Synthesis and modelling of Tungsten catalysts for alkene metathesis

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Summary

The aim of this study was to investigate, theoretically and experimentally, the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalyst and to synthesise ‘cage’ alicyclic ligands that will help retain the catalyst during the membrane separation process. Furthermore, molecular modelling was used in order to explain the metal-ligand coordination, the active sites in carbosilane dendritic catalysts and to investigate the mechanistic steps of the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalyst in the metathesis of 1-octene.

The W(O-2,6-C₆H₃X₂)₂X₄ (X = Cl, Br and Ph) catalytic system has been reported in literature, and the complex with X = Cl substituent was found to have higher activity than the complex with Br and Ph substituents. However, the complex with Br and Ph substituents were found to have high selectivity but lower activity. The metathesis of 1-octene by the W(O-2,6-C₆H₃Cl₂)₂Cl₄ system was investigated and the results matched well with literature. A theoretical study was done on the metathesis mechanism of 1-octene in the presence of carbosilane dendritic catalysts and the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system. The electronic energy profiles were plotted by using a Potential Energy Surface (PES) scan. The preferred routes in the activation steps and in the catalytic cycles were predicted. The activation steps of the two carbosilane dendritic catalysts are different from the activation step of the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalyst, but the catalytic cycle is in agreement with that of W(O-2,6-C₆H₃Cl₂)₂Cl₄. Electronic energy gaps, orbital symmetry and the orientation of ligands or 1-octene with metal complexes were calculated and analysed. A striking observation is that in the coordination of the metal complex with either the ligand or 1-octene the smallest energy gap of the frontier orbitals is always between the lowest unoccupied molecular orbitals (LUMO) of the metal complex and the highest occupied molecular orbitals (HOMO) of the ligand/alkene. It was also observed on the energy profiles that the heptylidene species is more stable than the methylidene species.

Two ‘cage’ alicyclic compounds which differ in their periphery, the “cage divinyl ether” and “cage dialyl ether” were synthesised and obtained in good yields. Attempts to synthesise dendritic catalysts/complexes with these ligands as cores of the dendritic catalysts were undertaken. An electrophilic addition reaction of HCl and Cl₂ on the double bonds was observed. An energy gap analysis of these ligands with the W(O-2,6-C₆H₃Cl₂)₂Cl₄ system was undertaken. It was found that the LUMO of W(O-2,6-C₆H₃Cl₂)₂Cl₄ and the HOMO of the “cage alicyclic compounds” showed a good possibility of coordination. However, the orbital symmetry and orientation of the metal and ligand does not permit the coordination of the ligands with the metal complex. In-situ metathesis of “cage alicyclic compounds” as ligands with W(O-2,6-C₆H₃Cl₂)₂Cl₄ as catalyst did not give any metathesis products.
Samevatting

Die doel van die studie was om die W(O-2,6-C₆H₃Cl₂)₂Cl₄ katalisator teoreties en eksperimenteel te ondersoek en om ‘hok’ alisikliese ligande te sintetiseer wat kan help om die katalisator terug te hou gedurende ‘n membraanskeidingproses. Verder is molekuulmodellering gebruik om die metal-ligandinteraksie en die aktiewe posisies in die karbosilaan dendritiese katalisatore te verduidelik, sowel as die mekanistiese stappe van die W(O-2,6-C₆H₃Cl₂)₂Cl₄ katalisator in die metatese van 1-okteen te onderzoek.

