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THE SYNTHESIS, CHARACTERIZATION AND
METATHESIS REACTIVITY OF COMPOUNDS (WITH AT
LEAST ONE PENDANT ALKENE GROUP) OF IRON,
RUTHENIUM AND IRIDIUM

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UNIVERSITY OF CAPE TOWN

2008

A THESIS SUBMITTED TO THE

UNIVERSITY OF CAPE TOWN

In fulfilment of the requirements for the degree of
Master of Science

By

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2008

DECLARATION

I declare that this thesis **The synthesis, characterization and metathesis reactivity of compounds (with at least one pendant alkene group) of iron, ruthenium and iridium** is my original work and has not been presented for the award of any other degree at any university. All sources of information consulted and quoted have been acknowledged by means of a full reference.

signature removed

Lancelot Lungelo Mpatho Mbatha

26 August 2008

University of Cape Town

TABLE OF CONTENTS

Acknowledgements.....	vi
Abbreviations.....	vii
Conference Contributions.....	vii
Abstract	ix

CHAPTER 1: APPLICATIONS OF OLEFIN METATHESIS TO ORGANOMETALLIC SUBSTRATES

1.1 Introduction	1
1.2 Well-defined catalyst systems.....	3
1.2.1 Fischer metal carbenes.....	5
1.2.2 Schrock's Mo catalyst (the first well-defined metathesis catalyst).....	6
1.2.3 Ruthenium-based metathesis catalysts.....	7
1.2.3.1 The development of Grubbs' 1 st generation catalyst.....	7
1.2.3.2 Grubbs' 2 nd generation catalyst.....	8
1.3 Mechanism of ruthenium catalyzed olefin metathesis	
1.3.1 Grubbs' 1 st generation catalyst.....	10
1.3.2 Grubbs 2 nd generation catalyst.....	11
1.4 Applications to organometallic substrates.....	13
1.4.1 Recent applications of ring closing metathesis to organometallic substrates.....	14
1.4.1.1 Template directed synthesis.....	14
1.4.1.2 <i>ansa</i> -Metallocenes.....	18
1.4.1.3 RCM chemistry of transition metal complexes with olefin containing phosphine ligands.....	19

1.4.1.4 Bis(alkenyl) compounds.....	22
1.4.2 Recent applications of cross metathesis to organometallic substrates.....	23
1.5 Conclusions.....	29
1.6 Aims and objectives.....	30
1.7 References.....	31

CHAPTER 2: INTRODUCTION TO THE SYNTHESIS OF THE SUBSTRATES AND THEIR METATHESIS REACTIVITY

2.1 Preparation of substrates

2.1.1 Compounds of the type $\text{LRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (49) – (51) (where L = Cp or Cp*).....	36
2.1.2 Preparation of complexes of the type $\text{Cp}^*(\text{L})\text{IrCl}_2$, (69) – (72)...	37
2.1.3 Preparation of acyl complexes of the type $\text{RC}(\text{O})\text{Fe}(\text{CO})(\text{L})\text{Cp}$, (62 – 65).....	37

2.2 Investigating olefin metathesis reactivity

2.2.1 The metathesis route for the synthesis of homo-bimetallic compounds of the types $\text{L}(\text{CO})_2\text{M}\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}\text{ML}(\text{CO})_2$ (M = Fe or Ru; L = Cp* or Cp), (52) – (61); and $\text{Cp}^*(\text{Cl})_2\text{Ir}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_m\text{PPh}_2\}\text{Ir}(\text{Cl})_2\text{Cp}^*$, (73) – (75).....	38
2.2.2 The ring-closing metathesis reactivity of the chiral acyl iron complexes of the type, $\text{LFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ (n = 3 – 4, m = 3, 4 and 6), (66) – (68).....	41
2.3 References.....	42

CHAPTER 3: SYNTHESIS, CHARACTERISATION OF SOME TRANSITION-METAL COMPLEXES WITH AT LEAST ONE PENDANT ALKENE GROUPS

3.1 The synthesis of ruthenium alkenyl compounds of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$; compounds (49) – (51).....	45
3.1.1 IR Spectroscopy of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 5); (49) – (51).....	46
3.1.2 NMR spectroscopy of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 7); (49) – (51).....	47
3.1.3 Elemental analysis of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (49) – (51).....	50
3.2 Synthesis of iron compounds of the type $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$, (62) – (65).....	51
3.2.1 IR spectroscopy of $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($n = 2, 3$, or 4 ; $m = 2, 3, 4$, or 6); (62) – (65).....	52
3.2.2 NMR spectroscopy of $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_3\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$, (62) – (65).....	54
3.2.3 Elemental analysis of $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_3\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$, (62) – (65).....	56
3.3 The synthesis of iridium complexes of the type $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$; compounds (69) – (72).....	57
3.3.1 NMR spectroscopy of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($m = 2, 3, 4$, and 6); (69) – (72).....	59
3.3.2 Elemental analysis of compounds (69) – (72) and mass spectral analysis of compounds (69), (71), and (72).....	61
3.4 Conclusion.....	63

3.5 References.....	64
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CHAPTER 4: METATHESIS REACTIVITY OF COMPOUNDS (WITH AT LEAST ONE PENDANT ALKENE GROUP) OF IRON, RUTHENIUM AND IRIDIUM

4.1 Synthesis of ruthenium and iron based homo-binuclear compounds, LM(CO) ₂ {(CH ₂) _n CH=CH(CH ₂) _n }(CO) ₂ ML; compounds (52) – (61).....	66
4.1.1 IR spectroscopy of LM(CO) ₂ {(CH ₂) _n CH=CH(CH ₂) _n }(CO) ₂ ML (n = 3 – 6; M = Ru or Fe; and L = η ⁵ -C ₅ (CH ₃) ₅ or η ⁵ -C ₅ H ₅).....	68
4.1.2 NMR spectroscopy of LM(CO) ₂ {(CH ₂) _n CH=CH(CH ₂) _n }(CO) ₂ ML (n = 3 – 6; M = Ru or Fe; and L = η ⁵ -C ₅ (CH ₃) ₅ or η ⁵ -C ₅ H ₅).....	70
4.1.3 Mass spectrum of Cp*Fe(CO) ₂ {(CH ₂) ₅ CH=CH(CH ₂) ₅ }(CO) ₂ FeCp* (56) and Elemental analysis of LM(CO) ₂ {(CH ₂) _n CH=CH(CH ₂) _n }(CO) ₂ ML (where L = Cp or Cp*); compounds (52) – (62).....	73
4.2 Self metathesis reaction of iridium compounds of the type Cp*Ir(Cl) ₂ {PPh ₂ (CH ₂) _m CH=CH ₂ }, catalyzed by Grubbs' first or second generation ruthenium catalysts; compounds (73) – (75).....	75
4.2.1 NMR spectroscopy of [Cp*Ir(Cl) ₂] ₂ [μ- {PPh ₂ (CH ₂) _m CH=CH(CH ₂) _m PPh ₂ }], (73) – (75).....	76
4.2.2 Mass spectral analysis of [Cp*Ir(Cl) ₂] ₂ [μ- {PPh ₂ (CH ₂) ₄ CH=CH(CH ₂) ₄ PPh ₂ }], (75) and elemental analysis of compounds (73) – (75).....	77
4.3 Ring-closing metathesis reactivity of compounds of the type CpFe(CO){C(O)(CH ₂) _n CH=CH ₂ }{PPh ₂ (CH ₂) _m CH=CH ₂ }; (62) – (65).....	79
4.3.1 IR spectroscopy of compounds (66) – (68).....	80

4.3.2 NMR spectroscopy of compounds (66) – (68).....	80
4.3.3 Elemental analysis of compounds (66) – (68).....	82
4.4 Conclusion.....	82
4.5 References	83

CHAPTER 5: EXPERIMENTAL

5.1 General.....	85
5.2 Preparation of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3, 5$); compounds (49) – (51).....	86
5.3 Preparation of $[\text{LM}(\text{CO})_2]_2[\mu\text{-}\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}]$, ($L = \text{Cp}$ or Cp^* , $M = \text{Fe}$ or Ru ; $n = 3 - 6$); compounds (52) – (61).....	89
5.4 Preparation of $\text{CpFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($n = 2, 3, 4$ and $m = 2 - 4$, or 6); compounds (62) – (65).....	97
5.5 Preparation of compounds (66) – (68).....	101
5.6 Preparation of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($m = 2, 3, 4$, or 6); compounds (69) – (72).....	104
5.7 Preparation of $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2[\mu\text{-}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_m\text{PPh}_2\}]$ ($m = 2$, 3 , or 4); compounds (73) – (75).....	108
5.8 References.....	111

ACKNOWLEDGEMENTS

My Supervisors:

I want to thank Prof. John Moss and Dr. Gregory Smith for their assistance throughout the period of my program. All the lessons learned will help me undertake future challenge with confidence and wit.

Funding:

To my sponsors, the NRF and the GOOT Scholarship for affording me the opportunity to undertake my studies at UCT.

My Family:

To my mother, Mageba Zulu; my sisters Londi, Ayo, and Lihle; my brother Lungisane 'Bostosto', I thank you all for your love, understanding and support (especially for the financial support). JAH bless each and every one of you.

Technical Staff at UCT:

To the NMR staff, Pete and Noel, thank you for all the work you did, the useful advices, and especially for keeping up with me. To Pierro, for doing the elemental analysis.

UCT Organometallic Research Group:

I want to thank all the members of the Organometallic Research Group for making my time in the laboratory an enjoyable learning experience. I, also, want to give a special thanks to Dr. Akella Sivaramakrishna for his assistance and his most valued input to my work.

My God:

Finally, I want to thank the Christ in whom I can do all things.

ABBREVIATIONS

Cp = cyclopentadienyl

Cp* = pentamethylcyclopentadienyl

M⁺ = molecular ion

IR = infrared

Me = methyl

m/z = mass to charge ratio

NMR = nuclear magnetic resonance

Ph = phenyl

Ar = aromatic group

hrs = hours

R = alkyl

Fp = CpFe(CO)₂

Fp* = Cp*Fe(CO)₂

THF = tetrahydrofuran

DCM = dichloromethane

Mes = 2,4,6-trimethylphenyl

Is = 2,4,6-tri-isopropylphenyl

IR Spectroscopy

ν = stretching vibration

s = strong

m = medium

w = weak

NMR spectroscopy

s = singlet

d = doublet

dd = doublet of doublets

t = triplet

dt = doublet of triplets

m = multiplet

br s = broad singlet

br m = broad multiplet

CONFERENCE CONTRIBUTIONS

Mbatha L. L., Moss J. R., Smith G., Sivaramakrishna A., and Clayton H. S.;
August 2006 **The dimerization of Fe-alkenyl complexes using
Grubbs' 2nd Generation catalyst.** Cape Organometallic Symposium,
Cape Town, South Africa. Poster presentation.

Mbatha L. L., Moss J. R., Smith G., Sivaramakrishna A., and Clayton H. S.;
August 2006, **The dimerization of Fe-alkenyl complexes using
Grubbs' 2nd Generation catalyst.** 37th International Conference on
Coordination Chemistry, Cape Town, South Africa. Poster
presentation.

Mbatha L. L., Moss J. R., Smith G., Sivaramakrishna A., and Clayton H. S.;
August 2006, **The dimerization of Fe-alkenyl complexes using
Grubbs' 2nd Generation catalyst,** 15th international Symposium on
Homogeneous Catalysis, Sun City, South Africa. Poster presentation.

Mbatha L. L., Moss J. R., Smith G., Sivaramakrishna A., and Clayton H. S.;
July 2007, **The synthesis of homo-binuclear and hetero-binuclear
complexes bridged by unsaturated hydrocarbon chains,**
South African Chemical Institute (Inorg 007), Cape Town, South
Africa. Poster presentation.

ABSTRACT

This thesis reports on the synthesis, characterisation and metathesis reactivity studies of (i) ruthenium and iron mono(alkenyl) complexes of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ (M = iron or ruthenium, $\text{L} = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$ and $n = 2 - 6$), **41** – **51**; (ii) iridium complexes of the type $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($m = 2 - 4$ and 6), **69** – **72**; and (iii) bis(alkenyl) acyl complexes of the type $\text{CpFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($n = 3 - 4$, $m = 3, 4$ and 6), **62** – **65**.

Reaction of the ruthenium dicarbonyl anion, $[\text{CpRu}(\text{CO})_2]^-$ with bromoalkenes of the type $\text{Br}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ led to the formation of complexes $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 5), **49** – **51**. Preparation of the related complexes of iron $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($\text{L} = \text{Cp}$ or Cp^*) **41** – **48** have been reported.

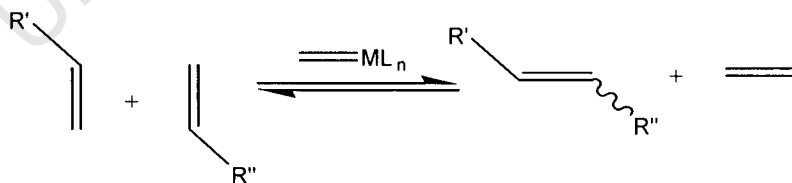
Treatment of the iridium dimer $[\text{Cp}^*\text{IrCl}_2]_2$ with phosphine ligands $\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2$ yields complexes $\text{Cp}^*\text{IrCl}_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($m = 2, 3, 4$, or 6) **69** – **72**. Catalytic intermolecular coupling reactions of iron and ruthenium complexes **41** – **48**, **50** – **51**, and iridium complexes **69** – **71** assisted by Grubbs' 1st or 2nd generation catalysts gave the desired dimers, **52** – **61** and **73** – **75**.

Reaction of iron mono(alkenyl) complexes $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3, 4$) with phosphine ligands $\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ($m = 2, 3, 4$, or 6) led to migratory alkyl insertion, affording novel iron acyl complexes where there are two pendant and different alkene groups attached to the chiral iron atom, $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ **62** – **65**. Catalytic intramolecular ring-closing reactions of **63** – **65** in the presence of Grubbs 1st or 2nd generation catalysts gave the corresponding metallacycles, **66** – **68**.

CHAPTER 1: APPLICATIONS OF OLEFIN METATHESIS TO ORGANOMETALLIC SUBSTRATES

1.1 Introduction

The development of alkene metathesis from a laboratory interest to a crucial synthetic tool in organic, organometallic and polymer chemistry has attracted profound attention in the chemistry fraternity. Pioneers in this field were awarded the Nobel Prize in 2005.¹ Olefin metathesis is an organic reaction which involves the cleavage and reformation of a double bond (Scheme 1.1). Olefin metathesis was first used in petroleum reformation for the synthesis of higher olefins from the α -olefins resulting from the Shell higher olefin process (SHOP). Catalysts were usually derived from a reaction of metal halides with alkylation agents, for example WCl_6 -EtOH-EtAlCl₂.^{1a-f, 2} Late-transition metal alkylidene complexes, such as ruthenium alkylidenes, have driven this synthetic tool into the forefront of carbon-carbon bond-forming methods. This is largely because of the functional group tolerance of these catalysts, and stability in air.^{1a-f, 2}



Scheme 1.1

Many commercial products that contain organic molecules have at least one carbon-carbon double bond or if one is not present in the product, it is likely that an olefin was used in its preparation.^{1b} An important part of organic synthesis is the reliable and

efficient formation of carbon-carbon bonds.^{1b} Olefin metathesis allows for such reactions to take place in the presence of transition metal carbene complexes, such that in a single step new carbon-carbon bonds can be formed.

The development of well-defined (and functional-group tolerant) ruthenium based catalyst systems allows for fully functionalized molecules to undergo metathesis either in a laboratory or on a large industrial scale. Each improvement in the catalytic activity, lifetime, functional group tolerance and selectivity has resulted in new applications being discovered.¹ Olefin metathesis is considered to be in line with the goals of green chemistry in three ways, and these include (i) providing a more efficient route over traditional methods to carbon-carbon bond formation and avoiding by-products; (ii) by enabling the use of renewable resources; and (iii) by providing a means to attain environmentally friendly products.^{1a-f, 3 - 6}

In the past two decades, the olefin metathesis reaction has been applied in virtually every arena of chemical synthesis. This has been largely promoted by the commercial availability of catalysts which have significant air, moisture and functional group tolerance.⁶ However, despite the large body of research with regards to olefin metathesis chemistry, the application of this reaction to metal-containing substrates is much less explored although attracting a growing interest.⁷ In the early studies by Mohr *et al.* they utilized a combination of transition metal based template strategy and ring-closing metathesis to access, novel [2]catenanes.^{8,9}

A number of research groups have actively pursued the development of improved derivatives of the original catalysts, as well as novel systems and these have opened-up new areas of chemistry in terms of activity, chemo-, regio-, and stereo-selectivity whilst at the same time, addressing important factors such as catalyst stability, ease of synthesis and functional group tolerance.¹⁰

As shown in Table 1.1 below, there are at least five important classes of olefin metathesis type chemistry and these include (i) Cross metathesis (CM), (ii) ring-closing metathesis (RCM), (iii) Ring opening metathesis (ROM), (iv) ring-opening metathesis polymerization (ROMP) and (v) acyclic diene metathesis (ADMET) polymerization.

Table 1.1: Examples of some fundamental metathesis reactions

Entry	Synthetic Route
(i) CM	
(ii) RCM	
(iii) ROM	
(iv) ROMP	
(v) ADMET	

1.2 Well-defined catalyst systems for alkene metathesis

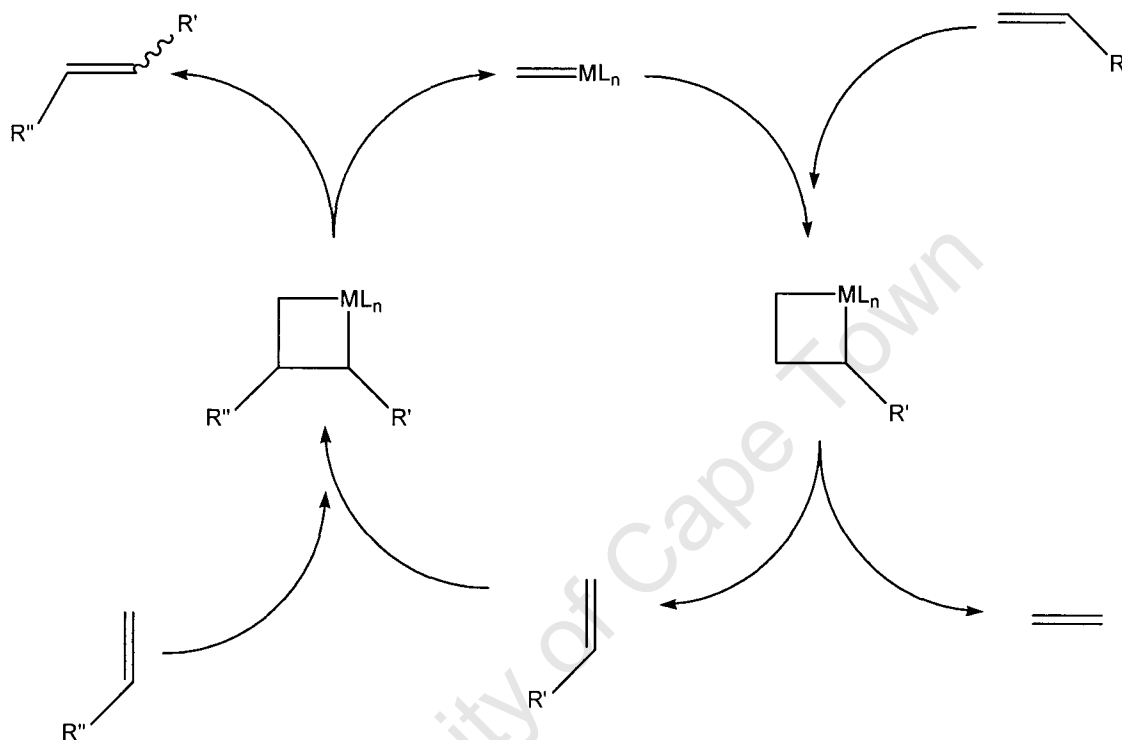
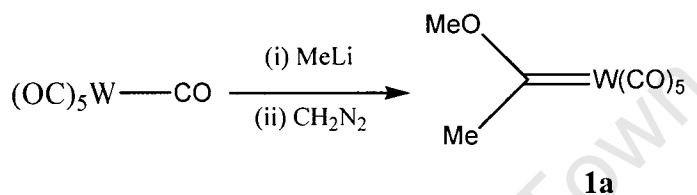


Figure 1.1: Mechanism of olefin metathesis

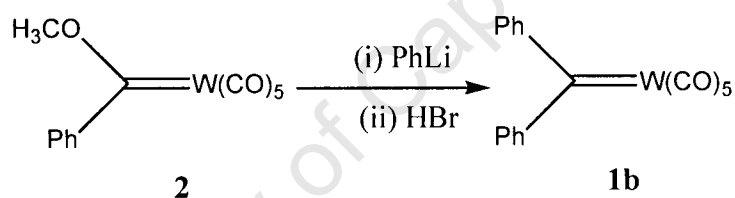
In the early 1960's, olefin metathesis was carried out via the use of group six metals supported on an oxide support (such as WO_3/SiO_2) or group six metal chlorides (such as WCl_3) combined with an alkylating agent and a Lewis acid;² as well as group 7 metal oxides (for example $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$).¹¹ These systems were ill-defined and the mechanism was not well understood at the time. Hérrison and Chauvin first proposed a 'carbene/metallacyclobutane' mechanism which suggested that the metathesis reaction proceeds via a series of metal-carbene and metallacyclobutane complexes as intermediates (Figure 1.1).¹² Further studies by Katz on related systems provided more support for the Chauvin mechanism.^{13a} It was such developments in mechanistic

understanding and in knowledge of the intermediates involved that enabled research groups to use rational design to access better catalyst systems.^{6,13b-c}

1.2.1 Fischer metal carbenes



Scheme 1.2 (a)



Scheme 1.2 (b)

Fischer metal carbenes played a pivotal role in the understanding of the olefin metathesis mechanism. These, were found to initiate olefin metathesis, the polymerization of acetylene, and the rearrangement of enynes.² The first transition-metal carbene complex isolated in 1964 was a Fischer carbene,^{14a} Complex **1a** (Scheme 1.2(a)). Complex **1a** was obtained from the reaction of CH_3Li and $W(CO)_6$, to yield a water-soluble anion, which can be precipitated as its tetramethylammonium salt. Precipitation of the salt from aqueous solution followed by protonation and subsequent methylation with CH_2N_2 , gives $W(CO)_5(COCH_3)(CH_3)$ **1a** (Scheme 1.2(a)).^{14a} Looking at the reaction Scheme 1.2(b), in 1973 Casey *et al.* showed that if complex **2**^{14b} is reacted with phenyllithium and then HBr, it gives (diphenylcarbene)pentacarbonyltungsten **1b**.^{14c} Whereas **1a** is unreactive, **1b** was found to initiate metathesis at temperatures of 40°C or less.^{14d}

1.2.2 Schrock's Mo Catalyst

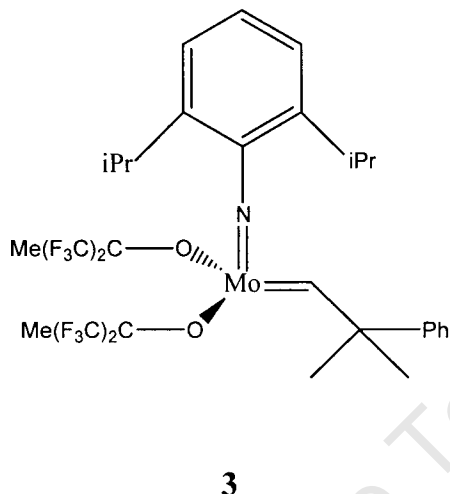


Figure 1.2: An example of a Schrock type molybdenum metathesis catalyst

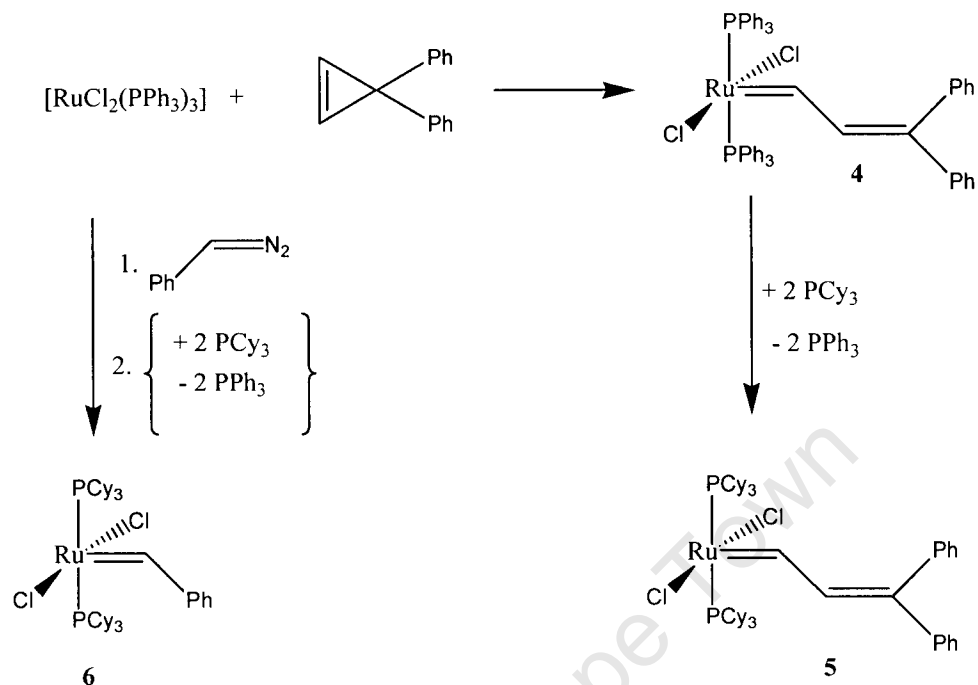
Studies by Schrock resulted in the development of a number of very efficient molybdenum and tungsten catalyst systems.^{2,15} Schrock's molybdenum carbene **3** (Figure 1.2) was the first well-defined metathesis catalyst reported in the literature.^{15a-e} Catalyst **3** has a high activity towards both terminal and internal olefins, and catalyzes the RCM reaction for sterically demanding and electron poor substrates.¹⁶ The reactivity of **3** could be fine-tuned by altering the alkoxide ligands.¹⁵ The molybdenum catalysts can impart stereochemical control over the formation of *anti*- and *syn*-rotamers.² Despite the activity of the Schrock catalyst systems, the use of early transition metals required that the catalyst be handled in an inert atmosphere. The oxophilicity of the metal center rendered these catalyst systems intolerant to a number of functional groups, and that coupled with a short lifetime and the difficulty in synthesis prompted researchers to look for alternative catalyst systems.

1.2.3 Ruthenium-based metathesis catalysts

The development of ruthenium-based metathesis catalysts started with the goal of preparing interesting polymeric structures.^{1b,2} Ruthenium halide based catalysts for the polymerization of highly strained olefins were discovered in the mid 1960's. The preference of ruthenium for soft Lewis bases and π -acids such as olefins, over hard bases such as oxygen-based ligands, is responsible for its high tolerance to air and water.^{1b} With these ill-defined ruthenium halide catalyst systems, metathesis reactions could be carried out in protic solvents and in air. However, it was not until 1992 that Grubbs and coworkers developed the first well-defined ruthenium-based olefin metathesis catalyst, complex **4**.¹⁷

1.2.3.1 The development of Grubbs' 1st Generation catalyst

With the understanding that olefin metathesis must occur via the formation of metal carbenes, complex **4** was prepared by Nguyen and Grubbs. Complex **4** was isolated from the reaction of diphenylcyclopropene with $\text{RuCl}_2(\text{PPh}_3)_3$ (Scheme 1.4). This became the first well-defined, metathesis-active ruthenium alkylidene complex. Complex **4** could effectively catalyze the polymerization of norbornenes in protic media.¹⁸ Although boasting of high activity and versatility with regards to functional group tolerance, catalyst **4** was limited to highly strained monomers.⁴ An even more active catalyst, complex **5** was isolated when the PPh_3 ligands in **4** were replaced by the basic and larger PCy_3 (Cy = cyclohexyl) (Scheme 1.3).^{3,17} However, the availability of complexes **4** and **5** was hindered by the difficulty in the synthesis of diphenylcyclopropene.



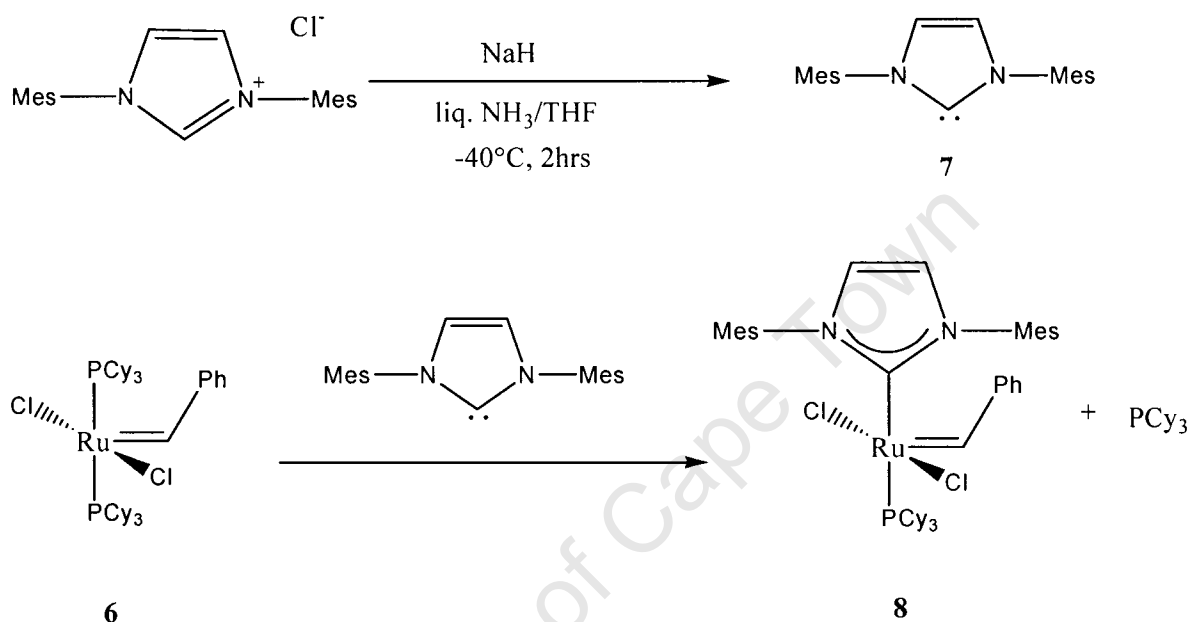
Scheme 1.3

Such synthetic challenges prevented large scale production of the afore-mentioned catalysts. Finally, the benzylidene catalyst **6** was isolated from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with the diazo alkyl- and aryl-diazoalkane compounds and later replacing the two PPh_3 ligands with PCy_3 (Scheme 1.3). Complex **6** could be produced commercially on multikilogram scale.^{19a-c} Catalysts **4**, **5** and **6**, were found to be tolerant to diverse functional groups such as alcohols, acids, esters and aldehydes.²⁰ Complexes **5** and **6** are not sensitive to moisture, air or solvent impurities.^{21a} However, none of these latter catalysts are as reactive as the Schrock catalyst **3**.

