe-alkyl bond of compounds of the type $Cp(CO)_2Fe$-R (R = alkyl).[43-48] A number of mechanistic studies have shown that the alkyl group migrates from the iron centre to the coordinated CO, in a "migratory insertion" reaction.[43-45] The thermal reaction of $Cp(CO)_2Fe$-R compounds with tertiary phosphines promotes "CO insertion" to afford chiral complexes of the type $Cp(PR'_3)(CO)FeCOR$.[46-48]

A proton α to the acyl function of $Cp(PPh_3)(CO)FeCOCH_3$ can readily be abstracted with a strong base to form the corresponding metal acyl enolate species.[49-51] Functionalisation of these acyl-iron enolates occurs with high stereoselectivity and has been extensively used in organic synthesis[47] and in the preparation of mono[49-51] and binuclear[52] hydrocarbyl compounds [Scheme 1.5].



[Fe] = Cp(PPh$_3$)(CO)Fe
M = Mo, Cr

Scheme 1.5 Elaboration of the iron-acyl enolate.

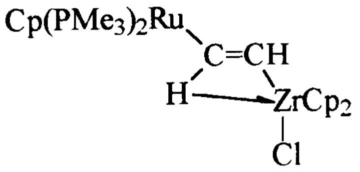
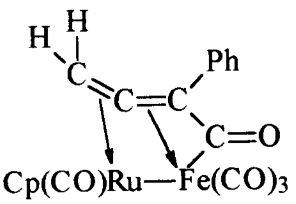
The diversity shown by the iron-containing hydrocarbyl compounds is also found with some hydrocarbyl compounds with ruthenium and manganese metal centres. The synthesis and chemical reactivities of ruthenium and manganese containing hydrocarbyl compounds are briefly discussed in the following sections.

1.2.2 Ruthenium-containing hydrocarbyl compounds

The reactivity of some ruthenium hydrocarbyl compounds has been shown to resemble that of the iron analogues.[53-55] The reaction of the alkyl complexes of the type, Cp(CO)$_2$RuR (R = Me, Et and Bu) with tertiary phosphines, for example, results in the "insertion of CO" into the metal-alkyl bond to yield crystalline compounds with the general formula Cp(PR'$_3$)(CO)RuCOR.[55] Similar results have been found for the iron analogues, but under much milder conditions.[45] In contrast, the reaction of the transition metal alkyls with CO shows a different behaviour. Thus $Cp(CO)_2FeCH_3$ reacts with CO to form the acyl derivative, $Cp(CO)_2FeCOCH_3$ while the ruthenium analogue is rather unreactive in this regard.[43]

As with the iron-containing hydrocarbyl complexes, a number of mono- and binuclear ruthenium hydrocarbyl compounds have been synthesized via diverse synthetic routes. These reactions are summarized in Table 1.2.

Table 1.2 Synthetic routes to some ruthenium-containing hydrocarbyl complexes.

Reactants	**Products**	**References**
$[CpRu(CO)_2]^-$ + CH_3I	$Cp(CO)_2RuCH_3$	53
$Ru(CO)ClH(PPh_3)_3$ + phenylacetylene, pent-1-yne *or* diphenylacetylene	$Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ R = H, R'= C_3H_7, Ph R = R' = Ph	56
$[CpRu(CO)_2]^-$ + $PhC{\equiv}CCH_2Cl$	$Cp(CO)_2RuCH_2C{\equiv}CPh$	57
$Ru(CO)ClH(PPh_3)_3$ + HgR_2 R = *p*-tolyl	$RuRCl(CO)(PPh_3)_2$ R = *p*-tolyl	58
$CpRu(CO)_3^+$ + 4 $NaBH_3CN$	$Cp(CO)_2RuCH_2OH$	54
$[CpRu(CO)_2]^-$ + $Cl_2(CH_2)_2$ *or* $[CpRu(CO)_2]^-$ + $[Cp(CO)_2RuC_2H_4]PF_6$	$Cp(CO)_2Ru(CH_2)_2Ru(CO)_2Cp$	59
$Cp(CO)_2Ru(CH_2)_5Ru(CO)_2Cp$ + 2 PPh_3	$Rp'(CH_2)_5Rp'$ Rp' = $Cp(CO)(PPh_3)Ru$	60
$Cp(PMe_3)_2RuC{\equiv}CH$ + $Cp_2Zr(H)Cl$		61
$Cp(CO)_2RuCH_2C{\equiv}CPh$ + $Fe_2(CO)_9$		62

1.2.3 Manganese-containing hydrocarbyl compounds

The first reported manganese-containing hydrocarbyl compound was methyl manganesepentacarbonyl, $(CO)_5MnCH_3$, prepared in 1957.[63] It was synthesized via the reaction between sodium manganesepentacarbonyl and methyl iodide [Eq. 1.13].

$$Na[Mn(CO)_5] + CH_3I \longrightarrow (CO)_5MnCH_3 + NaI \qquad (1.13)$$

Manganese alkyl compounds are classic examples of compounds that undergo "carbonyl insertion"[64-66], a key step in many catalytic cycles. Compounds of the type $(CO)_5MnR$ (R = alkyl) undergo a number of well reported reactions which are summarized in Table 1.3.

In addition to the preparation of mononuclear hydrocarbyl compounds, binuclear hydrocarbyl compounds have also been synthesized. King attempted to synthesize the binuclear hydrocarbyl compound $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$.[67] The attempt however, did not afford the expected compound, instead he proposed the isolated compound to have the structure shown in Figure 1.3.

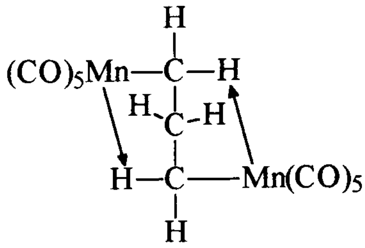
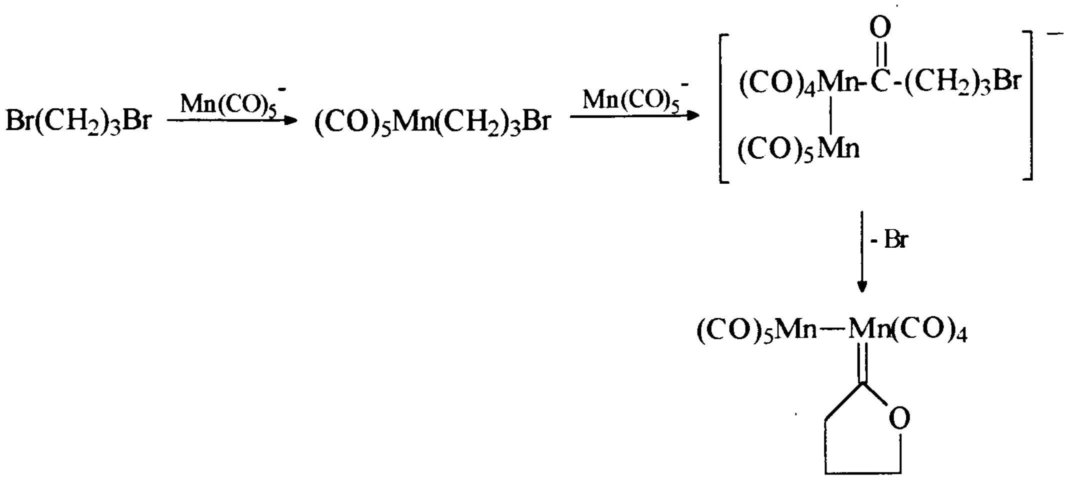


Figure 1.3 The structure of the compound $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$, originally proposed by King.

This product was however later shown to be a cyclic metal-carbene, which is shown in Eq. 1.14 and the structure of which was first elucidated by Casey and Anderson.[68]

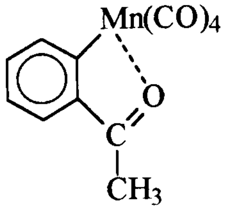


(1.14)

The μ-alkanediyl compound, $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$ has since been prepared successfully by the reaction of $TFO(CH_2)_3OFT$ ($TF = SO_2CF_3$) with $K[Mn(CO)_5]$ in a substitution reaction.[69] Moss *et al.*[70] used a different synthetic route to prepare a series of longer chain binuclear compounds $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n)\}$ (n = 4-6). They first prepared the μ-diacyl compounds $[(CO)_5Mn(O)C(CH_2)_nC(O)Mn(CO)_5]$ (n = 4-6), then using thermal decarbonylation isolated the corresponding μ-alkanediyl compounds [Eq. 1.15].

$$
\begin{array}{l}
2\,Na[Mn(CO)_5] + ClCO(CH_2)_nCOCl \longrightarrow (CO)_5Mn(O)C(CH_2)_nC(O)Mn(CO)_5 \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \Delta \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad [Mn(CO)_5]_2\{\mu\text{-}(CH_2)_n\} \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad n = 4\text{-}6
\end{array}
\qquad (1.15)
$$

Table 1.3 Some reactions of Manganese pentacarbonyl alkyl compounds of the type, $Mn(CO)_5R$.

Reagents	**Products**	**References**
1. Neutral Ligands		
$P(C_6H_5)_3$, alkylamines, alkenes, alkynes and CO	A range of acetylmanganese compounds with general structure $(CO)_4LMnCOR$, are obtained (L = neutral ligand)	65,66,71
2. Acids		
A. Protic Acids HBF_4, CF_3SO_3H, HBr	$[(CO)_5Mn]X$ (X = BF_4, SO_3CF_3 and Br)	72
CF_3COOH in the presence of CO	$(CO)_5MnCOR$	73
B. Lewis Acids		
$AlBr_3$, $AlCl_3$ in the presence of CO	$(CO)_5MnCOR$	74,75
3. Anions		
I^-, $Mn(CO)_5^-$, $Re(CO)_5^-$	$[(CO)_4XMnCOR]^-$ X = I, $Mn(CO)_5$, $Re(CO)_5$	64,76
4. Transition metal hydrides		
$CpMo(CO)_3H$, $Re(CO)_5H$ and $CpW(CO)_3H$	$(CO)_4(s)Mn\text{-}ML_n$ + RCHO ML_n = $CpMo(CO)_3$, $Re(CO)_5$ and $CpW(CO)_3$ s = solvent	77
5. Substituted phenyl groups		
$MeC(O)C_6H_5$	 + RH + CO	78

1.3 The scope of this project

The aim of the project was to synthesize hydrocarbyl complexes which can possibly act as model compounds in catalytic processes such as the Fischer-Tropsch reaction, Hydroformylation, the Monsanto-acetic acid process and Ziegler-Natta polymerization.

The synthesis of mononuclear hydrocarbyl compounds of the type $L(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6, L = Cp and Cp*), $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ are reported in this thesis. These hydrocarbyl compounds were fully characterized by microanalysis, IR, ^1H and ^{13}C NMR spectroscopy and mass spectrometry. In addition to the synthesis, the reactivity of these mononuclear hydrocarbyl compounds under various conditions was also investigated. The reactions performed on the η^1-alkenyl compounds include the β-hydride abstraction on $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6), and the hydrozirconation of some of the alkenyl compounds, $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3). The investigations on the ω-hydroxyalkyls include the protonation of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6, 8), the bromination of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 8) and the reaction of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-5,8) with trifluoromethanesulfonic anhydride.

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CHAPTER 2

THE SYNTHESIS AND CHARACTERIZATION OF η^1-ALKENYL COMPLEXES OF IRON

2.1 Introduction

2.1.1 Definition of η^1-alkenyl transition metal compounds and the motivation for the study.

η^1-Alkenyl transition metal compounds are hydrocarbyl complexes where an alkene ligand is sigma-bonded to a transition metal. The class of η^1-alkenyl compounds investigated in this thesis contains a terminal double bond and have the general structure shown below:

$$L_nM(CH_2)_yCH{=}CH_2$$

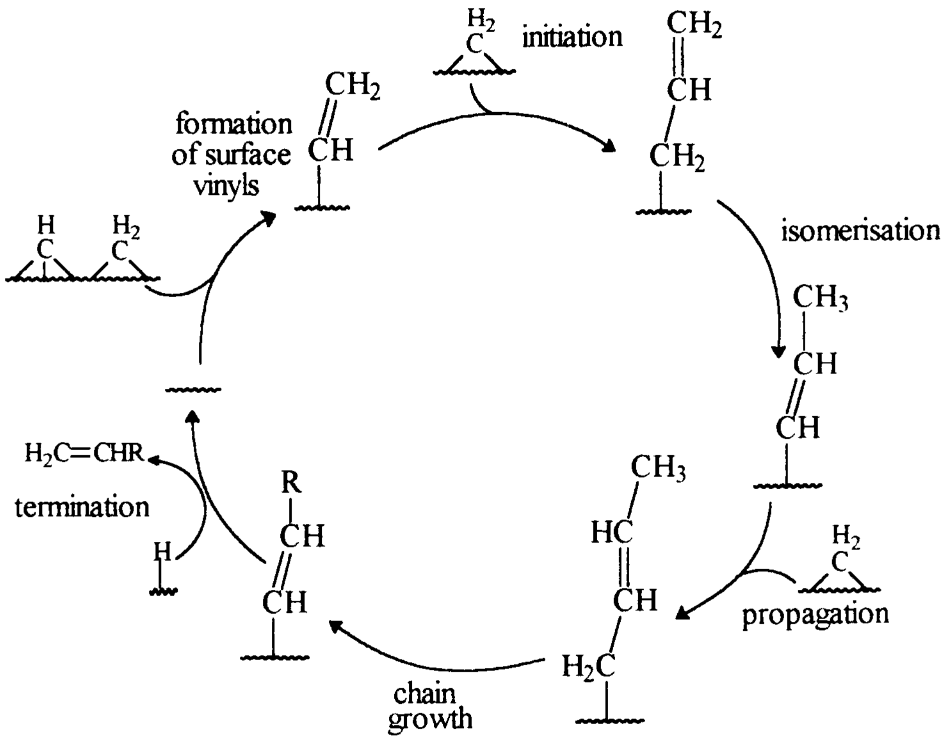
$$y \geq 2$$

L_nM = transition metal and its associated ligands.

Figure 2.1 η^1-Alkenyl transition metal complexes.

The above-mentioned η^1-alkenyl complexes can act as potential model compounds for intermediates in catalytic processes catalyzed by transition metal species.[1-5] Some of these processes include, the hydrogenation of alkenes to alkanes, carbonylation of alkenes to acyl species, alkene metathesis and the polymerization and dimerization of α-olefins.

One of the proposed mechanisms for the Fischer-Tropsch process is the alkenyl mechanism shown in Scheme 2.1.[5] This mechanism suggests that the formation of surface vinyls by the coupling of surface methynes and methylenes is an integral part in the Fischer-Tropsch polymerization of surface methylenes. η^1-Alkenyl compounds may be used to model a number of steps in this cycle, which include amongst others, the isomerization of allyl species to alkenyl analogues, chain growth and chain termination.[2,3]



Scheme 2.1 The alkenyl mechanism for chain growth in the Fischer-Tropsch process.

In addition to the perceived role of η^1-alkenyl complexes in catalytic processes, the study of η^1-alkenyl complexes in its own right, is an exciting and ever-growing field.[6-11]

2.1.2 An overview of previous work

Green *et al.* synthesized a series of η^1-allyl compounds containing different transition metal centres [Figure 2.2].[6-8]

$$L_nMCH_2CH{=}CH_2$$
$$L_nM = CpFe(CO)_2, CpMo(CO)_3, CpW(CO)_3$$

Figure 2.2 Some examples of η^1-allyl compounds.

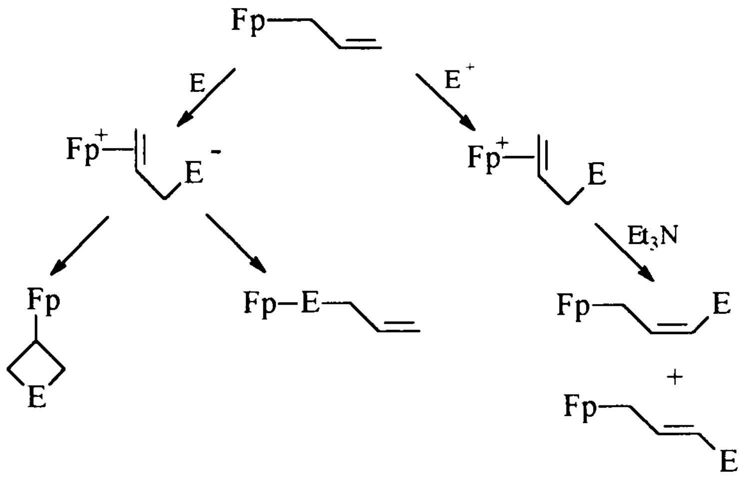
These compounds were synthesized by the reaction of the sodium salts of the transition metal carbonyls with allyl chloride [Eq. 2.1].

$$\mathrm{Na[L_nM]} + \mathrm{CH_2{=}CHCH_2Cl} \longrightarrow \mathrm{L_nMCH_2CH{=}CH_2} + \mathrm{NaCl}$$

$$\mathrm{L_nM} = \mathrm{CpFe(CO)_2, CpMo(CO)_3, CpW(CO)_3} \qquad (2.1)$$

The ability of the η^1-alkenyl complexes to act as model compounds for catalytic intermediates, prompted a number of reactivity studies on these compounds.[9,11] Green *et al.*[9] synthesized and investigated the photolytically and thermally induced decomposition of $Cp(CO)_2Fe(CH_2)_2CH{=}CH_2$. Mapolie *et al.*[11] prepared compounds of the type $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3) and studied the hydrogenation, hydroformylation and hydroboration thereof.

η^1-Alkenyl complexes have also evoked great interest because of their ability to be further functionalized to new hydrocarbyl complexes.[10,12-16] For example, Rosenblum *et al.*[10,14] reacted $Cp(CO)_2FeCH_2CH{=}CH_2$ with neutral and charged electrophiles, which resulted in the formation of η^1-allyl-substituted compounds [Scheme 2.2].

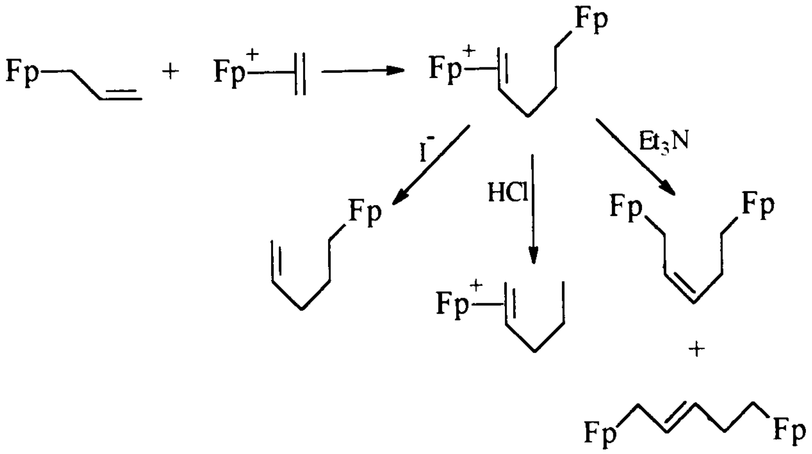


E	E^+
SO_2	$MeSO_2$-
$CH_2=SO_2$	$(MeO)_3C$-
$MeO_2CN=SO_2$	MeO_2C-

Fp = $CpFe(CO)_2$

Scheme 2.2 Functionalization of $Cp(CO)_2FeCH_2CH=CH_2$.

Homobinuclear hydrocarbyl compounds have also been synthesized via the elaboration of $Cp(CO)_2FeCH_2CH=CH_2$ with cationic $[CpFe(CO)_2(\eta^2\text{-olefin})]^+$ compounds.[12] The subsequent transformation of the intermediate, under various conditions, resulted in the formation of mono- and binuclear hydrocarbyl products as summarized in Scheme 2.3.



Fp = CpFe(CO)2

Scheme 2.3 Transformation of $Cp(CO)_2FeCH_2CH{=}CH_2$.

Longer chained η^1-alkenyl compounds have not previously been prepared. Therefore, there exists an informational void on longer chain η^1-alkenyl species especially where the carbon chain length exceeds five. These complexes could possibly act as model compounds for intermediates in the formation of C_3-C_{18} olefinic products in the Fischer-Tropsch process and other polymerization reactions. In this thesis we report on the preparation of η^1-alkenyl species of the type $L_nM(CH_2)_yCH{=}CH_2$ ($L_nM = (\eta^5\text{-}C_5H_5)Fe(CO)_2$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$, $y = 2\text{-}4,6$), and also on a study to further functionalize some of these compounds.

2.2 Results and discussion

The compounds **1-4**,**7** and **8** were isolated as orange-yellow oils, while **5** and **6** were obtained as stable yellow crystals with low melting points. These compounds were formed via the reaction between the sodium salts of the transition metal carbonyls and the appropriate n-bromo-1-alkene.

$$Na[L_nM] + Br(CH_2)_yCH{=}CH_2 \longrightarrow L_nM(CH_2)_yCH{=}CH_2 + NaBr$$

1 $y = 2$ $L_nM = Fp$
2 $y = 3$ $L_nM = Fp$
3 $y = 4$ $L_nM = Fp$
4 $y = 6$ $L_nM = Fp$
5 $y = 2$ $L_nM = Fp^*$
6 $y = 3$ $L_nM = Fp^*$
7 $y = 4$ $L_nM = Fp^*$
8 $y = 6$ $L_nM = Fp^*$
$Fp = (\eta^5\text{-}C_5H_5)CpFe(CO)_2$
$Fp^* = (\eta^5\text{-}C_5Me_5)Fe(CO)_2$ (2.2)

The compounds **1-8** are light sensitive and they decompose slowly in the presence of light and air. They can however be stored at about -20 °C for several weeks without significant signs of decomposition. All the compounds were characterized by IR, ^1H and ^{13}C NMR spectroscopy, as well as microanalysis and mass spectrometry, details of which are given in Tables 2.1-2.8.