Die W(O-2,6-C₆H₃X₂)₂X₄ (X = Cl, Br en Ph) katalitiese sisteem is in die literatuur geraporteer, en daar is gevind dat die kompleks met X = Cl substituent ‘n hoër aktiwiteit het as dié met Br en Ph substituente. Daar is egter gevind dat die met Br en Ph substituente hoër selektiwiteit maar laer aktiwiteit. Die metatese van 1-okteen met die W(O-2,6-C₆H₃Cl₂)₂Cl₄ sisteem is ondersoek en die resultate stem goed ooreen met dié in literatuur. ‘n Teoretiese studie is op die metatese-meganisme van 1-okteen in die teenwoordigheid van karbosilaan dendritiese katalisatore en die W(O-2,6-C₆H₃Cl₂)₂Cl₄ katalitiële sisteem uitgevoer. Die elektroniese energieprofiële is gestip deur van ‘n Potensiële Energie Oppervlak (Potential Energy Surface, PES) skandering gebruik te maak. Die voorkeurroetes in die aktiveringstappe en katalitiese siklusse is voorspel. Die aktiveringstap van die twee karbosilaan dendritiese katalisatore verskil van die aktiveringstap van die W(O-2,6-C₆H₃Cl₂)₂Cl₄ katalisator, maar hul katalitiese siklusse stem ooreen met die van W(O-2,6-C₆H₃Cl₂)₂Cl₄. Elektroniese energie gapings, orbitaalsimmetrie en die orientasie van ligande of 1-okteen met metaalkompleksie is bereken en geanaliseer. ‘n Opvallende waarneming is dat in die koördinasie van die metaalkompleks met of die ligand of 1-okteen die kleinste energie gaping van die grensorbitale altyd tussen die laagste ongevulde molekuulorbitaal (LUMO) van die metaalkompleks en die hoogste gevulde molekuulorbitaal (HOMO) van die ligand/alkeen is. Daar is ook op die energieprofiële waargeneem dat die heptilideen spesies meer stabile is as die metilideen spesies.

Twee ‘hok’ alisikliese verbinding wat in die periferie verskil, die “hokdivinieleter” en “hokdiallieleter” is gesintetiseer en in goeie opbrengs verkry. Pogings om dendritiese katalisatore/kompleksie met hierdie ligande as kerne te berei is ondernem. ‘n Elektrofiele addisie van HCl of Cl₂ oor die dubbelbindings is waargeneem. ‘n Energiegaping-analise van hierdie ligande met die W(O-2,6-C₆H₃Cl₂)₂Cl₄ sisteem is onderneem. Daar is gevind dat die LUMO van W(O-2,6-C₆H₃Cl₂)₂Cl₄ en die HOMO van die “hokalisikliese verbinding” ‘n groot moontlikheid van koördinasie vertoon. Maar die orbitaalsimmetrie en oriëntasie van die metal en ligand verhoed koördinasie van die ligand met die metaalkompleks. In-situ metatese van “hokalisikliese
verbindings" as ligande met W(O-2,6-C₆H₃Cl₂)₂Cl₄ as katalisator het egter geen metatese produkte gegee nie.
# Table of contents

Acknowledgements...................................................................................................................i
Summary....................................................................................................................................iii
Samevatting..........................................................................................................................v
Table of contents.................................................................................................................vii
List of abbreviations .............................................................................................................xi

## Chapter 1 Introduction and Aims of Study.................................................................1

1.1 Introduction.........................................................................................................................1

1.2 Aims and objectives............................................................................................................3

1.3 References..........................................................................................................................4

## Chapter 2 Literature Review.........................................................................................7

2.1 Introduction........................................................................................................................7

2.2 The development of alkene metathesis catalysts............................................................9

2.2.1 Tungsten(VI) aryloxide complexes..............................................................................9

2.2.2 Ligands..........................................................................................................................11

2.2.3 Dendritic catalysts..........................................................................................................13

2.2.4 Carbocyclic ‘cage’ compounds.....................................................................................15

2.3 Reaction mechanism of alkene metathesis.................................................................17

2.3.1 Pairwise mechanism.......................................................................................................17

2.3.2 Non-pairwise mechanism..............................................................................................19

2.4 Molecular modelling in alkene metathesis reactions...................................................20

2.5 References.......................................................................................................................22

## Chapter 3 Results and Discussions.............................................................................25

3.1 Introduction........................................................................................................................25

3.2 Metathesis reactions with W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system......................................26

3.3 Theoretical investigation of alkene metathesis...............................................................27

3.3.1 W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system.........................................................................27

3.3.2 Beerens catalyst............................................................................................................40

3.3.3 The G0-W₂ catalyst......................................................................................................46
3.4 The carbocyclic ‘cage’ catalysts .................................................................60
3.4.1 3,5-divinyl-4-oxahexacyclo[5.4.1.0^2,6.0^3,10.0^5,9.0^8,11]dodecane catalytic system .................................................................60
3.4.2 3,5-diallyl-4-oxahexacyclo[5.4.1.0^2,6.0^3,10.0^5,9.0^8,11]dodecane catalytic system .................................................................62
3.5 References .................................................................................................67