1.2.3.2 Grubbs' 2nd Generation catalysts

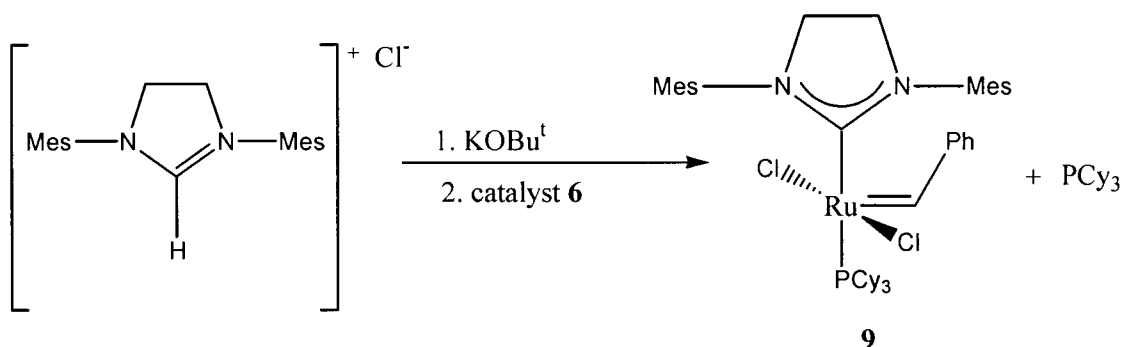
The catalysts of the type $(\text{PR}'_3)_2\text{Cl}_2\text{Ru}=\text{CHR}$ became a success in terms of ruthenium based catalysts. However, these well-defined and highly active metathesis catalysts were not active towards highly strained tri- and tetra- substituted olefins. By using complex **8**,

the productivity for ROMP could now reach a practical limit of 10^5 :1 monomer:catalyst ratio when using the above-mentioned ruthenium catalysts.^{2,21b}



Scheme 1.4

A large number of different research groups took part in the studies which led to the development of highly active but relatively stable metathesis catalysts.² It had already been shown through mechanistic studies, that $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ dissociates a PCy_3 ligand to give an active intermediate in the catalytic cycle. Attempts to use phosphine scavengers, such as CuCl_2 or HCl , with an aim of increasing the concentration of the active intermediate succeeded in enhancing activity, but it also sped up the rate of catalyst decomposition. The incorporation of N-heterocyclic carbene (NHC) ligands in place of one phosphine on **6** resulted in a series of highly active catalysts, for example, catalysts **8** or **9**, as shown in (Scheme 1.4)²² and (Scheme 1.5)^{23a} respectively. In Scheme 1.4 the imidazolynylidene ligand **7** was synthesized from the corresponding salt with sodium hydride in liquid ammonia, and was used without further purification.²²



Scheme 1.5

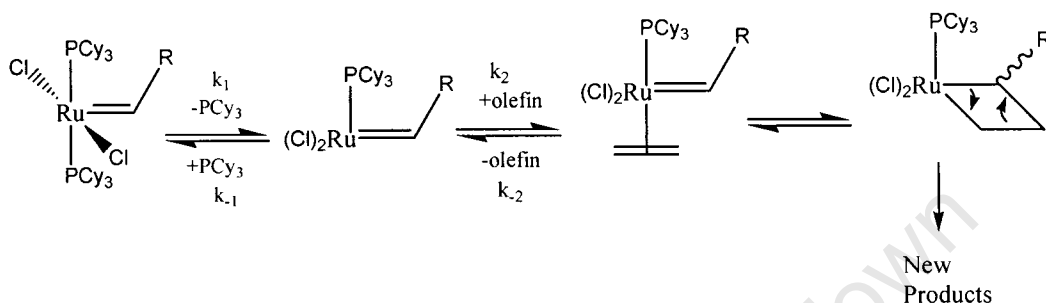
The enhanced metathesis activity was attributed to an increased catalyst turnover resulting from favourable electron donation and steric bulk of the relatively non-labile NHC ligand. The above-mentioned properties together facilitate the dissociative mechanism, the stabilization of both the 14-electron intermediate, and the 16-electron olefin complex. With these NHC-ligand-incorporating ruthenium complexes, the metathesis of tri- and tetra- substituted olefins became accessible.^{23a-b} The complexes are air stable and allow for a wide range of functional groups on the alkene substrate.²

1.3 Mechanism of ruthenium catalyzed olefin metathesis

1.3.1 Grubbs' 1st generation catalyst

Developments in the mechanistic studies of olefin metathesis has helped direct the design of new ligand systems that provide increased activity, improved functional group tolerance and a higher thermal stability. A dissociative mechanism has been supported by the aforementioned studies.^{24a} The first step is the dissociation of one PCy₃ ligand to afford a 14-electron mono-phosphine species (Scheme 1.6). However, this highly active

intermediate has only been observed in the gas phase, using mass spectrometric techniques.^{24b-d}



Scheme 1.6

The 14-electron species reacts with an olefin substrate to form a 16-electron monophosphine/olefin ruthenium complex. The coupling of the olefin and alkylidene ligands within the coordination sphere of the metal centre results in a metallacyclobutane. This highly strained metallacycle could rearrange in an intramolecular fashion, resulting either in new products or in the starting materials.²

1.3.2 Grubbs' 2nd generation catalyst

It has been established that the stronger sigma-donor ligands should facilitate dissociation, as well as stabilize the 14-electron intermediate resulting in enhanced catalytic activity. The development of mono(NHC) complexes, where one PCy₃ ligand is replaced by an a bulky NHC group led to the discovery of the so-called 2nd generation Grubbs' catalysts. The increased stability of the 2nd as compared to the 1st generation type catalysts is attributed to the slow propagation rate (i.e. k₋₁/k₂). Thus the Grubbs' 2nd generation catalyst systems remain in the catalytic cycle for longer. The strong donor ability of NHC ligands relative to tertiary phosphines allows the 2nd generation catalysts

to effect metathesis of electron poor and sterically hindered substrates. Hence, the catalytic activity is dependent on enhanced initiation and reduced propagation.^{2, 24e}

1.3.3 Other well-defined metathesis active catalysts

Studies in the Grubbs' group and others suggest that high catalytic activity often goes hand in hand with poor stability, and vice versa.² Figure 1.3 shows a selection of other well-defined metathesis active catalysts.

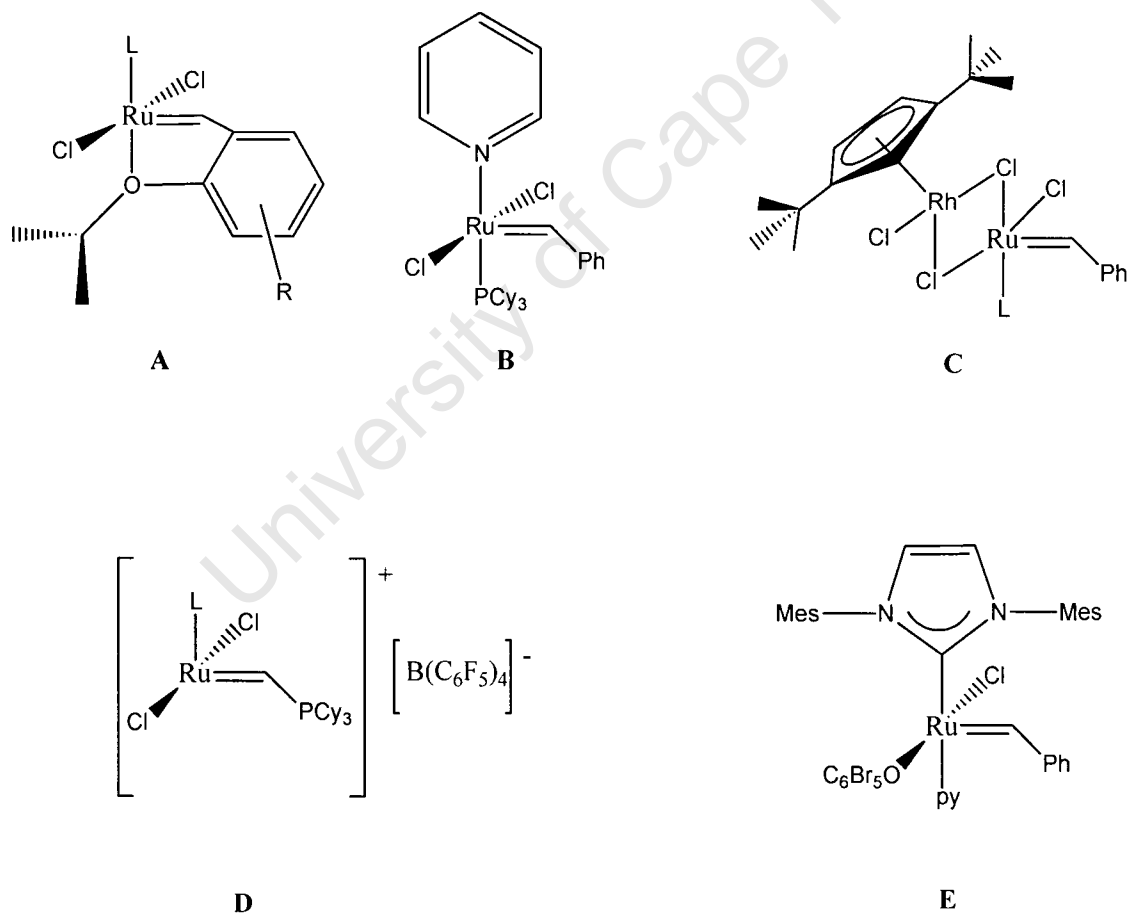


Figure 1.3: Selected examples of other well-defined, metathesis active ruthenium alkylidene catalysts (L = PR₃ or NHC)

The Hoveyda-Grubbs type catalyst **A** is obtained by replacing one of the phosphine ligands with an isopropoxy group attached to the benzene ring to either give the first (when $L = PR_3$) or the second (when $L = NHC$) generation Hoveyda-Grubbs catalysts. These complexes are highly stable, they exhibit slow initiation rates as a result of chelate stabilization.²⁵

The pyridine-coordinated complex **B**,^{26a} and the heterobimetallic complex **C**,^{26b} on the other hand exhibit high catalytic activity but this is accompanied by the fast rate of catalytic decomposition.² Romero and Piers reported a class of highly active 14-electron ruthenium olefin metathesis catalysts, of the type **D**. These complexes have a vacant coordination site, and hence provide rapid metathesis even at low temperatures.²⁷

It has been reported that Cl-bridged dimers are responsible for the deactivation of Grubbs-class catalysts containing two Cl groups.^{28a-b} For this reason, olefin metathesis catalysts containing alternative anionic ligands, such as complex **E**, have been prepared. Complex **E** has high activity, and is easy to remove.²⁹

1.4 Applications to organometallic substrates

Olefin metathesis has until recently been a synthetic tool for organic and polymer synthesis. However, not much work has been done in with regards to olefin metathesis applications to organometallic substrates. This brief review will therefore explore such developments in the areas of cross and ring-closing metathesis reactions. While the intramolecular variant of this reaction, ring-closing metathesis, has seen expanded use in synthesis, the intermolecular variant between two different alkenes, i.e., cross metathesis, has received significantly less attention.³⁰ In the studies by Alvares *et al.*³¹ it was demonstrated that the tungsten compounds underwent ring-closing metathesis with $WOCl_4/Ph_2SiH_2$ as the catalyst. Various metallocene-containing dendrimers, polymers,

and *ansa*-metallocenes have been prepared using either RCM, cross metathesis, or ring-opening metathesis polymerization.³²

1.4.1 Recent applications of Ring Closing Metathesis to organometallic substrates

The RCM protocol constitutes a versatile synthetic tool for the formation of carbon-carbon cycles,³³ and heterocycles.³⁴ The latter has found a greater number of successful applications probably due to the inherent Thorpe-Ingold effect in which the lone electron pair(s) in respective heteroatom may assist in aligning a productive conformation prior to the ring closure.³² A lot more work has thus been reported regarding the synthesis of oxo- and azacycles via RCM. This is useful in the synthesis of drug precursors and in the total synthesis of natural products.³⁵ Perhaps it is for similar reasons that the RCM protocol has seen more applications (as compared to the CM) in the case of organometallic substrates. Here we report advances in the synthesis of small to medium rings where at least one transition metal center is present in the substrate complex and/or in the final product.

1.4.1.1 Template-directed synthesis

A few reports in the literature describe the synthesis of macrocycles by metathesis of olefin substituted ligands in the coordination sphere of organometallic complexes whereby monometallic complexes were mainly used.^{9-10, 36-37} The work on template directed synthesis of macrocycles by RCM protocol exemplified one of the earliest applications of the use of the metathesis protocol to transition metal containing substrates (Figure 1.4).^{9,10}

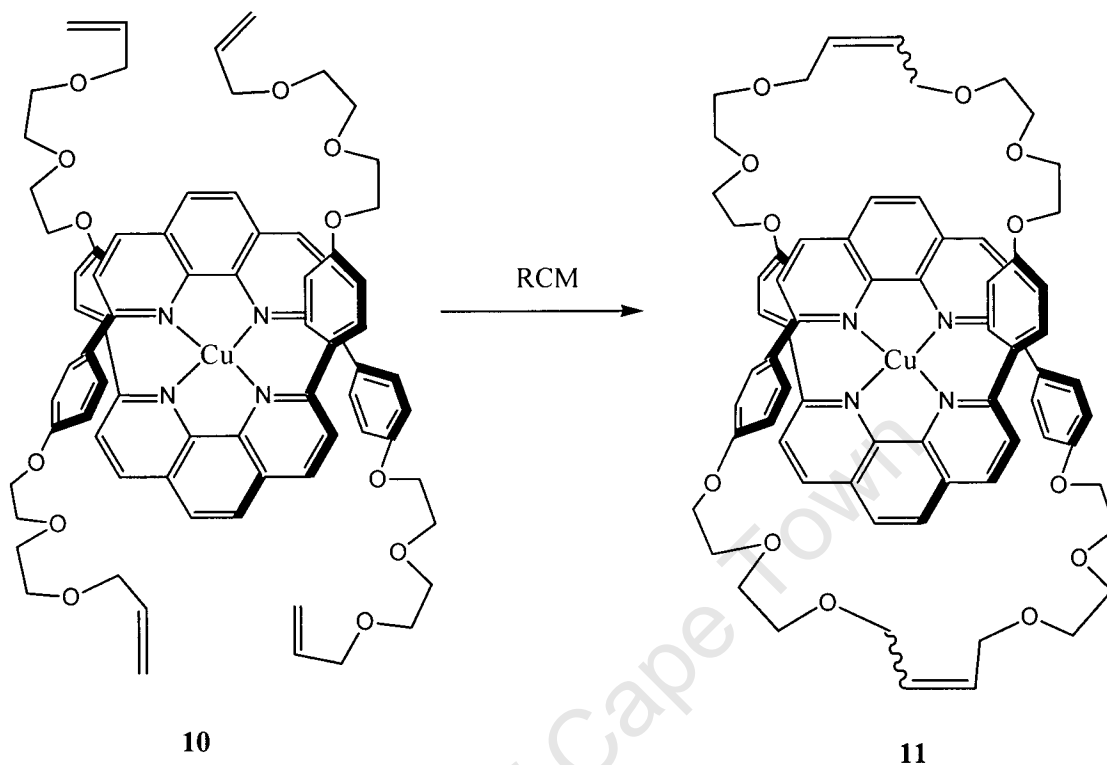
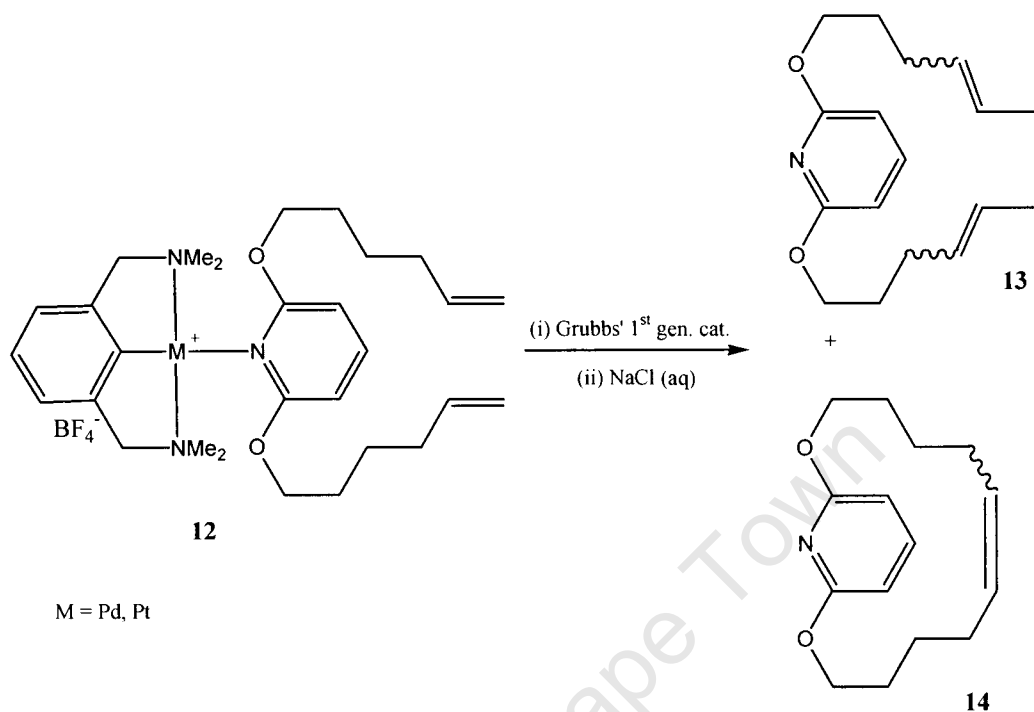


Figure 1.4: Cu-templated [2]catenane synthesis³⁷

In this work they detailed the generation of [2]catenanes using bis(olefin) appended 9,10-phenanthroline copper complexes via RCM, followed by demetalation. Up to 30-membered macrocycles were accessed via this route.

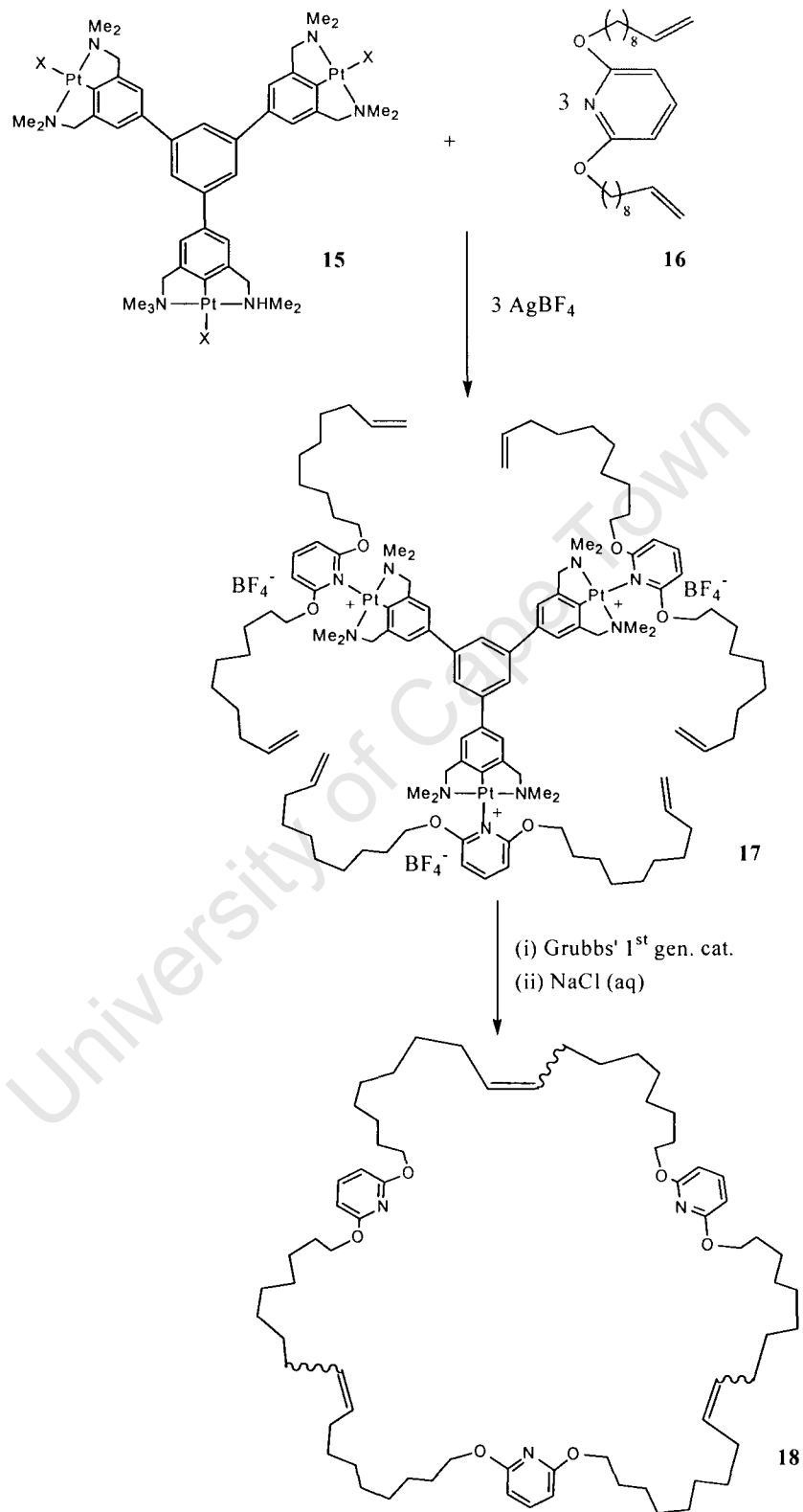
In later studies Spek, van Koten and co-workers detailed the use of pincer-ligand palladium and platinum complexes as protecting groups for bis-olefin substituted pyridines in RCM (Scheme 1.7).^{10, 37}



Scheme 1.7

The pincer-ligand complex **12** acts as a protected pyridine ligand which can undergo ring-closing metathesis, otherwise the free pyridines in solution would coordinate to the active site of the 14-electron catalyst species and in so-doing increasing the rate of catalyst-decomposition. The decomplexation by aqueous sodium chloride affords a pyridine-containing hetero-cycle **14**.

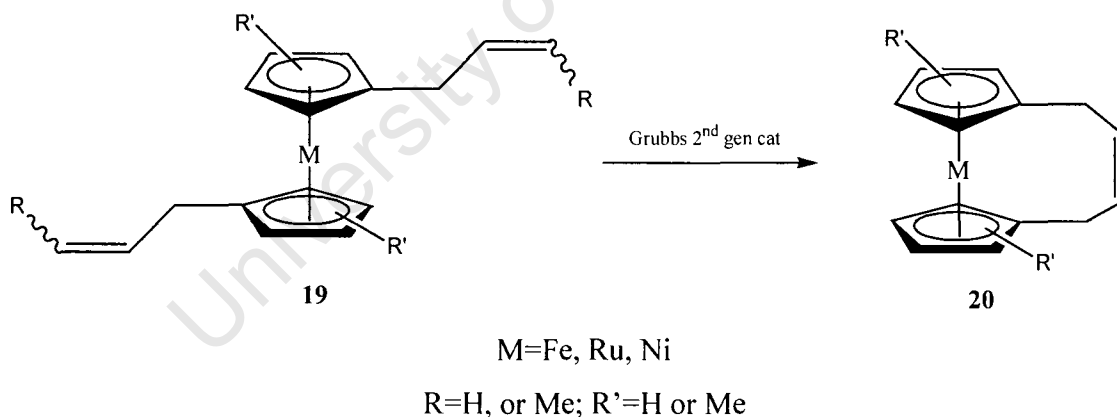
The reaction of NCN-Pt tri-pincer templates with three equivalents of 2,6-bis(9-decene-1-oxy)pyridine forms the templated precursor which when subjected to 5 mol% Grubbs 1st generation catalyst, followed by subsequent decomplexation of the pyridines with NaCl, afforded the macrocycle **18** (Scheme 1.8).³⁷



Scheme 1.8

1.4.1.2 *ansa*-Metallocenes

In recent years ring-closing metathesis has been successfully applied in the transition metal coordination sphere, providing access to novel inorganic and organometallic complexes (Scheme 1.9).³⁸ Connecting two cyclopentadienyl ligands in a bis(η^5 -cyclopentadienyl)metal complex is one of the most important methods to modify steric characteristics of a metallocene.³⁹ In addition, *ansa*-metallocenes of group III or group IV transition metals have been demonstrated to be useful catalyst precursors and reagents in polymerization reactions and in organic synthesis.³⁹ Ring-closing metathesis has been used for the preparation of *ansa*-metallocenes from metallocene precursors with two vinyl groups. Ogasawara *et al.*³⁹ reported the use of RCM for converting 1,1-diallylferrocene into the corresponding ferrocenophane **20** (Scheme 1.9).



Scheme 1.9

1.4.1.3 RCM chemistry of transition metal complexes with olefin containing phosphine ligands

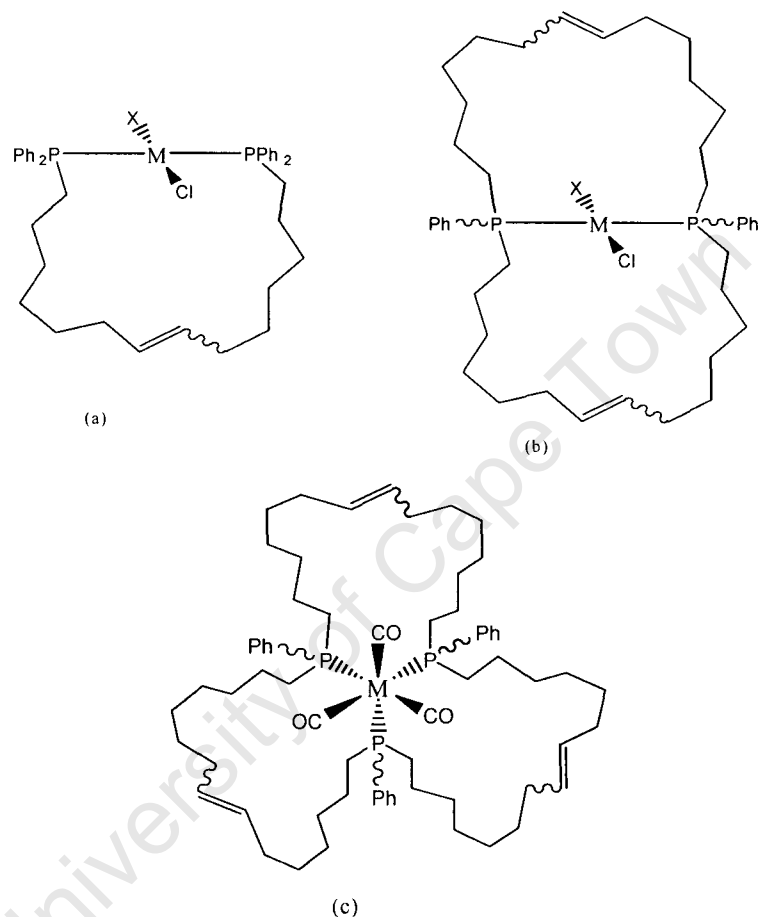


Figure 1.5: (a) mono-, (b) di- and (c) tricyclization products involving *trans*-spanning tertiary phosphine ligands.

The Gladysz group, in a series of papers have reported the preparation of olefin containing tertiary phosphine ligands where the number of terminal alkene moieties varies from one to three.⁴⁰⁻⁴³ The reaction of these ligands with transition metal complexes resulted in novel organo-transition metal complexes where the phosphorus atom is bonded to the metal center and the pendant olefin moiety is available for further manipulation. Subjecting the afore-mentioned organometallic complexes to the RCM

protocol afforded some novel ring complexes where the metal centre, two phosphine atoms and a number of $-\text{CH}_2-$ groups form part of the ring system (Figure 1.5). A few examples of such transformations include monomacrocyclizations involving *trans*-phosphine ligands each with terminal alkene moiety, dimacrocyclizations involving *trans*-phosphine ligands each with two terminal alkene moieties, and trimacrocyclization involving facial phosphine ligands each with two terminal alkene moieties.⁴⁰

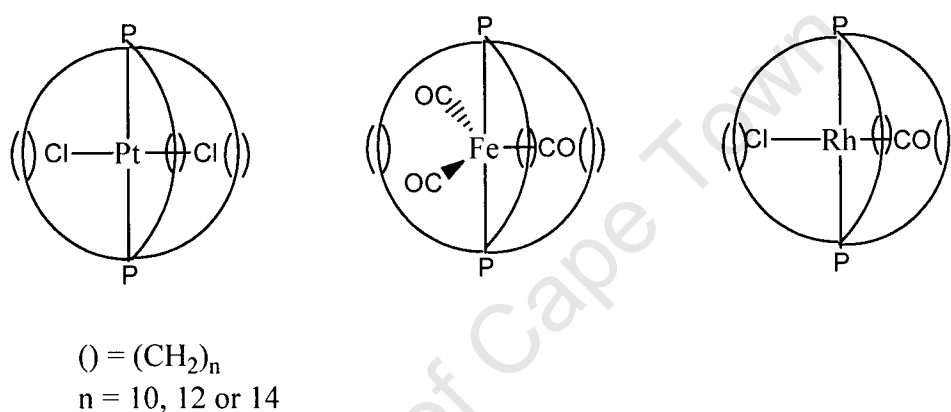
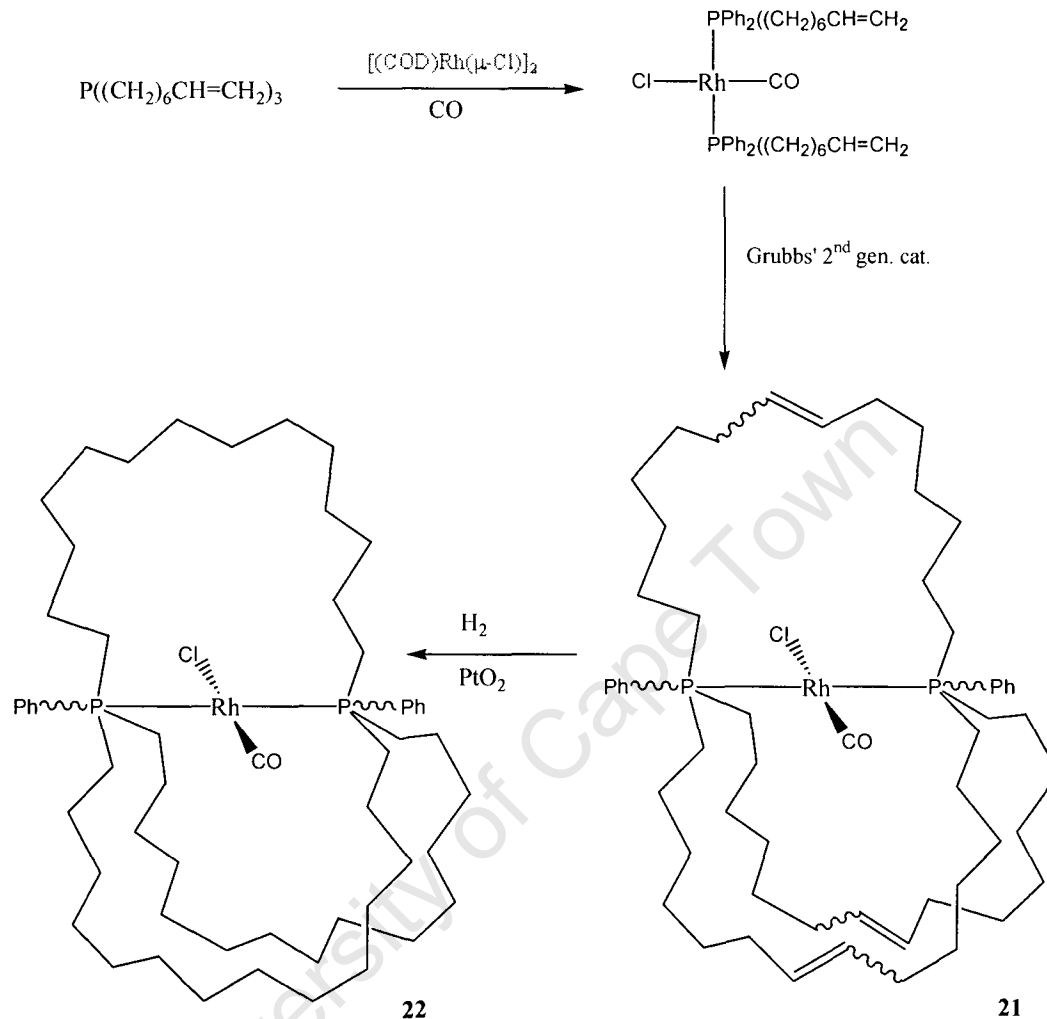