2.2.1 IR Spectra

The IR spectral data for the compounds **1-8** are summarized in Tables 2.1 and 2.2. The spectra of **1-4** in the ν(CO) region, resembles those of compounds of the type $CpFe(CO)_2R$, while those of the compounds **5-8** resemble the spectra of $Cp^*Fe(CO)_2R$ (R = alkyl). The ν(CO) frequencies for the $Cp^*Fe(CO)_2$ complexes are ~20 wavenumbers lower than those for the $CpFe(CO)_2$ analogues, which may be attributed an increased electron density brought about by the methyl substituted Cp ring. All spectra exhibit a medium intensity band in the region 1630-1640 cm^{-1}, which can be assigned to the (C=C) stretching frequency of the pendant alkene. The high values for the ν(C=C) for compounds **1-8** is indicative of terminal alkenes, whereas it has previously been found that ν(C=C) for coordinated alkenes appear about 100 wavenumbers lower.[6]

Table 2.1 Yields, microanalysis and IR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n =2-4,6) *i.e.* **1-4**

Compound number	**Yield (%)**	**Microanalysis [a] (%)**	**IR [b] (cm^{-1})**
1	76	C 56.83 (56.93)	2001(s), 1941(s) [c]
		H 4.96 (5.27)	1633(m) [d]
2	78	C 58.30 (58.57)	2001(s), 1943(s) [c]
		H 5.90 (5.73)	1637(m) [d]
3	80	C 59.26 (60.05) [e]	1999(s), 1939(s) [c]
		H 6.21 (6.15)	1639(m) [d]
4	80	C 61.43 (62.55) [e]	2000(s), 1941(s) [c]
		H 7.00 (6.94)	1639(m) [d]

[a] Calculated values in brackets
[b] Neat oil between NaCl plates (s = strong and m = medium)
[c] ν(CO)
[d] ν(C=C)
[e] Unstable compound, difficult to obtain acceptable microanalysis

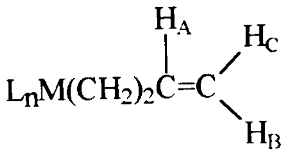
Table 2.2 Yields, microanalysis and IR spectral data for the compounds $Cp^*(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6) *i.e.* **5-8**

Compound number	**Appearance and melting point**[a]	**Yield (%)**	**Microanalysis**[b] **(%)**	**IR**[c] **(cm^{-1})**
5	yellow crystals 62-66°C	71	C 63.84 (63.58) H 7.60 (7.28)	1980(s), 1920(s)[d] 1633(m)[e]
6	yellow crystals 37-40°C	73	C 64.71 (64.56) H 7.59 (7.94)	1985(s), 1909(s)[d] 1638(m)[e]
7	bright yellow-orange oil	70	C 65.25 (65.50) H 8.38 (7.88)	1980(s), 1920(s)[d,f] 1641(m)[e]
8	bright yellow-orange oil	68	C 67.87 (67.64) H 8.65 (8.38)	1980(s), 1921(s)[d,f] 1641(m)[e]

[a] Melting point recorded on a Fischer-Johns hotstage apparatus
[b] Calculated values in brackets
[c] CH_2Cl_2 as solvent in NaCl solution cells, unless stated otherwise (s = strong and m = medium)
[d] ν(CO)
[e] ν(C=C)
[f] Neat oil between NaCl plates (s = strong and m = medium)

2.2.2 ^{1}H NMR Spectra

The spectra of compounds **1-8** exhibit resonances characteristic of species with vinylic protons.[17] These peaks are however not well resolved except for the butenyl compounds **1** and **5**. The proton assignments of the vinylic protons for **1** and **5** are based on the structure in Figure 2.3.



$L_nM = CpFe(CO)_2, Cp^*Fe(CO)_2$

Figure 2.3 The vinylic proton assignment for **1** and **5**.

The chemical shift difference for the protons H_A, H_B, and H_C indicates that these protons are magnetically non-equivalent. A multiplet at δ 5.8 ppm was assigned to the H_A proton. The two doublets in the region δ 4.8-4.9 ppm were assigned to H_B and H_C protons, with the *trans* (J_{BA}) and the *cis* (J_{CA}) coupling constants being 16 Hz and 10 Hz respectively. No geminal coupling (J_{BC}) was observed. The chain length or the change of the Cp ligand to the Cp* ligand had no significant influence on the chemical shift of the vinylic protons.

The protons of the carbon adjacent to the iron centre for compounds **1-4** and **5-8** were assigned to the peaks in the region δ 1.3-1.5 ppm and δ 0.92-0.95 ppm respectively. These protons exhibit an upfield shift of ~0.4 ppm upon the change of the Cp ligand to the methyl substituted Cp ligand. This can be attributed to the influence the Cp* ligand has on the electron density of the iron centre. The remaining protons were assigned to the peaks in the region δ 1.3-2.1 ppm. These assignments are outlined in Tables 2.3 and 2.4.

Table 2.3 ^{1}H NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) *i.e.* **1-4**

Compound number	**Chemical Shift** $^{a, b}$ **(δ ppm)**	**Assignment**
1	1.46 (br t, 2H, *J* = 8.4 Hz)	$FeC\underline{H}_2CH_2CH=CH_2$
	2.16 (br m, 2H)	$FeCH_2C\underline{H}_2CH=CH_2$
	4.75 (s, 5H)	$C_5\underline{H}_5$
	4.85 (d, 1H, $J_{CA,\ cis}$ = 10.4 Hz)	$Fe(CH_2)_2CH=C\underline{H}_2$
	4.95 (d, 1H, $J_{BA,\ trans}$ = 16 Hz)	$Fe(CH_2)_2CH=C\underline{H}_2$
	5.86 (m, 1H)	$Fe(CH_2)_2C\underline{H}=CH_2$
2	1.48 (br s, 4H)	$Fe(C\underline{H}_2)_2CH_2CH=CH_2$
	2.07 (br s, 2H)	$Fe(CH_2)_2C\underline{H}_2CH=CH_2$
	4.73 (s, 5H)	$C_5\underline{H}_5$
	4.94 (br m, 2H)	$Fe(CH_2)_3CH=C\underline{H}_2$
	5.82 (br m, 1H)	$Fe(CH_2)_3C\underline{H}=CH_2$
3	1.45 (br s, 6H)	$Fe(C\underline{H}_2)_3CH_2CH=CH_2$
	2.06 (br s, 2H)	$Fe(CH_2)_3C\underline{H}_2CH=CH_2$
	4.72 (s, 5H)	$C_5\underline{H}_5$
	4.94 (br m, 2H)	$Fe(CH_2)_4CH=C\underline{H}_2$
	5.80 (br m, 1H)	$Fe(CH_2)_4C\underline{H}=CH_2$
4	1.39 (br m, 10H)	$Fe(C\underline{H}_2)_5CH_2CH=CH_2$
	2.05 (br s, 2H)	$Fe(CH_2)_5C\underline{H}_2CH=CH_2$
	4.73 (s, 5H)	$C_5\underline{H}_5$
	4.96 (br m, 2H)	$Fe(CH_2)_6CH=C\underline{H}_2$
	5.80 (br m, 1H)	$Fe(CH_2)_6C\underline{H}=CH_2$

[a] $CDCl_3$ as solvent

[b] br = broad, s = singlet, t = triplet and m = multiplet

Table 2.4 ^{1}H NMR spectral data for the compounds $Cp^{*}(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6) *i.e.* **5-8**

Compound number	**Chemical Shift** [a, b] **(δ ppm)**	**Assignment**
5	0.94 (t, 2H, J = 8.4 Hz)	$FeC\underline{H}_2CH_2CH{=}CH_2$
	1.73 (s, 15H)	$C_5(C\underline{H}_3)_5$
	2.16 (m, 2H)	$FeCH_2C\underline{H}_2CH{=}CH_2$
	4.82 (d, 1H, $J_{CA,\,cis}$ = 10 Hz)	$Fe(CH_2)_2CH{=}C\underline{H}_2$
	4.94 (d, 1H, $J_{BA,\,trans}$ = 16.8 Hz)	$Fe(CH_2)_2CH{=}C\underline{H}_2$
	5.91 (m, 1H)	$Fe(CH_2)_2C\underline{H}{=}CH_2$
6	0.94 (t, 2H, J = 9 Hz)	$FeC\underline{H}_2(CH_2)_2CH{=}CH_2$
	1.51 (m, 2H)	$FeCH_2C\underline{H}_2CH_2CH{=}CH_2$
	1.72 (s, 15H)	$C_5(C\underline{H}_3)_5$
	2.08 (m, 2H)	$Fe(CH_2)_2C\underline{H}_2CH{=}CH_2$
	4.94 (m, 2H)	$Fe(CH_2)_3CH{=}C\underline{H}_2$
	5.84 (m, 2H)	$Fe(CH_2)_3C\underline{H}{=}CH_2$
7	0.94 (br s, 2H)	$FeC\underline{H}_2(CH_2)_3CH{=}CH_2$
	1.45 (m, 4H)	$FeCH_2(C\underline{H}_2)_2CH_2CH{=}CH_2$
	1.72 (s, 15H)	$C_5(C\underline{H}_3)_5$
	2.05 (m, 2H)	$Fe(CH_2)_3C\underline{H}_2CH{=}CH_2$
	4.93 (m, 2H)	$Fe(CH_2)_4CH{=}C\underline{H}_2$
	5.83 (m, 1H)	$Fe(CH_2)_4C\underline{H}{=}CH_2$
8	0.93 (br m, 2H)	$FeC\underline{H}_2(CH_2)_5CH{=}CH_2$
	1.32 (m, 8H)	$FeCH_2(C\underline{H}_2)_4CH_2CH{=}CH_2$
	1.71 (s, 15H)	$C_5(C\underline{H}_3)_5$
	2.03 (m, 2H)	$Fe(CH_2)_5C\underline{H}_2CH{=}CH_2$
	4.94 (m, 2H)	$Fe(CH_2)_6CH{=}C\underline{H}_2$
	5.80 (br m, 1H)	$Fe(CH_2)_6C\underline{H}{=}CH_2$

[a] $CDCl_3$ as solvent

[b] br = broad, s = singlet, t = triplet and m = multiplet

2.2.3 ^{13}C NMR Spectra

The ^{13}C NMR spectra of compounds **1-8** all exhibit similar trends. Peaks at δ 217 ppm and δ 219 ppm were assigned to the terminal carbonyls of the $CpFe(CO)_2$ and $Cp^*Fe(CO)_2$ complexes respectively. The vinylic carbons, ($=\underline{C}H_2$) and ($=\underline{C}H$) were assigned to the peaks in the regions δ 111-115 ppm and δ 137-144 ppm respectively. The relative chemical shifts of both the carbonyls and the unsaturated carbons, were not significantly affected by the increase in carbon chain length. The carbons α to the iron centre for the $Cp^*Fe(CO)_2$ complexes appear ~10 ppm downfield compared to those of the $CpFe(CO)_2$ analogues. This indicates that the α-carbons for the $Cp^*Fe(CO)_2$ compounds are influenced by the methyl substituents on the Cp ligand.[18] The other methylene carbons were assigned to the remaining peaks in the upfield region, as indicated in Tables 2.5 and 2.6.

Table 2.5 ^{13}C NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) *i.e.* **1-4**

Compound number	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
1	2.13	$Fe\underline{C}H_2CH_2CH=CH_2$
	41.83	$FeCH_2\underline{C}H_2CH=CH_2$
	85.32	$\underline{C}_5H_5$
	112.27	$Fe(CH_2)_2CH=\underline{C}H_2$
	142.53	$Fe(CH_2)_2\underline{C}H=CH_2$
	217.51	$\underline{C}O$

Table 2.5 (continued)

Compound number	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
2	3.05	$Fe\underline{C}H_2(CH_2)_2CH{=}CH_2$
	37.65	$FeCH_2\underline{C}H_2CH_2CH{=}CH_2$
	38.97	$Fe(CH_2)_2\underline{C}H_2CH{=}CH_2$
	85.30	$\underline{C}_5H_5$
	113.94	$Fe(CH_2)_3CH{=}\underline{C}H_2$
	139.15	$Fe(CH_2)_3\underline{C}H{=}CH_2$
	217.58	$\underline{C}O$
3	3.29	$Fe\underline{C}H_2(CH_2)_3CH{=}CH_2$
	33.53	$FeCH_2\underline{C}H_2(CH_2)_2CH{=}CH_2$
	33.93	$Fe(CH_2)_2\underline{C}H_2CH_2CH{=}CH_2$
	37.69	$Fe(CH_2)_3\underline{C}H_2CH{=}CH_2$
	85.29	$\underline{C}_5H_5$
	113.94	$Fe(CH_2)_4CH{=}\underline{C}H_2$
	139.94	$Fe(CH_2)_4\underline{C}H{=}CH_2$
	217.65	$\underline{C}O$
4	3.66	$Fe\underline{C}H_2(CH_2)_5CH{=}CH_2$
	28.92	$FeCH_2\underline{C}H_2(CH_2)_4CH{=}CH_2$
	29.03	$Fe(CH_2)_2\underline{C}H_2(CH_2)_3CH{=}CH_2$
	33.83	$Fe(CH_2)_3\underline{C}H_2(CH_2)_2CH{=}CH_2$
	34.70	$Fe(CH_2)_4\underline{C}H_2CH_2CH{=}CH_2$
	38.25	$Fe(CH_2)_5\underline{C}H_2CH{=}CH_2$
	85.31	$\underline{C}_5H_5$
	114.06	$Fe(CH_2)_6CH{=}\underline{C}H_2$
	139.36	$Fe(CH_2)_6\underline{C}H{=}CH_2$
	217.60	$\underline{C}O$

[a] $CDCl_3$ as solvent

Table 2.6 ^{13}C NMR spectral data for the compounds $Cp^{*}(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6) *i.e.* **5-8**

Compound number	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
5	9.34	$C_5(\underline{C}H_3)_5$
	12.55	$Fe\underline{C}H_2CH_2CH{=}CH_2$
	41.54	$FeCH_2\underline{C}H_2CH{=}CH_2$
	95.00	$\underline{C}_5(CH_3)_5$
	111.57	$Fe(CH_2)_2CH{=}\underline{C}H_2$
	144.19	$Fe(CH_2)_2\underline{C}H{=}CH_2$
	219.74	$\underline{C}O$
6	9.34	$C_5(\underline{C}H_3)_5$
	13.42	$Fe\underline{C}H_2(CH_2)_2CH{=}CH_2$
	37.20	$FeCH_2\underline{C}H_2CH_2CH{=}CH_2$
	40.04	$Fe(CH_2)_2\underline{C}H_2CH{=}CH_2$
	94.91	$\underline{C}_5(CH_3)_5$
	113.64	$Fe(CH_2)_3CH{=}\underline{C}H_2$
	139.78	$Fe(CH_2)_3\underline{C}H{=}CH_2$
	219.74	$\underline{C}O$
7	9.34	$C_5(\underline{C}H_3)_5$
	13.60	$Fe\underline{C}H_2(CH_2)_3CH{=}CH_2$
	33.78	$FeCH_2\underline{C}H_2(CH_2)_2CH{=}CH_2$
	37.34	$Fe(CH_2)_2\underline{C}H_2CH_2CH{=}CH_2$
	94.89	$Fe(CH_2)_3\underline{C}H_2CH{=}CH_2$
	92.80	$\underline{C}_5(CH_3)_5$
	113.80	$Fe(CH_2)_4CH{=}\underline{C}H_2$
	139.92	$Fe(CH_2)_4\underline{C}H{=}CH_2$
	219.85	$\underline{C}O$

Table 2.6 (continued)

Compound number	Chemical Shift [a] (δ ppm)	Assignment
8	9.34	$C_5(\underline{C}H_3)_5$
	14.11	$Fe\underline{C}H_2(CH_2)_5CH{=}CH_2$
	29.16	$FeCH_2\underline{C}H_2(CH_2)_4CH{=}CH_2$
	29.74	$Fe(CH_2)_2\underline{C}H_2(CH_2)_3CH{=}CH_2$
	33.95	$Fe(CH_2)_3\underline{C}H_2(CH_2)_2CH{=}CH_2$
	35.81	$Fe(CH_2)_4\underline{C}H_2CH_2CH{=}CH_2$
	37.83	$Fe(CH_2)_5\underline{C}H_2CH{=}CH_2$
	94.88	$\underline{C}_5(CH_3)_5$
	114.07	$Fe(CH_2)_6CH{=}\underline{C}H_2$
	139.66	$Fe(CH_2)_6\underline{C}H{=}CH_2$
	219.00	$\underline{C}O$

[a] $CDCl_3$ as solvent

2.2.4 Mass Spectra

The mass spectra of all the compounds exhibit similar trends and show molecular ions with the exception of compound **2**. The highest mass peak in the spectrum of **2** corresponds to $(M\text{-}CO)^+$ (m/z = 218), while the base peak observed in the spectrum, corresponds to $(CO)^+$ (m/z = 28). The base peak for **1**, **5** and **6** corresponds to $(M\text{-}2CO)^+$ and for **3** and **4** to $(M\text{-}2CO\text{-}[(CH_2)_nCH{=}CH_2])^+$. The base peak for the longer chained analogues **7** and **8**, were m/z = 270 and m/z = 298 respectively. These peaks could not be accounted for. It, however, appears that there are two fragmentation patterns for all the compounds. The major fragmentation pathway involves the sequential loss of the terminal carbonyls followed by the elimination of the hydrocarbon chain. The other observed decomposition pathway involves the elimination of the hydrocarbon chain followed by the loss of the terminal CO's. The assignment of the major peaks in the various spectra are summarized in Tables 2.7 and 2.8.

Table 2.7 Mass spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) *i.e.* **1-4**

	Relative intensities			
Ion [a]	**1** [b]	**2** [c]	**3** [d]	**4** [d]
M	8	-	7	4
M - CO	2	4	66	5
M - 2CO	100	7	-	45
M - 2CO - $[CH=CH_2]$	16	3	11	0.7
M - $(CH_2)_n$	2	1	-	1
M - 2CO - $(CH_2)_n$	73	5	29	5
M - $[(CH_2)_nCH=CH_2]$	9	4	-	11
M - CO - $[(CH_2)_nCH=CH_2]$	16	14	69	26
M - 2CO - $[(CH_2)_nCH=CH_2]$	73	38	100	100
Fe	95	30	88	75
Cp	-	7	7	2
CO	72	100	7	5

[a] All ions have a single positive charge, ion refers to suggested assignment, M = parent ion

[b] Peak intensities relative to *m/z* = 176

[c] Peak intensities relative to *m/z* = 28

[d] Peak intensities relative to *m/z* = 121

Table 2.8 Mass spectral data for the compounds $Cp^*(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6) *i.e.* **5-8**

	Relative Intensities			
Ion [a]	**5** [b]	**6** [c]	**7** [d,f]	**8** [e,g]
M	14	4	10	8
M - CO	2	30	9	9
M - 2CO	100	100	38	50
M - $[CH{=}CH_2]$	0.4	-	4	-
M - 2CO - $[CH{=}CH_2]$	20	-	9	-
M - $(CH_2)_n$	2	-	38	1
M - 2CO - $(CH_2)_n$	-	12	23	29
M - $[(CH_2)_nCH{=}CH_2]$	-	11	9	9
M - CO - $[(CH_2)_nCH{=}CH_2]$	20	28	26	29
M - 2CO - $[(CH_2)_nCH{=}CH_2]$	-	-	49	49
Fe	14	21	15	12
Cp*	8	19	15	15
CO	34	1	12	18

[a] All ions have a single positive charge, ion refer to suggested assignment, M = parent ion

[b] Peak intensities relative to $m/z = 246$

[c] Peak intensities relative to $m/z = 260$

[d] Peak intensities relative to $m/z = 270$

[e] Peak intensities relative to $m/z = 298$

[f] Base peak could not be accounted for

2.3 Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk tube techniques. $[CpFe(CO)_2]_2$, $[Cp^*Fe(CO)_2]_2$ and the n-bromo-1-alkenes were purchased from Aldrich. These chemicals were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under nitrogen. Melting points were recorded on a Fischer-Johns hotstage apparatus and are uncorrected. All chromatography was done on deactivated alumina 90 (70-230 mesh), obtained from Merck. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer and NMR spectra on a Varian XR 200 spectrometer operating at 200 MHZ, using tetramethylsilane as an internal standard (δ 0.00 ppm). Mass spectra were recorded on a V.G. Micromass 16F Spectrometer operating at 70 eV and using an accelerating voltage of 4 kV. Microanalyses were performed at the University of Cape Town.

2.3.1 Preparation of the compounds, $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2-4,6) *i.e.* 1-4

The general method for the preparation of the η^1-alkenyl compounds is outlined below.

A solution of $[CpFe(CO)_2]_2$ (1.00g; 2.26mmol) in THF (20ml) was stirred over a sodium amalgam (Na 3g; Hg 4ml) for 2h at room temperature. The resulting brown solution of Na[CpFe(CO)$_2$] (5.92mmol) was transferred to a second Schlenk tube to which the n-bromo-1-alkene, Br(CH$_2$)$_n$CH=CH$_2$ (n = 2-4,6) (5.92mmol) was added dropwise. The resulting brown green mixture was stirred at room temperature for 2h. The solvent was removed to obtain a green-grey solid, which was extracted with CH$_2$Cl$_2$ (2 x 30ml). This was filtered and the solvent removed on a rotary evaporator resulting in the formation of a yellow oil. The oil was dissolved in a minimum amount of hexane and chromatographed on a (5 x 1.5cm) alumina column using hexane as eluent. A yellow band moving close to the solvent front was collected. Removal of the solvent resulted in a yellow oil being obtained. The yellow oil was identified as the expected η^1-alkenyl product. Yields and characterization data of compounds **1-4** are given in Tables 2.1, 2.3, 2.5 and 2.7.

2.3.2 Preparation of the compounds, Cp*(CO)$_2$Fe(CH$_2$)$_n$CH=CH$_2$ (n = 2-4,6) *i.e.* 5-8

The pentamethyl analogues were prepared using the general method described below.

[Cp*Fe(CO)$_2$]$_2$ (0.50g; 1.03mmol) was dissolved in THF (15ml) and stirred at room temperature for 20h over a sodium amalgam (Na 0.3g; Hg 4ml). The red-brown solution was transferred to a second Schlenk tube followed by the dropwise addition of the n-bromo-1-alkene (2.07mmol). The resulting reaction mixture was stirred for 20h at room temperature and the reaction was followed with t.l.c. The solvent was removed to give a green residue which was extracted with CH_2Cl_2 (2 x 30ml) and filtered. Removal of the solvent from the filtrate gave a brown oil. The oil was extracted with hexane, to remove any insoluble material, and the extract chromatographed on an alumina column (5 x 1.5cm), with hexane as eluent. A fast moving yellow band was collected. The solvent was removed, yielding the expected $Cp^{*}Fe(CO)_2(\eta^1$-alkenyl) compound. The characterization data of compounds **5-8** are given in Tables 2.2, 2.4, 2.6 and 2.8.

2.5 References

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CHAPTER 3

THE SYNTHESIS AND CHARACTERIZATION OF ω-HYDROXYALKYL COMPOUNDS OF IRON

3.1 Introduction

3.1.1 Definition of ω-hydroxyalkyl compounds

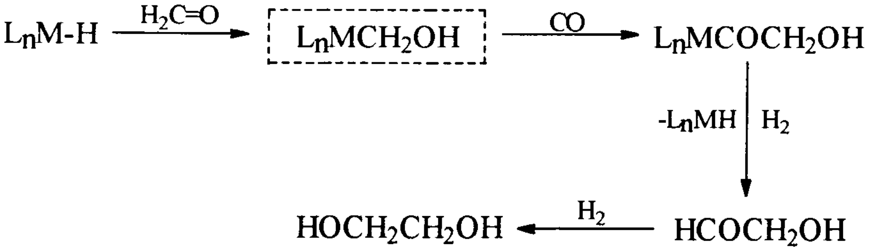
Transition metal ω-hydroxyalkyl complexes are compounds in which an alkyl group containing a terminal hydroxy moiety is sigma-bonded to the transition metal centre [Figure 3.1].

$$L_nM(CH_2)_yOH$$

L_nM = transition metal and its associated ligands.

Figure 3.1 Transition metal ω-hydroxyalkyl compounds.

ω-Hydroxyalkyl compounds have been implicated as intermediates in a number of catalytic cycles. Amongst these are the Wacker oxidation of ethylene, the Fischer-Tropsch process and the hydroformylation of formaldehyde.[1-3] The latter is illustrated in Scheme 3.1.