Chapter 4 Conclusions .........................................................................................69
4.1 Introduction .................................................................................................69
4.2 Theoretical and experimental study of W(O-2,6-C6H3Cl2)2Cl4 ................................69
4.3 W-carbosilane dendritic catalysts .................................................................69
4.4 Cage carbocyclic catalysts ............................................................................70
4.5 Recommendations .........................................................................................70
4.6 References .................................................................................................70

Chapter 5 Experimental .........................................................................................71
5.1 Solvents and reagents ..................................................................................71
5.1.1 Solvents .......................................................................................................71
5.1.2 Reagents .......................................................................................................71
5.2 Apparatus .......................................................................................................71
5.3 Experimental procedure .................................................................................73
5.3.1 Synthesis of pentacyclo[5.4.0.0^2,6.0^3,10.0^5,9]undecane-8,11-dione (8) ...........................................................................................................73
5.3.2 Synthesis of exo-8-exo-11-divinylpentacyclo[5.4.0.0^2,6.0^3,10.0^5,9]undecane-endoe-8-endo-11-diol (11) ................................................................................74
5.3.3 Synthesis of 3,5-divinyl-4-oxahexacyclo[5.4.1.0^2,6.0^3,10.0^5,9.0^8,11]dodecane (12) ...........................................................................................................75
5.3.4 Synthesis of exo-8-exo-11-diallylpentacyclo[5.4.0.0^2,6.0^3,10.0^5,9]undecane-endoe-8-endo-11-diol (13) ................................................................................76
5.3.5 Synthesis of 3,5-diallyl-4-oxahexacyclo[5.4.1.0^2,6.0^3,10.0^5,9.0^8,11]dodecane (3) ...........................................................................................................77
5.3.6 Purification of WCl6 .......................................................................................77
5.3.7 Synthesis of W(O-2,6-C6H3Cl2)2Cl4 ................................................................78
5.3.8 Synthesis of ‘cage’ compound catalysts ......................................................78
5.4 Metathesis reactions .......................................................................................79
5.4.1 W(O-2,6-C₆H₃Cl₂)₂Cl₄ complex ................................................................. 79
5.4.2 ‘Cage’ compound catalysts ................................................................. 79
5.5 Analysis ................................................................................................. 80
5.5.1 Gas Chromatography (GC) ................................................................. 80
5.5.2 Gas Chromatography-Mass Spectrometry (GC-MS) ......................... 82
5.5.3 Infrared spectroscopy (IR) ................................................................. 82
5.5.4 Nuclear Magnetic Resonance spectroscopy (NMR) ......................... 82
5.6 Computational details ........................................................................ 83
5.6.1 Hardware ......................................................................................... 83
5.6.2 Software ......................................................................................... 83
5.7 References ......................................................................................... 84

Appendices: ............................................................................................... 85
Appendix A: IR spectra ................................................................. 85
Appendix B: GC-MS spectra ............................................................ 91
Appendix C: ¹H NMR spectra ............................................................. 99
Appendix D: ¹³C NMR spectra ............................................................ 104
## List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMET</td>
<td>Acyclic diene metathesis polymerization</td>
</tr>
<tr>
<td>CM</td>
<td>Cross metathesis</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DNP</td>
<td>Double numeric polarization</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HNMR</td>
<td>Hydrogen-1 nuclear magnetic resonance spectroscopy</td>
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<tr>
<td>IP</td>
<td>Isomerisation products</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
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<td>Norbornene</td>
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<td>NHC</td>
<td>N-heterocyclic carbene</td>
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</tr>
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<td>ROM</td>
<td>Ring-opening metathesis</td>
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</tr>
<tr>
<td>Rf</td>
<td>Response factor</td>
</tr>
<tr>
<td>SCF</td>
<td>Self consistent field</td>
</tr>
<tr>
<td>SRNF</td>
<td>Solvent Resistant Nanofiltration</td>
</tr>
<tr>
<td>SMP</td>
<td>Secondary metathesis products</td>
</tr>
<tr>
<td>SM</td>
<td>Self metathesis</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin-layer chromatography</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
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Chapter 1. Introduction and Aims of Study

1.1 Introduction

The term metathesis is derived from the Greek words *meta* (change) and *tit hemi* (place). In chemistry it refers to a reaction in which the carbon-carbon double bonds in alkenes are broken and rearranged in a statistical fashion to form new alkenes.¹