Figure 1.6: Gyroscope-like molecules prepared via RCM

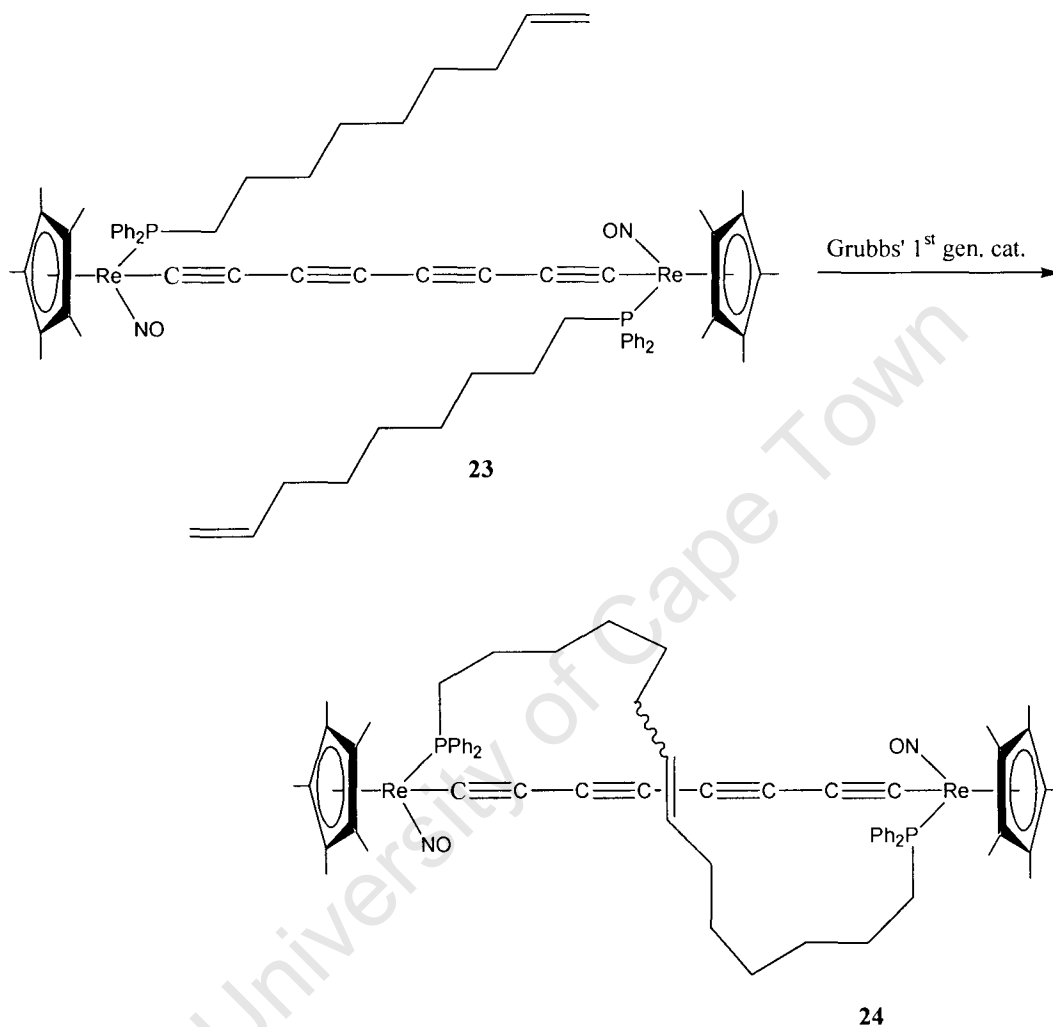
Gyroscope-like molecules with rotating components consisting of three spoke stators that enclose neutral transition metal rotators have been prepared via the RCM route, such complexes feature in many molecular devices.⁴¹

These complexes resemble those shown in **Figure 1.6**, where the transition metal is encased in *trans*-spanning diphosphine stators. The diphosphine stators consist of three $(\text{CH}_2)_n$ “spokes” that are generated by alkene metathesis/hydrogenation sequences such as the example shown in Scheme 1.10.^{41-42a-b}



Scheme 1.10

Platinum and rhenium complexes of the type $\text{L}_n\text{MC}_8\text{ML}_n$, **24**, (where $\text{L}_n = \text{Cp}^*$, NO , and $\text{PPh}_2(\text{CH}_2)_7\text{CH}=\text{CH}_2$; and $\text{M} = \text{Re}$) with sterically-protected sp carbon chains were obtained via olefin metathesis as in the example shown in (Scheme 1.11) below.⁴³ In the case where $\text{M} = \text{Pt}$, each $\text{L}_n\text{PtC}_8\text{PtL}_n$ fragment features two olefin-containing $\text{PPh}_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$ ligands which can cyclize in two ways (i.e. from ring-closing between phosphine ligands on opposite Pt atoms; or from ring-closing between phosphine ligands on the same Pt atom).⁴³

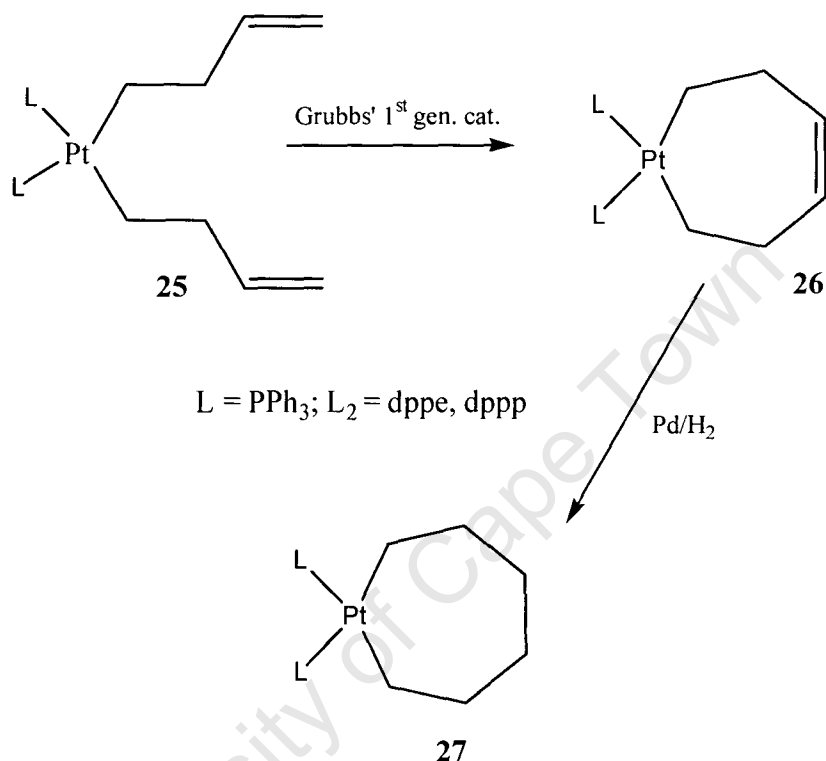


Scheme 1.11

1.4.1.4 Bis(alkenyl) compounds

In the Moss group, Sivaramakrishna *et al.*^{44-45a-b} described some new applications of ring closing metathesis (RCM) with bis(alkenyl) compounds, $L_mPt\{(CH_2)_nCH=CH_2\}_2$ (where L_m = other ligands, and $n \geq 2$). Scheme 1.12 shows an example of an intramolecular ring closing metathesis reaction involving two pendant arms of a bis(alkenyl) platinum

complex to form a platinacycloheptene, which is then hydrogenated to afford the corresponding platinacycloheptane **27**.^{45a-b}

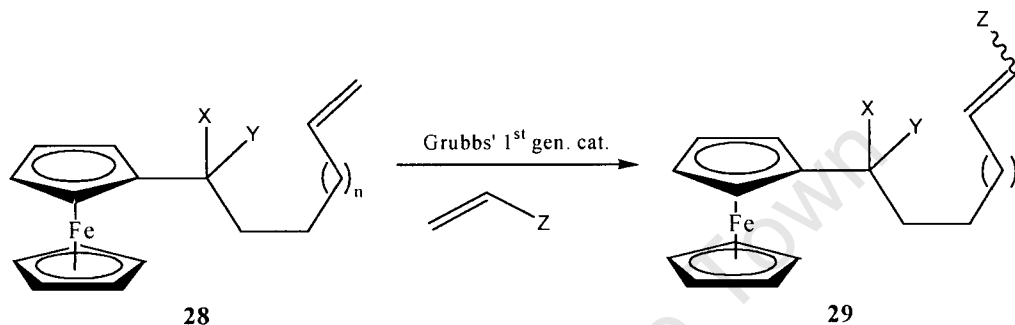


Scheme 1.12

1.4.2 Recent applications of cross metathesis to organometallic substrates

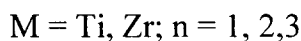
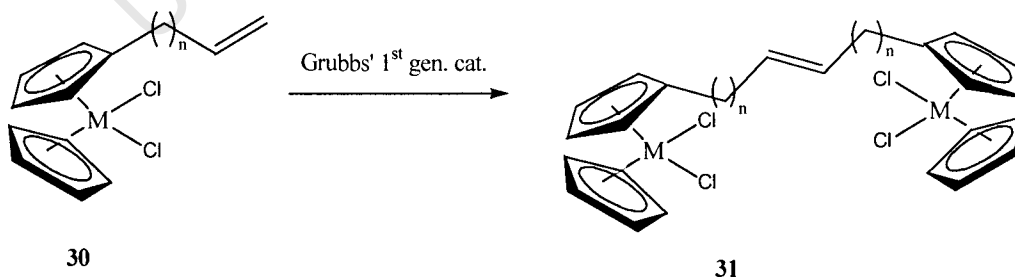
Cross metathesis (CM) has become a powerful alternative to the Wittig-olefination, in part because it requires milder conditions. However, unlike the entropically favored RCM protocol, CM is associated with more challenges in terms of selectivity. The formation of the cross metathesis products is always in competition with self-metathesis products.⁴⁶ Suppression of undesirable side products is therefore a prerequisite to success of CM reactions. The E/Z ratio of the newly formed double bond also needs to be predictable if not controllable. One of the useful methods which has been employed to control the

selectivity for the cross-metathesis products has been to functionalize terminal olefins with highly conjugated systems or nucleophilic species.⁴⁷ A useful method to effect the stereochemical outcome was introduced by Scheiner *et al.*⁴⁸ and it is based on the ring opening of strained ring systems such as norbornenes.



Scheme 1.13

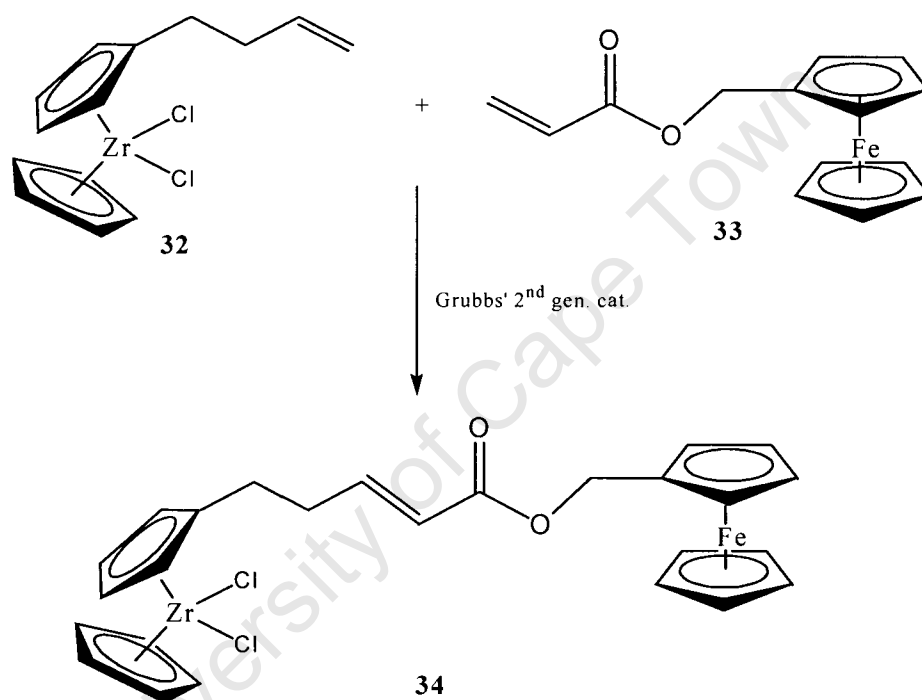
In 2000, Seshadri *et al.*³⁵ demonstrated the first application of cross-metathesis for the preparation of terminally unsaturated α -hydroxy- and α -ketoferrocenes (Scheme 1.13). In this work, it was found that 20 mol% of Grubbs' 1st generation catalyst, $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$, gave the cross metathesis product, **29**, in 59% yield (E:Z 1.6:1) along with 23% of self-metathesis product.³⁵



Scheme 1.14

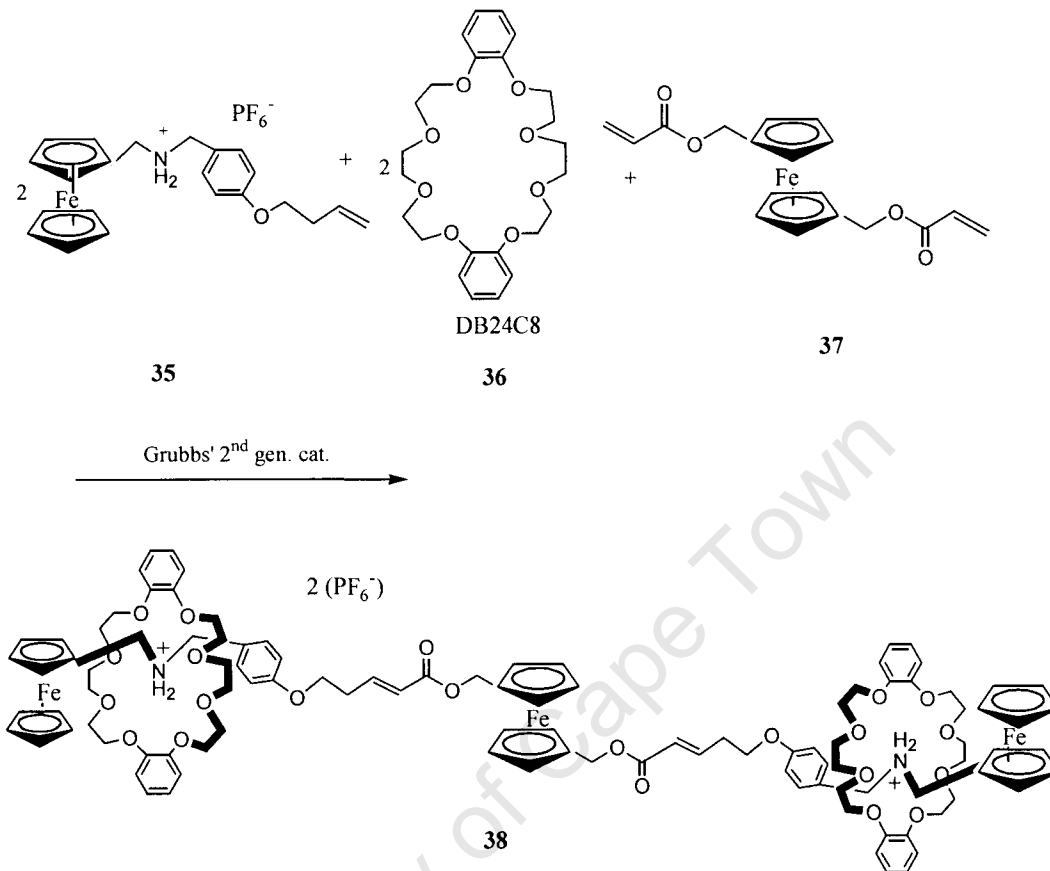
An intermolecular metathesis reaction for two metal complexes with vinyl pendant groups to form dinuclear metal complexes, accompanied by the elimination of ethylene.

Thus, mononuclear Zr and Ti complexes of the type $\text{CpMCl}_2\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ (where $n = 1, 2, 3$) were shown to undergo intermolecular metathesis, in the presence of Grubbs' 2nd or 1st generation catalysts to produce dinuclear complexes, **31**, with bridging ligands (Scheme 1.14).^{35,38,49-50}



Scheme 1.15

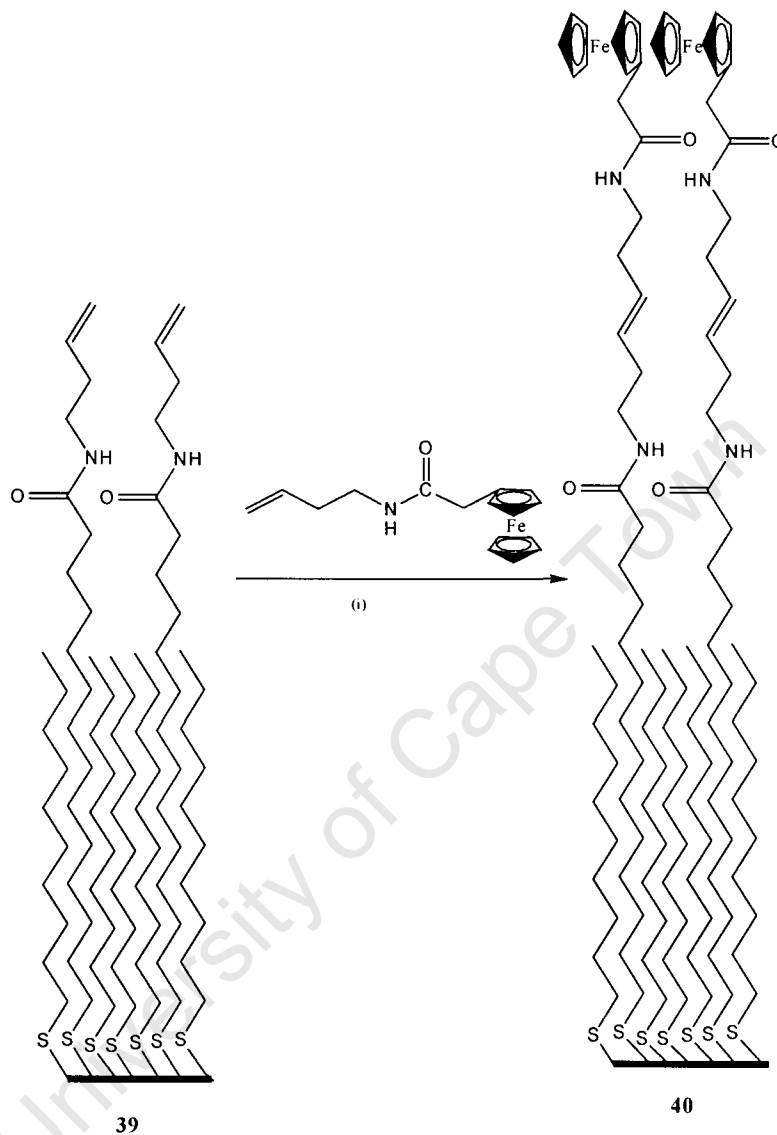
Kuwabara *et al.*⁵⁰ successfully prepared a Zr/Fe heterodinuclear complex (**34**) (where the two metal centers are bridged by a biscyclopentadienyl ligand) via the cross metathesis reaction of $\text{CpZrCl}_2\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)\text{CH}=\text{CH}_2\}$ and ferrocenylmethyl acrylate in the presence Grubbs' 2nd generation catalyst (Scheme 1.15).⁵⁰



Scheme 1.16

A [3]rotaxane (**38**) having one ferrocenylene and two ferrocenyl groups in the axle component was prepared via an end-capping cross-metathesis reaction in the presence of Grubbs' second generation catalyst as shown in Scheme 1.16 above.⁵¹

Brooksby *et al.* showed that surface-confined ferrocenyl complexes (**40**) can be prepared via a cross-metathesis reaction between the surface-bound olefins and the free olefins in solution (scheme 1.17).⁵² Olefin cross metathesis was used to functionalize polyolefin dendrimers, polymers and gold nanoparticles using Grubbs' second generation catalyst.⁵³



Scheme 1.17: (i) DCM, 50%, Grubbs' 2nd gen. catalyst

Ruthenium catalyzed cross metathesis protocol has also been applied in the dimerization of tetraplatinum cluster units of the type $[\text{Pt}_4(\mu\text{-OCOCH}_3)_7\{\mu\text{-OCO}(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ to afford the corresponding octaplatinum clusters (Figure 1.7(a)).⁵⁴ The self metathesis of diruthenium clusters with a single $(\text{CH}_2)_n\text{CH}=\text{CH}_2$ fragment gave tetraruthenium complexes as shown in Figure 1.7(b) below.³²

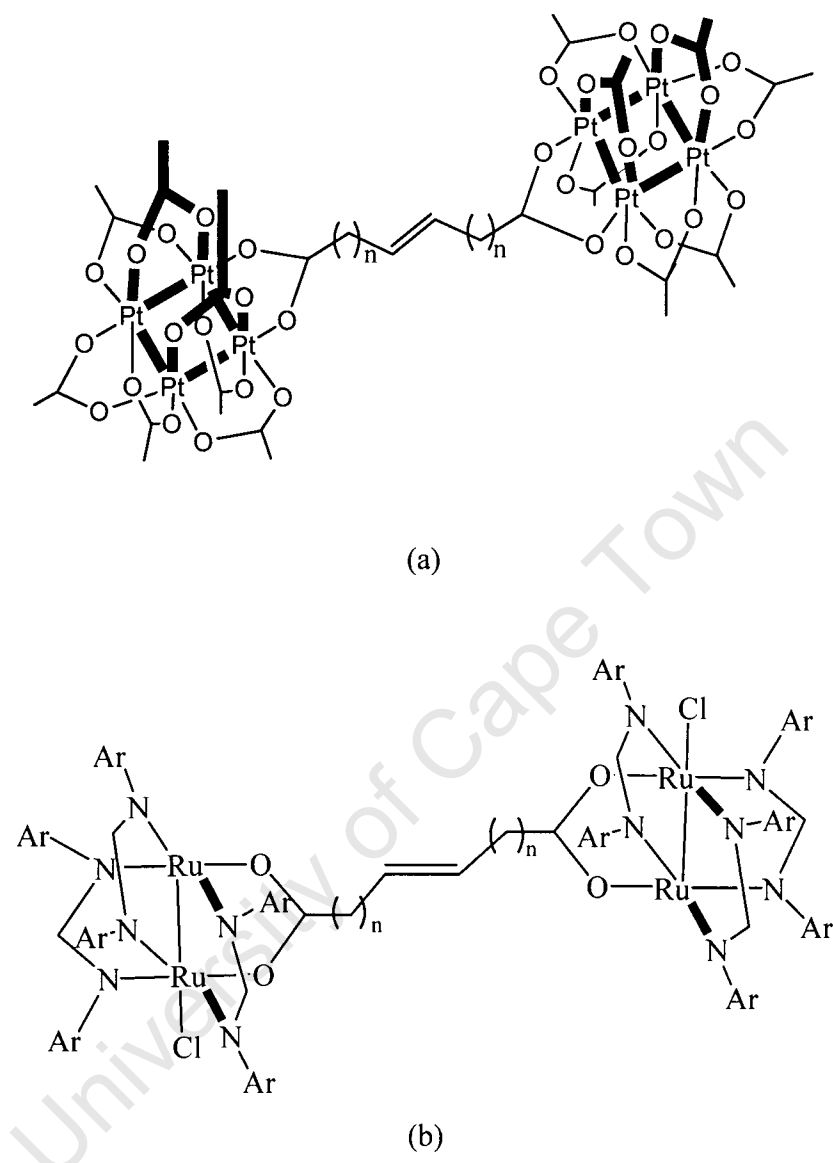


Figure 1.7: Examples of cluster complexes obtained via the cross (self) metathesis catalyzed by Grubbs' ruthenium catalysts. (a) Octaplatinum and (b) tetraruthenium cluster complexes ($n = 1-3$ in each case).^{32,54}

1.5 Conclusions

The story of olefin metathesis is one of scientific achievement or victory. The metathesis reaction has come a long way, from laboratory success on a small scale to viable commercialized products produced on a large industrial scale. The recent advances in its applications make it difficult even to imagine the discipline of synthetic chemistry without such a versatile tool. In 2005, the pioneers of this field received a Nobel Prize in chemistry. The catalyst systems have since seen great improvements, from the ill-defined metal-salts of group six and group seven transition metals to the well-defined catalyst systems of Schrock and Grubbs where the ligands can be altered to fine-tune or control the reactivity. Better understanding of the mechanistic details led to the discovery that metallocarbenes play a significant role in the catalytic cycle. This discovery allowed many research groups to focus their energies in trying to isolate (and later develop) metallocarbenes to function as possible catalysts or catalyst precursors.

In its early days, the metathesis reaction was mainly used to effect polymerization of strained carbocycles via ROMP, or for the transformation of propene into ethylene and butane. The isolation of Schrock's molybdenum and later Grubbs' ruthenium catalysts provided catalysts with enhanced metathesis activity. The ruthenium systems were found to be more stable and tolerant towards different functional groups and hence found more applications in all spheres of organic and polymer synthesis. Of late, a number of research groups have reported successful applications of the metathesis protocol to organometallic substrates. Both the RCM and CM type reactions have been reported, but these are very limited especially in comparison to those of polymer or organic synthesis. However, even with regards to organometallic substrates, the potential is great and so are the possibilities.

1.6 Aims and objectives

The general aims of this project were (i) to prepare novel homo-binuclear complexes where the two metals are bridged by an unsaturated hydrocarbon chain via the cross metathesis reaction of the mononuclear complexes having one pendant alkene group, and (ii) to prepare novel metallacyclic complexes of iron via the intramolecular ring-closing metathesis reaction of bis(alkenyl) complexes.

- The primary objectives of this project was to synthesize complexes (with at least one pendant alkene group) of ruthenium (of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, $n = 2, 3, \text{ or } 5$) iridium (of the type $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$, $m = 2, 3, 4 \text{ or } 6$) and iron (of the types (i) $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, $n = 3 - 6$, $\text{L} = \text{Cp or Cp}^*$ and (ii) $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$, $n = 2, 3 \text{ or } 4$ and $m = 2, 3, 4 \text{ or } 6$). In Chapter 3, we, therefore, discuss the preparation and the characterization of the above-mentioned complexes.
- The secondary objectives of this project were to investigate the metathesis reactivity (as discussed in Chapter 4) of these complexes; and by so doing, prepare novel (i) binuclear complexes (via cross metathesis) where the two metals are connected by unsaturated hydrocarbon bridges, and (ii), prepare novel metallacyclic complexes (via ring-closing metathesis) where iron, an acyl group and a hydrocarbon chain form part of the ring system.

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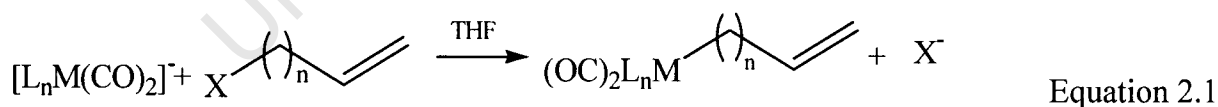
CHAPTER 2: AN INTRODUCTION TO THE SYNTHESIS OF THE SUBSTRATES AND THEIR METATHESIS REACTIVITY

2.1 Preparation of the substrates

2.1.1 Compounds of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$

Complexes of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ (M = iron or ruthenium, L = Cp or Cp* and $n = 2 - 6$) with one metal-carbon σ -bond can be prepared by nucleophilic attack of the carbonylmetallates, (i.e. $[\text{L}_n\text{M}(\text{CO})_2]^-$, L_n = ancillary ligands) on compounds of the type $\text{X}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ (X = halide,^{1,2} tosylate² or other good leaving groups) as shown in the Equation 2.1 below.

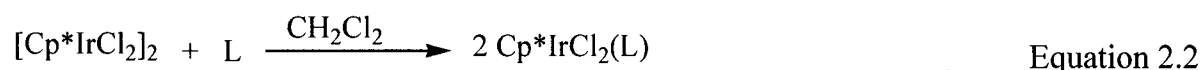
Reactivity studies such as β -hydride abstraction,^{2,3} photolysis,³ thermal decomposition,³ hydrogenation⁴ and hydroformylation,⁴ etc. have been reported for $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ compounds.



Iron complexes of the type $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ have been reported previously.¹ The ruthenium analogs are however new. These latter compounds were prepared by following a method similar to the one used for the synthesis of the related complexes of iron.¹ The reaction of the ruthenium carbonyl anion $[\text{CpRu}(\text{CO})_2]^-$ (prepared by stirring the dicarbonylcyclopentadienyl ruthenium dimer over a sodium amalgam) with corresponding bromoalkenes resulted in the formation of complexes of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$.

2.1.2 Preparation of complexes of the type Cp*(L)IrCl₂

The iridium dimer complex, [Cp*IrCl₂]₂ reacts with donor ligands in polar solvents to give Cp*(L)IrCl₂ (for example, L = PPh₃) as shown in the Equation 2.2 below.⁵

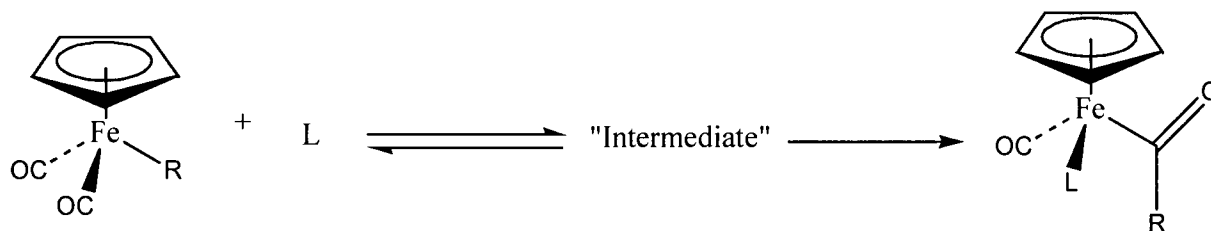


Novel iridium complexes of the type Cp*Ir(Cl)₂{PPh₂(CH₂)_mCH=CH₂} were prepared by stirring the iridium dimer [Cp*IrCl₂]₂ with the corresponding donor ligands PPh₂(CH₂)_mCH=CH₂ (m = 2, 3, 4, and 6) in dichloromethane at room temperature. This resulted in the formation of novel iridium complexes where the iridium atom is coordinated to the phosphorus atom to leave the pendant alkene moiety available for further manipulation.