Scheme 3.1 Hydroformylation of formaldehyde.

3.1.2 An overview of previous work

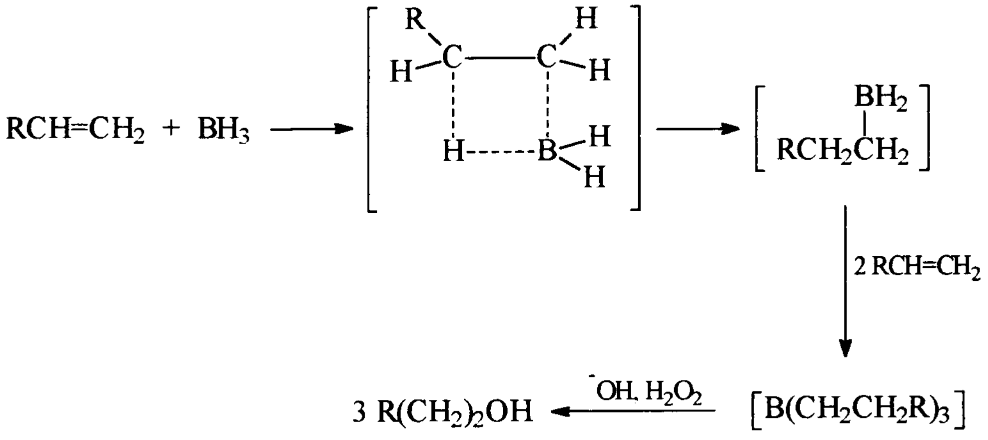
A number of synthetic routes to different ω-hydroxyalkyl complexes have been reported.[1,4-10] However, most of the reports investigated hydroxymethyl compounds.[4-8] These hydroxymethyl compounds can be formed by the facile hydride reduction of coordinated carbon monoxide.[5] This particular reaction may be related to a key step in the Fischer-Tropsch process which involves the reduction of CO in the presence of transition metals.[1] Only a few investigations on longer chained ω-hydroxyalkyls have been reported.[9,10] Studies investigating ω-hydroxyalkyl compounds are summarized in Table 3.1.

Recently Mapolie *et al.*[10] reported the preparation of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) via the oxidative-hydroboration reaction of the η^1-alkenyl compounds, $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3).

$$Cp(CO)_2Fe(CH_2)_nCH{=}CH_2 \xrightarrow[NaOH,\ H_2O_2]{BH_3.\ THF} Cp(CO)_2Fe(CH_2)_{n+2}OH$$

$$n = 2 \text{ and } 3 \qquad (3.1)$$

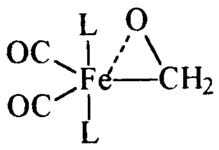
This reaction is based on the concept that olefinic hydrocarbons are readily hydroborated and upon oxidation, alcohols are formed.[11,12] The hydroboration of alkenes takes place through a four centered cyclic transition state. The subsequent addition of hydrogen peroxide in a basic solution cleaves the carbon-boron bond with the addition of a hydroxy group [Scheme 3.2].



Scheme 3.2 The oxidative-hydroboration of olefinic hydrocarbons.

Our aim was to transform compounds **1-5** to form new functionalized mononuclear hydrocarbyl compounds. The synthetic approach was to subject compounds **1-5** to oxidative-hydroboration conditions to yield the longer chained ω-hydroxyalkyl compounds of the type $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$. These compounds could possibly act as model compounds for the formation of C_4-C_8 oxygenated products in the Fischer-Tropsch process.

Table 3.1 Some known ω-hydroxyalkyl compounds.

Reagents	ω-Hydroxyalkyl compounds	Reference
$[CpM(CO)_3]^+$ + $NaBH_3CN$ M = Fe and Ru	$Cp(CO)_2MCH_2OH$ M = Fe and Ru	4
$[Cp^*Ru(CO)_3][BF_4]$ + $NaBH_4$	$Cp^*(CO)_2RuCH_2OH$	5
$[Cp^*Fe(CO)_3][PF_6]$ + $NaBH_4$	$Cp^*(CO)_2FeCH_2OH$	6
$[Cp^*Re(NO)(CO)_2][PF_6]$ + $NaBH_4$	$Cp^*Re(NO)(CO)CH_2OH$	7
 + HCl / Et_2O L = $P(OCH_3)_3$	$(CO)_2L_2ClFeCH_2OH$ L = $P(OCH_3)_3$	8
$(CO)_5MCH(C_6H_5)OSi(CH_3)_3$ + HX / H_2O M = Mn and Re, X = Cl, F	$(CO)_5MCH(C_6H_5)OH$ M = Mn and Re	1
$B[Co]^-$ + $X(CH_2)_2OH$ B = pyridine, X = Br [Co] = bis(dimethylglyoximato) cobalt	$B[Co](CH_2)_2OH$	9
$Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ + BH_3 + ^-OH + H_2O_2 n = 2 and 3	$Cp(CO)_2Fe(CH_2)_nOH$ n = 4 and 5	10

3.2 Results and discussion

The ω-hydroxyalkyl compounds **9-13** were isolated from the oxidative-hydroboration reactions of the η^1-alkenyl compounds **1-5**, as shown below.

$$L_nM(CH_2)_yCH{=}CH_2 \xrightarrow[\text{NaOH. H}_2\text{O}_2]{\text{BH}_3\cdot\text{THF}} L_nM(CH_2)_{y+2}OH$$

1	$y = 2$, L_nM = Fp	**9**	$y = 2$, L_nM = Fp
2	$y = 3$, L_nM = Fp	**10**	$y = 3$, L_nM = Fp
3	$y = 4$, L_nM = Fp	**11**	$y = 4$, L_nM = Fp
4	$y = 6$, L_nM = Fp	**12**	$y = 6$, L_nM = Fp
5	$y = 2$, L_nM = Fp*	**13**	$y = 2$, L_nM = Fp*

$$\text{Fp} = (\eta^5\text{-}C_5H_5)Fe(CO)_2$$
$$\text{Fp*} = (\eta^5\text{-}C_5Me_5)Fe(CO)_2 \qquad (3.2)$$

Compounds **9-12** were isolated as brown-yellow oils. These oils were unstable and decomposed rapidly in solution and in the presence of air or light. It was also found that the longer chained ω-hydroxyalkyls were less stable than the shorter chained analogues. Thus, for compounds **11** and **12** it was not possible to obtain acceptable microanalysis. This was not a problem for the shorter chain compounds. The methyl substituted cyclopentadienyl compound **13**, was isolated as a pale yellow powder. The compound is stable at room temperature and in solution, provided it is kept in the absence of air.

The compounds **9-13** were fully characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, as well as microanalysis and mass spectrometry. The characterization data for these compounds are given in Tables 3.2-3.6.

3.2.1 IR Spectra

The IR spectra of compounds **9-13** show similar trends. They contain two sharp bands in the ν(CO) region, which are similar to those of the starting η^1-alkenyl compounds. This is an indication that the metal environment remains unchanged after the oxidative-hydroboration reaction. The ν(CO) frequency of the $Cp^*Fe(CO)_2$ complex **13**, appears ~20 wavenumbers lower than that of the analogous $CpFe(CO)_2$ compound, which may be attributed to the change in the electron density at the iron centre upon changing from the Cp ligand to the methyl substituted Cp ligand.

A strong broad band in the region 3355 cm^{-1} was assigned to the ν(O-H) frequency of the hydroxy functionality. Furthermore, the spectra show the absence of bands in the region around 1630 cm^{-1} , which is normally assigned to the ν(C=C) stretching frequency. This shows that the organic chain is no longer unsaturated.

Table 3.2 Yields, microanalysis and IR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ *i.e.* **9-13**

Compound number	**Appearance**	**Yields (%)**	**Microanalysis** [a] **(%)**	**IR** [b] **(cm^{-1})**
9	yellow-brown oil	70	C 52.65 (52.83) H 5.60 (5.64)	1934(s), 2000(s) [c] 3355(br) [d]
10	yellow-brown oil	64	C 54.42 (54.57) H 6.20 (6.11)	1935(s), 1997(s) [c] 3355(br) [d]
11	yellow-brown oil	60	e	1934(s), 1997(s) [c] 3355(br) [d]
12	yellow-brown oil	61	e	1938(s), 1996(s) [c] 3354(br) [d]
13	pale yellow powder 62-65 °C [g]	61	C 60.05 (59.68) H 7.50 (7.79)	1919(s), 1979(s) [c,f]

[a] Calculated values in brackets

[b] Neat film between NaCl plates, unless stated otherwise, (s = strong and br = broad)

[c] ν(CO)

[d] ν(O-H)

[e] unstable oil, not possible to obtain acceptable microanalysis

[f] CH_2Cl_2 as solvent in NaCl solution cells

[g] Melting point on a Fischer-Johns hotstage melting point apparatus

3.2.2 ^{1}H NMR Spectra

The ^{1}H NMR spectra of all the compounds exhibit similar trends, except for compound **13**, the spectrum of which contains signals similar to those of a methyl substituted cyclopentadienyl compound of the type Cp*$(CO)_2Fe(CH_2)_nX$ (X = halogen).[13] The peaks are broad and not well defined which may be due to the unstable nature of the ω-hydroxyalkyls.

The five cyclopentadienyl protons of compounds **9-12** were assigned to a single peak in the region δ 4-5 ppm. Again an increase in the carbon chain length had no significant influence on the position of this peak. The protons of the carbon adjacent to the hydroxy group were assigned to the signal in the region δ 3.4-3.7 ppm. This signal appears downfield due to the deshielding effect of the hydroxy group.

The remaining protons were assigned to the signals in the region δ 1-1.8 ppm. The peak for the hydroxy proton in the spectrum of the Cp*$Fe(CO)_2$ complex, at δ 1.1 ppm, could be clearly distinguished from the other methylene protons, while for the $CpFe(CO)_2$ compounds this was not the case. Nelson[5] also assigned the alcoholic proton of the ω-hydroxyalkyl compound, Cp*$Ru(CO)_2CH_2OH$, to the peak at 0.88 ppm. Normally the aliphatic alcohols show an OH signal at a position 4-5 ppm. The observation that the OH proton is more shielded in the $Cp^*Fe(CO)_2$ ω-hydroxyalkyls should be further investigated.

Table 3.3 ^1H NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ *i.e.* **9-13**

Compound number	**Chemical Shift** [a, b] **(δ ppm)**	**Assignment**
9	1.45 (br d, 7H)	$Fe(C\underline{H}_2)_3CH_2O\underline{H}$
	3.64 (br s, 2H)	$Fe(CH_2)_3C\underline{H}_2OH$
	4.73 (s, 5H)	$C_5\underline{H}_5$
10	1.41 (br s, 9H)	$Fe(C\underline{H}_2)_4CH_2O\underline{H}$
	3.62 (br s, 2H)	$Fe(CH_2)_4C\underline{H}_2OH$
	4.66 (br s, 5H)	$C_5\underline{H}_5$
11	1.43 (br s, 11H)	$Fe(C\underline{H}_2)_5CH_2O\underline{H}$
	3.61 (br s, 2H)	$Fe(CH_2)_5C\underline{H}_2OH$
	4.55 (br s, 5H)	$C_5\underline{H}_5$
12	1.1-1.6 (br m, 15H)	$Fe(C\underline{H}_2)_7CH_2O\underline{H}$
	3.5-3.7 (br s, 2H)	$Fe(CH_2)_7C\underline{H}_2OH$
	4.6-4.8 (br s, 5H)	$C_5\underline{H}_5$
13	1.1 (br s, 1H)	$Fe(CH_2)_4O\underline{H}$
	1.72 (br s, 21H)	$Fe(C\underline{H}_2)_3CH_2OH$, $C_5(C\underline{H}_3)_5$
	3.65 (br s, 2H)	$Fe(CH_2)_3C\underline{H}_2OH$

[a] $CDCl_3$ as solvent
[b] br = broad, s = singlet, d = doublet and m = multiplet

3.2.3 ^{13}C NMR Spectra

The ^{13}C NMR spectra of all the compounds exhibit similar trends, except for the methyl substituted cyclopentadienyl compound **13**. Peaks in the region of δ 217 ppm were assigned to the terminal carbonyl groups of the compounds **9-13**. The hydrocarbon chain length or the change in the iron environment had no significant effect on the chemical shifts of these peaks.

The carbon atom α to the iron centre in the $CpFe(CO)_2$ compounds, was assigned to the peaks in the region δ 3-4 ppm. The α-carbon for the $Cp^*Fe(CO)_2$ complex appears at δ 11.39 ppm. The chemical shift difference of ~8 ppm between the $CpFe(CO)_2$ complex and that of the $Cp^*Fe(CO)_2$, indicates that the α-carbon for the $Cp^*Fe(CO)_2$ complex is influenced by the methyl substituted Cp ligand.

The chemical shift for the carbons α to the iron centre of **9-12** compares favourably with that of the chemical shift for $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$,[14] which was reported to be at δ 3.8 ppm. Again the increase in chain length had no significant influence on the chemical shift of the α-carbons for the ω-hydroxyalkyl series, $Cp(CO)_2Fe(CH_2)_nX$ ($X = OH$, $n = 4\text{-}6,8$). Moss *et al.*[13] synthesized a series of functionalized alkyl compounds of the type $Cp(CO)_2Fe(CH_2)_nX$ (X = Br and I, $n = 3\text{-}10$). The trends observed for these haloalkyl compounds are different to what we find for the ω-hydroxyalkyl compounds. The afore-mentioned workers found that an increase in chain length influences the chemical shift of the carbon α to the iron centre. They suggested that this was due to an interaction between the halogen and the metal centre as illustrated in Figure 3.2.[13,15]

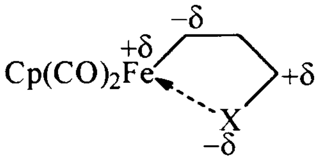


Figure 3.2 The proposed interaction between the halogen and the iron centre.

Figure 3.2 shows the polarization of the metal-carbon bond induced by the electronegative halogen. This polarization causes a partial negative charge on the α-carbon resulting in a upfield shift. The polarization decreases with an increase in chain length, since the interaction between the halogen and the iron centre weakens. It results in a less shielded α-carbon. This effect was not as obvious with the ω-hydroxyalkyl species. The reported chemical shift for the α-carbon of $Cp(CO)_2Fe(CH_2)_4Br$[13] appears at δ 1.34 ppm while the α-carbon of $Cp(CO)_2Fe(CH_2)_4OH$, was assigned to the peak at δ 3.12 ppm.

The carbon atoms adjacent the hydroxy group for **9-13**, were assigned to the peaks in the region δ 62-63 ppm. These carbons were much more deshielded than the corresponding carbons of the ω-haloalkyls, $Cp(CO)_2Fe(CH_2)X$ (X = Br and I, n = 3-10)[13], which were reported to be in the region δ 33-36 ppm. The large chemical shift difference between the carbons adjacent to the hydroxy group and that of the carbons adjacent to the halogens indicates that the hydroxy group is more electron withdrawing.

The remaining carbons were assigned to the peaks in the region δ 7-39 ppm as outlined in Table 3.4.

Table 3.4 ^{13}C NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ *i.e.* **9-13**

Compound number	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
9	3.12	$Fe\underline{C}H_2(CH_2)_3OH$
	34.70	$FeCH_2\underline{C}H_2(CH_2)_2OH$
	38.45	$Fe(CH_2)_2\underline{C}H_2CH_2OH$
	62.48	$Fe(CH_2)_3\underline{C}H_2OH$
	85.40	$\underline{C}_5H_5$
	217.60	$\underline{C}O$
10	3.25	$Fe\underline{C}H_2(CH_2)_4OH$
	30.71	$FeCH_2\underline{C}H_2(CH_2)_3OH$
	32.47	$Fe(CH_2)_2\underline{C}H_2(CH_2)_2OH$
	37.92	$Fe(CH_2)_3\underline{C}H_2CH_2OH$
	63.10	$Fe(CH_2)_4\underline{C}H_2OH$
	85.30	$\underline{C}_5H_5$
	217.62	$\underline{C}O$
11	3.41	$Fe\underline{C}H_2(CH_2)_5OH$
	25.40	$FeCH_2\underline{C}H_2(CH_2)_4OH$
	32.83	$Fe(CH_2)_2\underline{C}H_2(CH_2)_3OH$
	34.49	$Fe(CH_2)_3\underline{C}H_2(CH_2)_2OH$
	38.14	$Fe(CH_2)_4\underline{C}H_2CH_2OH$
	63.05	$Fe(CH_2)_5\underline{C}H_2OH$
	85.28	$\underline{C}_5H_5$
	217.64	$\underline{C}O$

Table 3.4 (continued)

Compound number	Chemical Shift [a] (δ ppm)	Assignment
12	3.64	$\mathrm{Fe\underline{C}H_2(CH_2)_7OH}$
	25.69	$\mathrm{FeCH_2\underline{C}H_2(CH_2)_6OH}$
	29.28	$\mathrm{Fe(CH_2)_2\underline{C}H_2(CH_2)_5OH}$
	29.43	$\mathrm{Fe(CH_2)_3\underline{C}H_2(CH_2)_4OH}$
	32.75	$\mathrm{Fe(CH_2)_4\underline{C}H_2(CH_2)_3OH}$
	34.73	$\mathrm{Fe(CH_2)_5\underline{C}H_2(CH_2)_2OH}$
	38.22	$\mathrm{Fe(CH_2)_6\underline{C}H_2CH_2OH}$
	63.02	$\mathrm{Fe(CH_2)_7\underline{C}H_2OH}$
	85.26	$\mathrm{\underline{C}_5H_5}$
	217.68	$\mathrm{\underline{C}O}$
13	7.35	$\mathrm{C_5(\underline{C}H_3)_5}$
	11.39	$\mathrm{Fe\underline{C}H_2(CH_2)_3OH}$
	31.64	$\mathrm{FeCH_2\underline{C}H_2(CH_2)_2OH}$
	36.90	$\mathrm{Fe(CH_2)_2\underline{C}H_2CH_2OH}$
	61.15	$\mathrm{Fe(CH_2)_3\underline{C}H_2OH}$
	92.98	$\mathrm{\underline{C}_5(CH_3)_5}$
	217.81	$\mathrm{\underline{C}O}$

[a] $CDCl_3$ as solvent

3.2.4 Mass Spectra

The mass spectra of the compounds **10-13** all exhibit molecular ions, except for **9** which shows a highest mass peak representing, the species $(M\text{-}CO)^+$ ($m/z = 222$).

Two major fragmentation patterns were observed in the mass spectra of these compounds. The one pathway involves the sequential loss of the terminal carbonyl groups, followed by the loss of the alcohol functionality either through the elimination of H_2O or through direct loss of the hydroxy group. The hydrocarbon chain is then subsequently eliminated. The second fragmentation pathway involves the initial loss of the terminal CO's followed by the elimination of the hydrocarbon chain.

The base peak for compounds **9-11** and **13** corresponds to the species $(M\text{-}2CO\text{-}C_nH_{2n})^+$. This may suggest that a possible fragmentation pathway involves one which give rise to ions in which the Fe-OH bond is formed. Thus there might exist some sort of interaction between the iron centre and the hydroxy group, under these conditions.

The spectrum of **13** shows that the loss of the Cp* ligand yields low intensity ions, unlike compounds **9-12**, where the decomposition route corresponding to the loss of the Cp ligand is favoured.

The assignments of the major peaks in the mass spectra of compounds **9-12** and **13** are summarized in Tables 3.5 and 3.6 respectively.

Table 3.5 Mass spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) *i.e.* **9-12**

	Relative Intensities			
Ion [a]	**9** [b]	**10** [b]	**11** [b]	**12** [c]
M	-	3	3	1
M - CO	0.6	7	9	8
M - 2CO	30	25	32	32
M - 2CO - OH	8	4	6	2
M - 2CO - H_2O	16	26	32	9
M - 2CO - OH - $C_{½n}H_n$	14	2	20	24
M - 2CO - C_nH_{2n}	100	100	100	16
M - 2CO - OH - C_nH_{2n}	61	22	8	12
M - 2CO - Cp	22	3	5	0.4
M - 2CO - Cp - OH	3	1	1	2
M - 2CO - Cp - H_2O	51	3	8	8
M - 2CO - CpH - C_3H_6	-	1	52	100
M - 2CO - Cp - C_nH_{2n}	2	21	12	10
M - 2CO - Cp - OH - C_nH_{2n}	42	19	68	56

[a] All the ions have a single positive charge, ion refers to suggested assignment, M = parent ion

[b] Peak intensities relative to *m/z* = 138

[c] Peak intensities relative to *m/z* = 142

Table 3.6 Mass Spectral data for the compound $Cp^*(CO)_2Fe(CH_2)_4OH$ *i.e.* **13**

Ion [a]	**Relative Intensities** [b]
M	3
M - CO	8
M - 2CO	16
M - 2CO - OH	5
M - 2CO - OH - $C_{½n}H_n$	4
M - 2CO - C_nH_{2n}	100
M - 2CO - OH - C_nH_{2n}	44
M - 2CO - Cp*	1
M - 2CO - Cp* - H_2O	1
M - 2CO - Cp* - OH - C_nH_{2n}	14

[a] All ions have a single positive charge, ion refers to suggested assignment, M = parent ion

[b] Peak intensities relative to *m/z* = 208

3.3 Conclusion

The η^1-alkenyl compounds, $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ ($n = 2\text{-}4,6$) and $Cp^*(CO)_2Fe(CH_2)_2CH{=}CH_2$ were successfully functionalized to the ω-hydroxyalkyl complexes, $Cp(CO)_2Fe(CH_2)_nOH$ ($n = 4\text{-}6,8$) and $Cp^*(CO)_2Fe(CH_2)_4OH$ under oxidative-hydroboration conditions. These compounds were fully characterised by IR, ^1H NMR, ^{13}C NMR spectroscopy as well as microanalysis and mass spectrometry.

The relative ease of conversion of the η^1-alkenyl compounds indicate that they are useful precursors for further derivatization to other functionalized alkyls.

3.4 Experimental

All the reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. $BH_3 \cdot THF$ and H_2O_2 were purchased from Aldrich and BDH Limited respectively. These chemicals were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under nitrogen prior to its use. Chromatography was done on deactivated alumina 90 (70-230 mesh), purchased from Merck. Melting points were recorded on a Fischer-Johns hotstage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer and NMR spectra on a Varian XR 200 spectrometer operating at 200 MHZ, using tetramethylsilane as internal standard (δ 0.00 ppm). Mass spectra were recorded on a V.G. Micromass 16F Spectrometer operating at 70eV and using accelerating voltage of 4kV. Microanalyses were performed at the University of Cape Town.

3.4.1 Preparation of the compounds, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) and $Cp^*(CO)_2Fe(CH_2)_4OH$ *i.e.* 9-13

The oxidative-hydroboration of compound **1**, as described below, outlines the general procedure used.