Metal-catalysed alkene metathesis have a huge impact on organic synthesis, and is one of the most often used chemical transformation processes.² In 1966 Natta (Nobel Prize in Chemistry, 1963) and co-workers showed that combinations of tungsten hexachloride with either triethylaluminium or diethylaluminium chloride polymerize cycloheptene, cyclooctene and cyclododecene.³ The following year Calderon and co-workers reported their extension of these findings to other cycloalkenes using a mixture of tungsten hexachloride and ethylaluminium chloride as an initiator.⁴,⁵ Calderon suggested that the polymerization of cyclic alkenes to polyalkenes and the disproportionation of acyclic alkenes are the same type of reaction and named the reaction alkene metathesis.⁶ The contribution of metathesis reaction in the 21st century is still evident. Yves Chauvin, Robert H. Grubbs and Richard R. Schrock were awarded the Nobel Prize in Chemistry in 2005 for their outstanding work in the field of alkene metathesis.⁷

There are however three kinds of catalytic systems namely, homogeneous, heterogeneous and biological catalysts. Homogeneous catalysts offer high catalytic activity and selectivity. In homogeneous catalysis the metal complex is available to the substrate when the catalyst is completely soluble in the reaction media, however recovery is generally more difficult.⁸-¹⁰ In this study we will focus on homogeneous catalysis.

The most important homogeneous catalyst systems for metathesis are derived from compounds of the non-italised nine transition metals shown in Table 1.1; those shown in bold are generally the most effective.¹
Table 1.1 Transition metals used for metathesis catalysts.

<table>
<thead>
<tr>
<th>IVb</th>
<th>Vb</th>
<th>Vlb</th>
<th>VIIb</th>
<th>VIII</th>
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<tr>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Co</td>
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<tr>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
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<tr>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
</tr>
</tbody>
</table>

Traditional tungsten pre-catalyst for metathesis is WCl$_6$/EtAlCl$_2$.$^{11-13}$ Basset et al. introduced tungsten catalytic systems W(O-2,6-C$_6$H$_3$X$_2$)$_2$X$_4$ (X = Cl, Br and Ph) which are active, stable and can be handled in air.$^{16,17}$ High activities are obtained in the presence of co-catalysts like R$_n$AlCl$_{3-n}$, R$_4$M (R = methyl or butyl, M = Sn or Pb) alkyltinhydrides.$^{12,13,16,17}$

The cost and problematic separation of homogeneous catalysts from reaction products in solution has hampered the commercialisation of many excellent homogeneous catalysts. This leads to an increasing need for recycling. One possibility is the use of dendritic catalysts or catalytic dendrimers such as 1 and 2 below.$^{16-20}$ Catalytic dendrimers show kinetic behaviour, activity and selectivity of a homogeneous catalyst, with the advantage of the heterogeneous catalyst, that they can be removed from the reaction mixture by solvent resistant nanofiltration (SRNF) membrane techniques (Figure 1.1) and therefore can be recycled.$^{19,21-24}$

![Chemical structures](image-url)
One disadvantage of dendritic catalysts is that they have a flexible skeleton. This means that they change in size and shape in solution and this may cause the dendritic catalysts to escape through the pores of the nanofiltration membrane. This drawback can be overcome by the incorporation of aromatic or alicyclic molecules as ligands, which will help maintain the dendrimer shape in solution. Alicyclic hydrocarbons, especially the carbocyclic ‘cage’ compounds, for example, could be used to prepare derivatives with the diallyl ether functionality that can serve as three dimensional cores and also as ligands for the catalysts. These compounds can be used to synthesise novel alicyclic diene derivatives with stable and rigid polycyclic carbon skeletons. These ligands would have a less flexible skeleton, addressing the problem stated above.

**1.2 Aims and objectives**

The aim of this study is to synthesise a $\text{W(O-2,6-C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}_4$ catalyst with cage alicyclic hydrocarbons as ligands, test its metathesis behaviour and investigate the reaction mechanism theoretically.
To achieve this, the following objectives are set:

- An extensive literature study on large and bulky compounds, and especially their use as ligands in homogeneous catalysis must be conducted;
- the 'cage' alicyclic compounds must be synthesised;
- the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalysts with cage alicyclic hydrocarbons as ligands must be synthesised;
- the above mentioned catalysts must be tested for metathesis activity of 1-octene; and
- the nature of the active species of the Basset's, Beerens's³³ (1), Mbhele's³⁴ (2) and the above mentioned catalysts, and their mode of formation must be elucidated by means of computational methods.