2.1.3 Preparation of acyl complexes of the type RC(O)Fe(CO)(L)Cp

The chemistry of CO migratory insertion into metal alkyl bonds, in the presence of a donor ligand (L) is an important carbon-carbon bond-forming step in a number of catalytic reactions including methanol carbonylation to acetic acid, and alkene hydroformylation.^{7,8} The reaction (Scheme 2.1) has been well-studied and well-reported by a large number of research groups.^{2,8,9} In Chapter 3 we report the use of this chemistry in order to access novel acyl complexes of iron having two pendant and different alkene moieties bonded to the iron centre. These complexes were prepared by refluxing the complexes of the type CpFe(CO)₂{(CH₂)_nCH=CH₂} (n = 2, 3, and 4) and the ligands PPh₂(CH₂)_mCH=CH₂ (m = 2, 3, 4, and 6) in acetonitrile resulting in the isolation of complexes RC(O)Fe(CO)(L)Cp (R = -(CH₂)_nCH=CH₂, L = PPh₂(CH₂)_mCH=CH₂). Previously, a similar synthetic method had been used to prepare a series of related acyl

complexes, where (R = Et or Prⁱ; L = PPh₃, PPh₂Me).^{9a-c}



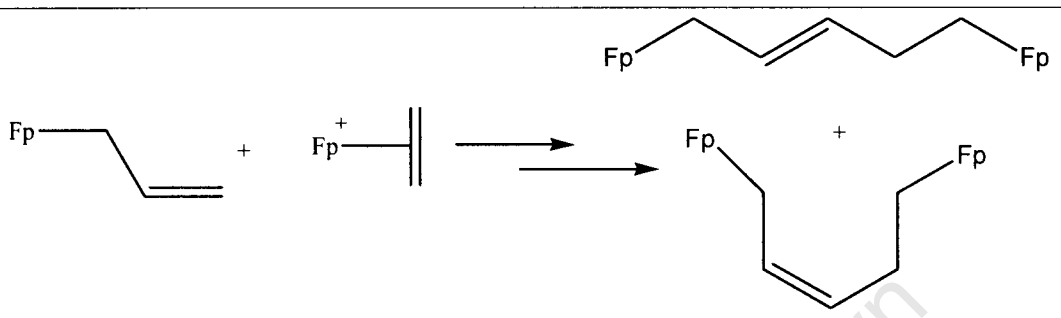
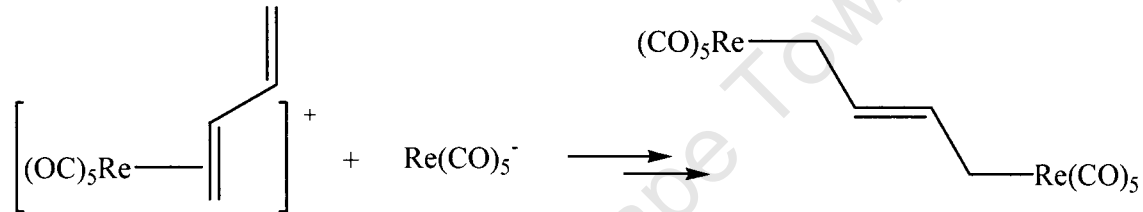
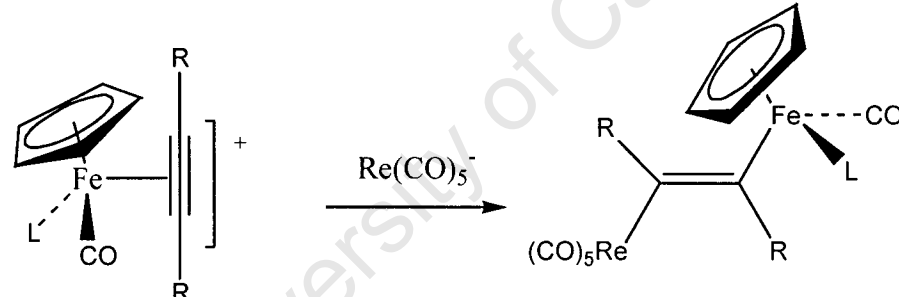
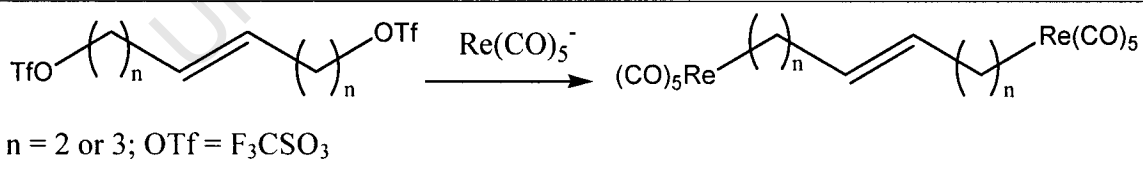
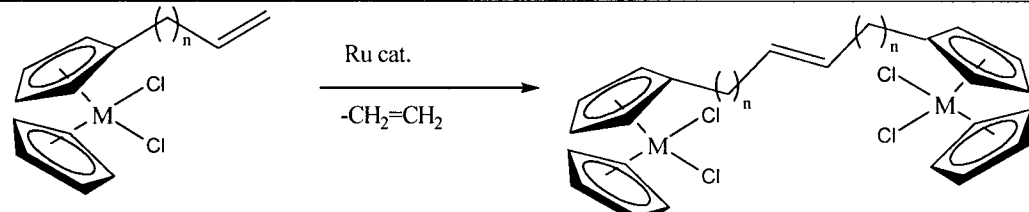
Scheme 2.1

2.2 Investigating olefin metathesis reactivity of the substrates

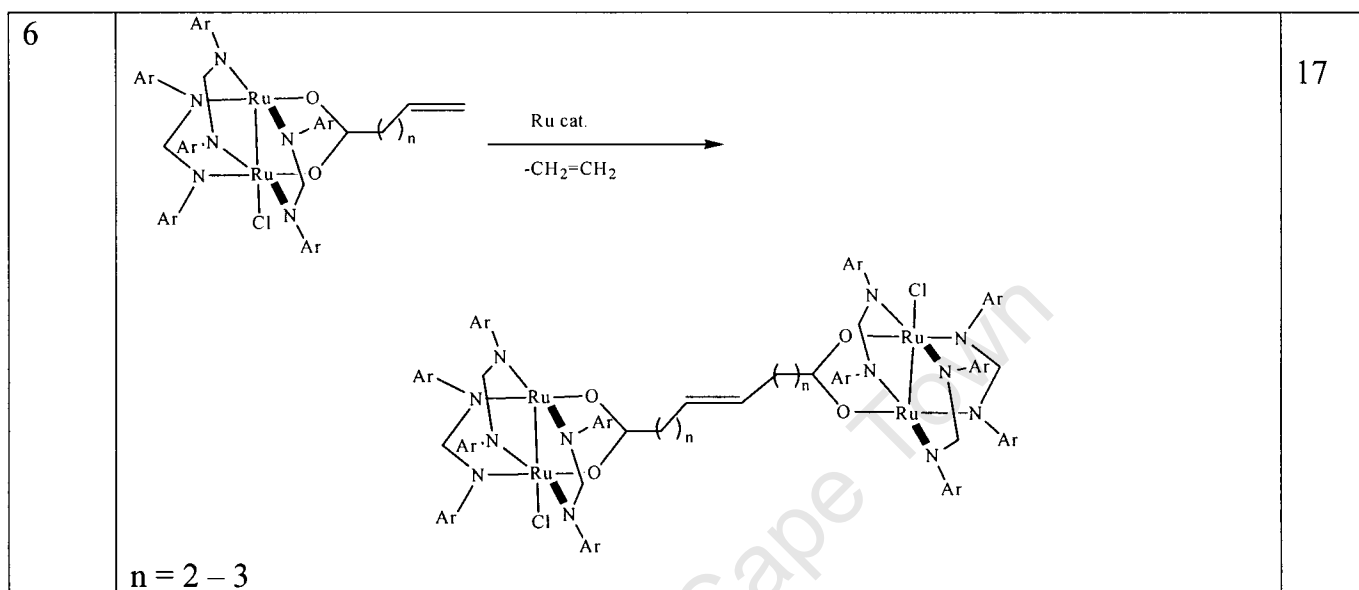
2.2.1 Metathesis route for the synthesis of homo-bimetallic compounds of the types $L(\text{CO})_2\text{M}(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{ML}(\text{CO})_2$ (M = Fe or Ru; L = Cp* or Cp); and $\text{Cp}^*(\text{Cl})_2\text{IrPPh}_2(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{PPh}_2\text{Ir}(\text{Cl})_2\text{Cp}^*$.

Bimetallic hydrocarbon bridged complexes of the type $L_n\text{M}(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{ML}_n$ (ML_n = metal and associated ligands, or metal cluster complex) with unsaturated bridging units containing more than four carbon atoms and one double bond are not well-reported in the literature.¹⁰⁻¹⁷ Such complexes make it possible to introduce new functional groups by addition reactions or to bind other electrophilic metal fragments to the alkene group.¹¹ In 1980 Lennon *et al.* described the preparation of the bimetallic iron complex by condensation of the $\text{CpFe}(\text{CO})_2(\eta^1\text{-allyl})$ complex with the $[\text{CpFe}(\text{CO})_2(\eta^2\text{-olefin})]^+$ cation (Table 2.1, entry 1). The dinuclear condensation product is cationic, but the $\text{Fp}(\eta^1\text{-allyl})$ moiety could be easily regenerated by treating with triethylamine to afford *cis*- and *trans*- geometric isomers.¹⁰

Table 2.1: A summary of bimetallic complexes with unsaturated hydrocarbon bridges

Entry	Synthetic route	Ref.
1	 <p>Reaction scheme showing the synthesis of a bimetallic complex with an unsaturated hydrocarbon bridge. The reactants are a ferrocene-terminated alkene and a ferrocene-terminated alkyne. The product is a bimetallic complex where two ferrocene units are bridged by a trans-alkene.</p>	10
2	 <p>Reaction scheme showing the synthesis of a bimetallic complex with an unsaturated hydrocarbon bridge. The reactants are a ferrocene-terminated alkene and a rhenium pentacarbonyl anion. The product is a bimetallic complex where two rhenium pentacarbonyl groups are bridged by a trans-alkene.</p>	12
3	 <p>Reaction scheme showing the synthesis of a bimetallic complex with an unsaturated hydrocarbon bridge. The reactants are a ferrocene-terminated alkyne and a rhenium pentacarbonyl anion. The product is a bimetallic complex where a ferrocene unit and a rhenium pentacarbonyl group are bridged by a trans-alkene.</p> <p>R = Me, Ph, L = PPh₃, P(OPh)₃</p>	13
4	 <p>Reaction scheme showing the synthesis of a bimetallic complex with an unsaturated hydrocarbon bridge. The reactants are a ferrocene-terminated alkene with triflate end groups and a rhenium pentacarbonyl anion. The product is a bimetallic complex where two rhenium pentacarbonyl groups are bridged by a trans-alkene.</p> <p>n = 2 or 3; OTf = F₃CSO₃</p>	14
5	 <p>Reaction scheme showing the synthesis of a bimetallic complex with an unsaturated hydrocarbon bridge. The reactants are a ferrocene-terminated alkene and a ruthenium catalyst. The product is a bimetallic complex where two ferrocene units are bridged by a trans-alkene.</p> <p>n = 1-4, M = Ti, Zr</p>	15

(Table 2.1 cont.)



Beck *et al.* isolated the 2-butene-1,4-diyl-bridged carbonylrhenium complex via the addition of $[\text{Re}(\text{CO})_5]^-$ to η^2 -coordinated 1,3-butadiene (Table 2.1, entry 2).¹² Beck *et al.* also reported on the preparation of hetero-bimetallic complexes (with bridging carbon-carbon double bond) by nucleophilic attack of carbonylmetalates on coordinated unsaturated hydrocarbons (Table 2.1, entry 3).¹³

The bis(triflate) method was later shown to be the route of choice if hydrocarbon bridges longer than six carbons in a chain were desired.¹⁴ Lindner *et al.* prepared such complexes by reacting $[\text{Re}(\text{CO})_5]^-$ with the corresponding bis(triflates) (Table 2.1, entry 4).¹⁴

It was only recently that Seshadri *et al.* showed that olefin metathesis can be applied to the metallocene complexes with one pendant terminal alkene moiety to access novel bimetallic complexes where the two metallocene moieties are connected by an unsaturated hydrocarbon chain (Table 2.1, entry 5).¹⁵ Ohashi¹⁶ and Chen¹⁷ independently prepared (via self metathesis) platinum¹⁶ and ruthenium¹⁷ cluster compounds where two

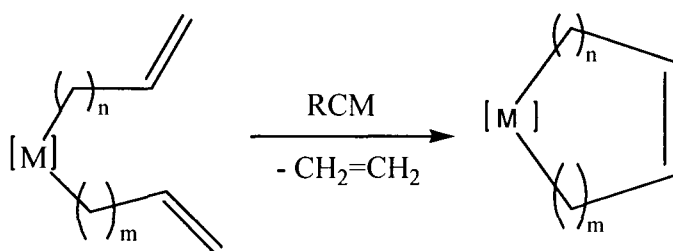
cluster groups are linked by an unsaturated hydrocarbon chain (Table 2.1, entry 6).

In Chapter 4 we describe the preparation of homodinuclear complexes in which the transition metals are linked by unsaturated hydrocarbon chains. These complexes were prepared by the self metathesis of either $LM(CO)_2\{(CH_2)_nCH=CH_2\}$ ($L = \eta^5-C_5H_5$ or $\eta^5-C_5(CH_3)_5$; $M = Ru$ or Fe) or $Cp^*(Cl)_2Ir\{PPh_2(CH_2)_mCH=CH_2\}$. In the former alkenyl complexes of iron or ruthenium there exists a metal-carbon σ -bond, whereas in the latter complexes of iridium, the metal is only bonded to the phosphorus atom. The mono-alkenyl complexes of ruthenium (i.e. **49** – **51**) are new, whereas the iron complexes have been reported before.¹ According to our knowledge, the metathesis reactivity of the abovementioned alkenyl complexes has not been reported previously. Compounds (**41**) – (**51**) reacted with Grubbs' ruthenium catalysts in a cross metathesis fashion to afford the corresponding bimetallic products (See section 4.1).

2.2.2 The ring-closing metathesis reactivity of the chiral acyl iron complexes of the type, $CpFe(CO)\{C(O)(CH_2)_nCH=CH_2\}\{PPh_2(CH_2)_mCH=CH_2\}$ ($n = 3 - 4$, $m = 3, 4$ and 6)

As discussed in Chapter 1, the applications of catalytic ring-closing metathesis to metal containing substrates (Scheme 2.2) have been extensively investigated¹⁸ especially when compared to the cross metathesis protocol.

In Chapter 4 (see Section 4.3) we discuss the ring closing metathesis reaction of the new chiral acyl iron compounds of the type $CpFe(CO)\{C(O)(CH_2)_nCH=CH_2\}\{PPh_2(CH_2)_mCH=CH_2\}$ ($n = 3$ or 4 , $m = 3, 4$ and 6), where the two olefin arms are of different functionalities (as shown in Scheme 4.3).



Scheme 2.2

2.3 References

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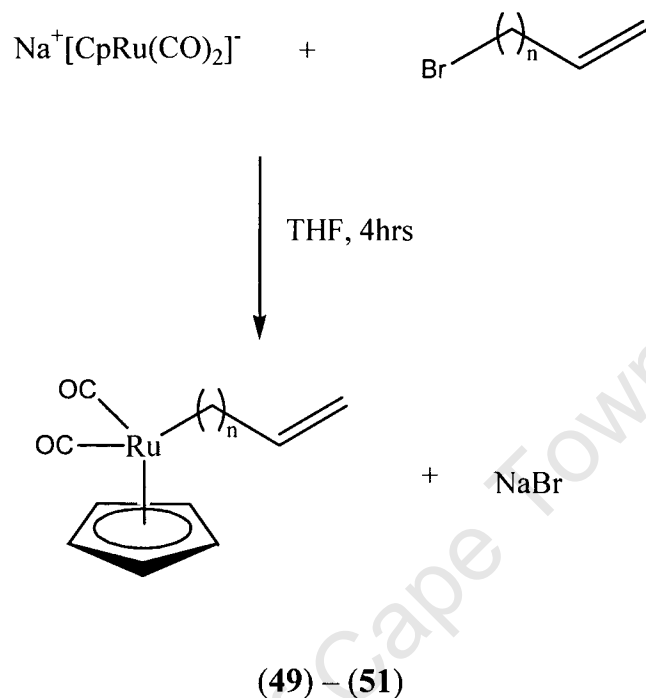
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CHAPTER 3: SYNTHESIS AND CHARACTERISATION OF SOME TRANSITION-METAL COMPLEXES WITH AT LEAST ONE PENDANT ALKENE GROUP

3.1 The synthesis of ruthenium alkenyl compounds of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$; compounds (49) – (51)

The preparation of complexes of the type $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, ($\text{L} = \text{Cp}$ or Cp^*) (41) – (48), has been previously reported.¹ The complexes $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3, \text{ and } 5$), (49) – (51), were prepared by following a similar route (except for minor changes regarding time and temperature) to the one used for the preparation of the analogous iron complexes.¹ The reaction of $\text{Na}^+[\text{CpRu}(\text{CO})_2]^-$ with $\text{Br}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ (as shown in Scheme 3.1) in THF at 0°C under an inert atmosphere yielded the ruthenium alkenyl complexes (49) – (51) in moderate to high yields.

These compounds were purified by column chromatography on a Florisil column. Eluting with hexane resulted in the isolation of the ruthenium mono(alkenyl) complexes in moderate to good yields (Table 3.1). All the complexes were isolated as yellow or yellow to brown oils; and were found to be stable towards light and air. These properties are similar to those of related haloalkyl complexes of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{X}\}$ ($n = 3 - 5$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$), previously reported by Friedrich *et al.*²



Scheme 3.1

3.1.1 IR spectroscopy of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 5)

The IR data for compounds (49) – (51) are given in Table 3.1. The IR spectrum was recorded in dichloromethane and is in good agreement with the values previously reported for related compounds.^{2a-b} All compounds show two strong terminal carbonyl bands (at frequencies 2013 or 2011 and 1945 or 1946 cm^{-1}) in their IR spectra. There are no significant variations as the chain length increases.

As shown in (Figure 3.1) the newly prepared ruthenium complexes gave rise to peaks that are slightly shifted to higher frequencies (or stronger CO bond) as compared to previously reported iron analogues.¹ This shift towards higher frequencies can be

ascribed to the lower electron density on the ruthenium centre resulting from the increase in atomic radius and therefore, less electron density available for back-bonding into the π^* orbital of the CO ligand.

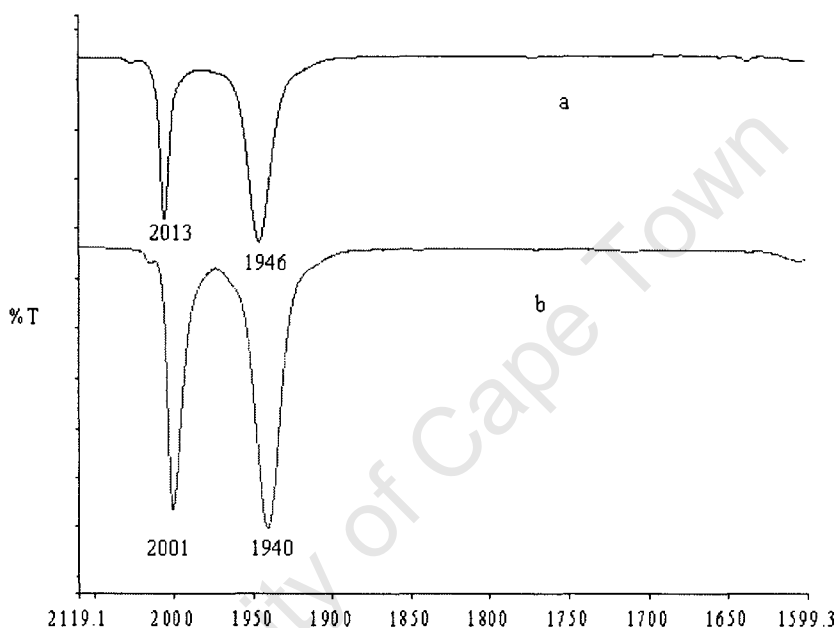


Figure 3.1: The spectra were recorded in DCM (cm^{-1}), in the terminal $\nu(\text{C}=\text{O})$ region; (a) the newly synthesised $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$ and (b) the previously reported complexes, $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$.¹

TABLE 3.1: Data for the compounds, $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$

Compound No	n	Yield (%)	$\nu(\text{CO})/\text{cm}^{-1}$ ^a	
49	2	82	2013 (s)	1946(s)
50	3	71	2011(s)	1945 (s)
51	5	79	2011 (s)	1946 (s)

(a) in CH_2Cl_2 solution

3.1.2 NMR spectroscopy of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 7)

^1H NMR spectroscopy

The mono(alkenyl) compounds (49) – (51) were characterized by proton NMR spectroscopy. These complexes give signals which are characteristic of species containing an alkene moiety. The signals characteristic of the terminal alkene functional groups gave distinct sets of resonances at δ 4.80 – 5.00 ppm ($=\text{CH}_2$) and δ 5.72 – 5.90 ppm ($\text{CH}=\text{}$) integrating for two and one protons respectively.

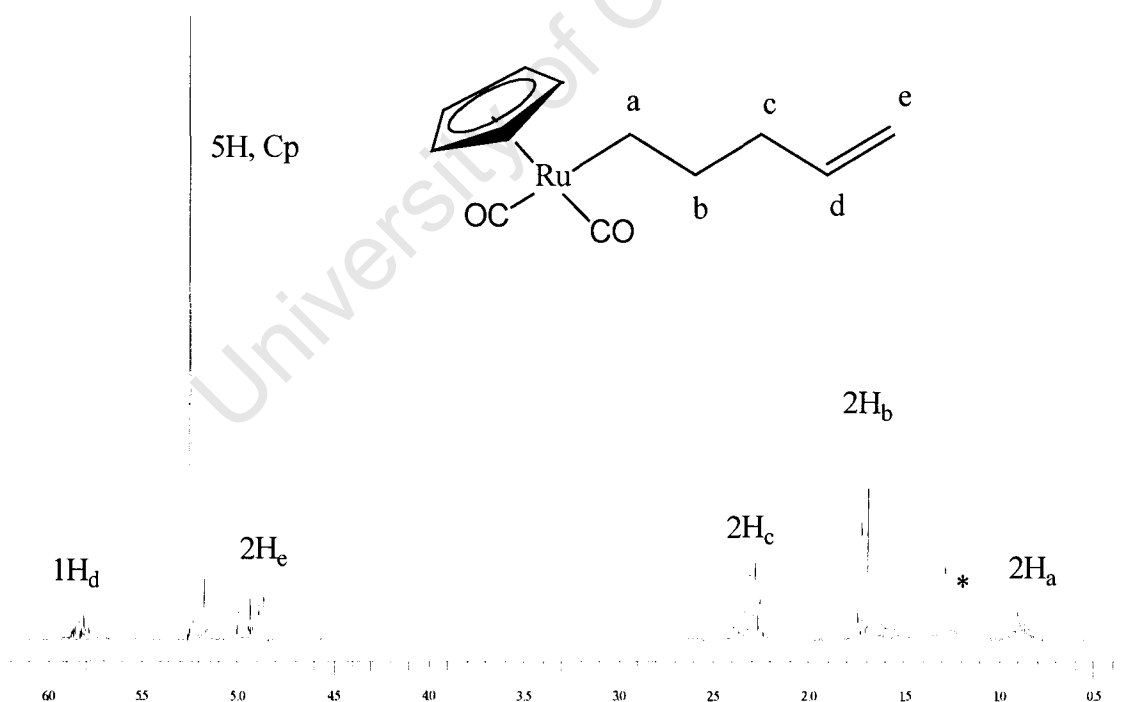


Figure 3.2: ^1H NMR spectrum of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (* = solvent)

The ^1H NMR spectra show the expected chemical shifts and peaks corresponding to the

alkenyl chains. The chemical shift corresponding to the Cp moiety appears as a singlet at δ 5.24 or 5.25 ppm for five protons of the Cp ring.

Protons of the carbons directly bonded to the metal centre were assigned to peaks in the region δ 0.85 – 0.89 ppm (Ru- $\underline{\text{C}}\text{H}_2$ -). These α -methylene protons appear in this high field region as a result of shielding from the electron density on the metal centre. Similar shifts have been previously reported for related compounds.^{2a}

The protons on the carbon adjacent to the alkene group gave resonances at δ 2.10 – 2.40 ppm ($\underline{\text{C}}\text{H}_2\text{CH}=\text{)$ as expected.^{1a} These are shifted to low field compared to other methylene protons and this is a result of de-shielding by the electron-withdrawing alkene group.

The other protons of the hydrocarbon chain appeared as broad multiplets at δ 1.5 – 1.60 ppm ($-\underline{\text{C}}\text{H}_2-$), the integration being the only way to distinguish between compounds of different hydrocarbon chain length. The integrations of the resonances in all the spectra were in good agreement with expected values. The assignments compared well with those of similar compounds in the literature.^{2a-b,3}

¹³C NMR Spectroscopy

Compounds (49) – (51) were also characterized by ¹³C NMR spectroscopy. ¹³C NMR spectra gave further information on the ruthenium alkenyl complexes and this served to further support the assignments given in the ¹H NMR spectral analysis. Resonances for the alkene carbons were observed in the region δ 139 – 143 ppm ($\underline{\text{C}}\text{H}=\text{)$ and δ 112 – 114 ppm ($=\underline{\text{C}}\text{H}_2$) as expected.^{1a}

The signals due to the Cp carbons appeared at δ 88.3 – 88.5 ppm, which is in good agreement with reported chemical shifts for similar complexes.³ Resonances that correspond to the carbons directly bonded to ruthenium atom (i.e. Ru- $\underline{\text{C}}\text{H}_2$ -) appeared

furthest up-field in the region δ -2.5 – -4.9 ppm. This is an expected region for carbon atoms bonded to the ruthenium atom and similar shifts have been previously reported for analogous complexes.^{2a-b,3} The signals for the carbons of the terminal carbonyl groups are located at δ 202 – 203 ppm as expected. Other signals resulting from the hydrocarbon chain appeared in the region δ 29 – 40 ppm ($-\underline{\text{C}}\text{H}_2-$), which agrees well with those previously reported for related compounds.^{2a-b,3}

3.1.3 Elemental analysis of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (49) – (51)

Ruthenium alkenyl compounds were also characterized by elemental analysis as shown in Table 3.2 below. The percentage values found are in good agreement with the calculated values.

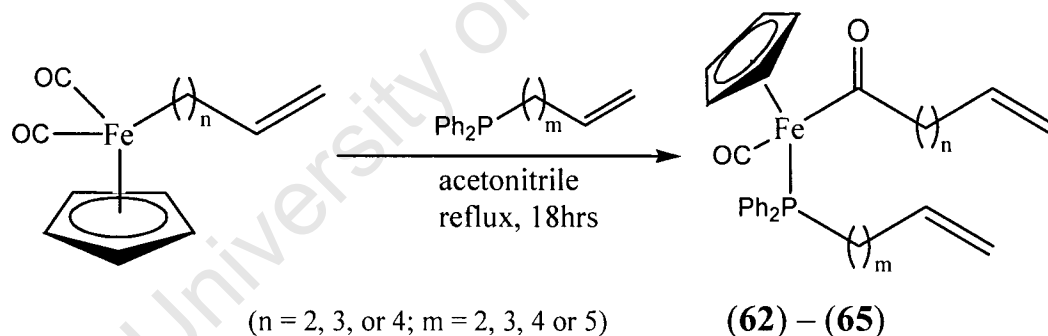
Table 3.2: elemental analysis data of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (49) – (51)

Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
49	47.65	47.40	4.36	4.33
50	49.47	49.44	4.84	4.80
51	52.65	52.20	5.68	5.68

3.2 Synthesis of iron compounds of the type

$\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$; compounds (62) – (65)

The Fe-carbon σ -bond is capable of undergoing a facile migratory carbon monoxide insertion reaction. In this way, bis(alkenyl) acyl compounds of the type $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ were prepared by refluxing the iron alkenyl compounds $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3$ or 4) with phosphine ligands of the type $\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ($m = 2, 3, 4$ or 6) in acetonitrile (Scheme 3.2). The preparation of the phosphine ligands used has been reported by Bauer *et al.*⁵ The new acyl compounds are generally more stable than their alkenyl precursors.



Scheme 3.2

All the reactions were carried out by using about 10% excess of the ligand in order to ensure the complete conversion of the starting mono(alkenyl) precursors. Product formation was indicated by the disappearance of the two strong peaks corresponding to the starting iron mono(alkenyl) precursors in the terminal carbonyl region of the IR spectra. This was accompanied by the appearance of a new strong peak at lower frequencies of the terminal carbonyl region as well as a second medium peak due to the

acyl carbonyl group.

The complexes were purified by column chromatography on an alumina column. Elution with dichloromethane/hexane mixture at the ratio of 50/50 gave compounds (62) – (65) in moderate to high yields as shown in Table 3.3. The compounds were isolated as yellow to brown oils except for the compound 62 (where $n = m = 2$) which was isolated as a low-melting yellow-brown solid.

TABLE 3.3: Data for Compounds (62) – (65)

Compound No	Chain length	Yield (%)	$\nu(\text{CO})/\text{cm}^{-1}$ ^a		³¹ P NMR δ (ppm)
62	$n = m = 2$	85	1913 (s)	1602 (m)	71.65
63	$n = m = 3$	68	1911 (s)	1596 (m)	71.61
64	$n = m = 4$	87	1914 (s)	1597 (m)	71.64
65	$n = 4, m = 6$	96	1913 (s)	1602 (m)	71.60

(a) in CH_2Cl_2 solution

3.2.1 IR spectroscopy of

$\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($n = 2, 3, \text{ or } 4$; $m = 2, 3, 4, \text{ or } 6$)

The IR spectral data for compounds (62) – (65) are given in Table 3.3. The IR spectra showed an expected single terminal carbonyl band in the region $1911 - 1914 \text{ cm}^{-1}$ (See Figure 3.3, (b)). As shown in Figure 3.3, the terminal carbonyl band in graph (b) is at a slightly lower frequency when compared to the two terminal carbonyl bands in spectrum

(a) and this position reflects the donor characteristics of the incoming ligand, which is a better donor ligand than the carbonyl group.

Shifts to lower frequencies suggests that the CO bond is weaker in the acyl compounds than in their alkenyl precursors. This is a direct result of having a better donor ligand (or one less CO ligand) which increases the electron density on the metal available to be donated into the π^* orbital of the CO ligand, in that way weakening the CO bond. A second band of medium intensity found in the $1597 - 1602 \text{ cm}^{-1}$ region was assigned to the acyl carbonyl group. Both these assignments are in agreement with what has been reported previously for related compounds.⁶⁻¹⁰

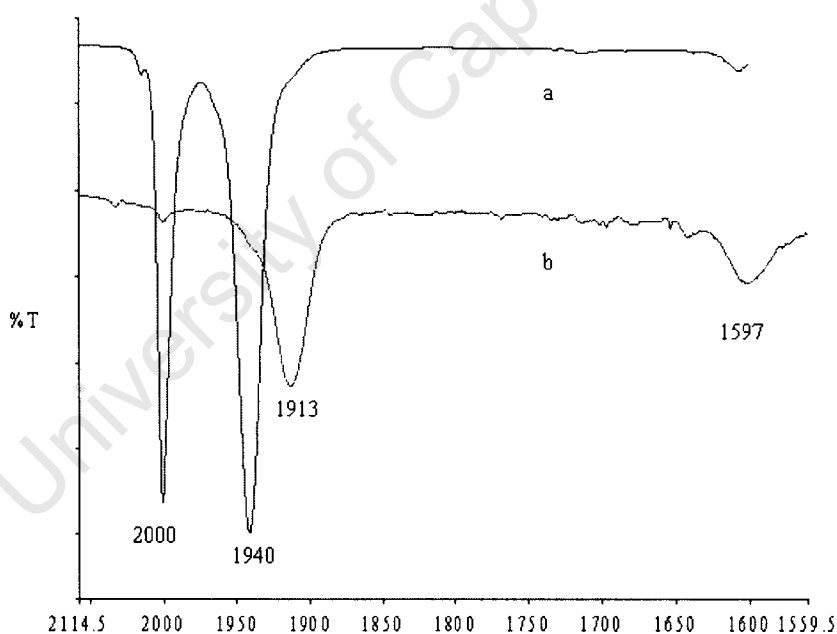


Figure 3.3: IR spectra were recorded in DCM (cm^{-1}). (a) $\text{CpFe}(\text{CO})_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$; and (b) $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_3\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$.

3.2.2 NMR spectroscopy of

$\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_n\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (62) – (65).

³¹P NMR spectroscopy

³¹P NMR spectroscopy was also instrumental in monitoring the progress of the reactions as well the characterization of compounds (62) – (65). The disappearance of the singlet due to the free phosphine ligand in the region δ -14 – -20 ppm indicates that there is no free ligand in the product. This was accompanied by the appearance a new singlet due to the coordinated phosphine in the region δ 70 – 72 ppm (Fe-P).