1 (0.22g; 0.9mmol) was transferred to a Schlenk tube and dissolved in a minimum amount of THF (3ml). The yellow solution was cooled to 0°C and 1M $BH_3 \cdot THF$

(0.9ml; 0.9 mmol) was added dropwise. The yellow solution changed colour to a lighter yellow. The reaction mixture was then warmed to room temperature and stirred for a further 2h. Water (2 drops) was added followed by the addition of 3M NaOH (0.6ml). The mixture foamed excessively. After the foaming had ceased, 30% H_2O_2 (0.2ml) was added dropwise. The yellow mixture immediately changed to orange and this was then refluxed for 2h after which it was cooled to room temperature. The reaction mixture was filtered to remove any undissolved salts. The filtrate was dried over $MgSO_4$, which was filtered off after standing for a few minutes. Removal of the solvent from the filtrate,using a rotary evaporator, resulted in a yellow oil. This was dissolved in a minimum amount of CH_2Cl_2 and transferred to an alumina column (5 x 1.5cm). Elution with CH_2Cl_2 yielded two bands. The first band was collected and after removal of the solvent a yellow oil was obtained. The oil was identified as unreacted starting material. The second slower moving band was then collected. A yellow oil was isolated upon removal of the solvent. The oil was found to be the oxidative-hydroboration product **9**.

Compounds **2-5** were reacted in a similar manner yielding compounds **10-13**. Yields and characterization data for compounds **9-13** are given in Tables 3.2-3.6.

3.5 References

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CHAPTER 4

THE REACTIVITY OF η^1-ALKENYL HYDROCARBYL COMPOUNDS OF IRON

4.1 The hydrozirconation of the η^1-alkenyl hydrocarbyl compounds, $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3).

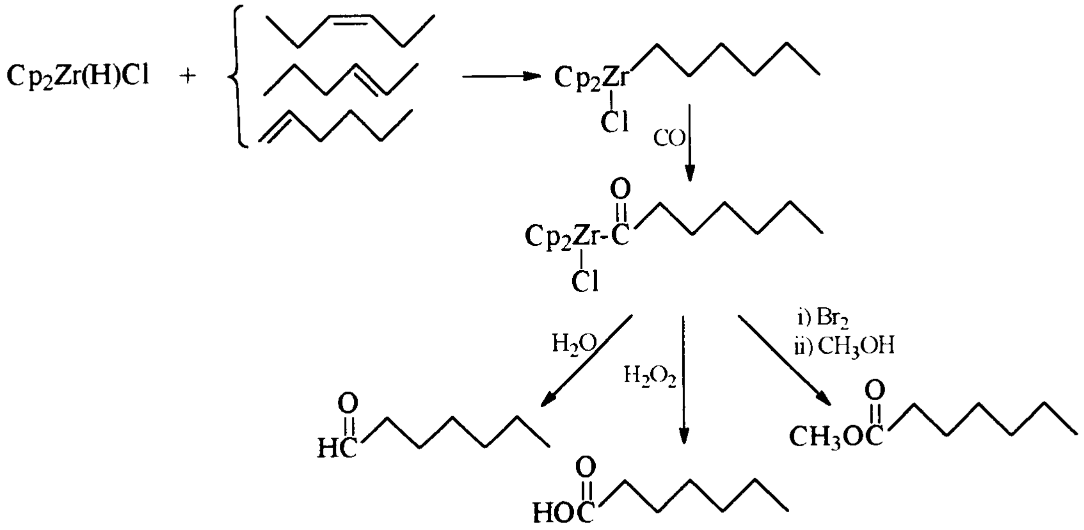
4.1.1 Introduction

Hydrozirconation involves the insertion of an unsaturated hydrocarbon into the Zr-H bond of zirconium hydride compounds.[1] The hydrozirconation reactions of the zirconium compound, $Cp_2Zr(H)Cl$ with unsaturated hydrocarbons have been extensively investigated by Wailes and Schwartz.[2-5] The hydrozirconation reagent $Cp_2Zr(H)Cl$, which they investigated, was synthesized via the reaction of Cp_2ZrCl_2 with the lithium complex LiAl(O-*tert*-$C_4H_9)_3H$ or $LiAlH_4$ [Eq. 4.1].[2]

$$Cp_2ZrCl_2 + LiAl(O\text{-}tert\text{-}C_4H_9)_3H \xrightarrow{THF} Cp_2Zr(H)Cl + LiCl + Al(O\text{-}tert\text{-}C_4H_9)_3 \tag{4.1}$$

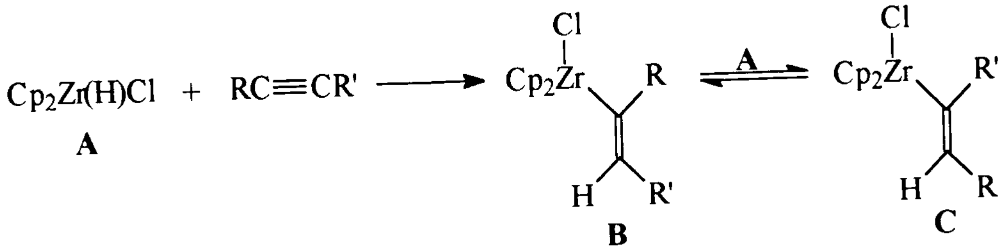
Schwartz *et al.* utilized hydrozirconation as a convenient way to transform olefins and acetylenes into a variety of desirable organic products.[3-5] Some transformations are shown in Scheme 4.1.[4] This scheme illustrates the hydrozirconation of olefins followed by subsequent CO insertion. Different carbonyl-containing organic compounds were obtained, depending on the work-up procedure.

The scheme also illustrates that hydrozirconation occurs with high regiospecificity *i.e.* the hydrozirconation of isomeric olefins give a single alkylzirconium compound.[4] This is due to the bulky Cp_2ZrCl moiety which dictates that the zirconium centre is attached to the sterically least or more hindered, accessible position of the olefin. The process involves the addition of Zr-H to the olefin moiety irrespective of whether it is a terminal or internal alkene. In the case of an internal alkene, the initial Zr-alkyl undergoes β-hydride transfer to produce a new alkene in which the double bond has shifted to the α position. Subsequent Zr-H addition and alkene elimination ultimately leads to a Zr-alkyl species in which we have an n-alkyl group.[5] The procedure occurs rapidly at room temperature whereas the analogous organoboration of internal olefins proceeds slowly at elevated temperatures.[5]



Scheme 4.1 The hydrozirconation of isomeric olefins.

Schwartz *et al.*[6] also demonstrated the high regio- and stereoselectivity of hydrozirconation by reacting $Cp_2Zr(H)Cl$ with asymmetrical disubstituted acetylene compounds. They found that for each asymmetrical acetylene compound two *cis* vinylzirconium complexes were formed [Eq. 4.2]. Subsequent treatment of the vinylzirconium mixture with $Cp_2Zr(H)Cl$, catalyzed the conversion to the isomer with the highest regioselectivity as shown in Table 4.1.[6]



$R = CH_3, R' = CH_3CH_2CH_2$

$R = CH_3, R' = (CH_3)_2CHCH_2$

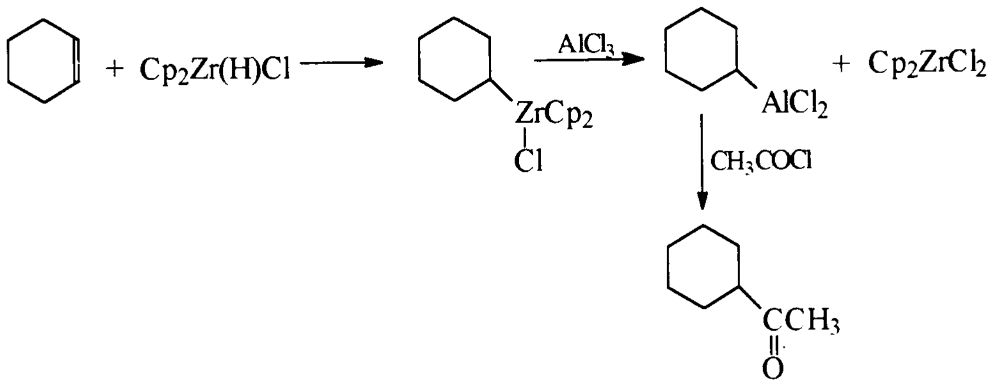
$R = CH_3, R' = (CH_3)_2CH$ (4.2)

Table 4.1 The hydrozirconation of some asymmetrical acetylene compounds.[6]

Acetylene (RC≡CR′)	Product Ratio (**B**:**C**)[a]	
	Initially observed	After treatment with **A**
$R = CH_3, R' = CH_3CH_2CH_2$	69:31	91:9
$R = CH_3, R' = (CH_3)_2CHCH_2$	55:45	95:5
$R = CH_3, R' = (CH_3)_2CH$	84:16	98:2

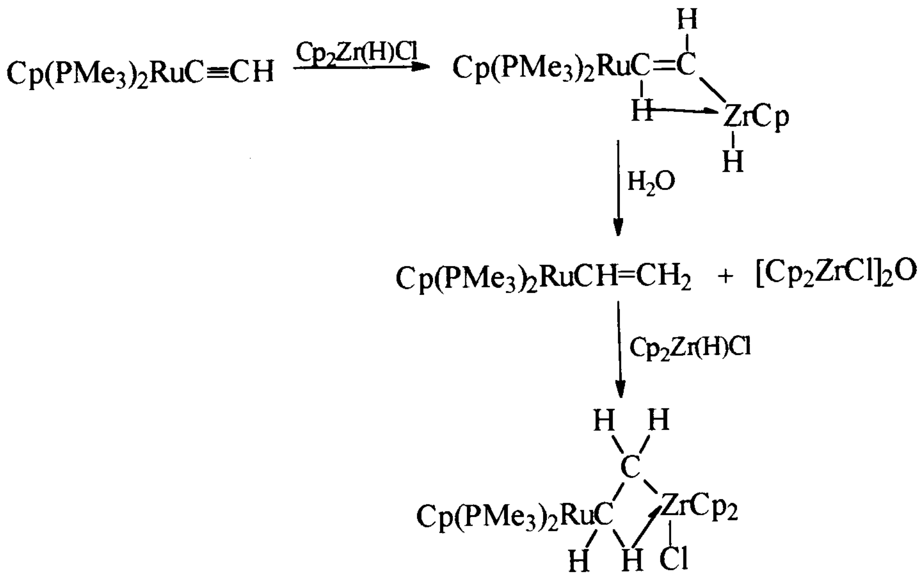
[a] See Eq. 4.2

The usefulness of hydrozirconation in organic synthesis has further been broadened by reports that hydrozirconated products can be transmetalated with cyanocuprate and aluminum halides to form reactive organometallic compounds.[7,8] The resulting hydrozirconation-transmetalation products *viz.* organoaluminiums and organocuprates, are both alkylating agents.[7,8] Several features of the hydrozirconation-($AlCl_3$)-transmetalation reactions are noteworthy.[7] The reaction occurs with high regioselectivity. Mixtures of isomeric olefins give a single zirconium-containing compound and the subsequent transmetalation affords only the corresponding organoaluminium compound. The organoaluminium compounds can be used as precursors in organic synthesis.[7] The hydrozirconation-transmetalation-alkylation sequence, for example, was used to effect ketone formation through the acylation of an organoaluminium compound with an acid chloride [Eq. 4.3].[7]



(4.3)

Hydrozirconation reactions have also been used to synthesize binuclear hydrocarbyl compounds.[9,10] The hydrozirconation of the unsaturated ruthenium hydrocarbyl complexes, $Cp(PMe_3)_2RuCH{=}CH_2$ and $Cp(PMe_3)_2RuC{\equiv}CH$, resulted in the formation of C_2-bridged early / late heteronuclear hydrocarbyl compounds [Scheme 4.2].[10]



Scheme 4.2 The hydrozirconation of some unsaturated ruthenium complexes.

The importance of hydrozirconation

The hydrozirconation of unsaturated hydrocarbons has been demonstrated to be of high value in organic synthesis.[3-6] Alkenes and acetylene compounds have been transformed under mild conditions into various products via alkylzirconium and alkenylzirconium intermediates respectively.[3-6] These intermediates may act as model compounds for a number of catalytic processes. An example, which was earlier demonstrated in Scheme 4.1, is the alkylzirconium compound which readily undergoes CO insertion.[4] This reaction may model a step in the reduction of CO in the Fischer-Tropsch process, or it may model CO insertion which is important in a number of catalytic processes *e.g.* the Monsanto acetic acid process.[11,12] Hydrozirconation of olefins, which involves alkene insertion into a Zr-H bond, may also be used to model some steps in the Ziegler-Natta polymerization reaction.[1]

Early / late hydrocarbyl complexes, as were formed during the hydrozirconation of the unsaturated ruthenium containing hydrocarbyl compounds [Scheme 4.2], have ignited increased interest.[13-16] The early/late heterobimetallic complexes combine the Lewis acidity of the oxophilic early metals with that of the known abilities of the late metals for hydrogenation.[13] These compounds have therefore extensively been investigated as models for species in important metal-catalyzed reactions *e.g.* carbon monoxide reduction in the Fischer-Tropsch process.[16]

4.1.2 Synthetic approach

The hydrozirconation of unsaturated hydrocarbons is well recorded.[3] We therefore investigated the hydrozirconation of the η^1-alkenyl compounds $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3), with the aim of producing early / late transition metal hydrocarbyl complexes of the type, $Cp(CO)_2Fe(CH_2)_{n+2}ZrCp_2(Cl)$ (n = 2 and 3) as shown in Eq. 4.4.

$$\underset{\substack{\mathbf{1}\quad n = 2\\ \mathbf{2}\quad n = 3}}{Cp(CO)_2Fe(CH_2)_nCH{=}CH_2} + Cp_2Zr(H)Cl \longrightarrow \underset{\substack{\mathbf{14}\quad n = 2\\ \mathbf{15}\quad n = 3}}{Cp(CO)_2Fe(CH_2)_{n+2}ZrCp_2(Cl)} \qquad (4.4)$$

4.1.3 Results and discussion

We expected to isolate the heterobinuclear hydrocarbyl compounds **14** and **15** [Eq. 4.4], since the successful hydrozirconation of alkenes is well recorded.[3] Instead the compounds $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4), $[Cp_2ZrCl]_2O$ and starting material were isolated. The iron alkyls of the type $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) were isolated as unstable orange-yellow oils that decomposed in the presence of air. $[Cp_2ZrCl]_2O$ was isolated as an off white powder, which was stable at room temperature in the presence of air. The identity of the oxo-bridged zirconium dimer was confirmed by comparing its ^1H, ^{13}C NMR and mass spectrum with those previously reported.[17] The spectral data of $[Cp_2ZrCl]_2O$ are summarized in the Experimental Section 4.3.

We speculate that the binuclear hydrocarbyl compounds **14** and **15** were indeed formed, but that they were fairly unstable and could thus not be isolated. *In-situ* decomposition of **14** and **15** lead to the formation of the iron alkyl compounds of the type $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) and $[Cp_2ZrCl]_2O$. We suspect that the alkyl compounds are formed as a result of the hydrolysis of the Zr-alkyl bond in compounds **14** and **15**.

Previous reports on zirconiumalkyl compounds indicated that the Zr-C bonds are extremely reactive towards protic reagents. The reaction of the zirconiumalkyls with water, often atmospheric, proceeds according the equation below.[2]

$$2\ Cp_2Zr(Cl)CH_3 + H_2O \longrightarrow [Cp_2ZrCl]_2O + 2\ CH_4 \qquad (4.5)$$

We are of the opinion that a similar reaction occurs in the case of **14** and **15** and that hydrolysis probably occurs during the work-up procedure. In an attempt to exclude all traces of water, we repeated the above reactions. The entire work-up procedure was carried out under ultra-dry nitrogen using ultra-dry solvents. A yellow oil was obtained after removal of the solvent *in-vacuo*. The NMR spectrum of this oil was obtained in a sealed NMR tube which had been loaded in a nitrogen purged glove-bag. The ^1H NMR data for the compound is discussed below.

^{1}H NMR Spectra of Hydrozirconation Products

The ^{1}H NMR spectra obtained for the hydrozirconated samples of **1** and **2** exhibit similar trends. Peaks in the region δ 6-6.3 ppm were assigned to the cyclopentadienyl protons attached to the zirconium centre. The fact that more than one peak is observed in this region is indicative of a mixture of zirconium compounds. Peaks at δ 4.8 ppm and δ 5.8 ppm were assigned to the vinylic protons of the unreactive starting material.[18] The spectra also exhibit peaks characteristic of the chemical shift of Zr-C$\underline{H}_2$, in the region δ 0.8-0.92 ppm.[5]

In conclusion, the ^{1}H NMR spectra show that the starting material was not completely consumed. The reaction solution contains mixtures of zirconium compounds, which possibly may include $Cp_2Zr(H)Cl$, $[Cp_2ZrCl]_2O$ and the expected compounds **14** and **15**. However, since this was not very conclusive, we had to conduct some other experiments to confirm our suspicions that **14** and **15** were indeed formed to some extent.

It was decided to subject **14** and **15** to *in-situ* transformations. **14** and **15** were oxidized which resulted in the formation of the ω-hydroxyalkyl compounds, $Cp(CO)_2Fe(CH_2)_nOH$ ($n = 4$ and 5). The oxidation of zirconiumalkyls is a known reaction which leads directly to the formation of alcohols.[19]

Attempts at oxidative-hydrozirconation of **1** and **2** afforded a mixture of products in both cases. For both of the compounds, the hydrolysis products, $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) and the expected alcohols, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) were isolated as indicated in Eq. 4.6.

$$\begin{tikzcd}
\mathrm{Cp(CO)_2Fe(CH_2)_nCH{=}CH_2 + Cp_2Zr(H)Cl} \arrow[r] & \text{"}\mathrm{Cp(CO)_2Fe(CH_2)_{n+2}ZrCp_2(Cl)}\text{"} \arrow[d, "\mathrm{H_2O_2,\ NaOH}"] \\
 & \mathrm{Cp(CO)_2Fe(CH_2)_{n+2}OH} + \mathrm{Cp(CO)_2Fe(CH_2)_{n+1}CH_3}
\end{tikzcd}$$

(4.6)

The isolation of a mixture of products, indicates that two competitive pathways are operative during the reaction. The alcohols were formed via an oxidative-hydrozirconation reaction while the alkanes were formed as a result of the hydrolysis of the Zr-C bond, with the introduction of water into the system from the basic medium required for the oxidation of the alkylzirconium. The ω-hydroxyalkyl species, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) and the iron-alkyls, $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) were isolated as unstable brown-yellow oils that decompose in the presence of air. The ^1H NMR and IR characterization data for the compounds, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) and $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) were in good agreement with those of authentic samples. The IR and ^1H NMR spectra of the expected products of the oxidative-hydrozirconation reactions are briefly discussed and are summarized in the Experimental Section 4.3.

The fact that the ω-hydroxyalkyl compounds, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) were isolated, is further evidence for the existence of $Cp(CO)_2Fe(CH_2)_{n+2}ZrCp_2(Cl)$ (n = 2 and 3) in solution.

IR Spectra of the Oxidative-hydrozirconation Products

The IR spectra of the oxidative-hydrozirconation products of **1** and **2**, show two sharp bands in the ν(CO) region at 1940 and 2000 cm^{-1} , which are similar to those of the starting material. This is an indication that the metal environment remained unaffected during the oxidative-hydrozirconation reaction. A strong band in the region 3350 cm^{-1}, assigned to the ν(O-H), was also observed. The absence of a band in the region ~1630 cm^{-1}, which can be assigned to the ν(C=C), indicates that we no longer have an unsaturated organic fragment.

^{1}H NMR Spectra Oxidative-hydrozirconation Products

The ^{1}H NMR spectra of the isolated products, show peaks that are broad and unresolved. However these resemble the spectra of the expected ω-hydroxy alkyls. The spectra exhibit peaks at δ 3.6 ppm which were assigned to the protons adjacent to the hydroxy functionality. The peaks at δ 4.7 ppm and in the region δ 1-1.8 ppm were assigned to the cyclopentadienyl protons and the remaining methylene protons respectively.

4.1.4 Conclusion

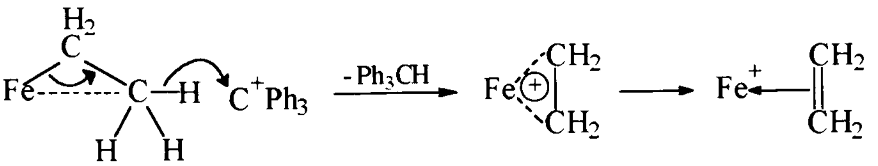
The hydrozirconation of the η^1-alkenyl compounds does not yield the expected binuclear compounds **14** and **15**, instead the hydrolysis products of **14** and **15** *viz.* $Cp(CO)_2Fe(CH_2)_nCH_3$ (n = 3 and 4) and $[Cp_2ZrCl]_2O$ were obtained. The *in-situ* oxidation of **14** and **15** to the corresponding ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) however confirmed their existence in solution.

Comparison of the oxidative-hydrozirconation reaction of **1** and **2** with that of the oxidative-hydroboration reaction of the same compounds (Chapter 2), shows that the latter is more efficient in the preparation of ω-hydroxyalkyl compounds. Yields from the oxidative-hydroboration reactions exceed 60% while the those for the oxidative-hydrozirconation reactions were low *e.g.* the yield for $Cp(CO)_2Fe(CH_2)_5OH$ was only 16%. The low yields for the oxidative-hydrozirconation reactions may possibly be attributed to the competing hydrolysis reaction of the zirconiumalkyl intermediate. Furthermore, the oxidative-hydroboration reaction does not exhibit the same sensitivity towards moisture, as was the case with the oxidative-hydrozirconation reaction. Therefore, stringent precautions to exclude moisture were not required. The oxidative-hydroboration reaction is thus a more convenient route for the conversion of η^1-alkenyl to ω-hydroxyalkyl compounds.

4.2 The reactivity of η^1-alkenyl compounds of iron towards β-hydride abstraction.

4.2.1 Introduction

Green and Nagy[20] have shown that β-hydride abstraction from compounds of the type $Cp(CO)_2FeR$ (R = alkyl) leads to the formation of $[CpFe(CO)_2(\eta^2\text{-olefin})]^+$ compounds.[20-22] They found that the hydride abstraction reaction is effected by trityl salts such as $Ph_3C^+PF_6^-$ or $Ph_3C^+BF_4^-$, as shown in Eq. 4.7.[20]



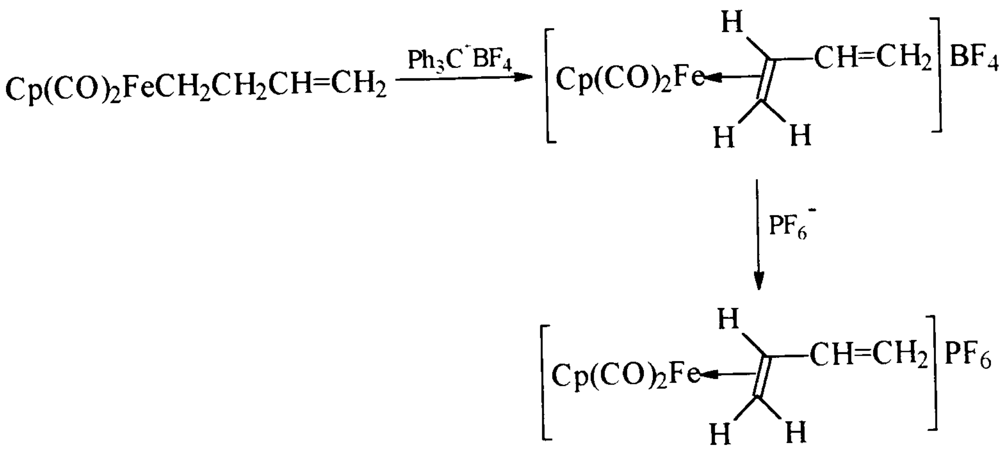
(4.7)

Later Moss *et al.*[23] also reacted the binuclear compounds, $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4-6) with $Ph_3C^+PF_6^-$, and in doing so isolated a series of cationic complexes of the type $\{[CpFe(CO)_2]_2[\mu\text{-}(C_nH_{2n-1})]\}PF_6$ (n = 4-6). Below is an example of one of these complexes where one iron atom is π-bonded and the other is σ-bonded to the organic chain.