1.3 References

34. Mbhele ZH, *Experimental Investigation of Dendritic Catalysts for Alkene Metathesis*, MSc Dissertation, North-West University, 2006
Chapter 2. Literature Review

2.1 Introduction

The term alkene metathesis was first introduced by Calderon in 1967 to describe the skeletal transformations of unsaturated hydrocarbons.¹ Alkene metathesis can be described as the interchange of carbon atoms between a pair of double bonds.² Alkene metathesis has developed to become an interdisciplinary field, comprising aspects of organic and inorganic chemistry, coordination and organometallic chemistry, homogeneous and heterogeneous catalysis, reaction kinetics, thermodynamics, chemical engineering and materials science.³

In 1931, Schneider and Frohlich⁸ observed the pyrolytic combination of propene molecules to form ethene and butene, which was a non-catalytic metathesis reaction. Although it is generally thought that Banks and Bailey⁹ discovered the metathesis reaction in 1964, Eleuterio¹⁰,¹¹ had already patented it in 1957. He observed the formation of a propene-ethene copolymer from propene in the presence of a MoO₃/Al₂O₃/LiAlH₄ catalytic system.¹¹ The first open publication on alkene metathesis was a report by Truett et al.¹⁵ in 1960 on the ring opening metathesis polymerisation (ROMP) of norbornene. Banks and Bailey applied the process of Evering and Peters¹²,¹³ for the transformation of propene into ethene and 2-butene on supported molybdenum oxide in 1964 in the Phillips Triolefin Process.¹⁴ The reaction was initially known as alkene disproportionation until the term ‘alkene metathesis’ was used in 1967 with the discovery of the first homogeneous WCl₆/EtOH/EtAlCl₂ catalytic system, which produced both metathesis and polymerisation products.¹ It was not until the discovery of heterogeneous and homogeneous catalysts, which could promote the reaction at lower temperatures and minimise side-reactions, that the potential of the metathesis reaction was realised.¹⁶ It is with transition metals that metathesis has become a very useful organic reaction.

In the presence of transition metal complexes, the metal carbene is generated and can be controlled to facilitate the metathesis reaction into subdivisions of metathesis (Figure 2.1).²,⁴,⁵ The switching of groups between two acyclic alkenes, i.e. homo- or self-metathesis (SM) and cross metathesis (CM); formation of dienes from cyclic and acyclic alkenes, i.e. ring-opening metathesis polymerization (ROMP); closure of large rings, i.e. ring-closing metathesis (RCM); polymerization of cyclic alkenes, i.e. acyclic diene metathesis polymerization (ADMET).
One of the most impressive features of the reaction is the fact that metathesis can be catalysed homogeneously and heterogeneously by catalysts containing the same elements.\textsuperscript{6} These reactions are generally reversible and thermoneutral, and equilibrium can be obtained in a matter of seconds.\textsuperscript{7}

The most important homogeneous catalyst systems are derived from transition metal complexes. Transition metal complexes have a central metal atom, with either ions or groups of atoms called ligands bonded to it. The ligands surround the metal atom and form a polyhedron with the metal in the centre. The most frequently observed geometries are octahedral, tetragonal pyramidal, trigonal pyramidal, tetrahedral and square planar.\textsuperscript{17} The range of effective transition metal compounds is continually being extended by the manipulation of ligands.\textsuperscript{2}
2.2 The development of alkene metathesis catalysts

Early developments in alkene metathesis involved the generation of active catalysts from MoO$_3$, WCl$_6$, W(O)Cl$_4$ and Re$_2$O$_7$ in the presence of alkylating agents (such as AlR$_3$, LiR, or SnR$_4$) or alumina in ethanol or chlorobenzene.$^{6,8,18,19}$ Despite tremendous advances in the area of alkene metathesis, there is still a need to develop more efficient catalysts, i.e. highly active, stable, stereoselective and compatible with functional groups.$^{20,21}$ This study will focus on obtaining a catalyst that could be separated from products by filtration without losing activity of the catalyst.