¹H NMR spectroscopy

The bis(alkenyl) compounds (62) – (65) prepared gave a similar pattern in their proton NMR spectra, and this served as an important guide in the characterization of these compounds. The aromatic protons appeared as broad multiplets at δ 7.20 – 7.70 ppm (PPh₂) which integrated for ten protons. The signals due to the terminal alkene protons appeared as two sets of multiplets at δ 4.82 – 4.96 ppm (=CH₂) and δ 5.64 – 5.86 ppm (CH=); these integrated for four and two protons respectively.

The peak due to the Cp group was observed as a singlet at δ 4.32 – 4.37 ppm for the five protons of the Cp ring, similar shifts have been reported for related compounds.^{1a,2a-b,6} This region is slightly up-field when compared to the region for the Cp protons of the mono(alkenyl) starting complexes which appeared at δ 4.71 – 4.73 ppm. The higher field shift also indicates the strong donor characteristic of the incoming phosphine ligand.

The signals for the protons on the carbon adjacent to the acyl group (-C(O)CH₂-) appeared in the δ 2.62 – 2.90 ppm region as a pair of multiplets integrating for two protons (see Figure 3.4). These particular signals are significant because they demonstrate that the two methylene protons are diastereotopic. This was expected, it occurs because of the chiral nature of the iron complex.

The protons adjacent to the alkene group appeared as broad multiplets in the region δ 1.94 – 2.38 ppm ($-\underline{\text{C}}\text{H}_2\text{CH}=\text{}$). Other methylene protons gave broad multiplets signals at δ 0.9 – 1.97 ppm ($-\underline{\text{C}}\text{H}_2-$). All the integrations agreed well with the suggested assignments

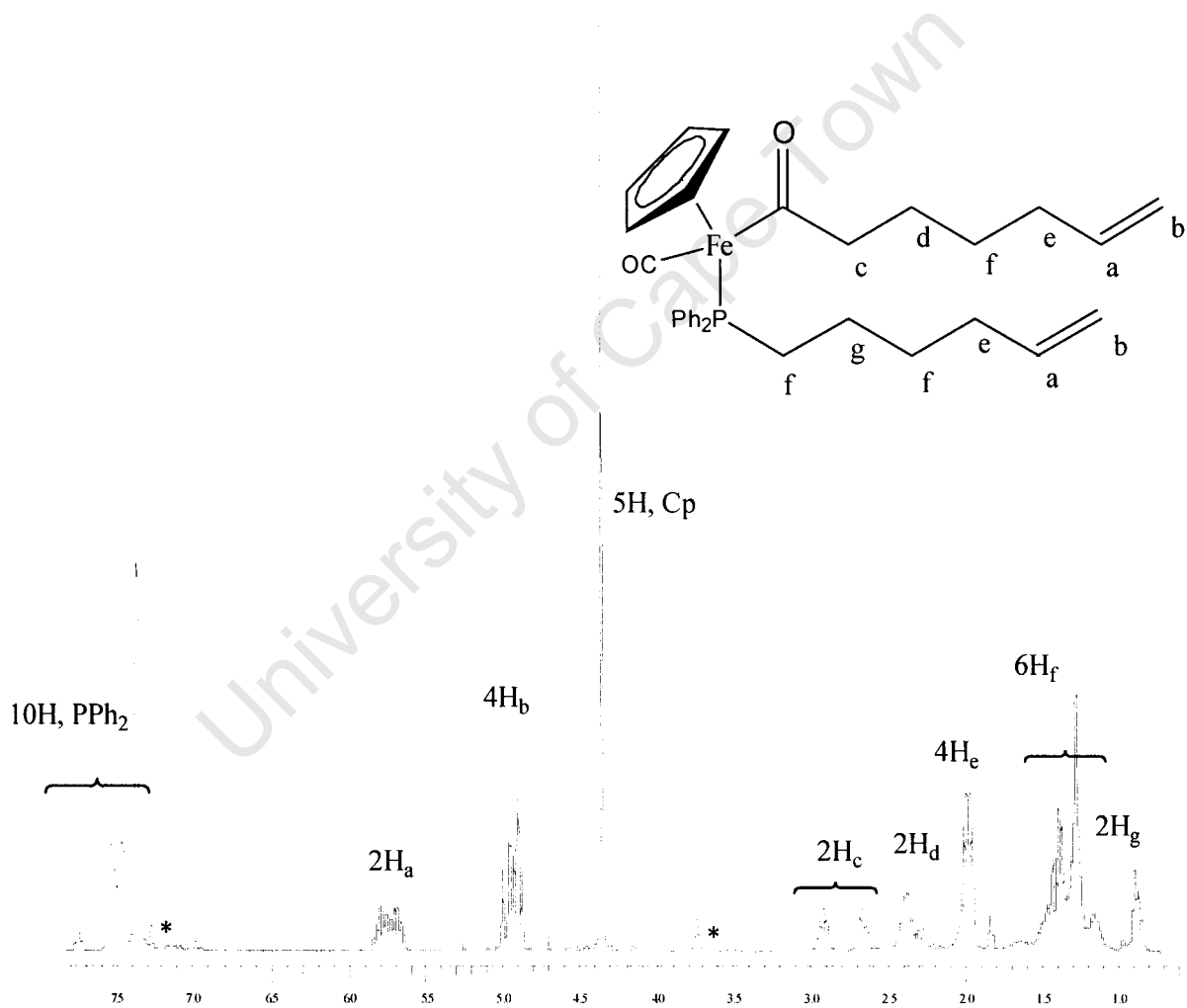


Figure 3.4: ^1H NMR spectrum of complex (64), (* = solvent)

¹³C NMR spectroscopy

The bis(alkenyl) compounds (62) – (65) were also characterized by ¹³C NMR spectroscopy. Complete assignments of the signals in ¹³C NMR spectra of the aforementioned compounds were possible. These gave additional information to further confirm the assignments made on the basis of the ¹H NMR spectra.

Resonances due to the carbonyl carbons were observed in the region δ 219 – 221 ppm and are independent of the methylene chain length. The signals due to the carbons of the pendant alkene group appeared at δ 138 – 140 ppm ($\underline{\text{C}}\text{H}=\text{}$) and δ 113 – 115 ppm ($=\underline{\text{C}}\text{H}_2$), which agrees well with what has been previously reported in the literature for similar compounds.^{1a}

Resonances for the carbons of the Cp group appeared at δ 84 – 85 ppm as expected.^{1a} The carbons of the aromatic group appeared in the region δ 126 – 136 ppm. The signals corresponding to the carbons adjacent to the carbonyl group appeared in the region δ 64 – 67 ppm ($-\text{C}(\text{O})\underline{\text{C}}\text{H}_2-$). Signals for the carbons of the hydrocarbon chain are observed at δ 22 – 33 ppm ($-\underline{\text{C}}\text{H}_2-$).

3.2.3 Elemental analysis of

$\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})(\text{CH}_2)_3\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$, (62) – (65).

Compounds (62) – (65) were also characterized by elemental analysis and these are listed in Table 3.4 below. The percentage content of carbon and hydrogen found were in good agreement with the calculated values.

Table 3.4. Elemental analysis data of compounds (62) – (65)

Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
62	68.58	68.38	6.18	6.40
63	69.61	69.52	6.65	6.69
64	70.46	70.44	7.07	7.90
64	71.22	71.18	7.42	7.44

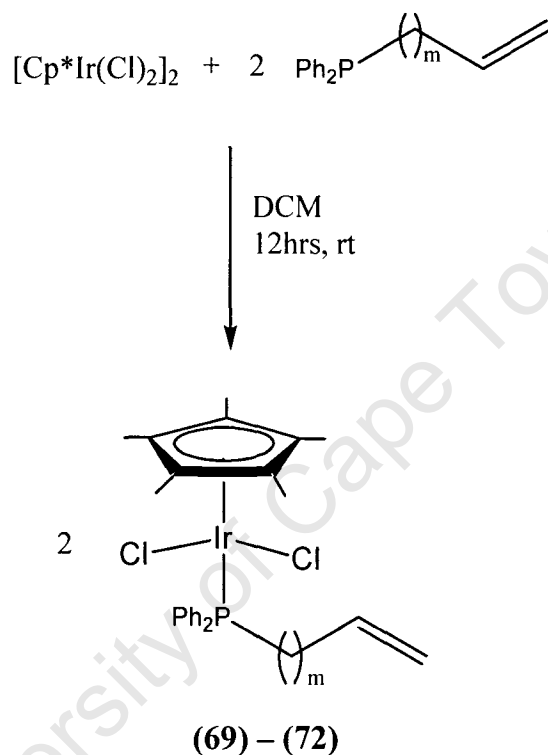
3.3 The synthesis of iridium complexes of the type

$\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$; compounds (69) – (72)

Complexes of the type $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$, (69) – (72), were obtained from the reaction of the iridium dimer, $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2$, with the phosphine ligands of the type $\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ($m = 2, 3, 4,$ and 6) in dichloromethane at room temperature under an inert atmosphere (Scheme 3.3). The reactions were monitored by ^{31}P NMR. The disappearance of the signal corresponding to the uncoordinated phosphine ligand was found to take place over 12hrs. This was accompanied by the appearance of the new singlet corresponding to the coordinated phosphorus atom in the region between δ -2 and -4 ppm.

The final products $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ were obtained as orange-yellow solids in good to high yields (see Table 3.5). The complexes were isolated by extracting

with toluene, followed by filtration to remove insoluble impurities. The filtrate was collected and the solvent removed to leave an orange-yellow solid which was subsequently washed with several portions of hexane to remove excess ligand precursor.



Scheme 3.3

The reaction products were fully characterized by a combination of elemental analysis, NMR, melting point, and in some instances mass spectrometry. The melting point values were found to be dependent on the length of hydrocarbon chain. The longer the hydrocarbon chain the lower the melting point (Table 3.5).

Table 3.5: Complexes of the type $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$

Compound No	m	Yield (%)	Mp ($^{\circ}\text{C}$)	^{31}P NMR/ ppm
69	2	42	177 – 179	-3.51
70	3	53	174 – 176	-2.08
71	4	82	147 – 148	-2.65
72	6	71	142 – 146	-2.49

3.3.1 NMR spectroscopy of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$ ($m = 2, 3, 4$ and 6)

^{31}P NMR spectroscopy

The ^{31}P NMR data for complexes (69) – (72) are given in Table 3.5. ^{31}P NMR spectroscopy was an invaluable tool for monitoring the progress of these reactions. The peaks for the coordinated phosphine ligands appear as singlets in the region $\delta -2 - -4$ ppm. Absence of the peaks in the region $-12 - -16$ ppm indicates that there are no free ligand residues remaining in the products.

^1H NMR spectroscopy

The ^1H NMR spectra of the Cp^* protons appeared in the region $\delta 1.34 - 1.35$ ppm as doublets with $J_{\text{P-H}}$ values between 2 and 3 Hz. Similar shifts and splitting patterns have been observed for analogous compounds with PH_2Mes , PH_2Is or PPh_3 as donor ligands.¹¹⁻

12

Signals characteristic of the alkene moiety appeared as a set of multiplets in the region $\delta 5.43 - 5.66$ ppm ($-\text{CH}=\text{}$) and $\delta 4.80 - 4.85$ ppm ($=\text{CH}_2$) for one and two protons respectively. Similar shifts have been previously reported for related compound.^{1a} The

signals due to aromatic protons occurred in the region δ 7.40 – 7.90 ppm (PPh_2) resonating for ten protons as expected.

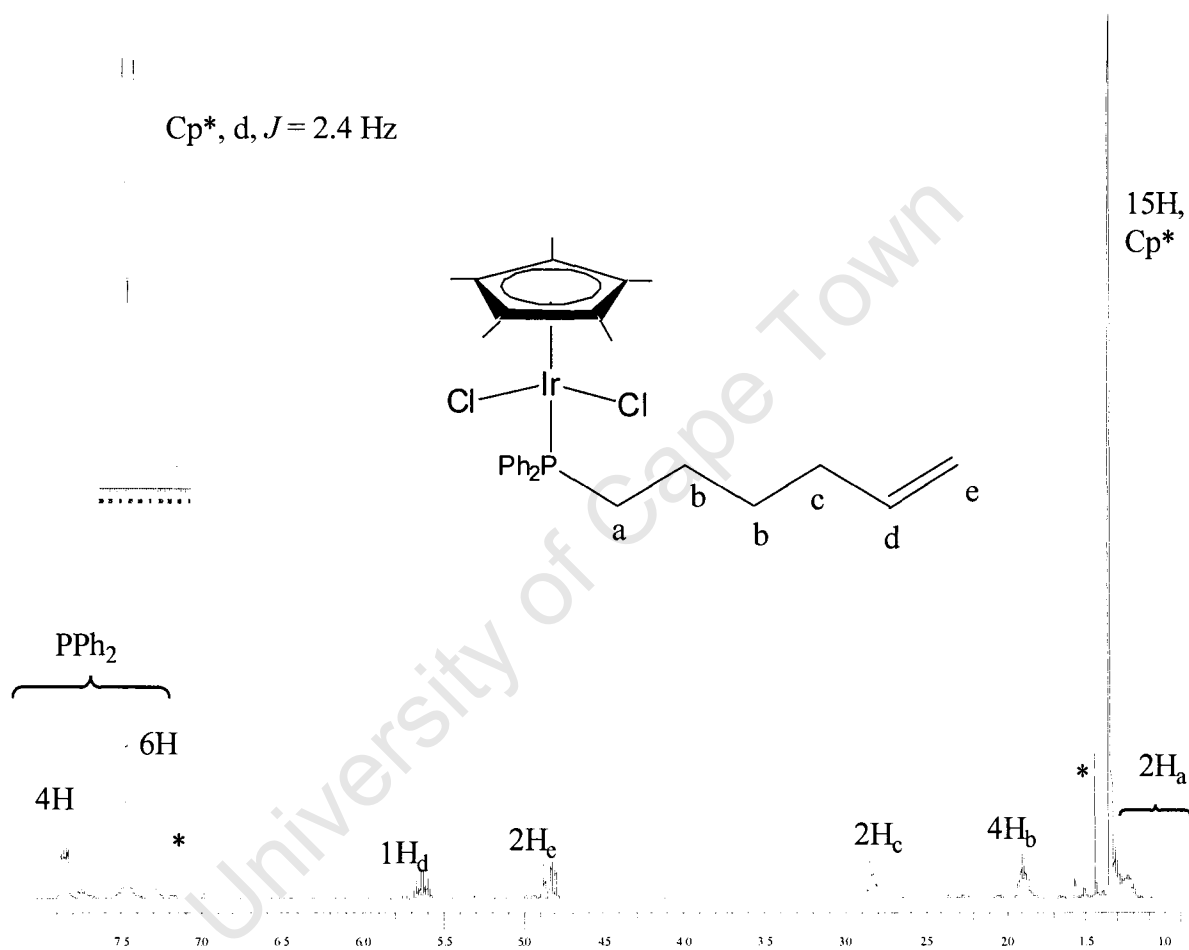


Figure 3.5: ^1H NMR spectrum of (71), (* = solvent).

The signals for the methylene protons adjacent to the alkene group were observed at δ 2.60 – 2.90 ppm ($-\text{CH}_2\text{CH}=\text{}$). The methylene protons adjacent to the phosphine group appeared at δ 1.20 – 1.40 ppm ($-\text{CH}_2\text{-P}$). This up-field position (relative to other methylene groups) is a result of shielding effect from the electron density on the phosphorus atom.

Other protons of the hydrocarbon chain appeared as broad multiplets in the region δ 1.6 – 1.9 ppm, integration being the only means of distinguishing between compounds with different chain lengths.

¹³C NMR spectroscopy

The iridium compounds (69) – (72) were also characterized by ¹³C NMR spectroscopy. All the ¹³C NMR spectral peaks could be assigned and these provided further support for the assignments given in the ¹H NMR spectral analysis.

The resonances for the Cp* (η^5 -C₅(CH₃)₅) were observed in the region δ 91– 92 ppm, for 15 protons. It was notable that this particular signal shifts slightly to the up-field as the value of n increases. The resonance signals due to the terminal alkene carbons appeared at δ 137 – 139 ppm (C=CH) and δ 114 – 115 ppm (CH₂=C). The peaks corresponding to the aromatic carbons were observed in the region δ 126 – 134 ppm (PPh₂). Located furthest up-field in the region δ 8.10 – 8.20 ppm were the signals corresponding to the methyl (CH₃) carbons of the Cp* group. The resonances resulting from other methylene carbons of the hydrocarbon chain were observed at δ 22 – 35 ppm (CH₂), as expected.^{1a,3}

3.3.2 Elemental analysis of compounds (69) – (72) and mass spectral analysis of compounds (69), (71), and (72)

Elemental analysis for compound (69) – (72) and mass spectral analysis for compounds (69), (71), and (72) were obtained. The (FAB) mass spectra of the complexes show similar fragmentation patterns (Table 3.6). Parent molecular ion (M⁺) peaks for compounds (69), (71), and (72) were observed at *m/e* 638, 666, and 694 respectively.

Table 3.6: Mass spectral data for compounds (69), (71) and (72)

Compound No	<i>m/e</i>	Relative peak intensities (%) ^a	Proposed assignment
69	638	18	Parent ion (M ⁺)
	603	4	IrC ₂₆ H ₃₂ PCl ⁺
	567	8	IrC ₂₆ H ₃₂ P ⁺
	432	4	IrC ₁₆ H ₁₇ P ⁺
	238	100	C ₁₆ H ₁₇ P ⁺
71	666	5	Parent ion (M ⁺)
	631	100	IrC ₂₈ H ₃₆ PCl ⁺
	596	8	IrC ₂₈ H ₃₆ P ⁺
	460	2	IrC ₁₈ H ₂₁ P ⁺
	268	54	C ₁₈ H ₂₁ P ⁺
72	694	18	Parent (M ⁺)
	659	100	IrC ₃₀ H ₄₀ PCl ⁺
	619	76	IrC ₃₀ H ₄₀ P ⁺
	488	10	IrC ₂₀ H ₂₅ P ⁺
	296	16	C ₂₀ H ₂₅ P ⁺

^aAll ions have a single positive charge; ion refers to suggested assignments.

All the spectra show peaks corresponding to the loss of two Cl atoms at *m/z* 567 (complex (69)), 596 (complex (71)) and 619 (complex (72)). The mass spectra of (69), (71) – (72) also show peaks corresponding to the loss of the Cp* ligand at *m/z* 432, 460 and 488 respectively. The peaks corresponding to the fragments [PPh₂(CH₂)_mCH=CH₂]⁺ (m = 2, 4, 6) were observed at *m/z* 238, 268 and 296. The elemental analysis data for compounds (69) – (72) are listed in Table 3.7 below. The percentage values found for carbon and hydrogen contents agreed well with the calculated values.

Table 3.7 Elemental analysis data of compounds (69) – (72)

Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
69	48.90	48.66	5.05	5.15
70	49.68	49.62	5.25	5.58
71	50.44	50.29	5.44	5.40
72	51.86	52.10	5.80	5.80

3.4 Conclusion

A series of ruthenium alkenyl compounds of the type $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ (59) – (51) have been prepared in a method similar to that used for the preparation of related iron alkenyl compounds.^{1a} Thus, the reaction of carbonyl ruthenium anions with corresponding bromoalkenes $\text{Br}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ led to the isolation of novel ruthenium compounds where a ruthenium-carbon σ -bond exists, and the olefin group is left available for further manipulations. The compounds were characterized by a range of spectroscopic and analytical methods. Compared to the analogous iron compounds these were found to be relatively more stable towards light and air. For possible future-work, reactivity studies such as UV irradiation and/or thermal decomposition could reveal interesting mechanistic trends. The results could be compared with those obtained from similar studies on iron compounds.^{1b-d} Iron alkenyl compounds of the type $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ (41) – (48) were prepared according to the literature method.^{1a}

We prepared the novel iron acyl compounds with two pendant and different olefin groups available to react in, for example, a metathesis fashion. The iron alkenyl complexes of the type $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ were reacted with tertiary phosphine ligands of the type $\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2$ to afford compounds (62) – (65).

The reaction of the iridium dimer $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2$ with two equivalents of ligands $\text{PPh}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ($m = 2, 3, 4,$ and 6) resulted in the formation of novel iridium compounds (69) – (72). In these, the phosphorus atom is σ -bonded to the iridium metal, to leave the olefin group available for further manipulations. Compounds (69) – (72) were isolated as high melting point orange-yellow solids, which were air stable. This work could have implications, for example, in catalytic and mechanistic studies involving the iridium bonded to a phosphorus ligand having a free olefin group.

3.5 References

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CHAPTER 4: METATHESIS REACTIVITY OF COMPOUNDS (WITH AT LEAST ONE PENDANT ALKENE GROUP) OF IRON, RUTHENIUM AND IRIDIUM

4.1 Synthesis of ruthenium and iron based homo-binuclear compounds, $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{ML}$; Compounds (52) – (61)

The self metathesis reaction of the complexes of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$, (41) – (51), (Scheme 4.1) in the presence of Grubbs' first (I) generation catalyst gave homo-binuclear complexes of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{ML}$, (52) – (61), The value of n was varied from 3 to 5; the ligand L was either $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$ and the metal M was either ruthenium or iron. (Scheme 4.1). In the new complexes two metal centres are connected by an unsaturated hydrocarbon chain having one carbon-carbon double bond in the middle of the chain.

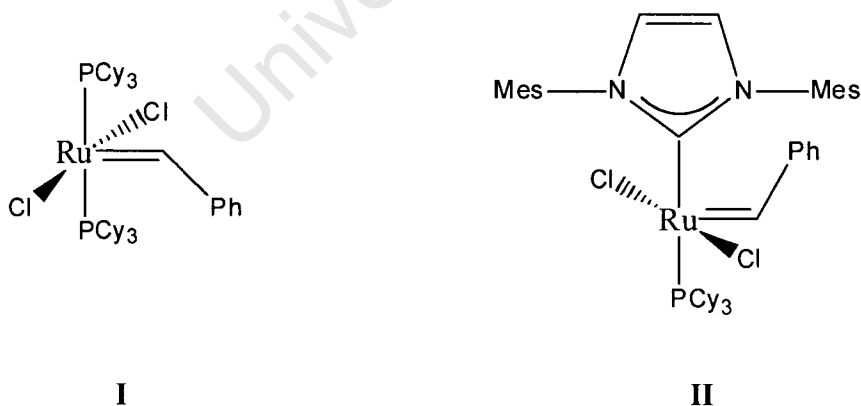
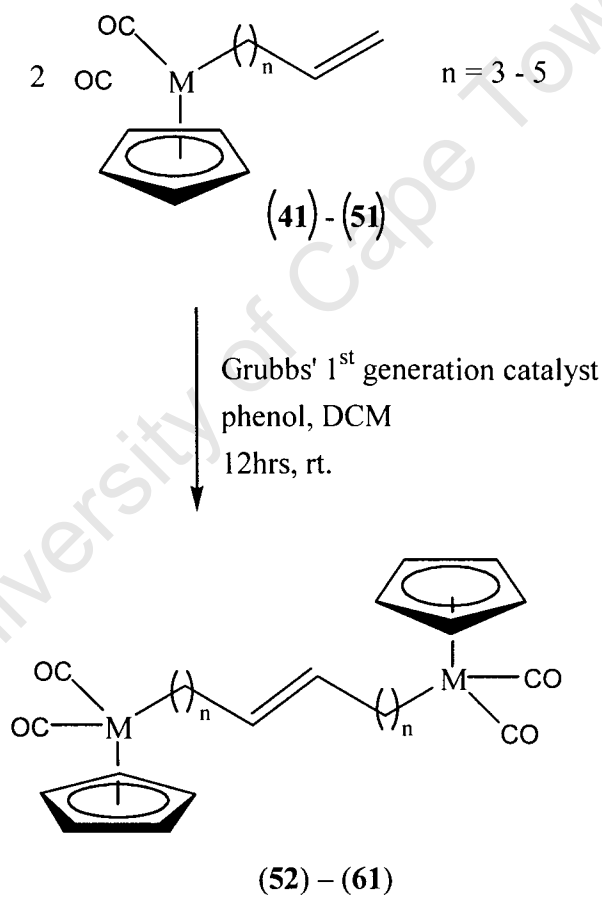


Figure 4.1: Grubbs' 1st generation catalyst (I) and Grubbs' 2nd generation catalyst (II)

The self metathesis products were isolated either as yellow-brown oils or low melting point solids for the iron-based compounds. The ruthenium-based compounds were however isolated as colourless oils. The yields varied from moderate to good as shown in Table 4.1. The complexes were found to be stable for extended periods when kept below 0°C, under an atmosphere of nitrogen.



Scheme 4.1

4.1.1 IR spectroscopy of $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{ML}$ ($n = 3 - 6$; $\text{M} = \text{Ru}$ or Fe ; and $\text{L} = \eta^5\text{-C}_5(\text{CH}_3)_5$ or $\eta^5\text{-C}_5\text{H}_5$)

The IR spectra were recorded in dichloromethane and are in good agreement with values previously reported for related compounds.^{1a-b,2} The IR spectral data for compounds (52) – (61) are given in the Table 4.1. All the compounds showed two strong carbonyl bands in the terminal carbonyl region. These carbonyl bands resembled the ones for the corresponding mono(alkenyl) complexes of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$.

TABLE 4.1: Data for the compounds $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{ML}$ (52) – (61) (note: for compounds (52) – (59), $\text{M} = \text{Fe}$; and $\text{L} = \eta^5\text{-C}_5(\text{CH}_3)_5$ only for even numbered compounds; compounds (60) and (61), $\text{M} = \text{Ru}$ and $\text{L} = \eta^5\text{-C}_5\text{H}_5$)

Compound No.	n	Yield (%)	Mp (°C)	ν(CO)/ cm ⁻¹		ν(C=C)/cm ⁻¹ ^a
52	3	53	oil	1979 (s)	1919 (s)	1602 (w)
54	4	55	84-90	1978 (s)	1917 (s)	1605 (w)
56	5	65	126-128	1979 (s)	1918 (s)	1605 (w)
58	6	60	oil	1978 (s)	1917 (s)	1605 (w)
53	3	56	oil	2001(s)	1940 (s)	1605 (w)
55	4	66	oil	2000 (s)	1940 (s)	1605 (w)
57	5	84	62-63	2000 (s)	1940 (s)	1605 (w)
59	6	52	oil	2001 (s)	1940 (s)	1604 (w)
60	3	86	oil	2012 (s)	1947 (s)	1604 (w)
61	5	61	oil	2013 (s)	1946 (s)	1603 (w)

(a) in CH_2Cl_2 solution

The terminal carbonyl bands for the di-iron compounds (52) – (59), were located at about 21 cm⁻¹ lower for Cp* compounds (where $\text{L} = \eta^5\text{-C}_5(\text{CH}_3)_5$) than for Cp compounds

(where $L = \eta^5\text{-C}_5\text{H}_5$) (See Figure 4.2).

This difference in $\nu(\text{CO})$ values is attributed to the higher electron density provided by the methyl groups in Cp^* containing complexes. Lower frequency also indicates that the CO bond is weaker in the Cp^* compounds. This is as a result of high electron density on the iron for the Cp^* compounds, which is back-donated into the π^* orbitals of carbonyl group.

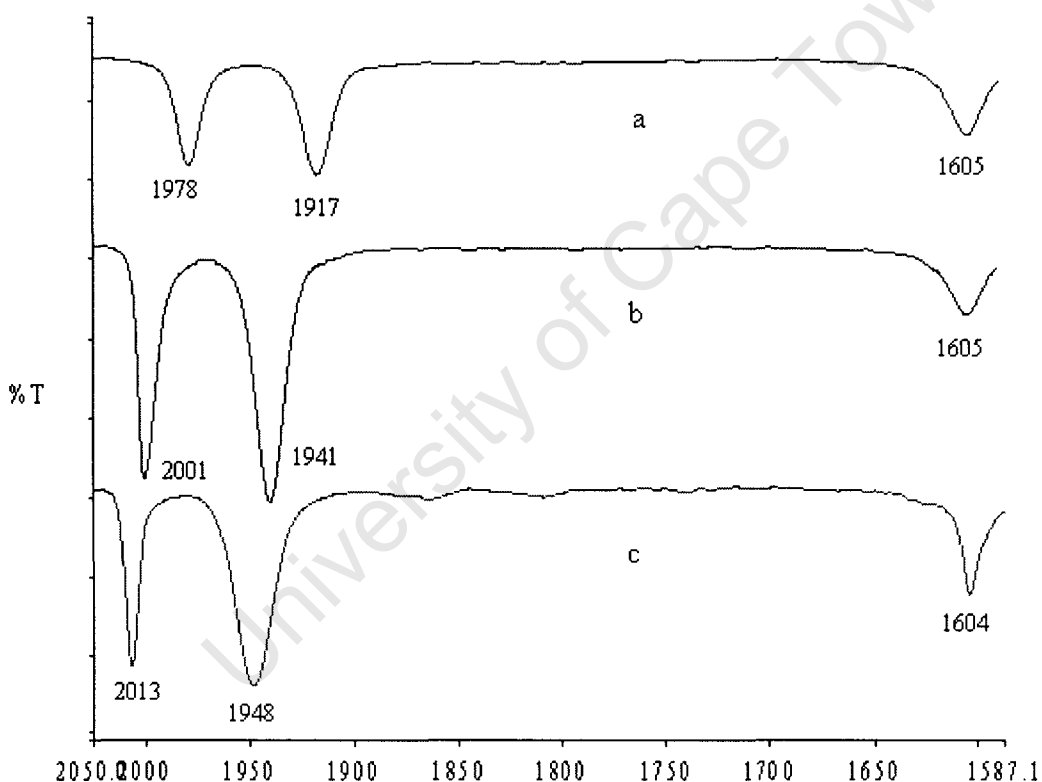


Figure 4.2: IR spectra of compounds $\text{LM}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\}(\text{CO})_2\text{ML}$, taken in DCM (cm^{-1}). (a) $M = \text{Fe}$, $L = \eta^5\text{-C}_5(\text{CH}_3)_5$, (b) $M = \text{Fe}$, $L = \eta^5\text{-C}_5\text{H}_5$, (c) $M = \text{Ru}$, $L = \eta^5\text{-C}_5\text{H}_5$.

In the di-ruthenium compounds $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{RuCp}$, (**60**) – (**61**), the terminal carbonyl bands appeared at slightly higher frequencies when compared to analogous di-iron Cp compounds (Figure 4.2(c)). The move to higher frequencies

suggests that the CO bond is much stronger in the di-ruthenium compounds. This is as a result of reduced electron density at the metal centre when going from iron to ruthenium in the abovementioned compounds. Similar trends have been reported in the literature for related compounds.¹⁻² All the bimetallic compounds showed weak $\nu(\text{C}=\text{C})$ signals at around 1600 – 1605 cm^{-1} .

4.1.2 NMR spectroscopy of $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\}(\text{CO})_2\text{ML}$ ($n = 3 - 6$; $\text{M} = \text{Ru}$ or Fe ; and $\text{L} = \eta^5\text{-C}_5(\text{CH}_3)_5$ or $\eta^5\text{-C}_5\text{H}_5$)

¹H NMR spectroscopy

Formation of bimetallic compounds was indicated by the appearance of the broad multiplet or the broad singlet at δ 5.31 – 5.42 ppm ($-\text{CH}=\text{}$) corresponding to the protons of the internal alkene group of the dimerized products. The appearance of this new peak was accompanied by the disappearance of the peaks at δ 4.8 – 4.9 ppm and δ 5.7 – 5.9 ppm which were due to the terminal alkene protons in mono(alkenyl) precursors. Figure 4.3 shows the ¹H NMR spectrum of complex (56). Similar shifts have been reported for related compounds.³⁻⁷ Many of the peaks are also similar to those shown by the starting materials.

Many peaks are broad and/or poorly resolved, and similar trends have been reported for related compounds.^{1a,3} The broadness of some peaks in the ¹H NMR spectra could also be attributed to the presence of paramagnetic iron species or to the fluxional nature of the alkenyl pendant.