Figure 4. 1 The cationic complex $\{[CpFe(CO)_2]_2[\mu\text{-}(C_4H_7)]\}^+$.

Green *et al.*[24] also performed a hydride abstraction reaction on the η^1-alkenyl complex, $Cp(CO)_2Fe(CH_2)_2CH{=}CH_2$ and isolated the compound,

$[Cp(CO)_2Fe(C_4H_6)]PF_6$ containing two alkene functionalities, one π-bonded to the iron centre and the other an uncoordinated terminal alkene moiety [Eq. 4.8].

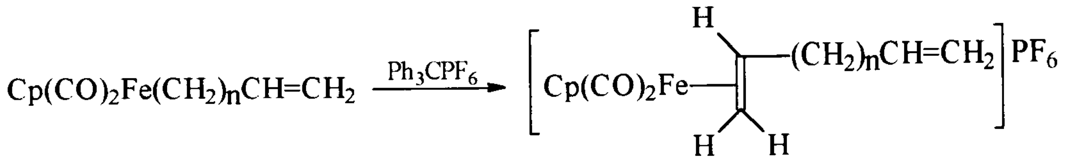


(4.8)

The previous reported isolation of $[Cp(CO)_2Fe(C_4H_6)]PF_6$ and our successful isolation of the longer chained η^1-alkenyl compounds, $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) prompted us to react these complexes with Ph_3CPF_6 to form longer chained $[CpFe(CO)_2(\eta^2\text{-diene})]^+$ compounds with the formula, $[Cp(CO)_2Fe(C_nH_{2n-2})]PF_6$ (n = 4-6,8).

4.2.2 Results and discussion

The reactions of $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) with Ph_3CPF_6 lead to the isolation of the compounds with the formula $[Cp(CO)_2Fe(C_nH_{2n-2})]PF_6$ (n = 4-6,8) as shown in Eq. 4.9.



1 n = 2
2 n = 3
3 n = 4
4 n = 6

16 n = 0
17 n = 1
18 n = 2
19 n = 4

(4.9)

Compounds **16-19** were isolated as microcrystalline solids. The colour of the compounds ranged from bright yellow for compound **16** to pale yellow for compound **19**. These compounds are stable at room temperature and in solution in the presence of air. They are insoluble in most organic solvents except acetone and acetonitrile. Yields for **16** and **17** were 72% and 71% respectively. Lower yields of 44% and 38% for **18** and **19** were obtained, respectively. This would seem to indicate that β-hydride abstraction for the longer chained η^1-alkenyl compounds, $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 4 and 6) is less effective compared to that of the shorter carbon chain η^1-alkenyl species.

IR Spectra

The compounds **16-19** were insoluble in most organic solvents. The IR spectrum of **16** was run as a nujol mull, in acetonitrile and as DRIFTS in KBr matrix. The spectrum run as DRIFTS exhibit well resolved peaks in the ν(CO) and ν(C=C) regions, while this was not the case for the other spectra. It was therefore decided to run the spectra of **16-19** as DRIFTS in KBr matrix.

The IR spectra of all the compounds exhibit similar trends. The spectra of compounds **16-19** contain two sharp bands in the ν(CO) region which are at higher wavenumbers than those of the starting material. This can be attributed to a decrease in the electron density of the cationic iron centre. The ν(CO) bands observed in the IR spectra are in good accord with those previously reported π-coordinated cationic iron compounds.[25]

Two medium intensity bands appear in the ν(C=C) region of the IR spectra. One of these bands, in the region 1623-1644 cm^{-1}, was assigned to the uncoordinated olefin. The other band was assigned to the π-coordinated olefin which appears about 100 wavenumbers lower, at 1518 cm^{-1}. This is in good agreement with what had previously been found.[26]

Table 4.2 Yields, microanalysis and IR data for the compounds, $[Cp(CO)_2Fe(C_nH_{2n-2})]PF_6$ (n = 4-6,8) *i.e.* **16-19**

Compound number	**Appearance**[a]	**Yields (%)**	**Microanalysis**[b] **(%)**	**IR**[c] **(cm^{-1})**
16	bright yellow crystals, decomposes 157-161°C	72	C 34.87 (35.17) H 2.88 (2.93)	2080(s), 2052(s) [d] 1624(m) [e], 1518(m)[f]
17	yellow crystals, decomposes 153-155°C	71	C 37.06 (36.95) H 3.35 (3.36)	2081(s), 2049(s) [d] 1639(m) [e], 1518(m) [f]
18	yellow powder, decomposes 157-161°C	44	C 39.30 (38.64) H 3.90 (3.74)	2076(s), 2045(s) [d] 1639(m) [e], 1518(m) [f]
19	pale yellow powder, decomposes 156-159°C	38	C 42.85 (41.69) H 4.62 (4.40)	2069(s), 2042(s) [d] 1643(m) [e], 1519(m) [f]

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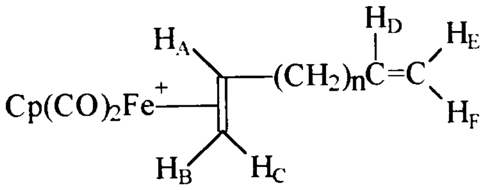
[a] Melting point obtained on a Fischer-Johns hotstage apparatus
[b] Calculated values in brackets
[c] DRIFTS in KBr matrix (s = strong and m = medium)
[d] ν(CO)
[e] ν(C=C) for terminal uncoordinated C=C
[f] ν(C=C) for coordinated C=C

^{1}H NMR

The ^{1}H NMR spectra of **16-19** in actetone-d_6, exhibit trends characteristic of vinylic system.[27] The peaks for the π-coordinated vinylic protons can be clearly distinguished, while the peaks for the uncoordinated alkene moiety are not well resolved. The proton assignments for **16-19** are based on the structure shown in Figure 4.2.



16 n = 0
17 n = 1
18 n = 2
19 n = 4

Figure 4.2 The vinylic proton assignments of **16-19**.

Two doublets in the region δ 3.6-3.9 ppm and δ 4.0-4.2 ppm, for **16-19**, were assigned to the H_C and H_B protons. These protons for **17-19** have *trans* (J_{CA}) and *cis* (J_{BA}) coupling constants of ~14 Hz and 8 Hz respectively. The chemical shifts of the *trans* protons (H_C) appear more upfield than the *cis* protons (H_B). This trend is observed for vinylic protons directly bonded to the metal centre.[27] The *trans* and *cis* coupling constants for **16**, the shorter carbon chain analog, are slightly lower at 13.2 Hz and 7.8 Hz respectively. It was also observed that the chemical shift difference between H_B and H_C protons for **16** is 0.2 ppm. The chemical shift difference between the H_B and H_C protons for the longer chain analogues, **17-19** is ~0.4 ppm. Similar results for the π-coordinated olefins were previously reported.[23,26,28] Rosenblum *et al.*[28] ascribed the large chemical shift difference to anisotropy effects associated with the cyclopentadienyl ring currents.

The vinylic protons in the region δ 4.9-6.0 ppm for **18** and **19** exhibit similar trends while the spectrum of **17** shows some differences which may be attributed to the peaks being unresolved. The spectrum of **16** in this region, shows trends which are different to **17-19**. The vinylic protons H_A, H_D, H_E and H_F were assigned using a COSY experiment together with previously reported data for both π-coordinated olefins[23,25,28] as well as data for the uncoordinated alkenes in Chapter 2. The COSY sprectra of **16** and **17** are given in the Appendix Section.

The ^1H NMR spectrum of **16** show a multiplet at δ 5.5 ppm which was assigned to the proton H_D. The protons H_A,H_E, H_F and the cyclopentadienyl protons in **16** were assigned to the broad peak at δ 5.9 ppm.

The ^1H nmr of compounds **18** and **19** show similar characteristics in the vinylic region between δ 4.9-6.00 ppm. The protons H_A, H_E and H_F for **17** all have chemical shifts in the same region at around δ 5.19 ppm. The signal for the H_D

proton is hidden under the broad Cp peak at δ 5.9 ppm. The ^1H NMR spectra of both **18** and **19** show a multiplet at ~δ 5 ppm which was assigned to the protons H_E and H_F. The H_A proton in both compounds was assigned to the peak at ~δ 5.3 ppm while the multiplet at ~δ 5.8 ppm was assigned to the H_D proton.

It was observed that the H_A proton for **17-19** appears at a chemical shift position similar to that of previously reported compounds containing π-coordinated olefins[23,25,28]. Similarly the chemical shift positions of the H_D, H_E and H_F protons were in good accordance with the data obtained for the uncoordinated terminal alkenes (Chapter 2). This was not the case for **16**. The differences observed in the spectrum of **16** may be attributed to the presence of a conjugated diene system, in which the chemical shift positions of the H_A, H_D, H_E and H_F protons are influenced. In constrast **17-19**, contain two isolated alkene functionalities which therefore do not have any conjugation and thus have no great influence on each other.

The peak assigned to the cyclopentadienyl protons of **16-19** appears at ~δ 5.8 ppm. The corresponding peak for the cyclopentadienyl protons of **1-4** (Chapter 2) appears at ~δ 4.7 ppm. This downfield chemical shift is due to the influence of the cationic iron centre.

The methylene protons in all the compounds give rise to peaks in the region ~δ 1.5-3.2 ppm. This trend is in agreement with previously reported data. It has been found that the methylene protons adjacent to the π-coordinated olefins[23] appear at ~δ 1.6 ppm. The methylene protons adjacent to the uncoordinated alkene appear further downfield at ~δ 2.1 ppm. The proton assignments are outlined in Table 4.3.

Table 4.3 ^{1}H NMR spectral data for the compounds $[Cp(CO)_2Fe(C_nH_{2n-2})]PF_6$ (n = 0-2,4) *i.e.* **16-19**

Compound number	**Chemical Shift** $^{a,\,b}$ **(δ ppm)**	**Assignment**
16	3.84 (d, 1H, $J_{CA,\,trans}$ = 13.2 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	4.04 (d, 1H, $J_{BA,\,cis}$ = 7.8 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	5.54 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)C\underline{H}{=}CH_2$
	5.90 (m, 8H)	$Fe(\eta^2\text{-}CH_2{=}C\underline{H})CH{=}C\underline{H}_2$, $C_5\underline{H}_5$
17	2.49 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)C\underline{H}_2CH{=}CH_2$
	3.18 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)C\underline{H}_2CH{=}CH_2$
	3.67 (d, 1H, $J_{CA,\,trans}$ = 14.6 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	4.14 (d, 1H, $J_{BA,\,cis}$ = 8 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	5.19 (m, 3H)	$Fe(\eta^2\text{-}CH_2{=}C\underline{H})CH_2CH{=}C\underline{H}_2$
	5.85 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)CH_2C\underline{H}{=}CH_2$
	5.91 (s, 5H)	$C_5\underline{H}_5$
18	1.65 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)C\underline{H}_2CH_2CH{=}CH_2$
	2.26 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)C\underline{H}_2CH_2CH{=}CH_2$
	2.42 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)CH_2C\underline{H}_2CH{=}CH_2$
	2.62 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)CH_2C\underline{H}_2CH{=}CH_2$
	3.63 (d, 1H, $J_{CA,\,trans}$ = 14.6 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	4.07 (d, 1H, $J_{BA,\,cis}$ = 8.4 Hz	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	5.04 (m, 2H)	$Fe(\eta^2\text{-}CH_2{=}CH)CH_2CH_2CH{=}C\underline{H}_2$
	5.24 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}C\underline{H})CH_2CH_2CH{=}CH_2$
	5.81 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)CH_2CH_2C\underline{H}{=}CH_2$
	5.91 (s, 5H)	$C_5\underline{H}_5$

Table 4.3 (continued)

Compound number	**Chemical Shift** [a, b] **(δ ppm)**	**Assignment**
19	1.51 (br m, 5H)	$Fe(\eta^2\text{-}CH_2{=}CH)(C\underline{H}_2)_4CH{=}CH_2$
	2.52 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)(C\underline{H}_2)_4CH{=}CH_2$
	2.82 (s, 2H)	$Fe(\eta^2\text{-}CH_2{=}CH)(C\underline{H}_2)_4CH{=}CH_2$
	3.65 (d, 1H, $J_{CA,\ trans}$ = 14.6 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	4.06 (d, 1H, $J_{BA,\ cis}$ = 8.2 Hz)	$Fe(\eta^2\text{-}C\underline{H}_2{=}CH)$
	4.95 (m, 2H)	$Fe(\eta^2\text{-}CH_2{=}CH)(CH_2)_4CH{=}C\underline{H}_2$
	5.31 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}C\underline{H})(CH_2)_4CH{=}CH_2$
	5.81 (m, 1H)	$Fe(\eta^2\text{-}CH_2{=}CH)(CH_2)_4C\underline{H}{=}CH_2$
	5.90 (s, 5H)	$C_5\underline{H}_5$

[a] Acetone-d_6 as solvent
[b] s = singlet, d = doublet and m = multiplet

^{13}C NMR

The ^{13}C NMR for **16-19**, obtained using acetone-d_6, exhibit similar trends. The π-coordinated vinylic carbons $(CH{=}\underline{C}H_2)$ and $(\underline{C}H{=}CH_2)$ were assigned to the peaks in the region δ 52-58 ppm and δ 85-92 ppm respectively. The chemical shifts compare favourably to similar compounds which have previously been reported.[25]

The uncoordinated vinylic carbons $(CH{=}\underline{C}H_2)$ and $(\underline{C}H{=}CH_2)$ were assigned to the peaks in the region δ 117-125 ppm and δ 135-142 ppm respectively. It was observed that for **16-18** there was a downfield chemical shift for the $(CH{=}\underline{C}H_2)$ carbons and an upfield chemical shift for the $(\underline{C}H{=}CH_2)$ carbons compared to the corresponding carbons of the starting material. This was not the case for **19**. The chemical shifts for both the vinylic carbons of **19** compare favourably with those of the starting material. The chemical shift differences for **16-18** indicate that during the reaction the electronic environment of the terminal vinylic carbons changed which could be attributed to the cationic iron centre.

The ^{13}C NMR spectra show two carbonyl absorptions at δ 209 ppm and δ 211 ppm. Rosenblum *et al.*[28] ascribed this to two different conformations in which the olefin axis is either near or in the group symmetry plane of the $CpFe(CO)_2$ group. This affords steric interactions between the carbonyl groups and the olefinic ligand, causing the carbonyls to have different electronic environments.

Table 4.5 ^{13}C NMR spectral data for $[\mathrm{Cp(CO)_2Fe(C_nH_{2n-2})]PF_6}$ (n = 0-2,4) *i.e.* **16-19**

Compound number	Chemical Shift [a] (δ ppm)	Assignment
16	52.71	$\mathrm{Fe(\eta^2\text{-}\underline{C}H_2{=}CH)CH{=}CH_2}$
	88.06	$\mathrm{Fe(\eta^2\text{-}CH_2{=}\underline{C}H)CH{=}CH_2}$
	90.22	$\mathrm{\underline{C}_5H_5}$
	124.66	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)CH{=}\underline{C}H_2}$
	137.71	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\underline{C}H{=}CH_2}$
	208.69	$\mathrm{\underline{C}O}$
	211.34	$\mathrm{\underline{C}O}$
17	40.09	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)\underline{C}H_2CH{=}CH_2}$
	54.66	$\mathrm{Fe(\eta^2\text{-}\underline{C}H_2{=}CH)CH_2CH{=}CH_2}$
	85.78	$\mathrm{Fe(\eta^2\text{-}CH_2{=}\underline{C}H)CH_2CH{=}CH_2}$
	90.19	$\mathrm{\underline{C}_5H_5}$
	118.02	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)CH_2CH{=}\underline{C}H_2}$
	137.02	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)CH_2\underline{C}H{=}CH_2}$
	209.26	$\mathrm{\underline{C}O}$
	211.13	$\mathrm{\underline{C}O}$
18	36.37, 36.92	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)(\underline{C}H_2)_2CH{=}CH_2}$
	55.25	$\mathrm{Fe(\eta^2\text{-}\underline{C}H_2{=}CH)(CH_2)_2CH{=}CH_2}$
	87.60	$\mathrm{Fe(\eta^2\text{-}CH_2{=}\underline{C}H)(CH_2)_2CH{=}CH_2}$
	90.09	$\mathrm{\underline{C}_5H_5}$
	116.36	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)(\underline{C}H_2)_2CH{=}\underline{C}H_2}$
	137.38	$\mathrm{Fe(\eta^2\text{-}CH_2{=}CH)(CH_2)_2\underline{C}H{=}CH_2}$
	209.19	$\mathrm{\underline{C}O}$
	211.41	$\mathrm{\underline{C}O}$

Table 4.5 (continued)

Compound number	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
19	30.75, 32.63	$Fe(\eta^2-CH_2=CH)(\underline{C}H_2)_4CH=CH_2$
	33.79, 36.78	$Fe(\eta^2-CH_2=CH)(\underline{C}H_2)_4CH=CH_2$
	54.89	$Fe(\eta^2-\underline{C}H_2=CH)(CH_2)_4CH=CH_2$
	88.92	$Fe(\eta^2-CH_2=\underline{C}H)(CH_2)_4CH=CH_2$
	90.07	$\underline{C}_5H_5$
	114.95	$Fe(\eta^2-CH_2=CH)(CH_2)_4CH=\underline{C}H_2$
	139.19	$Fe(\eta^2-CH_2=CH)(CH_2)_4\underline{C}H=CH_2$
	209.27	$\underline{C}O$
	211.50	$\underline{C}O$

[a] Acetone-d_6 as solvent

4.2.3 Conclusion

The reaction of $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2-4,6) with Ph_3CPF_6 leads to the isolation of $[Cp(CO)_2FeC_nH_{2n-2})]PF_6$ (n = 4-6,8). The yields obtained indicate that the carbon chain length influences product formation. The ^1H and ^{13}C NMR spectra for **16-19** suggest that a number of interactions exist *e.g.* interactions between the $CpFe(CO)_2$ centre and the olefinic ligands, which may influence the electronic environments of the hydrogens and carbons. Our future studies will include the investigation of the crystal structures of **16-19** to identify the conformations of these compounds.

4.3 Experimental

All reactions were performed under an atmosphere of ultra-dry nitrogen using standard Schlenk tube techniques. $Cp_2Zr(H)Cl$ and Ph_3CPF_6 were purchased from Aldrich, while H_2O_2 was purchased from BDH Limited. Tetrahydrofuran (THF), hexane and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen prior to use. CH_2Cl_2 and acetone were freshly distilled under nitrogen, from P_2O_5 and $CaCl_2$ respectively. All chromatography was done on deactivated alumina 90 (70-230 mesh), obtained from Merck. Melting points were recorded on a Fischer-Johns hotstage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer, Paragon 1000 FT-IR spectrophotometer and NMR spectra were recorded on a Varian EM 390 or a Gemini 2000 spectrometer operating at 90 and 300 MHz respectively. Tetramethylsilane was used as internal standard (δ 0.00 ppm) and $CDCl_3$ was generally used as solvent, except where stated otherwise. A V.G. Micromass 16F spectrometer operating at 70 eV and using an accelerating voltage of 4 kV was used to record mass spectra.

4.3.1 The hydrozirconation of $Cp(CO)_2Fe(CH_2)_nCH{=}CH_2$ (n = 2 and 3)

A mixture of **1** (0.39g; 1.68mmol) and $Cp_2Zr(H)Cl$ (0.47g; 1.83mmol) in THF (18ml) was stirred for 2-3h until the yellow suspension became a red-orange homogeneous solution. The solvent was removed *in-vacuo* resulting in a orange-yellow oil. The oil was extracted with hexane (3 x 30ml). After each extraction the yellow mother liquor was syringed off and filtered under nitrogen through a frit into a second Schlenk tube. The solvent was removed from the filtrate, leaving a yellow oil. The oil was identified as $Cp(CO)_2Fe(CH_2)_3CH_3$ but was contaminated with some starting material. This was confirmed by comparing the IR and ^1H NMR spectra with those of authentic samples of $Cp(CO)_2Fe(CH_2)_3CH_3$ and $Cp(CO)_2Fe(CH_2)_2CH{=}CH_2$.

A pale yellow powder remained in the reaction vessel. The powder was identified as the dimeric compound, $[Cp_2ZrCl]_2O$. It was confirmed by comparing its ^1H and ^{13}C NMR spectra as well as its mass spectrum with those previously reported. ^1H NMR (200 MHz, $CDCl_3$) δ 6.31 ppm (s, $C_5\underline{H}_5$); ^{13}C NMR (200 MHz, $CDCl_3$) δ 114.08 ppm ($\underline{C}_5H_5$); MS (*m/z* 462 (100%)) $Cp(Cl)Zr^{+IV}\text{-}O\text{-}Zr^{IV}(Cl)Cp_2$; microanalysis (calculated values in brackets) C 44.88% (45.36%), H 3.84% (3.78%).

The above procedure was also used for the hydrozirconation of **2**. Again a yellow oil and a pale yellow powder were isolated. The oil was identified as $Cp(CO)_2Fe(CH_2)_4CH_3$ which was also contaminated with some starting material. This was confirmed by comparison of its IR and ^1H NMR spectra with those of authentic samples of $Cp(CO)_2Fe(CH_2)_4CH_3$ and $Cp(CO)_2Fe(CH_2)_3CH{=}CH_2$. The pale powder was identified as $[Cp_2ZrCl]_2O$, with characterization data similar to those of the pale powder isolated from the hydrozirconation of **1**.