Signals corresponding to the Cp* protons appeared as singlets in the region δ 1.69 – 1.82 ppm and resonating for 30 protons. In the di-iron compounds, the Cp protons (Fe-Cp) appeared as singlets in the range δ 4.71 – 4.73 ppm, resonating for ten protons. In the di-

ruthenium compounds, the Cp protons (Ru-Cp) were observed in the range δ 5.23 – 5.24 ppm.

Notably, resonances for the protons of the Cp group attached to the ruthenium atom, Ru(η^5 -C₅H₅), are about δ 0.52 ppm down-field as compared to similar protons in the related iron compounds. This difference in chemical shifts is attributed to the decrease electron density on the metal when moving from iron to ruthenium.

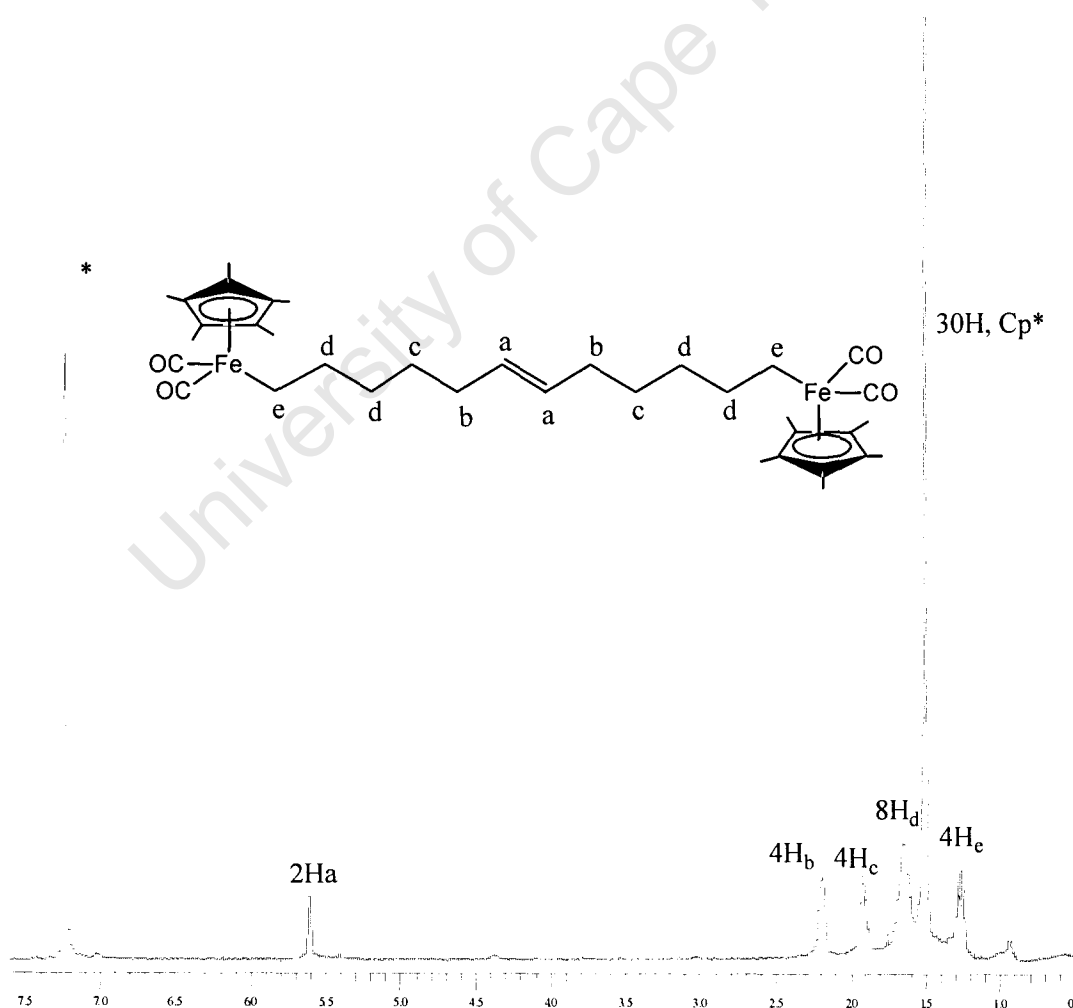


Figure 4.3: ¹H NMR spectrum (ppm) of compound 56. (* = solvent)

The methylene protons on the carbon atom adjacent to the metal centre (M-CH₂-) are more shielded than the other methylene protons in the bridging hydrocarbon chains. The signals of these protons appeared in the region δ 0.9 – 1.50 ppm (Fe-CH₂-) when the metal atom is iron. They appeared at δ 0.87 – 0.88 ppm (Ru-CH₂-) when the metal is ruthenium. These shifts agree well with those which were previously reported for similar compounds.^{1a-b,2,8} Other protons that are on the hydrocarbon chain appeared either as broad multiplets or poorly resolved multiplets in the region δ 1.50 – 1.80 ppm (-CH₂-).

¹³C NMR spectroscopy

The compounds (52) – (61) were also characterised by ¹³C NMR spectroscopy. It was possible to assign all the signals of the ¹³C NMR spectra and these provided more information to support the assignments suggested by the ¹H NMR analysis. Resonances for the internal alkene carbons were observed in the region δ 129 – 130 ppm (CH=) as expected.^{4,8}

The resonance signals for the carbons of the terminal carbonyl group appeared in the region δ 217 – 218 ppm (CpFeCO) for the iron complexes having the Cp ligand and in the region δ 219 – 221 ppm (Cp*FeCO) for those iron complexes having the Cp* ligand. Similar trends have been reported for related compounds.⁸ In the ruthenium-based complexes the carbonyl carbons were observed in the region δ 202 – 201 ppm (CpRuCO). The appearance of these carbonyl signals agree well with what is reported in the literature for related compounds.²

The peaks assigned to the Cp (η^5 -C₅H₅) carbons appeared at δ 85 – 86 ppm for the iron complexes and at δ 88 – 89 ppm for the ruthenium complexes. This behaviour relates well with that of the similar complexes in literature.^{1a, 2,8} The Cp* carbons are found in the regions δ 94 – 96 ppm (η^5 -C₅(CH₃)₅) and δ 8 – 10 ppm (η^5 -C₅(CH₃)₅). Similar chemical shift positions have been observed for related complexes.⁸

The signals due to the methylene carbons adjacent to the metal centre (M- $\underline{\text{C}}\text{H}_2$ -) were observed in the region δ 13 – 14 ppm (Cp*Fe- $\underline{\text{C}}\text{H}_2$ -) for the compounds having the Cp* ligands. They appeared at δ 3 – 5 ppm (CpFe- $\underline{\text{C}}\text{H}_2$ -) for the compounds having the Cp ligand. These carbons are expected to appear in these up-field regions as they are more shielded than the other carbons of the hydrocarbon chain. The effect of changing the donor ligand on the iron centre is noticeable, for instance, the shifts for the methylene carbons of the type Fe- $\underline{\text{C}}\text{H}_2$ - are furthest up-field for the Cp complexes than for Cp* complexes. Similar shifts have also been reported for related compounds.⁸

The signals of the carbons adjacent to the ruthenium centre appeared furthest up-field in the region δ -3 – -5 ppm (Ru- $\underline{\text{C}}\text{H}_2$ -). A similar chemical shift region has been observed for related complexes.⁸ Other carbons that form part of the hydrocarbon chain appeared at the region δ 22 – 40 ppm (- $\underline{\text{C}}\text{H}_2$ -) as expected.^{1a,2,8}

4.1.3 Mass spectrum of Cp*Fe(CO)₂{(CH₂)₅CH=CH(CH₂)₅}(CO)₂FeCp* (56) and elemental analysis of LM(CO)₂{(CH₂)_nCH=CH(CH₂)_n}(CO)₂ML (where L = Cp or Cp*); compounds (52) – (62)

Elemental analyses for compounds (52) – (62) and mass spectrometry (FAB) for compound (56) were obtained. The parent ion peak for compound (56) was observed at *m/e* 660. The mass spectrum shows a peak corresponding to the loss of two CO ligands at *m/e* 604. The peak at *m/e* 469 corresponds to the loss of the Cp* ligand.

Elemental analysis were performed on compounds (52) – (61), the percentage contents of carbon and hydrogen were in good agreement with expected values as shown in Table 4.3 below.

Table 4.2: Mass spectral data for the complex (56)

Compound No	<i>m/e</i>	Relative peak intensities (%) ^a	Proposed assignment
56	660	2	Parent iron [M^+]
	604	8	$Fe_2C_{34}H_{52}O_2^+$
	469	4	$Fe_2C_{24}H_{37}O_2^+$
	357	40	$FeC_{22}H_{37}^+$
	222	100	$FeC_{12}H_{37}^+$
	154	82	$C_{11}H_{22}^+$

^aAll ions have a single positive charge; ion refers to suggested assignments.

Table 4.3 Elemental analysis data of compound (52) – (61)

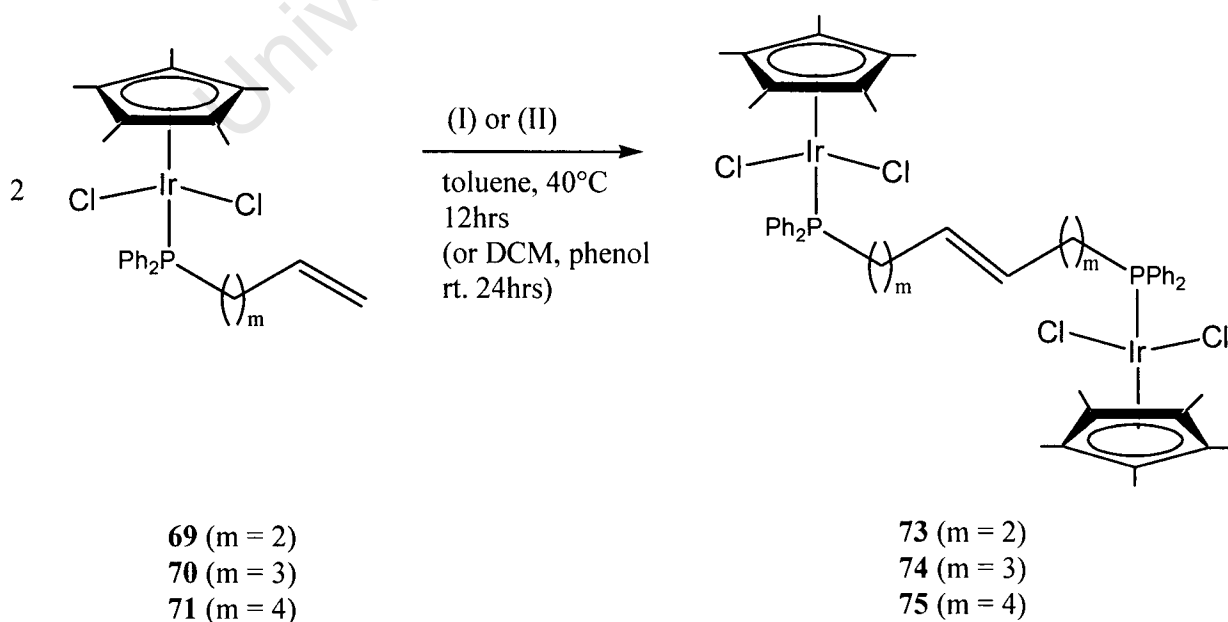
Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
52	63.60	63.58	7.33	7.77
53	56.93	56.13	5.21	5.65
54	64.57	64.60	7.70	7.68
55	58.57	58.56	5.73	5.91
56	65.46	65.77	7.93	8.12
57	60.03	60.08	6.20	6.01
58	66.28	66.32	8.10	6.37
59	61.34	61.37	6.60	6.68
60	47.65	47.67	4.36	4.46
61	51.14	51.24	5.28	5.35

4.2 Self metathesis reaction of iridium compounds of the type

$\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}_2\}$, catalyzed by Grubbs' first or second generation ruthenium catalysts; compounds (73) – (75)

As shown in Scheme 4.2, coupling of (69) by metathesis reaction of the alkene group was carried out by using Grubbs' second generation catalyst (II) at 40°C in toluene to give the dinuclear complex (73) in good yield. Complex (73) was purified by dissolving in minimum dichloromethane followed the addition of cold hexane until the precipitate formed.

The resulting precipitate was filtered, washed with portions of hexane and dried under vacuum. The self metathesis reaction of complexes (70) or (71) was carried out by stirring either complex in dichloromethane with Grubbs' first generation catalyst (I) and phenol as an additive. The resulting complexes (74) or (75) were purified using a similar method to the one used for complex (73) and these were obtained as yellow solids in good yields.



Scheme 4.2

4.2.1 NMR spectroscopy of $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2[\mu\text{-}\{\text{PPh}_2(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_m\text{PPh}_2\}]$, (73) – (75)

^{31}P NMR spectroscopy

The ^{31}P NMR spectral data are presented in the Table 4.4. Resonances for the Ir-P signal were observed in the region δ -1 to -4 ppm, as singlets. This chemical shift region is not different from the region where the monomer substrates appeared.

Table 4.4: Data for compounds (73) – (75)

Compound No	m	Yield (%)	Melting Point ($^{\circ}\text{C}$)	^{31}P NMR/ ppm
73	2	90	246 – 249	-2.44
74	3	68	190 – 194	-3.04
75	4	62	182 – 184	-1.95

^1H NMR spectroscopy

The proton NMR spectra of compounds (73) – (75) have characteristic patterns in the spectra that are common to all the complexes. Most signals are similar to the peaks of the starting monomeric precursors.

Appearance of the peaks due to the protons of the internal alkene group was accompanied by the disappearance of the protons corresponding to the terminal alkene group. These served as an indication to show that the metathesis reaction has reached completion, they appeared as broad multiplets or broad singlets in the region δ 4.8 – 5.1 ppm ($\text{CH}=\text{}$). Such behaviour has been reported for protons in a similar environment.³⁻⁷ Most peaks and chemical shifts are similar to those of the monomeric precursors.

Aromatic protons appeared in the region δ 7.0 – 8.0 ppm (PPh₂), for ten protons. Methyl protons of the Cp* group appeared in the region δ 1.32 – 1.34 ppm (η^5 -C₅(CH₃)₅) as doublets with the *J* values ranging between 1.9 and 2.5 Hz. Resonances for the methylene protons of the hydrocarbon chain were observed in the expected region δ 1.3 – 2.7 ppm (-CH₂-) as broad multiplets.^{3,6-7} The total integrations corresponded well with all the assignments given.

¹³C NMR spectroscopy

Compounds (73) – (75) were also characterized by ¹³C NMR spectroscopy. Complete assignments were possible and these agreed well with the assignments given in ¹H NMR spectroscopy. The resonance signals for the carbons of the alkene group appeared in the region δ 130 – 131 ppm (C=) as expected.³⁻⁷

The Cp* carbons appeared in the region δ 90 – 93 ppm (η^5 -C₅(CH₃)₅) and δ 8 – 9 ppm (η^5 -C₅(CH₃)₅). Carbons of the aromatic group were observed in the region δ 126 – 135 ppm (PPh₂). Resonances due to the carbons that are part of the hydrocarbon chain appeared in the region δ 27 – 40 ppm (-CH₂-) as expected.

4.2.2 Mass spectral analysis of [Cp*Ir(Cl)₂]₂[μ -{PPh₂(CH₂)₄CH=CH(CH₂)₄PPh₂}], (75) and elemental analyses of compounds (73) – (75)

Mass spectral data for complex 75 was obtained. The molecular ion peak for (75) was observed at *m/e* 1305. The peaks corresponding to the loss of one Cl were observed at *m/e* 1270. At peak at *m/e* 907 was assigned to the fragmentation of the [Cp*IrCl]⁺ group. A peak at *m/e* 872 was assigned to the fragment remaining after the loss of Cl from the [CpIrCl]⁺ species.

Table 4.5: Mass Spectral data for compound (75)

Compound No	m/e	Relative peak intensities (%) ^a	Proposed assignment
75	1305.3	3	Parent ion [M^+]
	1270	15	$Ir_2C_{54}H_{68}P_2Cl_3^+$
	907	10	$IrC_{44}H_{53}P_2Cl_2^+$
	872	85	$IrC_{44}H_{53}P_2Cl^+$
	528	12	$C_{34}H_{38}P_2^+$

^aAll ions have a single positive charge; ion refers to suggested assignments. Peak intensities relative to the base peak at $m/e = 363.4$

Table 4.6 below shows the elemental analysis data for compounds (73) – (75), the percentage values found for carbon or hydrogen content agree well with the expected values.

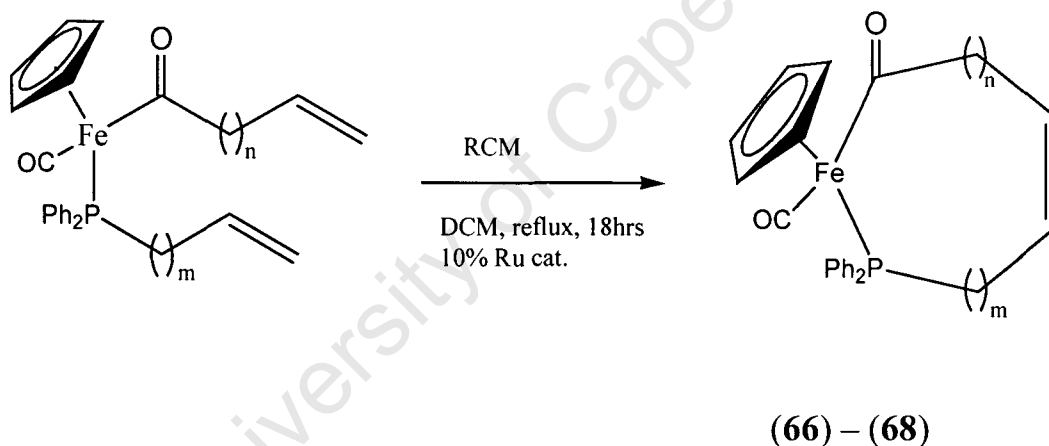
Table 4.6 Elemental analysis data for compounds (73) – (75)

Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
73	48.07	47.94	4.84	4.87
74	48.90	48.88	5.05	5.02
75	49.69	49.66	5.25	5.52

4.3 Metathesis reactivity of compounds of the type

$\text{CpFe(CO)\{C(O)(CH}_2)_n\text{CH=CH}_2\}\{\text{PPh}_2(\text{CH}_2)_m\text{CH=CH}_2\}$; compounds (62) – (65)

Compounds (66) – (68) were prepared by the ring closing metathesis reactions of the bis(alkenyl) compounds (63) – (65) using Grubbs' first generation (I) or second generation (II) catalysts. All the reactions were carried out in refluxing dichloromethane at catalyst loadings of 10 mmol% added in a batch-wise fashion (Scheme 4.3).



Scheme 4.3

The progress of the reactions was monitored by ¹H NMR spectroscopy. The reactions were stopped when the resonances resulting from the terminal alkene moiety became undetectable, and were replaced by the new signals corresponding to the internal alkene group. Purification of the compounds was carried out by column chromatography on an alumina column. Elution by a mixture of dichloromethane/hexane (50/50) resulted in a fast running yellow band. After removal of the solvent, complexes (66) and (68) were obtained, in reasonable yields (Table 4.7), as yellow oils; (67) which was obtained as a yellow-brown solid.

Table 4.7: Data for complexes (66) – (68)

Compound No	Chain length	Yield (%)	$\nu(\text{CO})/\text{cm}^{-1}$ ^a		³¹ P NMR δ (ppm)
66	n = m = 3	46	1913 (s)	1597 (m)	72.02
67	n = m = 4	38	1912 (s)	1596 (m)	71.94
68	n = 4, m = 6	87	1914(s)	1601 (m)	71.64

(a) in CH₂Cl₂ solution

4.3.1 IR spectroscopy of compounds (66) – (68)

IR spectral data for compounds (66) – (68) are listed in Table 4.7. The peaks for the terminal carbonyl groups gave strong signals in the range of 1912 – 1914 cm⁻¹. The second medium-sized bands belonging to the acyl carbonyl groups were observed in the range 1595 – 1602 cm⁻¹. The position of these bands in the IR spectra is in agreement with those of similar bands in related compounds of the type Cp(CO)Fe{C(O)R}PR'₃ in literature.⁸⁻⁹

4.3.2 NMR spectroscopy of (66) – (68)

³¹P NMR Spectroscopy

The ³¹P NMR spectral data for compounds (66) – (68) are listed in Table 4.7. As expected, the peaks appeared as a singlets in the region δ 71 – 73 ppm (Fe-P) which is a similar region as for the bis(alkenyl) precursors, complexes (63) – (65).

¹H NMR spectroscopy

Formation of the ring-closed products was indicated by the appearance of a broad multiplet or a broad singlet in the region δ 5.30 – 5.33 ppm (CH=). The appearance of

this new peak was accompanied by the disappearance of the peaks at δ 4.82 – 4.96 ppm, and δ 5.64 – 5.86 ppm, which correspond to the terminal alkene protons of bis(alkenyl) precursors.

The proton NMR spectra of the complexes also show signals in the δ 1.20 – 1.80 ppm ($\text{-CH}_2\text{-}$) region which are due to the methylene protons. The aromatic protons appeared in the range δ 7.20 – 7.90 ppm (PPh_2) as broad multiplets. The peaks due to the protons of the Cp ligand were detected as singlets in the range δ 3.84 – 4.40 ppm as expected.⁸⁻⁹

Protons adjacent to the acyl group were observed in the region δ 2.24 – 2.83 ppm as broad singlets ($\text{-C(O)CH}_2\text{-}$). Those protons adjacent to the alkene group appeared at δ 1.89 – 2.34 ppm ($\text{-CH}_2\text{CH=}$) as multiplets. Integrations were in agreement with the suggested assignments.

¹³C NMR spectroscopy

The complexes (66) – (68) were also characterized by ¹³C NMR spectroscopy. All the resonances were assigned and these provided more information to support the assignments given in the ¹H NMR spectroscopy. The signals at δ 130 – 132 ppm were assigned to the internal alkene (CH=) carbons. Resonances for the carbons of the carbonyl groups appeared in the region δ 200 – 220 ppm (CO). Signals corresponding to the Cp ($\eta^5\text{-C}_5\text{H}_5$) carbons were observed in the region δ 84 – 87 ppm, as expected. Carbons of the hydrocarbon chain appeared in the region δ 21 – 35 ppm. Resonances for those carbons adjacent to the carbonyl moiety were observed in the region δ 65 – 68 ppm ($\text{-C(O)CH}_2\text{-}$).

4.3.3 Elemental analysis of compounds (66) – (68)

Compounds (66) – (68) were also characterized by elemental analyses as shown in Table 4.8 below. The percentages found for carbon and hydrogen were in good agreement with the expected values.

Table 4.8 Elemental analysis data of compounds (66) – (68)

Compound No.	Carbon (%)		Hydrogen (%)	
	Calculated	Found	Calculated	Found
66	68.66	68.68	6.18	6.40
67	69.61	69.63	6.65	7.31
68	70.46	70.40	7.07	7.31

4.4 Conclusion

In conclusion, both the self metathesis and ring-closing metathesis have been realised on organometallic substrates with at least one pendant alkene group. These reactions represent rare applications of olefin metathesis to inorganic chemistry. Treatment of mono(alkenyl) compounds of the type $\text{LM}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ with Grubbs' 1st or 2nd generation catalysts resulted in bimetallic self metathesis products consisting of two metals bridged by unsaturated hydrocarbon chains. The homo-bimetallic compounds (52) – (59); ($\text{M} = \text{Fe}$, $\text{L} = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5(\text{CH}_3)_5$) were isolated as yellow oils or as low melting point solids. Compounds (60) and (61) ($\text{M} = \text{Ru}$, $\text{L} = \eta^5\text{-C}_5\text{H}_5$) were isolated as colourless oils.

The dimeric iridium compounds (73) – (75) were prepared by coupling of the monomeric iridium η^1 -alkenyl compounds (via self metathesis). These were isolated as high melting orange-yellow solids.

The metathesis method developed in this work provides an alternative for the preparation of homo-binuclear compounds where the two metal centres are connected by an unsaturated hydrocarbon bridge. The use of phenol as an additive improved the reactivity of Grubbs' 1st generation catalyst such that the metathesis reaction could be carried out at room temperature for those precursors (e.g. $\text{LFe}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$) which are not stable at elevated temperatures. Side reactions such as alkyl migration could leave the iron centre with a vacant coordination site that could form a bond with an alkene group in competition with the metathesis reaction. The self-metathesis method utilising a combination of Grubbs' 1st generation catalyst and phenol as an additive has been reported for organic substrates.¹⁵ The addition of phenol significantly extends the lifetime of Grubbs' 1st generation catalyst and this allows for the conversion of more accessible *cis*-products to thermodynamically stable *trans*- isomers.¹⁵ The efficiency of Grubbs' 1st generation catalyst versus Grubbs' 2nd generation catalyst has been discussed in Chapter One. However, the 1st generation catalyst is still the cheaper version even with an phenol additive and the combination is beneficial especially for self-metathesis reaction.^{15, 16}

The Grubbs' 2nd generation catalysts was a catalyst of choice regarding the RCM reactions which were carried-out at elevated temperatures which are not a suitable condition for Grubbs' 1st generation catalyst. Ring closure of compounds (63) – (65) occurred in a metathesis fashion in the presence of Grubbs' ruthenium catalysts to afford compounds (66) – (68). This work has implications in, for example, the applications of asymmetric ring-closing metathesis to transition metal containing substrates. Both E- and Z- geometries are possible, however more studies would have to be carried-out to determine the stereoselectivity of the ring-closure.

Characterization was done by NMR, IR, elemental analysis as well as mass spectral analysis (for selected compounds). Possible future-work would be to investigate the reactivity (such as addition and/or hydrogenation reactions) on the internal double-bond.

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4.5 References

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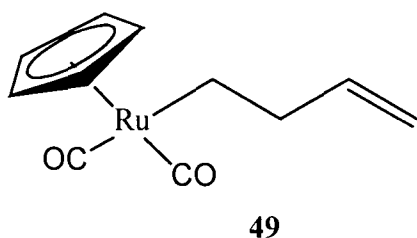
CHAPTER 5: EXPERIMENTAL

5.1 General

All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen unless otherwise stated. All solvents were of analytical grade and were dried by refluxing under an inert atmosphere over a suitable drying agent. THF and toluene were dried by refluxing over sodium wire and distilled from Na-benzophenone. Dichloromethane and acetonitrile were dried by refluxing over P₂O₅. Infrared spectra were recorded on a Paragon 1000 Fourier Transform Infrared Spectrometer. ¹H, ¹³C NMR and ³¹P NMR were recorded on Varian 300 and 400 spectrometers and all ¹H NMR chemical shifts are reported relative to the residual proton resonance in the deuterated solvents (all at 298 K in CDCl₃). Microanalyses were conducted at the University of Cape Town with a Thermo Flash 1112 Series CHNSO analyzer instrument. Mass spectra were recorded at the University of Witwatersrand or at the University of Cape Town. Melting points were recorded using a Kofler hot stage microscope (Riechert Thermovar). THF, dichloromethane, hexane, toluene and acetonitrile were purchased from Aldrich. Deuterated CDCl₃ was purchased from Aldrich and was used as it is. Florisil 60-100 mesh was purchased from Aldrich. Neutral aluminium oxide was purchased from Merck and was deactivated by washing with deionised water and drying in the oven at 120°C overnight. [Cp*IrCl₂]₂,¹ [CpRu(CO)₂]₂,² PPh₂(CH₂)_mCH=CH₂,³ and LFe(CO)₂{(CH₂)_nCH=CH₂}⁴ (for n = 3, 4, 5 or 6, and L = Cp or Cp*) were prepared by the reported methods. [CpFe(CO)₂]₂, Br(CH₂)_nCH=CH₂ as well as Grubbs 1st and 2nd generation catalysts were purchased from Aldrich. [Cp*Fe(CO)₂]₂ was purchased from Strem Chemicals.

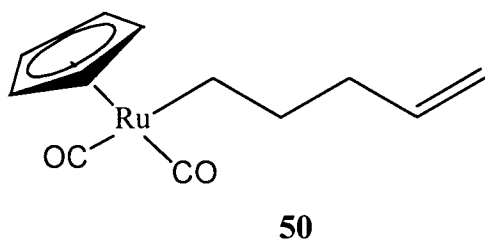
5.2 Preparation of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}$ ($n = 2, 3, \text{ or } 5$), compounds (49) – (51)

5.2.1 Preparation of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$ (49)



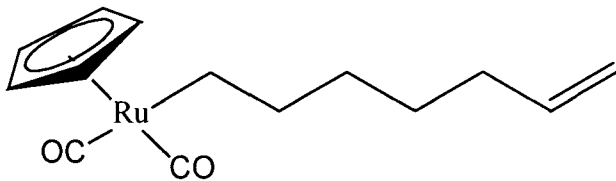
A solution of $[\text{RuCp}(\text{CO})_2]_2$ (1.00 g, 2.20 mmol) in THF (20 mL) was stirred over a sodium amalgam (0.5g Na, in 4 mL Hg) for 20hrs at room temperature. The resulting solution was transferred by a syringe to a second Schlenk tube and was cooled to 0°C in an ice bath. To this was added 4-bromo-1-butene (0.45 mL, 4.41 mmol) with stirring. The resulting mixture was stirred for 4hrs at 0°C . The solvent was removed under reduced pressure on a rotary evaporator to leave a brown residue. The brown residue was extracted with hexane (3 x 15 mL), filtered and the solvent removed under vacuum resulting in a yellow oil. The yellow oil was dissolved in dichloromethane (2 mL) and was transferred to a Florisil column (2.5 x 5cm). A yellow band was eluted with hexane. The removal of the solvent yielded a yellow oil which was identified as $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$ (49). Yield = 1.03 g, 82%. IR(DCM/ cm^{-1}): 2013 (s, $\nu(\text{CO})$) and 1946 (s, $\nu(\text{CO})$). δ_{H} (400 MHz, CDCl_3): 5.84 (m, 1H, $-\text{CH}=\text{}$), 5.24 (s, 5H, Cp), 4.85 (m, 2H, $=\text{CH}_2$), 2.32 (m, 2H, $-\text{CH}_2\text{CH}=\text{}$), 0.87 (br t, $J = 7.8$, 2H, $-\text{RuCH}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6, MHz): 202.22 (CO), 142.66 ($\text{CH}=\text{}$), 112.46 ($=\text{CH}_2$), 88.30 Cp, 43.47 ($\text{CH}_2\text{CH}=\text{}$), -4.86 (RuCH_2-). (Found: C, 47.40; H, 4.33. $\text{RuC}_{11}\text{H}_{12}\text{O}_2$ (277.26) requires: C, 47.65; H, 4.36%).

5.2.2 Preparation of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (**50**)



$\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (**50**) was synthesized in a procedure analogous to that of compound (**49**) above. A solution of $[\text{RuCp}(\text{CO})_2]_2$ (1.06 g, 2.40 mmol) in THF (20 mL) was stirred over a sodium amalgam (0.5 g Na, in 4 mL Hg) for 20hrs at room temperature. The reaction mixture was transferred to a second Schlenk tube and cooled to 0°C on an ice bath. To this was added 5-bromo-1-pentene (0.57 mL, 4.80 mmol), with stirring. The resulting mixture was stirred for 4hrs at 0°C . The work-up procedure is the same as that for (**49**) above. $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (**50**) was obtained as a yellow oil. Yield = 0.98 g, 71%, IR(DCM/ cm^{-1}): 2012 (s, $\nu(\text{CO})$) and 1947 (s, $\nu(\text{CO})$), δ_{H} (400 MHz, CDCl_3): 5.84 (m, 1H, $-\text{CH}=\text{}$), 5.24 (s, 5H, Cp), 4.93 (m, 2H, $=\text{CH}_2$), 2.14 (m, 2H, $-\text{CH}_2\text{CH}=\text{}$), 1.70 – 1.71 (m, 2H, $-\text{CH}_2-$), 0.85 (m, 2H, $-\text{RuCH}_2-$). $\delta_{\text{C}}(\text{H})$ (100.6, MHz) 202.22 (CO), 139.31 ($-\text{CH}=\text{}$), 113.99 ($=\text{CH}_2$), 88.47 (Cp), 38.63 ($-\text{CH}_2\text{CH}=\text{}$), 30.47 ($-\text{CH}_2-$) and -2.57 (RuCH_2-). (Found: C, 49.44; H, 4.80. $\text{RuC}_{12}\text{H}_{14}\text{O}_2$ (291.29) requires C, 49.48; H, 4.84%).