4.3.2 Oxidative-hydrozirconation of $Cp(CO)_2Fe(CH_2)_nCH=CH_2$ (n = 2 and 3)

A solution of **1** (0.43g; 1.85mmol) in THF (20ml) was added to $Cp_2Zr(H)Cl$ (0.52g; 2.02mmol). The yellow suspension was stirred for 2-3h until the mixture became red-orange and homogeneous. 3M NaOH (1.24ml) was added dropwise followed by the addition of 30% H_2O_2 (1.23 ml). This resulted in vigorous foaming of the reaction mixture. After the foaming ceased, the mixture was refluxed for 2h, during which time it turned dark brown with some black material coming out of solution. The mixture was cooled and filtered to remove the sticky black insoluble material. The resulting filtrate was dried over $MgSO_4$ and after a few minutes the mixture was filtered and the solvent removed to obtain an orange oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on an alumina column (6 x 1.5cm). Using hexane as eluent, a yellow band was isolated and upon removal of the solvent a yellow oil was obtained. The oil was identified as $Cp(CO)_2Fe(CH_2)_3CH_3$ (31%) which was confirmed by comparison of its IR and ^1H NMR spectra with those of an authentic sample. A second slower moving yellow band was collected by using CH_2Cl_2 as eluent. The solvent was removed leaving a yellow oil. The oil was identified as the expected oxidative-hydrozirconation product, $Cp(CO)_2Fe(CH_2)_4OH$ (32%). The identity of $Cp(CO)_2Fe(CH_2)_4OH$ was confirmed by comparing its characterization data with those of **9**, which we had prepared in Chapter 3. IR (neat oil between NaCl plates) $\nu_{(O\text{-}H)}$ 3350(br) cm^{-1}, $\nu_{(CO)}$ 1995(s) and 1933(s) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 4.69 ppm (s, 5H, $C_5\underline{H}_5$), δ 3.59 ppm (br s, 2H, $Fe(CH_2)_3C\underline{H}_2OH$), δ 1.3-1.7 ppm (br s, 7H, $Fe(C\underline{H}_2)_3CH_2O\underline{H}$).

The oxidative-hydrozirconation of **2** was carried out in a similar manner yielding the compounds, $Cp(CO)_2Fe(CH_2)_4CH_3$ (37%) and the oxidative-hydrozirconation product $Cp(CO)_2Fe(CH_2)_5OH$ (16%). The identity of $Cp(CO)_2Fe(CH_2)_4CH_3$ was confirmed upon comparison of its IR and ^1H NMR spectra with those of an authentic sample. The IR and ^1H NMR spectra of $Cp(CO)_2Fe(CH_2)_5OH$ were compared to those of compound **10**, which was prepared in Chapter 3. IR (neat oil between NaCl plates) $\nu_{(O\text{-}H)}$ 3350(br) cm^{-1}, $\nu_{(CO)}$ 1997(s) and 1940(s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.73 ppm (s, 5H, $C_5\underline{H}_5$), δ 3.63 ppm (br s, 2H, $Fe(CH_2)_4C\underline{H}_2OH$), δ 1.45 ppm (br s, 9H, $Fe(C\underline{H}_2)_4CH_2O\underline{H}$).

4.3.3 Preparation of $[CpFe(CO)_2(C_nH_{2n-2})]PF_6$ (n = 4-6,8) *i.e.* 16-19.

The β-hydride abstraction reaction of **1** is described below, to illustrate the general procedure used.

A solution of **1** (0.22g; 1.03mmol) in CH_2Cl_2 (5ml) was added dropwise to a solution of Ph_3CPF_6 (0.45g; 1.59mmol) in CH_2Cl_2 (10ml). The orange solution gradually changed to black with a yellow tint. The solution was left to stand for 18h at room temperature. Acetone was added to dissolve the black mixture. The product was precipitated out as a yellow solid by the addition of diethyl ether and it was subsequently filtered. The solid was dissolved in a minimum amount of acetone to which diethyl ether was added slowly, resulting in a yellow powder precipitating out of solution. The yellow powder was identified as the expected product $[Cp(CO)_2Fe(C_4H_6)]PF_6$, **16.**

In a similar manner, **17-19** were isolated. Yields and characterization data of these compounds are summarized in Tables 4.2-4.4.

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CHAPTER 5

REACTIONS OF SOME ω-HYDROXYALKYL COMPOUNDS OF IRON

5.1 The reaction of the ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ ($n = 4,5,8$), with trifluoromethanesulfonic anhydride.

5.1.1 Introduction

The ω-hydroxyalkyl compounds $Cp(CO)_2Fe(CH_2)_nOH$ ($n = 4,5,8$), were reacted with triflic anhydride, $(CF_3SO_2)_2O$ with the aim of forming compounds of the type, $Cp(CO)_2Fe(CH_2)_nOSO_2CF_3$ ($n = 4,5,8$). These alkyl triflate compounds are hydrocarbyl complexes containing a sigma-bonded alkyl group with a terminal trifluoromethanesulfonate (triflate) group as shown below:

$$L_nM(CH_2)_yOSO_2CF_3$$

L_nM = transition metal and its associated ligands.

Figure 5.1 The general structure of a transition metal alkyl triflate.

The alkyl triflate compounds also have many analogues in organic chemistry. The synthesis and reactivity of these organic triflates have been investigated extensively.[1-14] The interest in these triflate alkyl species is due to its high reactivity as an alkylating reagent in displacement reactions.[2,4,6,8] The ease of displacement of the triflate group can be attributed to its superior ability as a leaving group, which is caused by its electron-withdrawing substituents.[2,5,6,14]

Organic triflates have most commonly been synthesized by the reaction between the triflic anhydride and the corresponding alcohols as shown in Eq. 5.1.[1-3]

$$CH_3CH_2OH \xrightarrow[C_5H_5N]{(CF_3SO_2)_2O} CH_3CH_2OSO_2CF_3 \tag{5.1}$$

Some examples of reactions where organic triflates has been utilized are the alkylation of enolates[10], the palladium-catalyzed reactions of activated olefins[11,12] and the palladium-catalyzed cross coupling reactions of organoborane compounds.[13]

The good alkylating ability of organic triflates has also been applied in the synthesis of binuclear hydrocarbyl compounds.[15,16] Moss *et al.*[15] and Lindner *et al.*[16] prepared homonuclear μ-alkanediyl compounds via the reaction of transition metal anions with bis(triflate) alkyls in multiple displacement reactions [Eq. 5.2].

$$\begin{gathered} 2\,[L_nM]^- + CF_3SO_2O(CH_2)_3OSO_2CF_3 \longrightarrow L_nM(CH_2)_3ML_n \\ L_nM = Re(CO)_5 \text{ and } Mn(CO)_5 \end{gathered} \tag{5.2}$$

The synthesis of the homonuclear hydrocarbyl compound $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$, was deemed a breakthrough. The more general displacement reaction, that of the manganesepentacarbonyl anion with the dibromoalkyl $Br(CH_2)_3Br$, did not give the expected product but rather afforded a cyclic transition metal carbene.[17]

Transition metal compounds which contain coordinated triflate groups have also generated increased interest in recent years[18-23]. These compounds have been considered as valuable synthons in reactions where the facile triflate ligand can readily be displaced by ligands with greater nucleophilicity.[18] Numerous transition metal triflates have been synthesized. A few examples are : $Cp(CO)_2LMOSO_2CF_3$ (L = CO, PPh_3, $(MeO)_3P$, M = Mo and W), $Cp^*(CO)LRuOSO_2CF_3$ (L = CO and Me_3P), $L_nMOSO_2CF_3$ (L_nM = $CpFe(CO)_2$ and $Cp^*Fe(CO)_2$) and $Cp^*CO(Me_3P)FeOSO_2CF_3$.[20-23] These compounds were most commonly formed by the addition of triflic acid, $HOSO_2CF_3$ to transition metal methyl compounds [Eq. 5.3].[20,21]

$$L_nM{-}CH_3 \xrightarrow{HOSO_2CF_3} L_nM{-}OSO_2CF_3 + CH_4$$

L_nM = transition metal and its associated ligands. (5.3)

5.1.2 Synthetic approach

Our synthetic approach was to attempt the synthesis of metal-containing alkyl triflates of the type $Cp(CO)_2Fe(CH_2)_nOSO_2CF_3$ (n = 4-6,8), by reacting the ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) with triflic anhydride.

$$Cp(CO)_2Fe(CH_2)_nOH \xrightarrow[base]{(CF_3SO_2)_2O} Cp(CO)_2Fe(CH_2)_nOSO_2CF_3$$

$n = 4\text{-}6,8$ (5.4)

We had initially hoped that the alkyl triflates could be subsequently reacted with transition metal anions to produce binuclear μ-alkanediyl compounds [Eq.5.5].

$$Cp(CO)_2Fe(CH_2)_yOSO_2CF_3 + [L_nM]^- \longrightarrow L_nM(CH_2)_yFe(CO)_2Cp + {}^-OSO_2CF_3$$

$L_nM = Mn(CO)_5, CpFe(CO)_2, Re(CO)_5$
$y = 4\text{-}6,8$ (5.5)

As shown later, our attempts to synthesize a binuclear hydrocarbyl complex were not very successful and the expected product was isolated in only very low yield.

Our aim was also to compare the above reaction with the previously reported reaction of ω-haloalkyls of the type $Cp(CO)_2Fe(CH_2)_nX$ (X = Br, I, n = 3-6), with transition metal salts such as $Na[L_nM]$ (L_nM = $CpMo(CO)_3$, $CpW(CO)_3$ and $Re(CO)_5$) which yield binuclear hydrocarbyl compounds.[24,25] These reactions normally require long reaction times and the yields for the longer chained ω-haloalkyls are low. We envisioned that the alkyl triflates containing the labile triflate moiety, would be more reactive in the preparation of homo- and heteronuclear compounds, eliminating the problems previously experienced with the ω-haloalkyl complexes.

5.1.3 Results and discussion

Initially we attempted the synthesis of the alkyl triflates employing the triflic anhydride-pyridine method, used in the synthesis of organic triflates.[1-3] Attempts to isolate $Cp(CO)_2Fe(CH_2)_4OSO_2CF_3$ using this method, afforded sticky maroon-brown pastes with a distinctive pyridine smell. The IR spectra of some of these pastes show peaks in the ν(CO) region at ~ 2070(s) and 2021(s) cm^{-1}. The absorption peaks appear at high wavenumbers indicating that these pastes contained a species with some cationic nature. It was also previously found that pyridine often reacts with the triflic anhydride to form tar-like amine salts which causes problems with the purification of the products.[2]

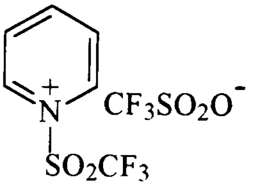


Figure 5.2 An example of a triflate amine salt.

To avoid these complications, sterically hindered bases such as 2,6-di-tert-butylpyridine[26] or polymer-bonded 2,6-di-tert-butylpyridine[27] which are incapable of reacting with the triflic anhydride have been recommended. However, inorganic bases such as Na_2CO_3, $NaHCO_3$ and K_2CO_3 have also previously been used as heterogeneous acid scavengers in the synthesis of organic triflates.[2,3] It was therefore decided that excess of Na_2CO_3 would be used in attempts to prepare the metal-containing alkyl triflates. Na_2CO_3 would physically adsorb the eliminated triflic acid by-product, and the resulting insoluble sodium salts could be easily separated from the reaction mixture via filtration.

The addition of triflic anhydride, to a methylene chloride solution of $Cp(CO)_2Fe(CH_2)_4OH$ in the presence of Na_2CO_3 at ambient temperature afforded $[CpFe(CO)_2]_2$ as the major product, while at 0°C, $Cp(CO)_2FeOSO_2CF_3$ was obtained. We suspect that both $[CpFe(CO)_2]_2$ and $Cp(CO)_2FeOSO_2CF_3$ were formed as a result of the iron-carbon bond cleavage of the expected iron alkyl triflate, mediated by the triflic acid by-product. The reaction at -70°C (ethanol/dry ice) resulted in a bright yellow solution which gradually changed colour to orange when it was allowed to warm to room temperature. We speculate that the colour change may be due to the conversion of the expected compound $Cp(CO)_2Fe(CH_2)_4OSO_2CF_3$ to $Cp(CO)_2FeOSO_2CF_3$. Again the iron-carbon bond cleavage is thought to be caused by the triflic acid by-product at higher temperatures. It however appears that at temperatures around -70°C the expected alkyl triflate remains intact.

In an attempt to prove the above, the reaction was repeated at -70°C and to the yellow mixture, the iron anion, $[CpFe(CO)_2]^-$ was added with the hope of forming the μ-alkanediyl compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$. The latter was indeed isolated but the yield of the product was extremely low [Eq. 5.6]. $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, was isolated as a yellow powder after recrystallisation which was done by dissolving the crude product in CH_2Cl_2 and adding hexane to the solution at -78°C (acetone/dry ice). The identity of the compound was confirmed by IR, ^1H NMR and ^{13}C NMR spectral information. The data are briefly discussed below and are summarized in the Experimental Section 5.4.

$$\begin{tikzcd}
Cp(CO)_2Fe(CH_2)_4OH \arrow[r, "(CF_3SO_2)_2O", "Na_2CO_3"'] & \text{"}Cp(CO)_2Fe(CH_2)_4OSO_2CF_3\text{"} \arrow[d, "{[CpFe(CO)_2]^-}"] \\
 & Cp(CO)_2Fe(CH_2)_4Fe(CO)_2Cp
\end{tikzcd}$$

(5.6)

IR Spectrum of the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$

The IR spectrum of the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, in the ν(CO) region resembles that of the starting material with two strong bands at 1999 and 1939 cm^{-1}. The IR spectrum shows no bands in the ν(O-H) region, indicating that the hydroxy functionality had been replaced.

^1H NMR Spectrum of the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$

The ^1H NMR spectrum of the symmetrical compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, exhibits two sharp singlets. The resonance at δ 1.48 ppm was assigned to the eight methylene protons while the peak at δ 4.72 ppm was assigned to the ten protons of the two cyclopentadienyl groups.

^{13}C NMR Spectrum of the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$

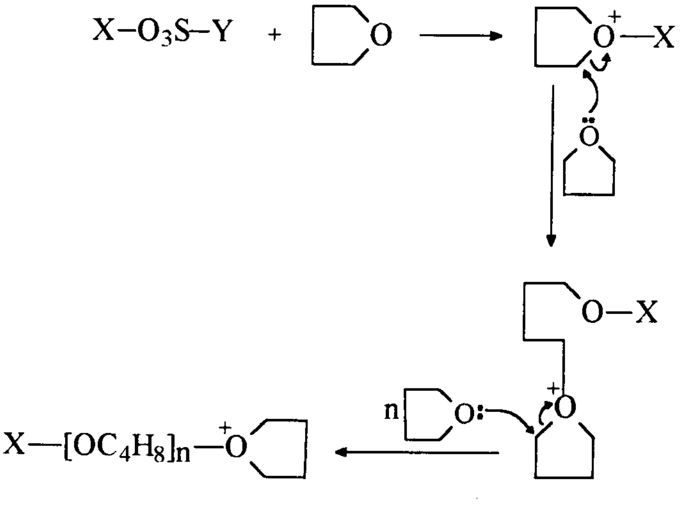
The ^{13}C NMR spectrum of the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, contains peaks at δ 3.76 ppm and δ 43.86 ppm which were assigned to the methylene carbons. The peak at δ 85.30 ppm was assigned to the cyclopentadienyl carbons.

The IR, ^1H NMR and ^{13}C NMR spectra are in good agreement with those of King's published results.[28] The yield was however very low, which was thought to be due to the low reactivity of the iron anion $[CpFe(CO)_2]^-$ at -70°C.

In order to try and improve the yield, the reaction time was increased. The increased time did not however improve the yield significantly. An increase from 2h to 4h resulted in an increase from 3% to 18%. A further increase to 9h gave an unexpectedly low yield of 8%. The isolated crude product was repeatedly recrystallized, at -78°C with the addition of hexane to the CH_2Cl_2 solution, which in turn affected the yield. Removal of the solvent from the mother liquor, obtained after the above recrystallisation, yielded a yellow oil. The yellow oily product was established by nmr as some sort of polymeric material. The spectral data of the polymeric material are summarized in Tables 5.1 and 5.2. The formation of this material is discussed below.

A reaction in which the iron anion, $[CpFe(CO)_2]^-$ was added to a mixture of $Cp(CO)_2Fe(CH_2)_4OH$ and triflic anhydride, was performed at -70°C. After warming the mixture to room temperature and stirring for an additional 15h at this temperature, a yellow oil was isolated. In a similar reaction, but in the absence of the iron anion, the same yellow oily product was isolated. This indicated that the iron anion did not participate in the formation of the yellow oil. The yellow oils were isolated as viscous sticky materials which solidified at -78°C. At -20°C, these materials transformed into a sticky paste. These oils were kept at -20°C for several months with minimal decomposition. The viscous nature and large amounts of these oils isolated, led us to believe that a polymerization reaction may be operative.

It had previously been reported that triflate containing compounds initiate THF ring-opening polymerization.[29,30] Kobayashi *et al.*[29] found that the superacid, ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$), initiated THF ring-opening polymerization, while Smith *et al.*[30] prepared dicationic polymers initiated by $(CF_3SO_2)_2O$. Smith *et al.* proposed a mechanism for the ring-opening polymerization of THF with $CH_3OSO_2CF_3$, $(CF_3SO_2)_2O$ and $(FSO_2)_2O$ as initiators. The mechanism proposed that during initiation an oxonium salt is generated via O-alkylation in the presence of esters or O-sulfonation when the anhydrides are used. This is followed by the propagation process, which involves successive nucleophilic attack at the α-carbon of the oxonium ion by the THF monomers as indicated in Scheme 5.1.

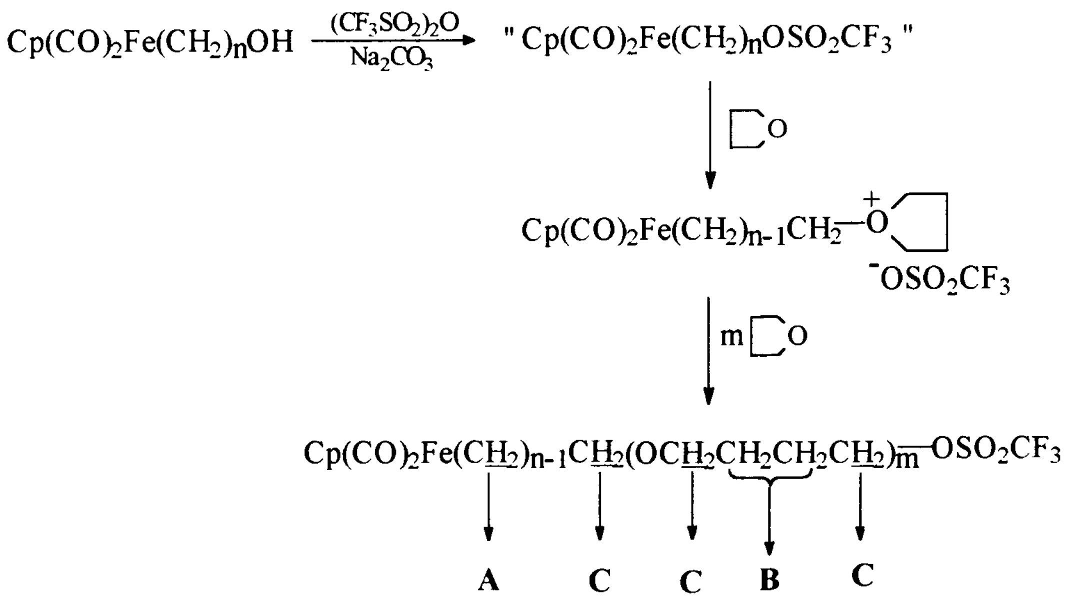


X = CH_3, FSO_2, CF_3SO_2; Y = F, CF_3

Scheme 5.1 The proposed mechanism for THF ring-opening polymerization.

The isolation of $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, confirmed that the alkyl triflate $Cp(CO)_2Fe(CH_2)_4OSO_2CF_3$ was formed [Eq. 5.6]. We deduce that in addition to the formation of the expected binuclear compound, the alkyl intermediate $Cp(CO)_2Fe(CH_2)_4OSO_2CF_3$ also initiates the ring-opening polymerization of THF (the solvent in which the iron anion was generated), to form polyethers with terminal triflate groups as well as a terminal organometallic group [Scheme 5.2].

Evidence confirming that the isolated yellow oils were organometallic polyethers were obtained from GPC studies, elemental analysis, ^1H NMR and IR spectroscopy. The charaterization data for the major fractions of the polyethers isolated as yellow oils, are summarized in Tables 5.1. and 5.2. Smaller fractions with similar IR and ^1H NMR spectral data were also isolated. We suspect that these fractions are oligomers or shorter chained polymers.



Scheme 5.2 The proposed formation of the transition metal-containing polyethers.

$Cp(CO)_2Fe(CH_2)_8OH$ was also reacted in a similar manner as $Cp(CO)_2Fe(CH_2)_4OH$, in the absence of $[CpFe(CO)_2]^-$, resulting in the formation of a viscous yellow oil. The oil was identified as the same type of polymeric material shown in Scheme 5.2. The oil solidified at -78°C and became a sticky paste at -20°C. The characterization data for the polymeric material, isolated when $Cp(CO)_2Fe(CH_2)_8OH$ was used as starting material, are summarized in Tables 5.1 and 5.2 (entry 3). The IR and ^1H NMR spectral data of this polymeric material exhibit similar trends to those of entries 1 and 2 in Tables 5.1 and 5.2. This indicates that the longer chained ω-hydroxyalkyl $Cp(CO)_2Fe(CH_2)_8OH$, was also converted to the corresponding triflate intermediate $Cp(CO)_2Fe(CH_2)_8OSO_2CF_3$. As was the case for the $Cp(CO)_2Fe(CH_2)_4OH$ species, the compound $Cp(CO)_2Fe(CH_2)_8OSO_2CF_3$ also initiates ring-opening polymerization of the solvent.

Elemental analysis, Gel Permeation Chromatography (GPC)

The elemental analysis as obtained from ICP studies indicated that the iron content of the polymeric material for entry 1 (Tables 5.1 and 5.2) was 3%. The average molecular weight (M_w) as determined by GPC analysis was 2807. The M_w and the proposed formula shown in Scheme 5.2 enabled us to determine the degree of polymerization *i.e.* the number of repeat units. This was found to be 33. Subsequently from the degree of polymerization, M_w and the formula indicated in

Scheme 5.2, the expected microanalysis of the polymer was determined. The calculated microanalysis of the polymers was C (62.65%) and H (10.04%), which compared favourably to that of the obtained microanalysis, C (62.92%) and H (10.27%).

From the GPC analysis it was found that the polydispersity (M_w/M_n) was 1.99, showing that the polymer had a fairly narrow molecular weight distribution.

The (M_w) of the polymeric material, obtained using $Cp(CO)_2Fe(CH_2)_8OH$ as starting material (Tables 5.1 and 5.2, entry 3), was found to be 9559, with a polydispersity (M_w/M_n) of 1.96, as determined by GPC. The repeat units as represented in Scheme 5.2, was determined to be 126. Thus the degree of polymerization was greater compared to when $Cp(CO)_2Fe(CH_2)_4OH$ was used as starting material (entries 1 and 2, Tables 5.1 and 5.2). It has previously been shown that THF ring-opening polymerization is largely determined by the ratio of initiator to monomer.[7] These previous studies found that a small ratio results in polymers with high degrees of polymerization. The conversion of $Cp(CO)_2Fe(CH_2)_8OH$ to $Cp(CO)_2Fe(CH_2)_8OSO_2CF_3$ was found to be less effective and thus a low level of triflate species was present. Since the triflate species is suspected of acting as an initiator in the polymerization process and since the initiator/monomer ratio was small, the degree of polymerization was found to be higher.

IR Spectra of the polymeric material in Table 5.1

The IR spectra for all the compounds in Table 5.1 appear to be the same. Two strong bands in the ν(CO) region at 2000 and 1940 cm^{-1} were observed and are at positions similar to that of the starting material. The spectra however also exhibit strong bands at 1113 cm^{-1} and in the region 3000-2800 cm^{-1} which were assigned to the aliphatic ether (CH_2OCH_2) and the alkyl frequencies respectively, of the repeat units.[3,7,31] The bands at ~1372 cm^{-1} and in the region 1430-1250 cm^{-1} were assigned to the stretching frequencies of the terminal triflate functionality.[1,31,32]

Table 5.1 IR and microanalysis data for the polymeric materials.

Entry	**ω-Hydroxyalkyl used to prepare the initiator**	**IR [a] (cm^{-1})**	**Microanalysis [b] (%)**
1	$Cp(CO)_2Fe(CH_2)_4OH$ [c]	1940(s), 2000(s)[d] 3000-2800(s, br) 1430-1488(m, br) 1370(s) 1210(m), 1250(m) 1112(s)	C (62.92) H (10.27)
2	$Cp(CO)_2Fe(CH_2)_4OH$	1938(s), 2000(s)[d] 3000-2800(s, br) 1430-1490(m, br) 1372(s) 1210(m), 1250(m) 1113(s)	C (64.79) H (10.73)
3	$Cp(CO)_2Fe(CH_2)_8OH$	1941(s), 1999(s)[d] 3000-2800(s, br) 1446-1490(m, br) 1372(s) 1209(m), 1250(m) 1113(s)	C (65.79) H (11.52)

[a] Neat oil between NaCl plates (br = broad, s = strong and m = medium)

[b] Obtained microanalysis

[c] $[CpFe(CO)_2]^-$ was added to the reaction mixture

[d] ν(CO) bands, other bands quoted are for the polyether units and the triflate functionality.

^1H NMR spectra of the polymeric material in Table 5.2

The ^1H NMR spectra for entries 1-3 in Table 5.2 exhibit similar trends. The signals appear as broad singlets with no splitting pattern discernible.

Referring to the structure of the polymer in Scheme 5.2, the peaks in the region δ 1.2-1.5 ppm were assigned to the methylene protons adjacent to the Fe centre marked **A**. These signals appear as weak singlets since the organometallic unit constitutes only a small fraction of the overall polymeric material. The singlet at δ 1.6 ppm was assigned to the alkyl protons of the repeat unit marked **B**. The protons of the carbons adjacent to the oxygen atom (marked **C**) were assigned to the singlet at δ 3.4 ppm. The peak for the cyclopentadienyl protons appears at δ 4.7 ppm.

Table 5.2 ^{1}H NMR spectral data for the polymeric material

Entry	**ω-Hydroxyalkyl used to prepare the initiator**	**^{1}H NMR [a, b] (δ ppm)**
1	$Cp(CO)_2Fe(CH_2)_4OH$ [c]	1.45 ***A*** 1.61 ***B*** 3.40 ***C*** 4.72 $C_5\underline{H}_5$
2	$Cp(CO)_2Fe(CH_2)_4OH$	1.45 ***A*** 1.61 ***B*** 3.40 ***C*** 4.72 $C_5\underline{H}_5$
3	$Cp(CO)_2Fe(CH_2)_8OH$	1-1.4 ***A*** 1.61 ***B*** 3.40 ***C*** 4.71 $C_5\underline{H}_5$

[a] $CDCl_3$ as solvent (s = singlet)

[b] All the peaks were broad singlets

[c] $[CpFe(CO)_2]^-$ was added to the reaction mixture

Since the use of THF as solvent leads to the formation of polymeric material, the preparation of $[CpFe(CO)_2]^-$ had to be done in another solvent. Diethyl ether was thus evaluated in this regard.

Attempts to prepare the compound $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, by preparing $[CpFe(CO)_2]^-$ in diethyl ether then adding it to the "$Cp(CO)_2Fe(CH_2)_4OSOCF_3$" solution, did not give the expected results. Instead a yellow oil, which was identified as $Cp(CO)_2Fe(CH_2)_4Cl$ was isolated. We later discovered that chloro-alkyl species could be obtained irrespective of whether the $[CpFe(CO)_2]^-$ anion was present or not in the reaction mixture. Similar results were also obtained for the longer carbon chain compound. Thus the reaction of $Cp(CO)_2Fe(CH_2)_5OH$ with triflic anhydride in diethyl ether leads to the isolation of $Cp(CO)_2Fe(CH_2)_5Cl$ [Eq.5.7].

$$\begin{tikzcd} \mathrm{Cp(CO)_2Fe(CH_2)_nOH} \arrow[r, "\mathrm{(CF_3SO_2)_2O}", "\mathrm{Na_2CO_3,\ CH_2Cl_2}"'] & \text{" }\mathrm{Cp(CO)_2Fe(CH_2)_nOSO_2CF_3}\text{ "} \arrow[d, "\text{diethyl ether}"] \\ & \mathrm{Cp(CO)_2Fe(CH_2)_nCl} \end{tikzcd}$$

$n = 4$ and 5 (5.17)

The longer chained chloro-alkyls of the type $Cp(CO)_2Fe(CH_2)_nCl$ ($n = 4$ and 5) have not previously been reported. The shorter chained analogue $Cp(CO)_2Fe(CH_2)_3Cl$, was however reported to be formed in the reaction between $[CpFe(CO)_2]^-$ and 1,3-dichloropropane in a single substitution reaction.[24] It is not entirely clear how the ω-haloalkyls $Cp(CO)_2Fe(CH_2)_nCl$ ($n = 4$ and 5), are formed in this reaction. It is however thought that possibly the intermediate alkyl triflate undergoes some sort of metathetical exchange reaction with the solvent, CH_2Cl_2 to produce the chloro-alkyl species.

The yield of $Cp(CO)_2Fe(CH_2)_5Cl$ was relatively low and a substantial amount of starting material was isolated, inferring that the conversion of the $Cp(CO)_2Fe(CH_2)_5OH$ to $Cp(CO)_2Fe(CH_2)_5OSO_2CF_3$ was less effective. The chloro-alkyl complexes, $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) were isolated as yellow unstable oils which rapidly decomposed in the presence of air and light to an insoluble brown residue.

The chloro-alkyl compounds were characterized by IR, ^1H and ^{13}C NMR spectroscopy as well as by mass spectrometry and elemental analysis. The characterization data are summarized in Tables 5.3-5.6, and are discussed below.

IR Spectra

$Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) in the ν(CO) region resembles that of the starting material, with two strong bands at 2000 cm^{-1} and 1940 cm^{-1}. The absence of a strong broad band around 3350 cm^{-1} shows that the hydroxy functionality of the starting material, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) had disappeared.

Table 5.3 IR and microanalysis data for the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5)

Entry	Starting ω-Hydroxyalkyls	Yield (%)	IR[a] (cm^{-1})	Microanalysis[b] (%)
1	$Cp(CO)_2Fe(CH_2)_4OH$[c]	45	1938(s), 2000(s)[d]	C 49.73 (49.25) H 5.03 (4.84)
2	$Cp(CO)_2Fe(CH_2)_4OH$	42	1938(s), 1999(s)[d]	C 49.54 (49.25) H 4.96 (4.84)
3	$Cp(CO)_2Fe(CH_2)_5OH$	23	1935(s), 1999(s)[d]	e

[a] Neat oil between NaCl plates (s = strong)
[b] Calculated values in brackets
[c] $[CpFe(CO)_2]^-$was added to the reaction mixture
[d] ν(CO)
[e] Compound unstable therefore acceptable analytical data could not be obtained

^{1}H NMR Spectra

The ^{1}H NMR spectra of $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) exhibit similar trends. The cyclopentadienyl protons were assigned to the signal at ~δ 4.7 ppm. The signal at δ 3.5 ppm was assigned to the protons of the carbons adjacent to the chlorine atom. These protons were more deshielded due to the electronegative nature of the chlorine atom. The protons of the carbon α to the iron were assigned to the peak at ~δ 1.4 ppm, while the remaining methylene protons were assigned to the peaks in the region δ 1.5-1.8 ppm.

Table 5.4 ^1H NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5)

Entry	Starting ω-Hydroxyalkyl	Chemical Shift [a, b] (δ ppm)	Assignment
1	$Cp(CO)_2Fe(CH_2)_4OH$[c]	1.44 (s, 2H)	$FeC\underline{H}_2(CH_2)_3Cl$
		1.54 (m, 2H)	$FeCH_2C\underline{H}_2(CH_2)_2Cl$
		1.80 (m, 2H)	$Fe(CH_2)_2C\underline{H}_2CH_2Cl$
		3.56 (t, 2H, *J* = 6.4 Hz)	$Fe(CH_2)_3C\underline{H}_2Cl$
		4.75 (s, 5H)	$C_5\underline{H}_5$
2	$Cp(CO)_2Fe(CH_2)_4OH$	1.44 (s, 2H)	$FeC\underline{H}_2(CH_2)_3Cl$
		1.57 (m, 2H)	$FeCH_2C\underline{H}_2(CH_2)_2Cl$
		1.80 (m, 2H)	$Fe(CH_2)_2C\underline{H}_2CH_2Cl$
		3.56 (t, 2H, *J* = 6.4 Hz)	$Fe(CH_2)_3C\underline{H}_2Cl$
		4.73 (s, 5H)	$C_5\underline{H}_5$
3	$Cp(CO)_2Fe(CH_2)_5OH$	1.45 (s, 6H)	$Fe(C\underline{H}_2)_3(CH_2)_2Cl$
		1.78 (m, 2H)	$Fe(CH_2)_3C\underline{H}_2CH_2Cl$
		3.52 (s, 2H)	$Fe(CH_2)_4C\underline{H}_2Cl$
		4.73 (s, 5H)	$C_5\underline{H}_5$

[a] $CDCl_3$ as solvent

[b] s = singlet, t = triplet and m = multiplet

[c] $[CpFe(CO)_2]^-$ was added to the reaction mixture

^{13}C NMR Spectra

The ^{13}C NMR spectra of the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) show similar trends. The cyclopentadienyl carbons and the CO were assigned to the peaks at δ 85 ppm and δ 217 ppm respectively.

The chain length seems to influence the chemical shift of the carbons α to the iron centre. The signal for the α-carbon of $Cp(CO)_2Fe(CH_2)_4Cl$ appears at δ 1.82 ppm, while the signal for the α-carbon of $Cp(CO)_2Fe(CH_2)_5Cl$ appears at δ 2.88 ppm. Moss *et al*[33] reported similar findings when they synthesized and investigated the series of ω-haloalkyl compounds of the type $Cp(CO)_2Fe(CH_2)_nX$ (X = Br and I, n = 3-10).

The carbons adjacent to the chlorine atom was assigned to the ^{13}C NMR signals in the region δ 44.88-45.33 ppm. The reported chemical shifts of the $\underline{C}H_2X$ carbons for the compounds $Cp(CO)_2Fe(CH_2)_nBr$ (n = 4 and 5), appear further upfield in the region δ 33.56-32.54 ppm.[33] This chemical shift difference may be ascribed to the more electron negative nature of the chlorine atom. The remaining methylene carbons were assigned to the peaks in the region δ 26-39 ppm.

Table 5.5 ^{13}C NMR spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5)

Entry	**Starting ω-Hydroxyalkyl**	**Chemical Shift** [a] **(δ ppm)**	**Assignment**
1	$Cp(CO)_2Fe(CH_2)_4OH$ [b]	1.82	$Fe\underline{C}H_2(CH_2)_3Cl$
		35.03	$FeCH_2\underline{C}H_2(CH_2)_2Cl$
		37.27	$Fe(CH_2)_2\underline{C}H_2CH_2Cl$
		44.88	$Fe(CH_2)_3\underline{C}H_2Cl$
		85.45	$\underline{C}_5H_5$
		217.75	$\underline{C}O$
2	$Cp(CO)_2Fe(CH_2)_4OH$	1.82	$Fe\underline{C}H_2(CH_2)_3Cl$
		35.03	$FeCH_2\underline{C}H_2(CH_2)_2Cl$
		37.27	$Fe(CH_2)_2\underline{C}H_2CH_2Cl$
		44.88	$Fe(CH_2)_3\underline{C}H_2Cl$
		85.44	$\underline{C}_5H_5$
		217.75	$\underline{C}O$
3	$Cp(CO)_2Fe(CH_2)_5OH$	2.88	$Fe\underline{C}H_2(CH_2)_4Cl$
		31.87	$FeCH_2\underline{C}H_2(CH_2)_3Cl$
		32.34	$Fe(CH_2)_2\underline{C}H_2(CH_2)_2Cl$
		37.34	$Fe(CH_2)_3\underline{C}H_2CH_2Cl$
		45.33	$Fe(CH_2)_4\underline{C}H_2Cl$
		85.45	$\underline{C}_5H_5$
		217.75	$\underline{C}O$

[a] $CDCl_3$ as solvent

[b] $[CpFe(CO)_2]^-$ was added to reaction mixture

Mass spectra

The mass spectra of the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5), appear to have similiar fragmentation pathways compared to those reported for the compounds $Cp(CO)_2Fe(CH_2)_nX$ (X = I, Br, n = 3-6).[33]

The spectra of $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) both exhibit molecular ions. The spectra of $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) both show peaks associated with the Cl-35 and Cl-37 isotopes. Each fragment shows two peaks and these fragments differ by two mass units. The most abundant peak for $Cp(CO)_2Fe(CH_2)_4Cl$ corresponds to $[CpFe]^+$ (*m/z* 121) and that for $Cp(CO)_2Fe(CH_2)_5Cl$ corresponds to $[CpFeCl]^+$ (*m/z* 156). The spectra exhibit peaks characteristic of $CpFe(CO)_2$ containing compounds. Peaks corresponding to $[CpFe(CO)_2]^+$ (*m/z* 177), $[CpFe(CO)]^+$ (*m/z* 149) and $[CpFe]^+$ (*m/z* 121) are present in the spectra.[34] These peaks indicate that one of the possible fragmentation pathways involves the elimination of the hydrocarbon chain followed by the loss of the chlorine atom. Another observed pathway involves the sequential loss of the carbonyls followed by three possible decomposition routes. These are (1) the elimination of the hydrocarbon chain to give $[CpFeCl]^+$ (*m/z* 156), (2) loss of CpH to give $[Fe(C_nH_{2n-1})Cl]^+$ and (3) the elimination of HCl to form $[CpFe(C_nH_{2n-1})]^+$.

Table 5.6 Mass spectral data for the compounds $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5)

Ion [b]	**Relative peak intensities** [a]	
	n = 4 [c]	**n = 5** [d]
M	6	9
M - CO	14	16
M - 2CO	22	33
M - 2CO - Cl	16	3
M - 2CO - HCl	23	23
M - $(CH_2)_n$	22	-
M - $(CH_2)_nCl$	16	14
M - 2CO - $(CH_2)_n$	98	100
M - CO - $(CH_2)_nCl$	28	32
M - 2CO - $(CH_2)_nCl$	100	99.5
M - 2CO - CpH	77	95
M - 2CO - CpH - HCl	70	47
M - 2CO - Cp - $(CH_2)_n$	29	23

[a] Each fragment shows two peaks associated with the Cl-35 and Cl-37 isotopes.

[b] All ions have a single positive charge, ion refers to suggested assignment, M = parent ion

[c] Peak intensities relative to *m/z* = 121

[d] Peak intensities relative to *m/z* = 156

5.1.4 Future Work

The serendipitous isolation of the polymeric material, $Cp(CO)_2Fe(CH_2)_n(O(CH_2)_4)_mOSO_2CF_3$ (n = 4 and 8) and the ω-haloalkyls $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) raised a few questions. Our future work would have to include kinetic and mechanistic investigations of these reactions which would shed more light on the formation of these compounds. Insight into these reactions would aid us to circumvent the problems we experienced using these solvent systems.

Penczek *et al.*[35] reported the preparation of a copolymer of 1,3,5-trioxane with 1,3-dioxolane using $(CF_3SO_2)_2O$ as initiator. We plan to copolymerize the THF-polymers with compounds such as 1,3,5-trioxane or 1,3-dioxolane using $Cp(CO)_2Fe(CH_2)_4OSO_2CF_3$ as initiator. These organometallic polymers would be characterized and their properties investigated.

5.1.5 Conclusion

The isolation of $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$, the ω-haloalkyls, $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) and the polymeric material, $Cp(CO)_2Fe(CH_2)_n(O(CH_2)_4)_mOSO_2CF_3$ (n = 4 and 8) confirmed that the ω-triflate alkyls, $Cp(CO)_2Fe(CH_2)_nOSO_2CF_3$ (n = 4,5, 8) were formed as unstable intermediates. The binuclear hydrocarbyl compound and the ω-haloalkyls were formed in reactions involving the facile displacement of the terminal triflate group. The polymeric materials on the other hand were formed when the ω-triflate alkyls, $Cp(CO)_2Fe(CH_2)_nOSO_2CF_3$ (n = 4 and 8) initiated THF ring-opening polymerization. Further work is required to fully elucidate the mechanistic details of the reactions.

In conclusion, our investigations indicated that the use of the alkyl triflates as reactive synthons in the preparation of binuclear hydrocarbyl compounds was not a viable synthetic approach. This is due to high reactivity of the alkyl triflates towards the solvents used.

5.2 The derivatization of some ω-hydroxyalkyls to the corresponding ω-haloalkyls.

5.2.1 Introduction

ω-Haloalkyls are transition metal compounds with an alkyl ligand containing a halogen atom on the terminal carbon. A number of ω-haloalkyls with different metal centres, alkyl chain lengths and halogens have previously been synthesized.[24,25,33,36,37]

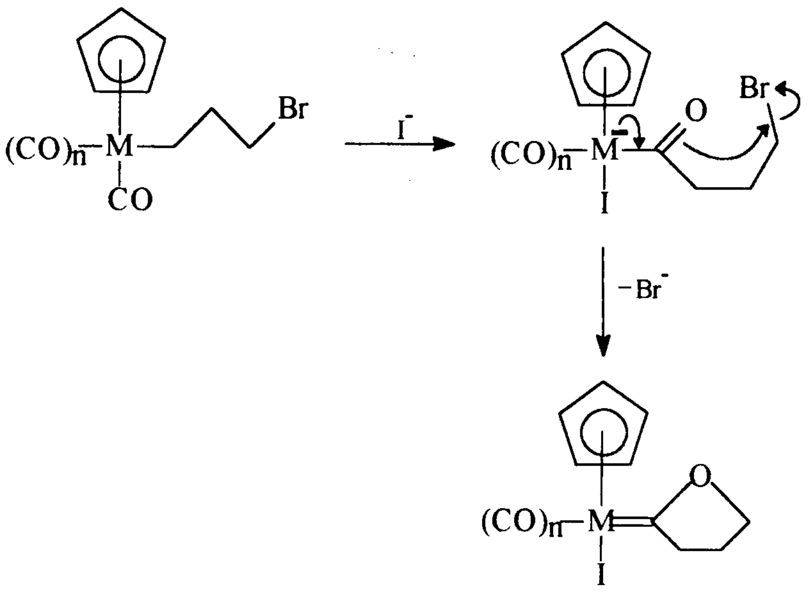
$$L_nM(CH_2)_yX$$

$L_nM = CpMo(CO)_3, CpW(CO)_3$ $y = 3, 4$ $X = Br$
$L_nM = CpFe(CO)_2$ $y = 3\text{-}10$ $X = Br, I$
$L_nM = Cp^*Fe(CO)_2$ $y = 3\text{-}5$ $X = Br, I$

Figure 5.3 Some examples of ω-haloalkyl compounds.

ω-Haloalkyls have been reported to act as useful precursor species in the formation of compounds which may act as model compounds for species in some catalytic cycles.[24,25,38,39] ω-Bromoalkyls have been utilized in the preparation of cyclic carbene complexes.[38,39] The carbene formation involved the attack of an iodide ion on the alkylbromide which induced migratory CO insertion. The intermediate acyl species undergoes rearrangement which involves the formation of a metal-carbon double bond, followed by cyclization and the concomitant expulsion of the bromide ion [Scheme 5.3].

Metal carbene species have been implicated as possible intermediates in the Fischer-Tropsch process.[40] It has been proposed that C-C bonds are formed via the insertion of a CO molecule into a metal carbon bond which ultimately leads to the formation of carbene compounds.



M = Mo n = 2
M = Fe n = 1

Scheme 5.3 The proposed cyclic carbene formation.

ω-Haloalkyls are also useful precursors in the preparation of mixed metal hydrocarbyl complexes.[24,25] Heterobinuclear hydrocarbyl compounds have been synthesized using the reaction of the transition metal sodium salts with ω-haloalkyls.

$$Cp(CO)_2Fe(CH_2)_yX + Na[ML_n] \longrightarrow Cp(CO)_2Fe(CH_2)_yML_n + NaX$$

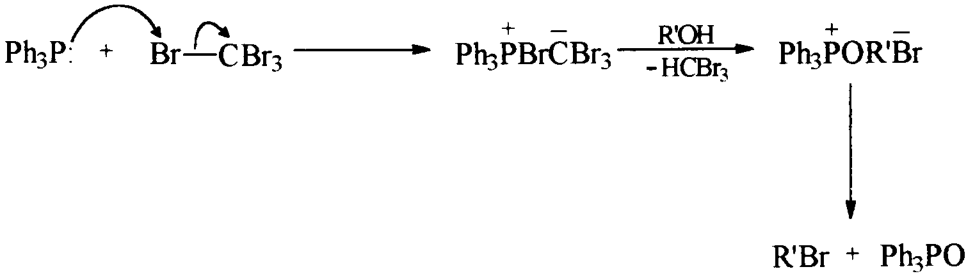
$$\begin{aligned} &ML_n = CpMo(CO)_3, CpW(CO)_3, Re(CO)_5 \\ &X = I, Br \\ &y = 3\text{-}6 \end{aligned} \qquad (5.8)$$

It has been discovered that mixed metal catalyst systems have higher activities, greater selectivities and better stabilities than the homonuclear catalyst systems.[41] This has motivated the synthetic and reactivity studies of heteronuclear hydrocarbyl compounds, where these compounds may act as catalyst precursors or may be used to model intermediates in mixed metal catalyst systems.[42]

5.2.2 Synthetic approach and motivation for the study.

ω-Haloalkyls of the type, $L_nM(CH_2)_yBr$ have previously been prepared via the reaction between transition metal salts and the appropriate dibromoalkanes in single substitution reactions.[24,25,33,36,37] This procedure required long reaction times. Furthermore the addition of $Br(CH_2)_nBr$ occurred at low temperatures.

Recently, reports on the bromination of dendrictic macromolecules containing hydroxy moieties were published.[43,44] These papers reported the fast, effective and convenient bromination of dendrimers containing hydroxy groups, using CBr_4 and PPh_3 as brominating agent. The conversion of the hydroxy containing compounds to the corresponding bromide complexes is based on the reactions reported by Hooz and Gilani in 1968.[45] The proposed bromination mechanism is illustrated below.



(5.9)

These findings initiated our investigations into the bromination of **9** and **12** utilizing CBr_4 and PPh_3.