5.2.3 Preparation of $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_5\text{CH}=\text{CH}_2\}$ (**51**)

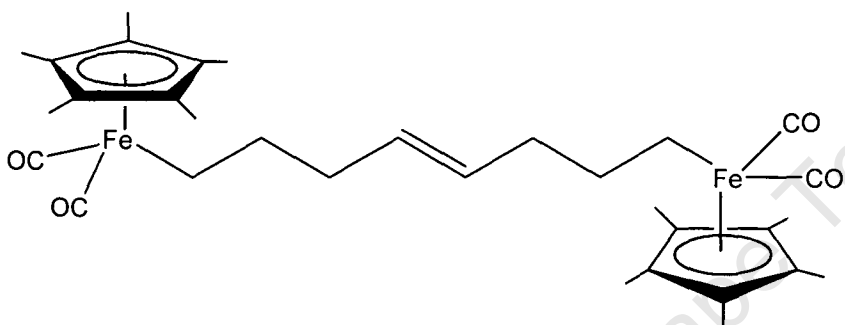


51

$\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_5\text{CH}=\text{CH}_2\}$ (**51**) was synthesized in a procedure analogous to that of complex (**49**) above. A solution of $[\text{RuCp}(\text{CO})_2]_2$ (1.24 g, 2.79 mmol) in THF (20 mL) was stirred over a sodium amalgam (0.5 g Na, in 4 mL Hg) for 20hrs at room temperature. The reaction mixture was transferred to a second Schlenk tube and cooled to 0°C on an ice bath. To this was added 7-bromo-1-heptene (0.85 mL, 5.58mmol), with stirring. The resulting mixture was stirred at 0°C for 4hrs. The work-up procedure is the same as for (**49**) above. $\text{CpRu}(\text{CO})_2\{(\text{CH}_2)_5\text{CH}=\text{CH}_2\}$ (**51**) was obtained as a yellow oil. Yield = 1.40 g, 79%, IR(DCM/ cm^{-1}): 2011 (s, $\nu(\text{CO})$) and 1946 (s, $\nu(\text{CO})$), δ_{H} (400 MHz, CDCl_3): 5.80(m, 1H, $-\text{CH}=\text{}$), 5.24(s, 5H, Cp), 5.00(m, 2H, $=\text{CH}_2$), 2.27 (m, $-\text{CH}_2\text{CH}=\text{}$), 1.23 – 1.92 (m, 6H, $-\text{CH}_2-$), 0.89 (m, 2H, RuCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6, MHz) 202.36($\underline{\text{C}}\text{O}$), 139.24($\underline{\text{C}}\text{H}=\text{}$), 113.98($=\text{CH}_2$), 88.45(Cp), 39.18, 33.87, 29.88, 26.09($-\text{CH}_2-$) and -3.51 ($\text{Ru}\underline{\text{C}}\text{H}_2-$). (Found: C, 52.20; H, 5.68. $\text{RuC}_{14}\text{H}_{18}\text{O}_2$ (319.35) requires C, 52.65; H, 5.68%).

5.3 Preparation of $[LM(CO)_2]_2 [\mu-\{(CH_2)_nCH=CH(CH_2)_n\}]$, (L = Cp or Cp*, M = Fe or Ru; n = 3 - 6); compounds (52) – (61)

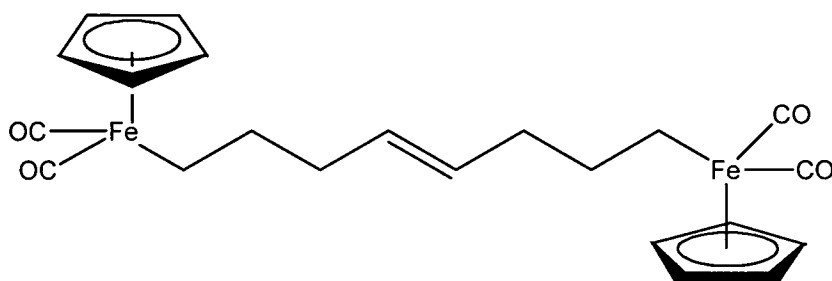
5.3.1 Preparation of $[Cp^*Fe(CO)_2]_2 [\mu-\{(CH_2)_3CH=CH(CH_2)_3\}]$ (52)



52

To a dichloromethane (15 mL) solution of $Cp^*Fe(CO)_2\{(CH_2)_3CH=CH_2\}$ (0.80 g, 2.53 mmol), and phenol (0.12 g, 1.26 mmol) was added Grubbs' 1st generation catalyst, $Cl_2Ru(=CHPh)(PCy_3)_2$ (0.052 g, 0.063 mmol). The mixture was stirred 12hrs at room temperature with a continuous flow of nitrogen. The solvent was removed under reduced pressure using a rotary evaporator to give a brown oil. The oil was dissolved in dichloromethane (2 mL) and chromatographed on an alumina column (6 x 2.5 cm). A yellow band was eluted using hexane/dichloromethane (50/50). Removal of solvent under reduced pressure gave compound **52** as a yellow-brown oil. Yield = 0.81 g, 53%. IR(DCM/cm⁻¹): 1979 (s, $\nu(CO)$), 1919 (s, $\nu(CO)$), 1602 (w, $\nu(C=C)$). δ_H (400 MHz, $CDCl_3$): 5.39 (m, 2H, $-CH=$), 1.98 (m, 4H, $-CH_2CH=$), 1.82 (s, 30H, Cp*), 1.34 (m, 4H, $-CH_2-$), 0.95 (m, 4H, $FeCH_2-$). $\delta_{C\{H\}}$ (100.6 MHz, $CDCl_3$): 220.01 (\underline{CO}), 130.32 ($\underline{CH=}$), 95.02 ($\eta^5-\underline{C}_5(CH_3)_5$), 37.89, 27.6 ($-\underline{CH}_2-$), 13.71 ($Fe\underline{CH}_2$), 8.98 ($-\underline{CH}_3$). (Found: C, 63.58; H, 7.77. $Fe_2C_{32}H_{44}O_4$ (604.3) requires C, 63.60; H, 7.33%).

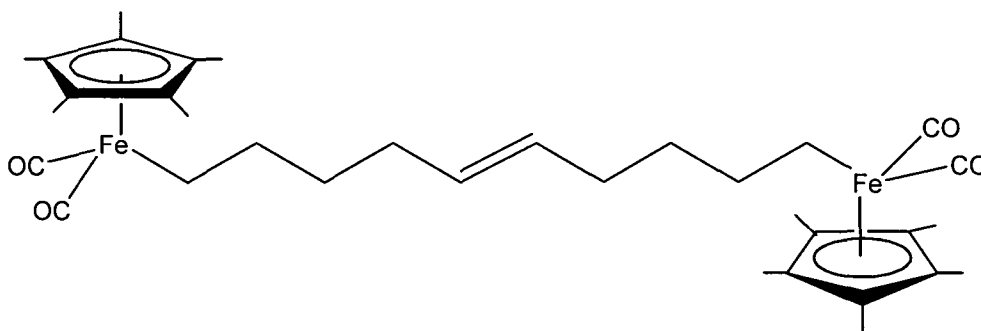
5.3.2 Preparation of $[\text{CpFe}(\text{CO})_2]_2[\mu\text{-}\{(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\}]$ (**53**)



53

A synthetic procedure similar to the one for **52** was used. To a dichloromethane solution (15 mL) of $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (1.02 g, 4.15 mmol), and phenol (0.19 g, 2.07 mmol) was added Grubbs' 1st generation catalyst, $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.11 g, 0.10 mmol). The same work-up procedure as the one used for **52** was followed. Compound **53** was obtained as a yellow oil. Yield = 0.96 g, 56%. IR(DCM/ cm^{-1}): 2001(s, $\nu(\text{CO})$), 1940(s, $\nu(\text{CO})$) and 1605(w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.39 (m, 2H, - $\text{CH}=\text{}$), 4.72 (s, 10H, Cp), 1.93 (m, 4H, - $\text{CH}_2\text{CH}=\text{}$), 1.35 (br s, 4H, - $\text{CH}_2\text{-}$), 0.96 (m, 4H, $\text{FeCH}_2\text{-}$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 217.52 ($\underline{\text{C}}\text{O}$), 131.06 ($\underline{\text{C}}\text{H}=\text{}$), 85.35 (Cp), 37.58, 29.96 ($\text{-CH}_2\text{-}$), 4.10 ($\text{FeCH}_2\text{-}$). (Found: C, 56.13; H, 5.65 $\text{Fe}_2\text{C}_{22}\text{H}_{24}\text{O}_4$ (464.08) requires C, 56.93; H, 5.21%).

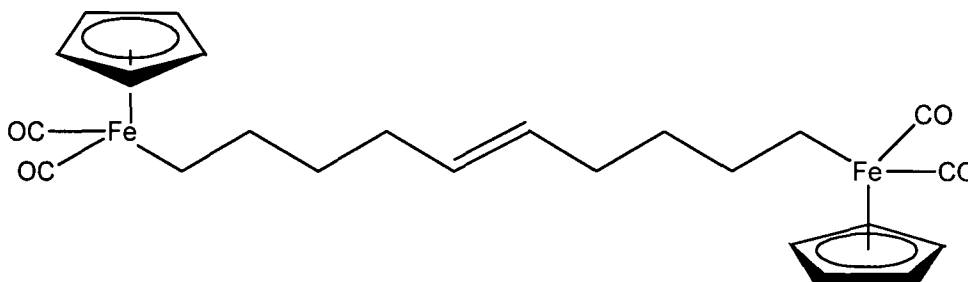
5.3.3 Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2[\mu\text{-}\{(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_4\}]$ (**54**)



54

Complex **54** was prepared using the same procedure as for **52**; to a dichloromethane (17 mL) solution of $\text{Cp}^*\text{Fe}(\text{CO})_2\{(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (1.72 g, 5.21 mmol), and phenol (0.25 g, 0.26 mmol) was added Grubbs' 1st generation catalyst $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.11 g, 0.13 mmol). After work-up (as described on section 5.3.1) the product was obtained as a yellow solid. Yield = 0.91 g, 55%. Mp: 84 – 90°C. IR (DCM/ cm^{-1}): 1978 (s, $\nu(\text{CO})$), 1917 (s, $\nu(\text{CO})$), 1605 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.37(m, 2H, $-\text{CH}=\text{}$), 1.95 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.74 (s, 30H, Cp^*), 1.36 (m, 8H, $-\text{CH}_2-$), 0.95 (m, 4H, FeCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 219.40 ($\underline{\text{C}}\text{O}$), 130.43 ($\underline{\text{C}}\text{H}=\text{}$), 94.75 ($\eta^5-\underline{\text{C}}_5(\text{CH}_3)_5$), 37.34, 35.82, 32.54 ($-\underline{\text{C}}\text{H}_2-$), 13.52 ($\text{Fe}\underline{\text{C}}\text{H}_2-$) 9.31 ($-\underline{\text{C}}\text{H}_3$). (Found: C, 64.60; H, 7.68; $\text{Fe}_2\text{C}_{34}\text{H}_{48}\text{O}_4$ (632.40) requires C, 64.57; H, 7.70%).

5.3.4 Preparation of $[\text{CpFe}(\text{CO})_2]_2 [\mu\text{-}\{(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_4\}]$ (**55**)

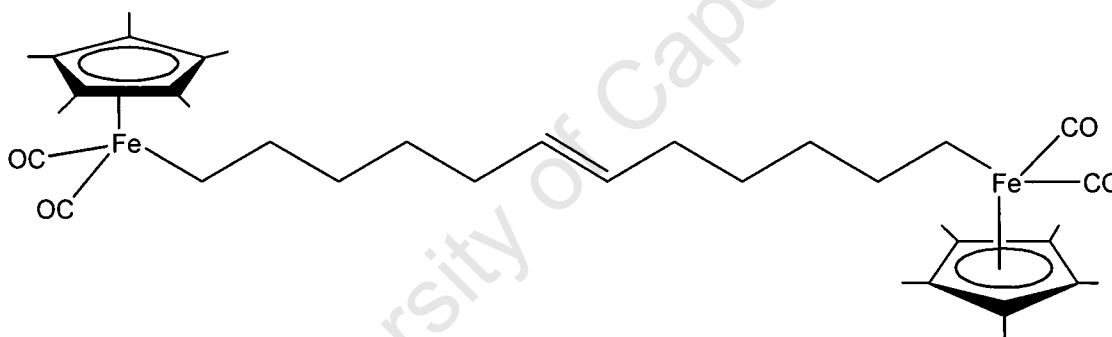


55

Complex **55** was prepared using the same procedure as for **52**; to a dichloromethane (15

mL) solution of $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (1.75 g, 6.73 mmol), and phenol (0.32 g, 3.41 mmol) was added Grubbs' 1st generation catalyst, $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.14 g, 0.17 mmol). After work-up (see section 5.3.1) the product was obtained as a yellow oil. Yield = 1.15 g, 66%. IR(DCM/ cm^{-1}): 2000 (s, $\nu(\text{CO})$), 1940 (s, $\nu(\text{CO})$), 1605 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.37 (m, 2H, $-\text{CH}=\text{}$), 4.72 (s, 10H, Cp), 1.97 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.45 (br s, 8H, $-\text{CH}_2-$), 0.94 (m, 4H, FeCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 217.78 ($\underline{\text{C}}\text{O}$), 130.33 ($\underline{\text{C}}\text{H}=\text{}$), 85.44 (Cp), 38.44, 34.47, 32.36 ($-\text{CH}_2-$), 3.84 (FeCH_2-). (Found: C, 58.56; H, 5.91. $\text{Fe}_2\text{C}_{24}\text{H}_{28}\text{O}_4$ (493.13) requires C, 58.57; H, 5.73%).

5.3.5 Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2 [\mu\text{-}\{(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_5\}]$ (**56**)

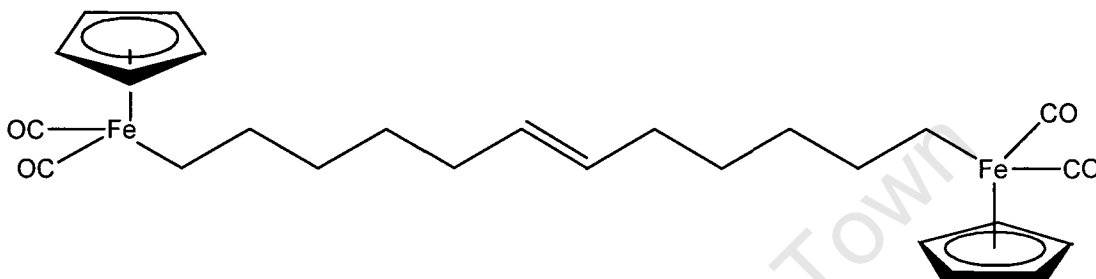


56

Complex **56** was prepared following the synthetic method used for the synthesis of **52** above; To a dichloromethane (15 mL) solution of $\text{Cp}^*\text{Fe}(\text{CO})_2\{(\text{CH}_2)_5\text{CH}=\text{CH}_2\}$ (0.92 g, 2.67 mmol), and phenol (0.13 g, 1.40 mmol) was added Grubbs' 1st generation catalyst, $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.05 g, 0.07 mmol). After a similar work-up (See section 5.3.1) **56** was obtained as a yellow oil. Yield = 0.57 g, 65%. IR(DCM/ cm^{-1}): 1979 (s, $\nu(\text{CO})$), 1918 (s, $\nu(\text{CO})$), 1605 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.39 (m, 2H, $-\text{CH}=\text{}$), 1.92 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.69 (s, 30H, Cp^*), 1.33 (m, 12H, $-\text{CH}_2-$), 0.95 (m, 4H, FeCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 219.98 (CO), 126.00 ($\underline{\text{C}}\text{H}=\text{}$), 94.52 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 39.64, 37.52, 35.68, 32.57 ($-\text{CH}_2-$), 13.73 (FeCH_2-), 9.19 ($-\text{CH}_3$). m/z (FAB) 660.5 (M^+).

(Found: C, 65.77; H, 8.12 Fe₂C₃₆H₅₂O₄ (660.45) requires C, 65.46; H, 7.93%).

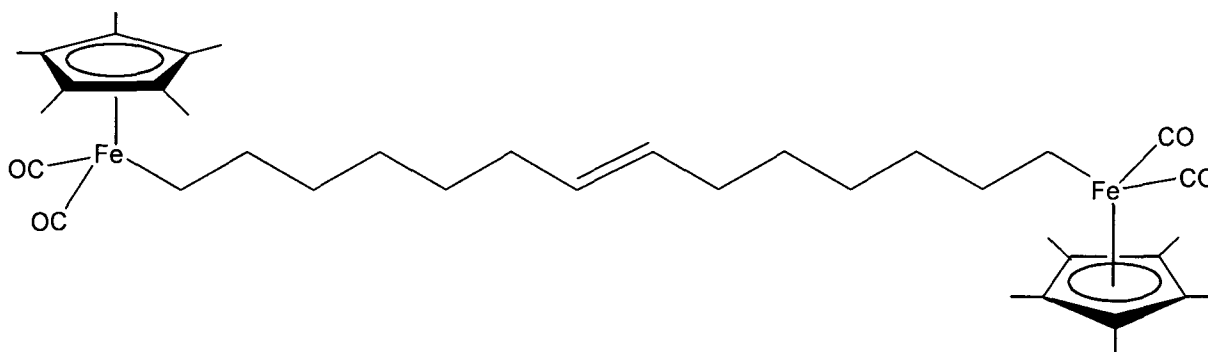
5.3.6 Preparation of [CpFe(CO)₂]₂ [μ-((CH₂)₅CH=CH(CH₂)₅)] (57)



57

The procedure used for the preparation of complex **52** was followed for the synthesis of **57**; To a dichloromethane (15 mL) solution of CpFe(CO)₂{(CH₂)₅CH=CH₂} (1.00 g, 4.50 mmol), and phenol (0.21 g, 2.20 mmol) was added Grubbs' 1st generation catalyst Cl₂Ru(=CHPh)(PCy₃)₂ (0.09 g, 0.11 mmol). After work-up (as outlined in section 5.3.1) the product was obtained as a yellow oil. Yield = 1.03 g, 84%. IR(DCM/cm⁻¹): 2000 (s, ν(CO)), 1940 (s, ν(CO)), 1605 (w, ν(C=C)). δ_H(400 MHz, CDCl₃): 5.36 (m, 2H, -CH=), 4.73 (s, 10H, Cp), 1.92 (m, 4H, -CH₂CH=), 1.33 (br m, 12H, -CH₂-), 0.94 (m, 4H, FeCH₂-). δ_C{H}(100.6 MHz, CDCl₃): 217.78 (C=O), 130.33 (CH=), 85.20 (Cp), 38.67, 34.69, 32.59, 29.55 (-CH₂-), 3.60 (FeCH₂). (Found: C, 60.08; H, 6.01. Fe₂C₂₆H₃₂O₄ (520.18) requires C, 60.03; H, 6.20%).

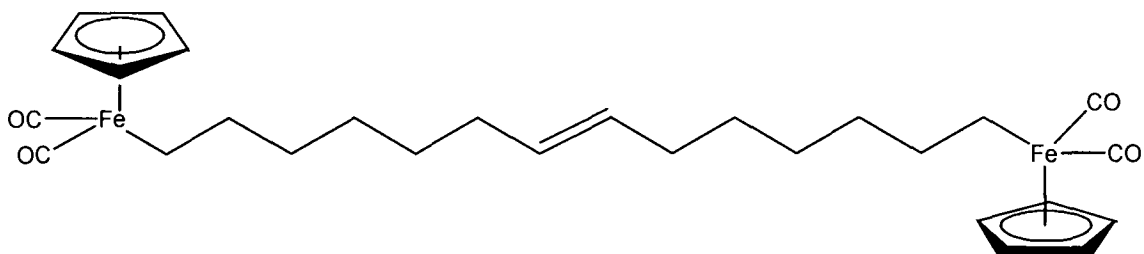
5.3.7 Preparation of [Cp*Fe(CO)₂]₂ [μ-((CH₂)₆CH=CH(CH₂)₆)] (58)



58

A synthetic procedure similar to the one used for the preparation of complex **52** was followed for the synthesis of **58**; to a dichloromethane (15 mL) solution of $(\text{Cp}^*)\text{Fe}(\text{CO})_2\{(\text{CH}_2)_6\text{CH}=\text{CH}_2\}$ (1.13 g, 3.16 mmol), and phenol (0.15 g, 1.60 mmol) was added Grubbs' $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.06 g, 0.08 mmol). After work-up (See section 5.3.1) the product was obtained as a yellow oil. Yield = 0.65 g, 60%. IR(DCM/ cm^{-1}): 1978 (s, $\nu(\text{CO})$), 1917(s, $\nu(\text{CO})$), 1605 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.36 (m, 2H, $\text{CH}=\text{}$), 1.95 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.69 (s, 30H, Cp^*), 1.40 (br s, 16H, $-\text{CH}_2-$), 0.92 (m, 4H, FeCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 201.09 (CO), 129.60 ($\text{CH}=\text{}$), 94.98 ($\eta^5-\text{C}_5(\text{CH}_3)_5$), 37.52, 35.87, 31.75, 28.59, 28.0 ($-\text{CH}_2-$), 13.69 (FeCH_2) 7.98 ($-\text{CH}_3$). (Found: C, 66.32; H, 6.37. $\text{Fe}_2\text{C}_{38}\text{H}_{56}\text{O}_4$ (690.52) requires C, 66.28; H, 8.17%).

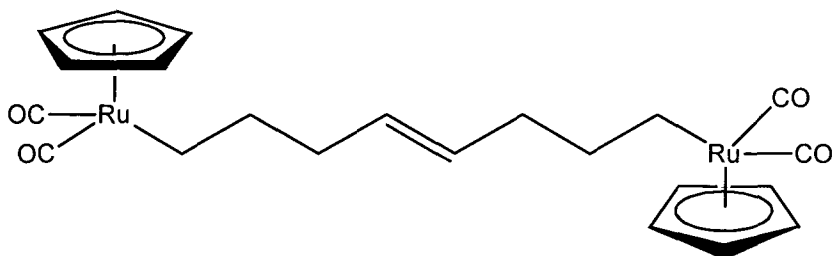
5.3.8 Preparation of $[\text{CpFe}(\text{CO})_2]_2[\mu\text{-}\{(\text{CH}_2)_6\text{CH}=\text{CH}(\text{CH}_2)_6\}]$ (**59**)



59

A synthetic procedure similar to the one used for the preparation of **52** was followed; to a dichloromethane (15 mL) solution of $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{CH}=\text{CH}_2\}$ (1.24 g, 4.31 mmol), and phenol (2.03 g, 2.20 mmol) was added Grubbs' 1st generation catalyst $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.09 g, 0.11 mmol). After work-up (see section 5.3.1) the product was obtained as a yellow oil. Yield = 0.64 g, 52%. IR(DCM/ cm^{-1}): 1978 (s, $\nu(\text{CO})$), 1917 (s, $\nu(\text{CO})$), 1605 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 5.38 (m, 2H, $-\text{CH}=\text{}$), 4.71 (s, 10H, Cp), 1.95 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.37 (br s, 16H, $-\text{CH}_2-$), 0.95 (m, 4H, FeCH_2-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 217.95 ($\underline{\text{C}}\text{O}$), 130.30 ($\underline{\text{C}}\text{H}=\text{}$), 85.25 (Cp), 37.16, 34.65, 32.60, 28.21, 27.63 ($-\text{CH}_2-$), 3.91 (FeCH_2). (Found: C, 61.37; H, 6.68. $\text{Fe}_2\text{C}_{28}\text{H}_{36}\text{O}_4$, (548.24) requires C, 61.34; H, 6.68%).

5.3.9 Preparation of $[\text{CpRu}(\text{CO})_2]_2[\mu\text{-}\{(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\}]$ (**60**)

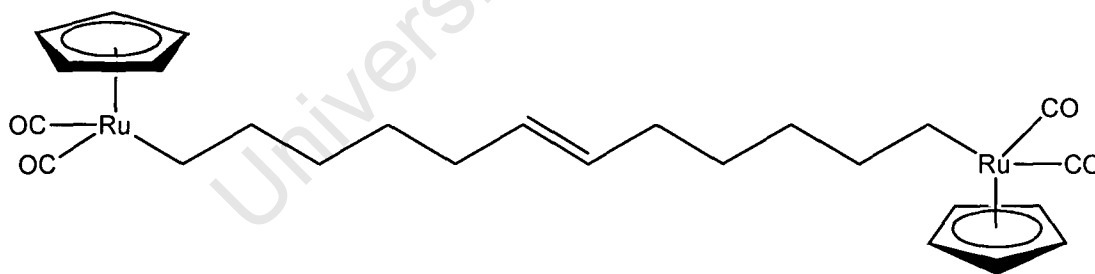


60

A Schlenk tube was charged with $\text{CpRu}(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (0.62 g, 2.13 mmol),

dichloromethane (15 mL), and phenol (0.11 g, 1.17 mmol). To this was added Grubbs' 1st generation catalyst, Cl₂Ru(=CHPh)(PCy₃)₂ (0.05 g, 0.58 mmol) followed by stirring at room temperature 12hrs. The continuous flow of N₂ was kept throughout the reaction time in order to remove access ethylene. Removal of the solvent under an oil pump vacuum resulted in a dark-brown residue. This was dissolved in minimum CH₂Cl₂ and transferred to a Florisil column and the colourless band was eluted with hexane. Removal of the solvent under reduced pressure left a colourless oil, which was identified as compound (**60**). Yield = 0.51 g, 86%. IR(DCM/cm⁻¹): 2012 (s, ν(CO)), 1947(s, ν(CO)), 1604 (w, ν(C=C)). δ_H(400 MHz, CDCl₃): 5.42 (m, 2H, -CH=), 5.24 (s, 5H, Cp), 2.24 (m, 4H, -CH₂CH=), 1.31 (br s, 4H, -CH₂-), 0.87 (m, 4H, RuCH₂-). δ_{C{H}}(100.6 MHz, CDCl₃): 202.10 (CO), 130.58 (CH=), 88.18 (Cp) 39.20, 31.89 (-CH₂-), -4.17 (RuCH₂). (Found: C, 47.67; H, 4.46. Ru₂C₂₂H₂₄O₄ (554.53) requires C, 47.65; H, 4.36%).

5.3.10 Preparation of [CpRu(CO)₂]₂ [μ-((CH₂)₅CH=CH(CH₂)₅)] (**61**)



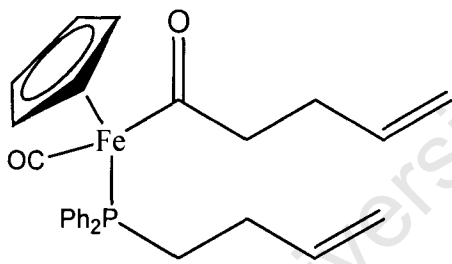
61

Complex **61** was synthesized following a procedure similar to the one used for the preparation of **60**. A Schlenk tube was charged with CpRu(CH₂)₅CH=CH₂ (0.60 g, 1.80 mmol), dichloromethane (15 mL), and phenol (0.10 g, 1.02 mmol). To this was added Grubbs' 1st generation catalyst Cl₂Ru(=CHPh)(PCy₃)₂ (0.04g, 0.50mmol) followed by stirring 12hours at room temperature. The continuous flow of N₂ was kept throughout the reaction time in order to remove ethylene by-product. After work-up (as described for

complex **60**) the product was obtained as a colourless oil. Yield = 0.34 g, 61%. IR(DCM/cm⁻¹): 2013 (s, $\nu(\text{CO})$), 1946 (s, $\nu(\text{CO})$), 1603 (w, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl₃): 5.41 (m, 2H, $-\text{CH}=\text{}$), 5.23 (s, 5H, Cp), 2.24 (m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.31-1.73 (br m, 12H, $-\text{CH}_2-$), 0.88 (m, 4H, RuCH₂-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl₃): 202.42 ($\underline{\text{C}}\text{O}$), 129.58 ($\underline{\text{C}}\text{H}=\text{}$). 88.68 (Cp), 39.98, 34.32, 32.97, 22.44 ($-\text{CH}_2-$), -3.28 (RuCH₂). (Found: C, 51.24; H, 5.35. Ru₂C₂₆H₃₂O₄ (610.64) requires C, 51.14; H, 5.28%).

5.4 Preparation of CpFe(CO){C(O)(CH₂)_nCH=CH₂}{PPh₂(CH₂)_mCH=CH₂} (n = 2, 3, 4 and m = 2, 3, 4, or 6); compounds (62) – (65)

5.4.1 Preparation of CpFe(CO){C(O)(CH₂)₂CH=CH₂}{PPh₂(CH₂)₂CH=CH₂} (62)

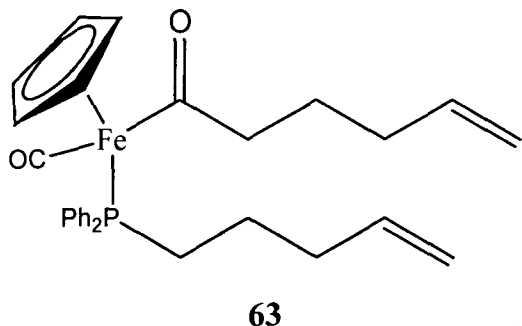


62

An acetonitrile (20 mL) solution of CpFe(CO)₂{(CH₂)₂CH=CH₂} (1.88 g, 8.1 mmol), and PPh₂(CH₂)₂CH=CH₂ (2.33 g, 8.90 mmol) in a 100 mL Schlenk flask was refluxed for 24hrs. After cooling to room temperature the solvent was reduced to 5 mL under vacuum. The resulting mixture was transferred to an alumina column (5 x 2.5 cm). Elution with dichloromethane/hexane mixture in the ratio of 50/50 resulted in a fast running yellow band. This was collected, and the solvent was removed under reduced pressure using a rotary evaporator to leave a yellow solid, Mp = 66 – 68°C. Yield = 3.21 g, 85%. IR: 1913 (s, $\nu(\text{CO})$), 1602 (m, $\nu(\text{C}=\text{C})$), δ_{H} (400 MHz, CDCl₃): 7.45 – 7.65 (br m, 10H, ArH), 5.86

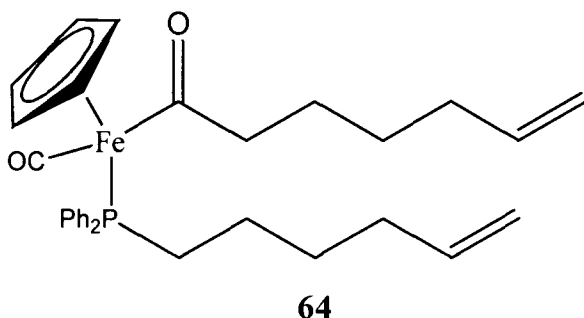
(br m, 2H, $\underline{\text{CH}}=$), 4.96 (br m, 4H, $=\underline{\text{CH}}_2$), 4.37 (s, 5H, Cp), 2.93 (m, 1H, $\text{C}(\text{O})\underline{\text{CH}}_a\text{H}_b-$), 2.83 (m, 1H, $\text{C}(\text{O})\text{CH}_a\underline{\text{H}}_b-$), 2.40 (br m, 2H, $\text{C}(\text{O})\text{CH}_2\underline{\text{CH}}_2-$), 1.97-2.20 (br m, 2H, $\underline{\text{CH}}_2\text{CH}=\text{)$, 1.20 (br m, 2H, $\text{P}\underline{\text{CH}}_2$), $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 220.2, 219.9 ($\underline{\text{C}}\text{O}$), 138.7, 137.8 ($\underline{\text{C}}\text{H}=\text{)$, 114.7, 113.9 ($=\underline{\text{C}}\text{H}_2$), 133.0, 132.8, 129.4, 128.6, ($\text{Ar}\underline{\text{C}}$) 84.40 (Cp), 64.84 ($\text{C}(\text{O})\underline{\text{C}}\text{H}_2-$), 29.6, 28.9, 28.2 ($-\underline{\text{C}}\text{H}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): 71.65 (Fe-P). (Found: C, 68.38; H, 6.40. $\text{FeC}_{27}\text{H}_{29}\text{O}_2\text{P}$ (472.32) requires C, 68.66; H, 6.18%).

5.4.2. Preparation of $\text{CpFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_3\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (63)



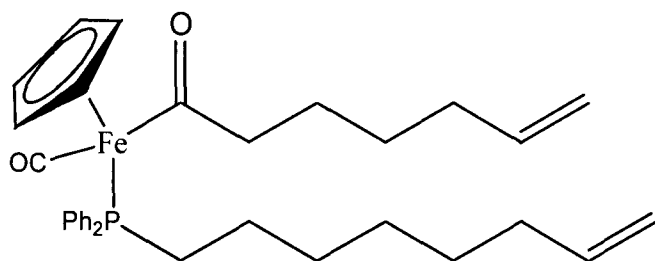
A synthetic procedure similar to the one used for the preparation of **62** was followed; an acetonitrile (20 mL) solution of $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (1.20 g, 4.90 mmol) and $\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (1.40 g, 5.50 mmol) was refluxed for 24hrs. after work-up (as described in section 5.4.1) the product was obtained as a yellow oil. Yield = 1.66 g, 68%, IR(DCM/ cm^{-1}): 1911 (s, $\nu(\text{CO})$) and 1596 (m, $\nu(\text{C}=\text{C})$) δ_{H} (400 MHz, CDCl_3): 7.40 – 7.80 (br m, 10H, ArH), 5.64 (br m, 2H, $\underline{\text{CH}}=$), 4.82 (br m, 4H, $=\underline{\text{CH}}_2$), 4.32 (s, 5H, Cp), 2.82 (m, 1H, $\text{C}(\text{O})\underline{\text{C}}\text{H}_a\text{H}_b-$), 2.63 (m, 1H, $\text{C}(\text{O})\text{CH}_a\underline{\text{H}}_b-$), 2.32 (br m, 2H, $\text{C}(\text{O})\text{CH}_2\underline{\text{C}}\text{H}_2-$), 1.96 (br m, 4H, $\underline{\text{C}}\text{H}_2\text{CH}=\text{)$, 1.21 – 1.58 (br m, 4H, $-\underline{\text{C}}\text{H}_2-$) $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 220.3, 219.9 ($\underline{\text{C}}\text{O}$), 138.7, 137.8 ($\underline{\text{C}}\text{H}=\text{)$, 114.7, 113.9 ($=\underline{\text{C}}\text{H}_2$), 132.1, 129.4, 127.9, 126.8 ($\text{Ar}\underline{\text{C}}$), 84.37 (Cp), 65.33 ($\text{C}(\text{O})\underline{\text{C}}\text{H}_2-$) 30.0, 29.3, 28.0, 26.2, 24.5 ($-\underline{\text{C}}\text{H}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): 71.61 (Fe-P). (Found: C, 69.52; H, 6.69. $\text{FeC}_{29}\text{H}_{33}\text{O}_4\text{P}$ (500.37) requires C, 69.61; H, 6.65%).

5.4.3 Preparation of $\text{CpFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_4\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (**64**)



Complex **64** was prepared following the same synthetic procedure as for **62** above; a 100 mL Schlenk flask was charged with $\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (2.00 g, 9.60 mmol), acetonitrile (20 mL), and $\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$ (2.07 g, 7.74 mmol). After work-up (as described for **62**) the product was obtained as a yellow oil. Yield = 3.05 g, 87%, IR(DCM/ cm^{-1}): 1914 (s, $\nu(\text{CO})$) 1597 (m, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 7.26 – 7.58 (br m, 10H, ArH), 5.64 (br m, 2H, $\text{CH}=\text{}$), 4.86 (br m, 4H, $=\text{CH}_2$), 4.36 (s, 5H, Cp), 2.84 (m, 1H, $\text{C}(\text{O})\text{CH}_2\text{H}_b$ -), 2.62 (m, 1H, $\text{C}(\text{O})\text{CH}_2\text{H}_a$ -), 1.96 (br m, 4H, $\text{CH}_2\text{CH}=\text{}$), 1.20 - 1.90 (br m, 10H, $-\text{CH}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 220.3, 219.9 (CO) 138.5, 138.7 ($\text{CH}=\text{}$), 114.5, 114.0 ($=\text{CH}_2$), 136.0, 133.0, 129.1, 127.9 (ArC), 84.32 (Cp), 66.38 ($\text{C}(\text{O})\text{CH}_2$ -), 32.9, 30.3, 29.6, 28.5, 24.7, 22.3, 22.0 ($-\text{CH}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): 71.64 (Fe-P). (Found: C, 70.44; H, 7.90. $\text{FeC}_{31}\text{H}_{37}\text{O}_2\text{P}$ (528.43) requires C, 70.46; H, 7.07%).

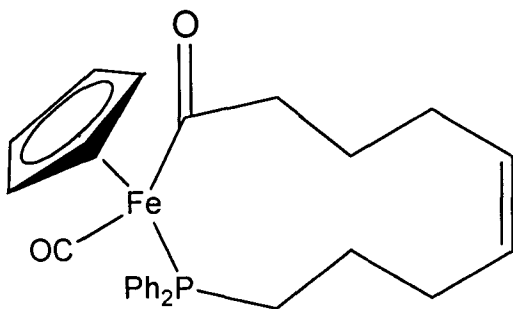
5.4.4 Preparation of $\text{CpFe}(\text{CO})\{\text{C}(\text{O})(\text{CH}_2)_4\text{CH}=\text{CH}_2\}\{\text{PPh}_2(\text{CH}_2)_6\text{CH}=\text{CH}_2\}$ (**65**)



Complex **65** was prepared using a synthetic procedure similar to the one followed for the preparation of **62**; a 100 mL Schlenk flask was charged with $\text{CpFe(CO)}_2\{(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (1.05 g, 4.04 mmol), acetonitrile (20 mL), and $\text{PPh}_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$ (1.44 g, 4.80 mmol). The mixture was refluxed for 24hrs. after work-up (same as for **62**) compound (**65**) was obtained as a brown oil. Yield: 2.17 g, 96%, IR(DCM/ cm^{-1}): 1913 (s, $\nu(\text{CO})$), 1601(m, $\nu(\text{C}=\text{C})$), δ_{H} (400 MHz, CDCl_3): 7.45 – 7.56 (br m, 10H, ArH), 5.74 (br s, 2H, $-\text{CH}=\text{}$), 4.82 (br m, 4H, $=\text{CH}_2$), 4.34 (s, 5H, Cp), 2.90 (br m, 1H, $-\text{C}(\text{O})\text{CH}_a\text{H}_b-$), 2.65 (br m, 1H, $-\text{C}(\text{O})\text{CH}_a\text{H}_b-$), 1.94 – 2.35 (br m, 4H, $\text{CH}=\text{}$), 1.20 – 1.63 (br m, 14H, $-\text{CH}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 220.20, 219.88 ($\underline{\text{C}}\text{O}$), 139.2, 138.8 ($\underline{\text{C}}\text{H}=\text{}$), 114.3, 113.6 ($=\underline{\text{C}}\text{H}_2$), 135.2, 132.0, 128.6, 126.7 (ArC), 84.33 (Cp), 65.79 ($\text{C}(\text{O})\underline{\text{C}}\text{H}_2-$), 31.3, 30.4, 29.6, 28.9, 28.0, 27.4, 26.4, 24.2, 23.2 ($-\underline{\text{C}}\text{H}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): 71.60 (Fe-P). (Found: C, 71.18; H, 7.44. $\text{FeC}_{33}\text{H}_{41}\text{O}_2\text{P}$ (556.47) requires C, 71.22; H, 7.42%).

5.5 preparations of compounds (66) – (68)

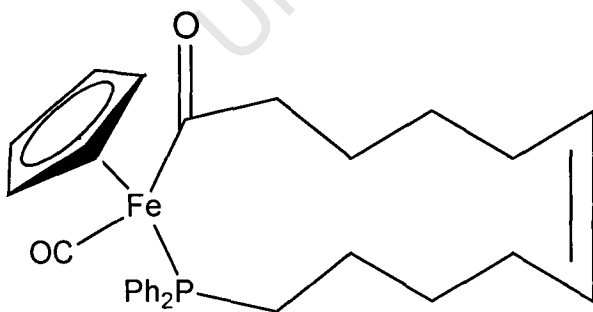
5.6.1 Preparation of compound (66)



66

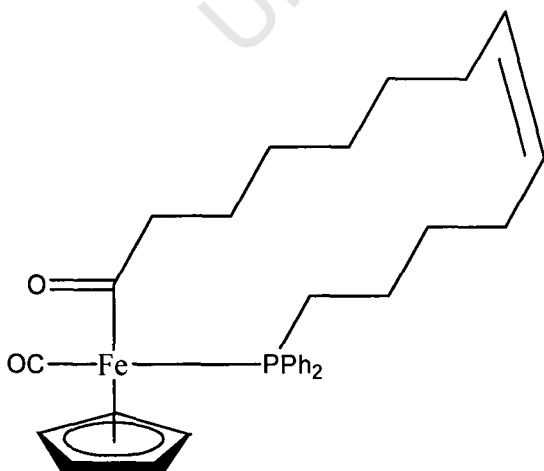
To a dichloromethane (20 mL) solution of **63** (1.56 g, 3.12 mmol), in a round bottom Schlenk flask was added Grubbs' 1st generation catalyst, Cl₂Ru(=CHPh)(PCy₃)₂ (0.19 g, 0.22 mmol). The mixture was refluxed for 12hrs. After cooling to room temperature, the mixture was filtered, and the solvent was removed under reduced pressure using a rotary evaporator to leave a dark-brown oil. The oil was dissolved in dichloromethane (2 mL) and was transferred to an alumina column (5 x 2.5 cm). Elution with dichloromethane/hexane mixture in the ratio of 50/50 resulted in a fast running yellow band. This was collected and the solvent was removed to leave a brown oil which was identified as **66**. Yield = 0.67 g, 46%. IR(DCM/cm⁻¹): 1913 (s, ν(CO)), 1597(m, ν(C=C)). δ_H(400 MHz, CDCl₃): 7.21 – 7.81 (br m, 10H, ArH), 5.23 (br m, 2H, -CH=), 4.28 (s, 5H, Cp), 2.37 (br m, 2H, -C(O)CH₂-) 1.89 (br m, 4H, -CH₂CH=), 1.21-1.60 (br m, 6H, -CH₂-). δ_{C{H}}(100.6 MHz, CDCl₃): 209.53 (C=O), 84.22 (Cp), 133.70, 129.07, 128.34, 127.4 (ArC), 67.89 (C(O)CH₂-), 131.74 (CH=), 30.34, 34.00, 37.66, 26.69, 27.67 (-CH₂). δ_{P{H}}(121 MHz, CDCl₃): 72.02 (Fe-P). (Found: C, 68.68; H, 6.40. FeC₂₇H₂₉O₂P (472.32) requires C, 68.66; H, 6.18%).

5.5.2 Preparation of compound (67)



A synthetic procedure similar to the one used for the preparation of complex **66** above was followed; to a dichloromethane (20 mL) solution of complex **64** (2.01 g, 3.80 mmol), was added Grubbs' 1st generation catalyst $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.22 g, 0.26 mmol) and the mixture was refluxed for 12hrs. After a similar work-up (See section 5.5.2) **67** was obtained as a yellow-brown solid. Yield = 0.73 g, 38%. Mp 170 – 173°C IR(DCM/ cm^{-1}): 1912 (s, $\nu(\text{CO})$), 1596 (m, $\nu(\text{C}=\text{C})$). δ_{H} (400 MHz, CDCl_3): 7.20-7.80 (br m, 10H, ArH), 5.32 (br m, 2H, $-\text{CH}=\text{}$), 4.33 (br s, 5H, Cp), 2.83 (br s, 2H, $-\text{C}(\text{O})\text{CH}_2-$), 2.34 (br m, 4H, $-\text{CH}_2\text{CH}=\text{}$), 1.21-1.80 (br m, 10H, $-\text{CH}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 217.22 ($\text{C}=\text{O}$), 84.86 (Cp), 137.52, 133.62, 129.73, 127.60 (ArC), 130.69, 130.0 ($\text{CH}=\text{}$), 65.12 ($\text{C}(\text{O})\text{CH}_2-$), 34.40, 33.5, 32.8, 32.22, 31.7, 30.0, 29.05 ($-\text{CH}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): 71.94 (Fe-P). (Found: C, 69.63; H, 7.31. $\text{FeC}_{29}\text{H}_{31}\text{O}_2\text{P}$ (500.37) requires C, 69.61; H, 6.65%).

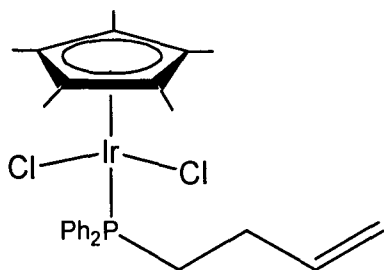
5.5.3 Preparation of compound (68)



Complex **68** was prepared following a method described for **66** above; to a dichloromethane (20 mL) solution of (**65**) (0.52 g, 0.93 mmol) was added Grubbs' 2nd generation catalyst (0.19 g, 0.22 mmol). The mixture was refluxed for 12hrs. After work-up (as outlined in section 5.6.1) the product was obtained as a yellow oil. Yield = 0.67 g, 73%. IR(DCM/cm⁻¹): 1914 (s, $\nu(\text{CO})$), 1601 (m, $\nu(\text{C}=\text{C})$), δ_{H} (400 MHz, CDCl₃): 7.62 – 7.80 (br m, 10H, ArH), 5.36 (br s, 2H, $\underline{\text{CH}}=$), 4.84 (s, 5H, Cp), 2.24 (br s, 2H, C(O) $\underline{\text{CH}}_2-$), 1.91 (br m, 4H, $\underline{\text{CH}}_2\text{CH}=\text{}$), 1.20 – 1.24 (br m, 14H, $-\underline{\text{CH}}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl₃): 204.00 ($\underline{\text{C}}\text{O}$), 86.27 (Cp), 132.08, 129.88, 127.70, 126.8 (Ar $\underline{\text{C}}$), 66.54 (C(O) $\underline{\text{C}}\text{H}_2-$), 130.87, 130.10 ($\underline{\text{C}}\text{H}=\text{}$), 35.81, 34.83, 31.17, 30.20, 29.71, 27.53, 26.06, 25.05, 21.67 ($-\underline{\text{C}}\text{H}_2-$). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl₃): 71.64 (Fe-P). (Found: C, 70.40; H, 7.31. FeC₃₁H₃₇O₂P (528.43) requires C, 70.46; H, 7.07%).

5.6 Preparation of Cp*Ir(Cl)₂{PPh₂(CH₂)_mCH=CH₂} (m = 2, 3, 4, or 6); compounds (**69**) – (**72**)

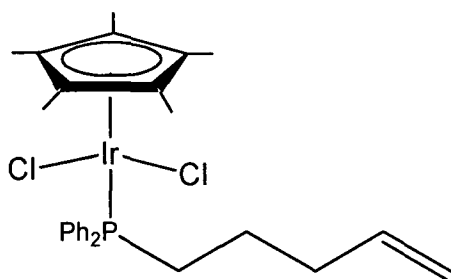
5.6.1 Preparation of Cp*Ir(Cl)₂{PPh₂(CH₂)₂CH=CH₂} (**69**)



69

To a solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.62 g, 0.78 mmol) in dichloromethane (15 mL) was added $\text{PPh}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (0.38 g, 1.58 mmol). The mixture was stirred for 12hrs at room temperature. The solvent was removed under reduced pressure using a rotary evaporator to leave an orange solid. This was extracted with methanol (4 x 15 mL), the extracts were combined, filtered and the solvent removed under reduced pressure on a rotary evaporator. The remaining orange residue was dissolved in dichloromethane (2 mL). Subsequent addition of hexane (4 mL) to the mixture resulted in an orange precipitate. This was filtered, and washed with (4 x 15 mL) portions of cold hexane. The precipitate was recrystallized from dichloromethane/hexane (50/50). Additional precipitate was obtained on leaving the washings for 24hrs at room temperature, this was combined with the original yield. The product was identified as $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$ (**69**). Yield = 0.42 g, 42%, Mp: 177–179°C, δ_{H} (400 MHz, CDCl_3): 7.85 (m, 4H, ArH), 7.45 (m, 6H, ArH), 5.65 (m, 1H, $\text{CH}=\text{}$), 4.84 (m, 2H, $=\text{CH}_2$), 1.98 (dt, $J = 6.4$ and 14.4 , 2H, $-\text{CH}_2\text{CH}=\text{}$), 1.35 (d, $J = 2.4$, 15H, Cp*), 1.34 (m, 2H, $-\text{PCH}_2-$), $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz): 138.3 ($\text{CH}=\text{}$), 114.5 ($=\text{CH}_2$), 133.9, 130.6, 128.9, 127.0 (ArC), 92.01 ($\eta^5-\text{C}_5(\text{CH}_3)_5$), 28.3, 26.4 ($-\text{CH}_2-$), 8.2 (CCH_3). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3) -3.51 (s, Ir-P). m/z (FAB) 638(M^+). (Found: C, 48.66; H, 5.15. $\text{IrC}_{26}\text{H}_{32}\text{PCl}_2$ (638.63) requires C, 48.89; H, 5.05%).

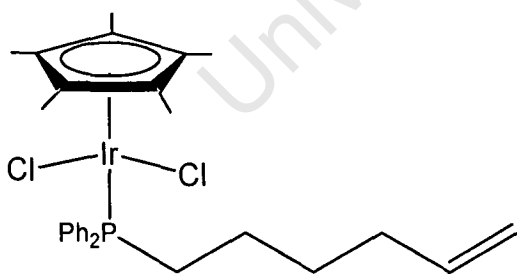
5.6.2 Preparation of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (**70**)



70

A similar synthetic procedure as the one used for the preparation of complex (69) above was followed. To a solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.62 g, 0.78 mmol) in dichloromethane (15 mL) was added $\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (0.41g, 1.61 mmol). The mixture was stirred for 12hrs at room temperature. After a similar work-up (as described in section 5.6.1) complex 70 was obtained as an orange solid. Yield = 0.27 g, 53%. Mp: 174–176°C. δ_{H} (400 MHz, CDCl_3): 7.87 (m, 4H, ArH), 7.44 (m, 6H, ArH), 5.60 (m, 1H, $\text{CH}=\text{}$), 4.84 (m, 2H, $=\text{CH}_2$), 1.97 (dt, $J = 7.5$ and 14.1, 2H, $-\text{CH}_2\text{CH}=\text{}$), 1.34 (d, $J = 2.0$, 15H, Cp^*), 1.33 (m, 4H, $-\text{CH}_2-$). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz) 137.1 ($\text{CH}=\text{}$), 114.8 ($=\text{CH}_2$), 133.9, 129.6, 128.0, 127.9 (ArC), 91.89 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 34.9, 26.4, 23.1 ($-\text{CH}_2-$), 8.10 (CH_3). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): -2.08 (Ir-P). (Found: C, 49.62; H, 5.58. $\text{IrC}_{27}\text{H}_{34}\text{PCl}_2$ (652.65) requires C, 49.68; H, 5.25%).

5.6.3 Preparation of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (71)

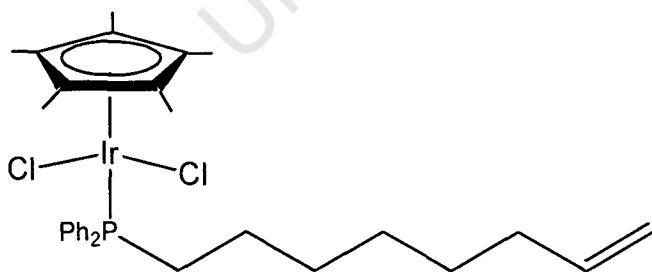


71

Complex 71 was prepared following a similar synthetic method as the one used for complex 69. To a solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.62 g, 0.78 mmol) in dichloromethane (15 mL) was added $\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$ (0.43 g, 1.60 mmol). The mixture was stirred for 12hrs at room temperature. After work-up (same as the one described for 69) the product

was obtained as an orange solid. Yield = 0.85 g, 82%. Mp: 147-148°C. δ_{H} (400 MHz, CDCl_3): 7.86 (m, 4H, ArH), 7.46 (m, 6H, ArH), 5.63 (m, 1H, CH=), 4.83 (m, 2H, =CH₂), 1.88 (m, 2H, -CH₂CH=), 1.34 (d, $J = 2.4$, 15H, Cp*), 1.27 – 1.32 (m, 6H, -CH₂-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz): 138.5 (CH=), 114.3 (=CH₂), 134.0, 130.6, 128.3, 126.2 (ArC), 91.86 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 33.13, 30.02, 26.4, 23.2 (-CH₂-), 8.14 (CH₃). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): -2.65. m/e (FAB): 666.8 (M^+). (Found: C, 50.29; H, 5.40. $\text{IrC}_{28}\text{H}_{36}\text{PCl}_2$ (666.7) requires C, 50.44; H, 5.44%).

5.6.4 Preparation of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_6\text{CH}=\text{CH}_2\}$ (72)



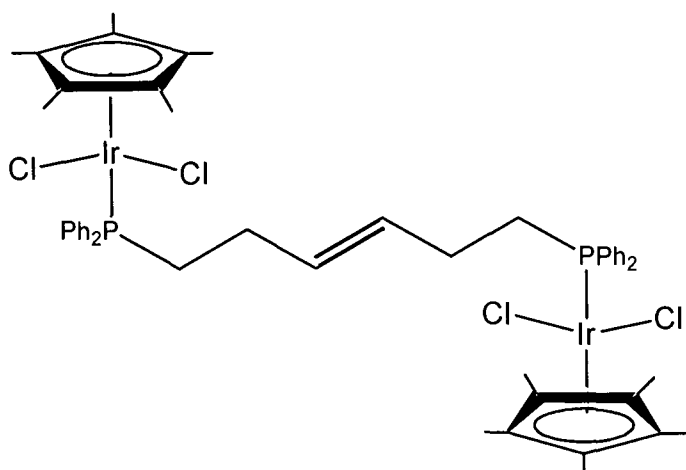
72

Complex 71 was prepared following a synthetic procedure similar to the one used for complex 69. To $[\text{CpIrCl}_2]_2$ (0.62 g, 0.78 mmol) in dichloromethane (15 mL) was added $\text{PPh}_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$ (0.43 g, 1.60 mmol). The mixture was stirred for 12hrs at room

temperature. After work-up (See section 5.6.1) the product was obtained as an orange solid. Yield = 0.75 g, 71%, Mp: 142 – 146°C, δ_{H} (400 MHz, CDCl₃): 7.90 (m, 4H, ArH), 7.42 (m, 6H, ArH), 5.43 (m, 1H, CH=), 4.84 (m, 2H, =CH₂), 1.98 (m, 2H, -CH₂CH=), 1.35 (d, $J = 2.4$, 15H, Cp*), 1.24 – 1.33 (br m, 10H, -CH₂-). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl₃): 139.1 (CH=), 114.8 (=CH₂), 134.4, 131.0, 129.2, 126.8, (ArC), 91.85 (η^5 -C₅(CH₃)₅), 32.3, 34.1, 30.2, 28.3, 26.4, 23.2 (-CH₂-), 8.20 (CH₃). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl₃): -2.49 (Ir-P). m/e (FAB): 694 (M⁺). (Found: C, 52.10; H, 5.80. IrC₃₀H₄₀PCl₂ (694.73) requires C, 51.86; H, 5.80%).

5.7 Preparation of [Cp*Ir(Cl)₂]₂[μ -{PPh₂(CH₂)_mCH=CH(CH₂)_mPPh₂}] (m = 2, 3, or 4) Compounds (73) – (75)

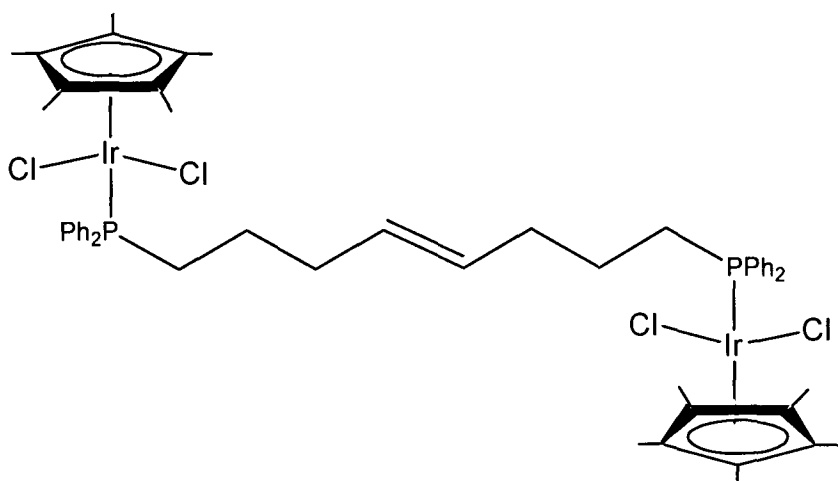
5.7.1 Preparation of [Cp*Ir(Cl)₂]₂[μ -{PPh₂(CH₂)₂CH=CH(CH₂)₂PPh₂}] (73)



73

To a solution of $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2\}$ (0.37 g, 0.58 mmol) in toluene (20 mL) was added Grubbs' 2nd generation catalyst (0.030 g, 0.034 mmol). The mixture was refluxed for 12hrs. After cooling to room temperature, the solvent was removed under reduced pressure leaving behind an orange solid. The solid was dissolved in dichloromethane (2 mL). Subsequent addition of hexane (4 mL) resulted in the product precipitating out as an orange solid. The mixture was filtered, and the orange solid was washed with cold hexane (4 x 5 mL), the solid was identified as compound (73). Yield = 0.33 g, 90%. Mp: 246 – 249°C. δ_{H} (400 MHz, CDCl_3): 7.79 – 7.86 (br m, 8H, ArH), 7.43 (br m, 8H, ArH), 7.17 (m, 4H, ArH), 5.04 (br m, 2H, CH=), 2.74 (br m, 4H, -CH₂CH=), 1.78 (br m, 4H, PCH₂-) 1.33 (d, $J = 2.3$, 30H, Cp*), $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 130.55 (CH=), 135.54, 129.60, 127.32, 126.20 (ArC), 92.03 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 33.63, 30.41 (-CH₂-), 8.27 (-CH₃) $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): -2.44 (Ir-P). (Found: C, 47.94; H, 4.87 $\text{Ir}_2\text{C}_{50}\text{H}_{60}\text{P}_2\text{Cl}_4$ (1249.21) requires C, 48.07; H, 4.84%).

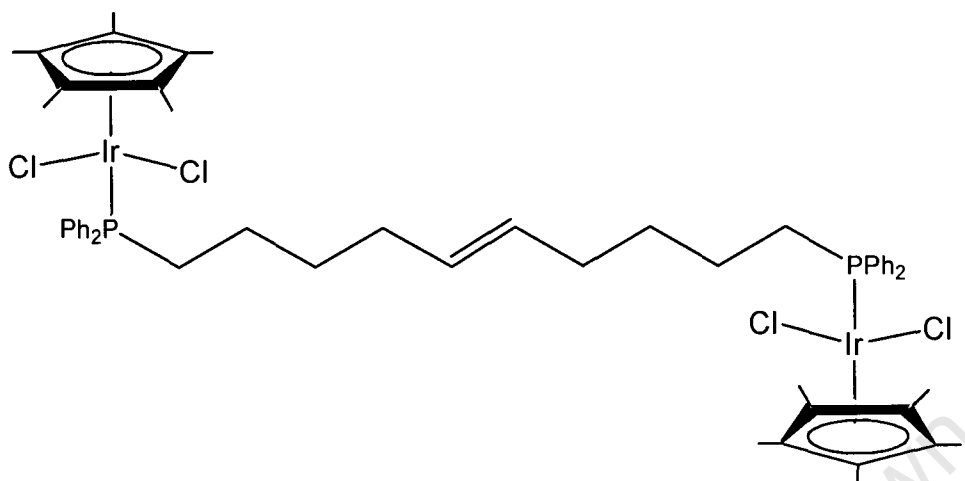
5.7.2 Preparation of $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2[\mu\text{-}\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{PPh}_2\}]$ (74)



74

A 100 mL Schlenk tube was charged with $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2\}$ (0.41 g, 0.63 mmol), dichloromethane (20 mL), and phenol (0.03 g, 0.32 mmol). To this was added Grubbs' $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ 1st generation catalyst (0.013 g, 0.16 mmol) and the mixture was stirred for 24hrs at room temperature under a continuous flow of nitrogen to remove evolved ethylene. The solvent was removed under reduced pressure leaving behind an orange solid. The solid was washed with cold hexane (4X5 mL) and dried in to give compound (74). Yield = 0.27 g, 68%. Mp: 190 – 194°C. δ_{H} (400 MHz, CDCl_3): 7.82 – 7.86 (br m, 8H, ArH), 7.43 (br m, 8H, ArH), 7.22 (m, 4H, ArH), 5.02(m, 2H, -CH=), 2.68 (br m, 4H, -CH₂CH=), 1.78 (m, 4H, -CH₂-), 1.34 (m, 4H, PCH₂-), 1.33 (d, $J = 2.4$, 30H, Cp*). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 130.29 (C=), 133.95, 125.42, 128.11, 127.4 (ArC), 91.54 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 40.00, 29.54, 27.77 (-CH₂-), 8.18 (-CH₃). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): -3.04 (Ir-P). (Found: C, 48.88; H, 5.02. $\text{Ir}_2\text{C}_{52}\text{H}_{64}\text{P}_2\text{Cl}_4$ (1277.27) requires C, 48.90, H, 5.05%).

5.7.3 Preparation of $[\text{Cp}^*\text{Ir}(\text{Cl})_2]_2[\mu\text{-}\{\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_4\text{PPh}_2\}]$ (75)



75

Similar to the preparation of compound (74) above; a Schlenk tube was charged with $\text{Cp}^*\text{Ir}(\text{Cl})_2\{\text{PPh}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2\}$ (0.41 g, 0.61 mmol), dichloromethane (20 mL), and phenol (0.031g, 0.31mmol). To this was added Grubbs' 1st generation catalyst, $\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2$ (0.013 g, 0.16 mmol) and the mixture was stirred for 24hrs at room temperature under a continuous flow of nitrogen. After work-up (as described for 74) the product was obtained as an orange solid. Yield = 0.27 g, 68%. Mp: 182 – 184°C. δ_{H} (400 MHz, CDCl_3): 8.08 – 7.92 (br m, 8H, ArH), 7.02 – 7.34 (br m, 8H, ArH), 6.91 (m, 4H, ArH), 4.89 (m, 2H, CH=), 1.60 (m, 4H, -CH₂CH=), 1.17 – 1.40 (m, 8H, -CH₂-), 1.35 (m, 4H, PCH₂-), 1.33 (d, $J = 1.95$, 30H, Cp*). $\delta_{\text{C}\{\text{H}\}}$ (100.6 MHz, CDCl_3): 130.04 (-CH=), 134.04, 131.60, 128.44, 127.0 (ArC), 91.87 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 32.16, 30.93, 27.03, 23.13 (-CH₂-), 8.26 (-CH₃). $\delta_{\text{P}\{\text{H}\}}$ (121 MHz, CDCl_3): -1.95 (Ir-P). (Found: C, 49.66; H, 5.52. $\text{Ir}_2\text{C}_{54}\text{H}_{68}\text{P}_2\text{Cl}_4$ (1305.32) requires C, 49.69; H, 5.25%).

5.8: References

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