5.2.3 Results and discussion

The ω-bromoalkyl compounds **20** and **21** were isolated as orange-yellow oils from the reactions of the corresponding ω-hydroxyalkyl compounds, **9** and **12** with PPh_3 and CBr_4 as shown below.

$$Cp(CO)_2Fe(CH_2)_nOH \xrightarrow[THF]{CBr_4,\ PPh_3} Cp(CO)_2Fe(CH_2)_nBr$$

$$\begin{array}{llll} \mathbf{9} & n = 4 & \mathbf{20} & n = 4 \\ \mathbf{12} & n = 8 & \mathbf{21} & n = 8 \end{array} \qquad (5.10)$$

The bromination of **9** and **12** were completed within 20 min. Both compounds **20** and **21** were isolated in good yield, indicating that the chain length does not influence the bromination process. The compounds **20** and **21** are unstable and readily decomposes in the presence of air.

The isolated bromo-alkyls were characterized by IR and ^1H NMR spectroscopy. The characterization data are in good agreement with previously published results.[33] The characterization data are summarized in the Experimental Section 5.4 and are briefly discussed below.

IR Spectra

The IR spectra of both compounds **20** and **21** exhibit similar trends. In the ν(CO) region there are two strong bands at 2000 cm^{-1} and 1940 cm^{-1}. These positions are similar to that of the starting material indicating that the metal centre is not affected during the bromination process. A peak at ~1430 cm^{-1} was assigned to the ν(C-Br). Furthermore the absence of a band in the region 3350 cm^{-1}, which is characteristic for the (O-H) stretching frequency, indicates that the hydroxy functionality was replaced by an halogen group.

^{1}H NMR Spectra

The ^{1}H NMR spectra of both compounds **20** and **21** show broad peaks which can be attributed to the unstable nature of the species. The spectra of the starting material and those of **20** and **21** show very little differences except for the protons of the carbon adjacent to the functional groups ($C\underline{H_2}X$). There was an upfield shift of ~0.2 ppm as X changed from OH to Br which was caused by the change in electronegativity.

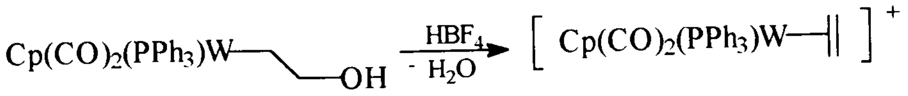
5.2.4 Conclusion

The bromination of the ω-hydroxyalkyls $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 8) with PPh_3 and CBr_4 afforded the ω-haloalklys, $Cp(CO)_2Fe(CH_2)_nBr$ (n = 4 and 8) in good yield. The reaction was fast and convenient while the chain length of the ω-hydroxyalkyls did not influence the bromination process.

5.3 The reactivity of ω-hydroxyalkyl iron compounds towards trifluoroacetic acid.

5.3.1 Introduction

The reaction of alcohols with protic acids often lead to protonation, dehydration and subsequent alkene formation.[46-48] Rosenblum *et al.*[47] and Beck *et al.*[48] have shown that the protonation of the organometallic alcohols $L_nM(CH_2)_2OH$ (L_nM = $CpFe(CO)_2$, $CpW(CO)_2(PPh_3)$), is a convenient method to form cationic [η^2-olefinic] compounds [Eq. 5.11].



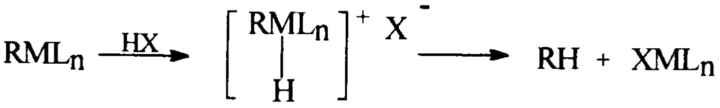
(5.11)

In this section we investigated the reaction of ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) with a protic acid *viz.* trifluoroacetic acid. The aim was to evaluate whether protonolysis occurs at the hydroxy group or at the metal centres.

5.3.2 Results and discussion

The reaction of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6, 8) with CF_3COOH afforded a brick brown powder, $Cp(CO)_2FeOCOCF_3$ which we suspect was formed via iron-carbon bond cleavage.

Numerous reports on the acid mediated metal-carbon bond cleavage of transition metal alkyl compounds have been published.[49-53] The proposed mechanism indicates that proton attack occurs at the metal centres followed by reductive elimination which leads to α-carbon cleavage [Eq. 5.12].[51-53]



$$RML_n \xrightarrow{HX} \left[\begin{matrix} RML_n \\ | \\ H \end{matrix}\right]^+ X^- \longrightarrow RH + XML_n$$

$HX = CF_3COOH, CF_3SO_2H, HBr$

RML_n = transition metal alkyl (5.12)

We propose that during the acidification of the ω-hydroxyalkyls, $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) the metal centre was firstly protonated followed by a reductive elimination reaction which resulted in the formation of $Cp(CO)_2FeOCOCF_3$. No attempts to isolate organic products were however made. $Cp(CO)_2FeOCOCF_3$, was identified from IR and ^1H NMR spectral data, which was in good accordance with previously reported data.[52] The characterization data are discussed below and are given in the Experimental Section 5.4.

IR Spectra

The IR spectrum $Cp(CO)_2FeOCOCF_3$ in the terminal ν(CO) region shows two strong bands at 2061 and 2015 cm^{-1}. These bands appear at higher wavenumbers than that of the starting ω-hydroxyalkyls, indicating that the iron centres now has a lower electron density. The spectrum also exhibits a strong band at 1685 cm^{-1} which was assigned to the acyl carbonyl ν(CO) of the trifluoroacetic acid ligand.

^{1}H NMR Spectra

The spectrum contains a sharp singlet at δ 5.1 ppm which can be assigned to the five cyclopentadienyl protons. This peak appears downfield compared to the corresponding peak in the starting material. The difference in chemical shift may be attributed to the influence the electron deficient iron centres have on the cyclopentadienyl ring. The absence of any other proton peaks indicated that the iron-alkyl bond had been cleaved.

5.3.4 Conclusion

The protonolysis of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6,8) with trifluoroacetic acid lead to the formation $Cp(CO)_2FeOCOCF_3$, which was formed via metal-carbon bond cleavage. Thus protonolysis occured at the metal centre as proposed in Eq. 5.12.

5.4 Experimental

All reactions were performed under an atmosphere of dry nitrogen using Schlenk tube techniques. $(CF_3SO_3)_2O$ was purchased from Sigma, while CBr_4 was purchased from Aldrich. CF_3COOH and PPh_3 were purchased from Merck and Riedel-de Haën respectively. Tetrahydrofuran (THF), hexane and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen prior to use. CH_2Cl_2 and acetone were freshly distilled from P_2O_5 and $CaCl_2$ respectively. Deactivated alumina 90 (70-230 mesh), purchased from Merck, was used in all chromatography. Melting points were performed on a Fischer-Johns hotstage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer, Paragon 1000 FT-IR spectrophotometer and NMR spectra were recorded on a Varian EM 390 or a Varian VXR 200 spectrometer operating at 90 and 200 MHz respectively. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) and $CDCl_3$ was used as solvent, except where stated otherwise. A V.G. Micromass 16F spectrometer operating at 70 eV and employing an accelerating voltage of 4 kV was used to record mass spectra.

5.4.1 Preparation of $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_4\}$

9 (0.43g; 1.72mmol) was dissolved in CH_2Cl_2 (20ml) and Na_2CO_3 (0.76g; 7.15mmol) was added. The yellow heterogeneous mixture was cooled to -70°C (ethanol/dry ice) to which $(CF_3SO_3)_2O$ (0.23ml; 1.72mmol) was added dropwise.

The mixture was stirred for 30-40 min. at -70°C. Na[CpFe(CO)$_2$] (1.72mmol generated in THF (20ml)) was added and the resulting grey-green mixture was stirred a further 2h at -70°C. The resulting mixture was warmed to room temperature. The solvent was removed and a brown-yellow solid was collected. It was extracted with CH$_2$Cl$_2$ (2 x 30ml) and filtered. Removal of the solvent from the filtrate resulted in an orange paste. The paste was dissolved in an minimum amount of hexane and chromatographed on an alumina column (5 x 1.5cm). Elution with hexane resulted in the isolation of a yellow solution. A sticky yellow powder was obtained when the solvent was removed. Elution with a hexane/CH$_2$Cl$_2$, (1:1) mixture as eluent resulted in the isolation of [CpFe(CO)$_2$]$_2$.

At -78°C the crude sticky yellow powder obtained from the hexane eluent, 'was dissolved in a minimum of CH$_2$Cl$_2$ followed by the addition of hexane. A yellow powder precipitated out of the solution and was later identified as the expected product, [CpFe(CO)$_2$]$_2${μ-(CH$_2$)$_4$} (yield 3%). IR (CH$_2$Cl$_2$ in NaCl solution cells) $\nu_{(CO)}$ 1999(s), 1939(s) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.49 ppm (s, 8H, [CpFe(CO)$_2$]$_2$-μ-(C$\underline{H}_2$)$_4$), δ 4.72 ppm (s, 10H, 2(C$_5\underline{H}_5$); ^{13}C NMR (200 MHz, CDCl$_3$) δ 3.76 ppm ([CpFe(CO)$_2$]$_2$-μ-{$\underline{C}$H$_2$(CH$_2$)$_2\underline{C}$H$_2$}), δ 43.86 ppm ([CpFe(CO)$_2$]$_2$-μ-{CH$_2$($\underline{C}$H$_2$)$_2$CH$_2$}), δ 85.30 ppm (2($\underline{C}_5$H$_5$)); Microanalysis (Calculated) C 52.74% (52.67%) and H 4.39% (4.49%).

After recrystillization the mother liquor was collected from which the solvent was removed to obtain a polymeric material. IR (neat film between NaCl plates) $\nu_{(CO)}$ 2000(s), 1940(s), (polyether units and triflate bands) 3000-2800(s), 1430-1480(m), 1370(s), 1210-1250(m), 1113(s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.40 ppm (s), 1.61 ppm (s), 3.40 ppm (s), 4.72 ppm (s).

5.4.2 The preparation of the metal-containing polyethers summarized in Tables 5.1 and 5.2

9 (0.37g; 1.47mmol) was dissolved in CH_2Cl_2 (15ml) followed by the addition of Na_2CO_3 (0.68g; 6.42mmol). The yellow suspension was cooled to -70°C (dry ice/ethanol) followed by the dropwise addition of $(CF_3SO_3)_2O$ (0.24ml; 1.47mmol). The mixture was stirred at -70°C for 30-40 min. THF (20ml) was added and the mixture was stirred for a further 5h at -70°C. It was then warmed to room temperature and stirred for an additional 15h at this temperature. The solvent was removed leaving a brown-orange oil. The oil was extracted with CH_2Cl_2 (2 x 30ml) and filtered to remove any inorganic salts. The solvent was removed from the filtrate resulting in an orange oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and chromotographed on an alumina column (7 x 1.5cm). Pure hexane and CH_2Cl_2/hexane mixtures were used to elute various fractions of yellow oils. A large fraction was also eluted with 10% acetone in CH_2Cl_2. The solvent was removed from all these fractions and in each case a viscous oil was obtained. The oil from the largest fraction was identified as an iron-containing polymer with a terminal triflate group. The characterization data for the polymeric material are summarized in Tables 5.1 and 5.2, entry 2. The smaller fractions which were also isolated as yellow oils exhibit similar characterization data.

The reaction was repeated using **12** as starting material. Similar results were obtained and the characterization data for the major product are summarized in Tables 5.1 and 5.2, entry 3.

5.4.3 The reaction of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 5) with $(CF_3SO_2)_2O$ in diethyl ether

9 (0.42g; 1.70mmol) was dissolved in CH_2Cl_2 (15ml) followed by the addition of Na_2CO_3 (1.34g; 12.67mmol). The yellow suspension was cooled to -70°C (dry ice and ethanol) and $(CF_3SO_3)_2O$ (0.30ml; 1.70mmol) was added dropwise. The mixture was stirred at -70°C for 30-40 min. followed by the addition of diethyl ether (20ml). The resulting yellow mixture was stirred for 5h at -70°C and subsequently warmed to room temperature. The solvent was removed and a yellow solid was obtained. It was extracted with CH_2Cl_2 (2 x 30cm), filtered and the solvent was removed from the extract to obtain a yellow oil. The oil was dissolved in a minimum amount of hexane and chromatographed on an alumina column (10 x 1.5cm). A yellow band was collected upon elution with hexane. The solvent was removed and a yellow unstable oil was isolated, which was later identified as $Cp(CO)_2Fe(CH_2)_4Cl$. Elution with CH_2Cl_2 resulted in the isolation of starting material.

The procedure outlined above was repeated for **10**. A yellow unstable oil which was identified as $Cp(CO)_2Fe(CH_2)_5Cl$ and starting material were isolated. The yields and characterization data for $Cp(CO)_2Fe(CH_2)_nCl$ (n = 4 and 5) are summarized in Tables 5.3-5.6.

5.4.4 Bromination of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4 and 8)

The procedure below outlines the general bromination method used.

12 (0.49g; 0.63mmol) and CBr_4 (0.23g; 0.70mmol) were dissolved in a minimum amount of THF (2ml) followed by the addition of PPh_3 (0.16g; 0.63mmol). The reaction mixture was stirred while the reaction was monitored by t.l.c. using hexane as eluent. After 5 min. an orange precipitate formed and after 20 min. the reaction was stopped. The reaction mixture was dissolved in hexane and transferred to a separating funnel, to which water (3 x 30ml) was added. The mixture was separated and the yellow hexane layer was collected. This was dried over $MgSO_4$, filtered and concentrated to obtain an orange-yellow oil. The oil was dissolved in a minimum amount of hexane and chromotographed on an alumina column (5 x 1.5cm) using hexane as eluent. A yellow band was collected and after removal of the solvent, a yellow oil was obtained which was identified as $Cp(CO)_2Fe(CH_2)_8Br$ **21** (64%). IR (neat oil between NaCl plates) $\nu_{(CO)}$ 2000(s) and 1940(s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.72 ppm (s, 5H, $C_5\underline{H}_5$), δ 3.41 ppm (br s, 2H, $Fe(CH_2)_7C\underline{H}_2Br$), δ 1.85 ppm (br s, 2H, $Fe(CH_2)_6C\underline{H}_2CH_2Br$), δ 1.44 ppm (br s, 12H, $Fe(C\underline{H}_2)_6(CH_2)_2Br$).

The bromination of **9** was carried out in a similar manner yielding a yellow oil, $Cp(CO)_2Fe(CH_2)_4Br$, **20** (60%). The ^1H NMR and IR spectra were compared with those of an authentic sample.

5.4.5 Protonolysis of $Cp(CO)_2Fe(CH_2)_nOH$ (n = 4-6, 8).

The protonolysis of **9** is described below. It outlines the general method used.

9 (0.36g; 1.42mmol) was dissolved in CH_2Cl_2 (8ml). The solution was cooled to 0°C followed by the addition of CF_3COOH (0.1ml; 1.42mmol) in CH_2Cl_2 (8ml). The ice bath was removed and the solution changed colour from yellow to orange. The reaction was stirred at room temperature for 4h. The solvent was removed which resulted in the isolation of an orange oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on an alumina column (5 x 1.5cm) using CH_2Cl_2 as solvent. An orange band was obtained and upon removal of the solvent a brick brown powder was isolated. The powder was identified as $Cp(CO)_2FeOCOCF_3$ (58%).

powder was isolated. The powder was identified as $Cp(CO)_2FeOCOCF_3$ (58%). Melting point (60-66°C); IR (CH_2Cl_2 in NaCl solution cells) terminal $\nu_{(CO)}$ 2061.04(s) and 2015.18(s) cm^{-1}, acyl $\nu_{(CO)}$ 1685.62(m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.10 ppm (s, 5H, $C_5\underline{H}_5$).

The protonolysis of **10-12** also resulted in the isolation of $Cp(CO)_2FeOCOCF_3$, in yields of 68%, 60% and 70% respectively.

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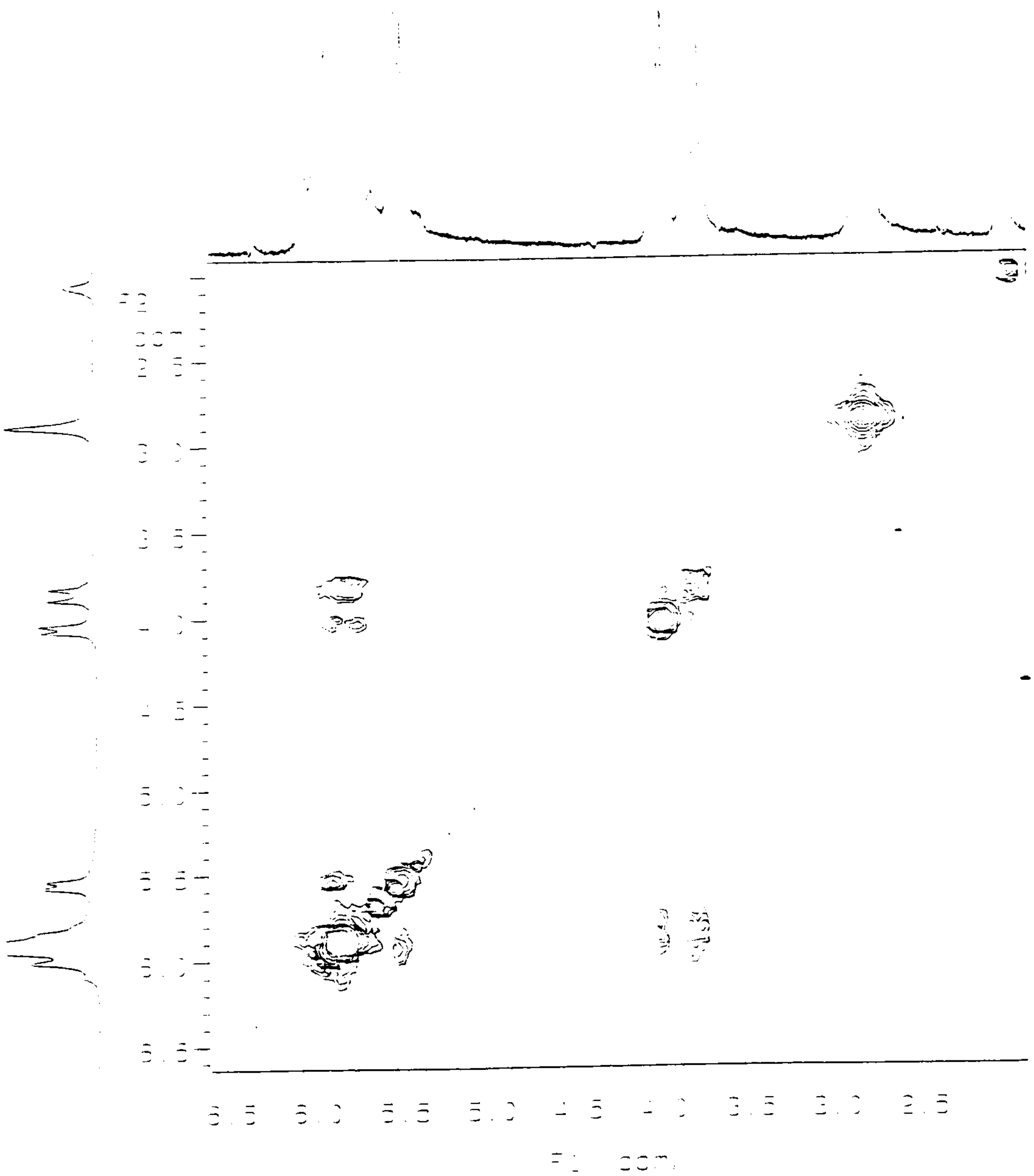
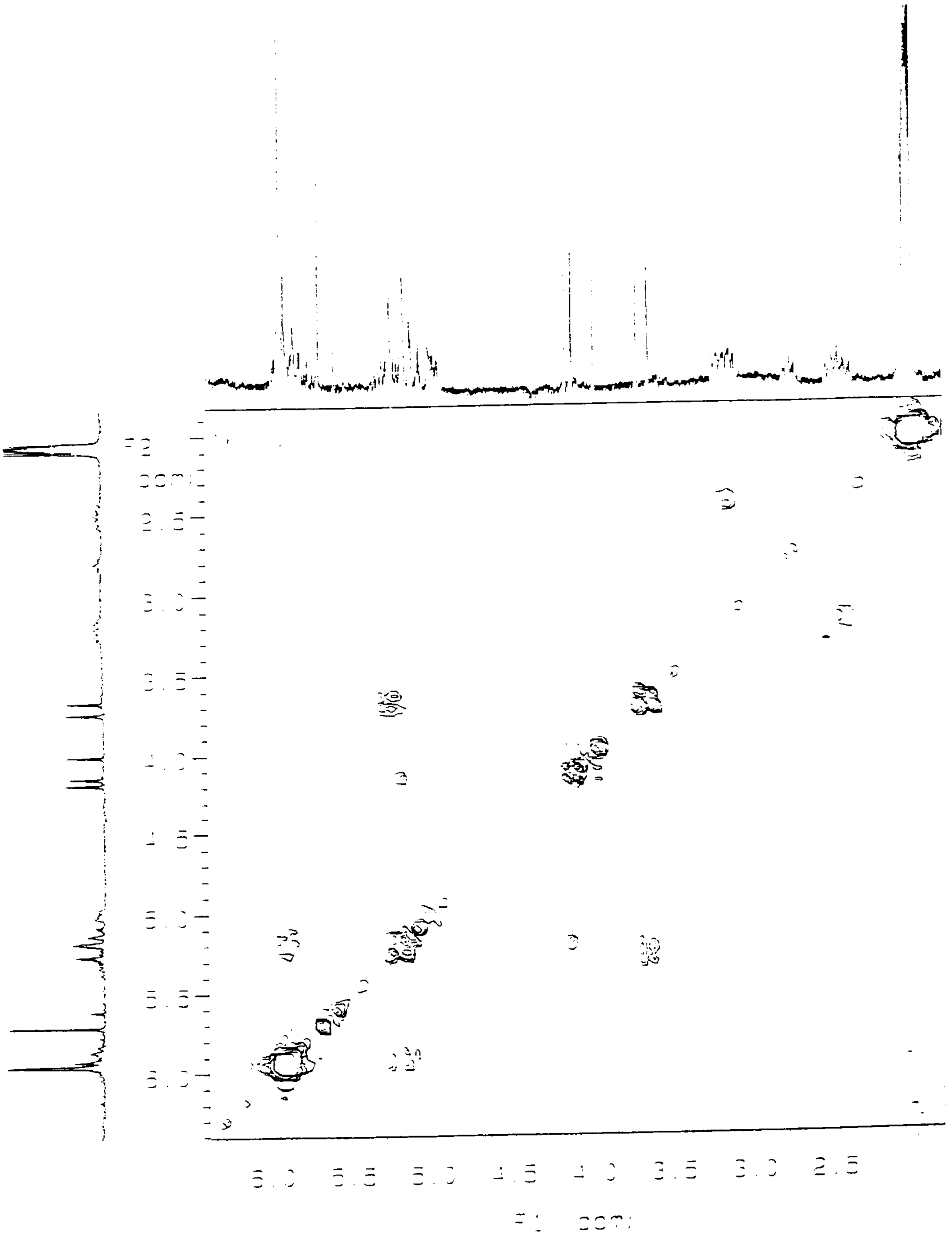
APPENDIX



Appendix 1 : The COSY spectra of the compound **16**, $[Cp(CO)_2Fe(C_4H_6)]PF_6$.



Appendix 2 : The COSY spectrum of compound **17**, $[Cp(CO)_2Fe(C_5H_8)]PF_6$.