2.2.1 Tungsten(VI) aryloxide complexes

The use of ethanol as an activator for metathesis in the WCl$_6$/EtAlCl$_2$ catalyst system is well known.$^{22}$ A number of phenoxides of tungsten have been documented$^{23-25}$ and were believed to show metathesis activity similar to that of the ethanol-activated WCl$_6$/EtAlCl$_2$ system.$^{23-25}$ The presence of the aromatic ring in the phenoxides also affords the possibility of making systematic changes in the steric and electronic properties of the ligands on the tungsten by incorporation of different substituents on the phenol.$^{26}$

The stereoselectivity of alkene metathesis have been investigated using cis and trans substrates since, in principle, they could elucidate the contribution of steric factors in the mechanism of metathesis.$^{22,27-29}$ Dodd and Rutt$^{30}$ found that by using acyclic alkenes, the consistency of the cis/trans ratios obtained for the products at zero conversion with a wide variety of catalysts, was an unexpected result. However, several explanations for that were given,$^{31-33}$ for example, metathesis of internal and terminal alkenes, as well as olefinic esters, can be achieved with the complexes W(OAr)$_2$Cl$_4$ (OAr = O-2,6-C$_6$H$_3$Me$_2$, O-2,6-C$_6$H$_3$(C$_6$H$_5$)$_2$, O-2,6-C$_6$H$_3$Br$_2$, O-2,6-C$_6$H$_3$Cl$_2$ and O-2,6-C$_6$H$_3$F$_2$) (Figure 2.2) associated with MR$_4$ (M = Sn, Pb; R = Me, n-Bu).$^{34}$
Figure 2.2 Tungsten(VI) aryloxide pre-catalyst with different substituents.\textsuperscript{34}

For \textit{cis}-2-pentene metathesis, many parameters play a role in the activity: the electron withdrawing property of the aryloxide ligand, the nature of the cocatalyst and the time of interaction between the precursor and the cocatalyst.\textsuperscript{34} For a given cocatalyst and a given time of interaction, the activity varies with the nature of the substituent in o,o'-'position on the aryloxide (X = CH\textsubscript{3} < C\textsubscript{6}H\textsubscript{5} < F < Cl < Br). For a given precursor complex and a given time of interaction, the activity increases with the nature of the cocatalyst in the following order: SnMe\textsubscript{4} < Sn(n-Bu)\textsubscript{4} < Pb(n-Bu)\textsubscript{4}. For a given catalyst and cocatalyst, there is an optimum time of interaction before introducing the alkene. The stereochemical results obtained with W(OAr)\textsubscript{2}Cl\textsubscript{4} and Pb(n-Bu)\textsubscript{4} show an increase of the stereoselectivity with the nature of the aryloxide substituents in the following order F \approx Cl < Br < Me < Ph.\textsuperscript{34}

In the late 90’s Vosloo et al.\textsuperscript{35,36} reported the tungsten compounds with the aryloxide ligands, i.e., W(O-2,6-C\textsubscript{6}H\textsubscript{3}X\textsubscript{2})\textsubscript{2}Cl\textsubscript{4} (X = Cl, Ph) and Bu\textsubscript{4}Sn, as catalytic systems for the metathesis of 1-alkenes of varying carbon lengths. They found that the catalytic system was activated at 85°C for 20 minutes prior to use and that the optimum metathesis activity with 1-alkenes was observed at 85°C and a Sn/W molar ratio = 3. They further summarized that the W(O-2,6-C\textsubscript{6}H\textsubscript{3}X\textsubscript{2})\textsubscript{2}Cl\textsubscript{4}/Bu\textsubscript{4}Sn catalytic system is very active for the metathesis of 1-alkenes with a carbon chain length of about six to eight and it favours a more polar solvent such as chlorobenzene. Alkylation of W(OAr)\textsubscript{2}Cl\textsubscript{4} by MR\textsubscript{4} (M = Sn, Pb; R = Me, n-Bu) has been investigated for the determination of the coordination sphere of the catalyst.\textsuperscript{34,35} The results obtained with M = Sn and OAr = O-2,6-C\textsubscript{6}H\textsubscript{3}Br\textsubscript{2} or O-2,6-C\textsubscript{6}H\textsubscript{3}Cl\textsubscript{2} suggest a process of double alkylation, \textalpha-H elimination and reductive elimination of alkene leading to SnR\textsubscript{3}Cl and W(OAr)\textsubscript{2}Cl\textsubscript{2}(CHR’) + RH (Scheme 2.1). Side reactions of \textbeta-H elimination which would give a tungsten species and an alkene were also observed.\textsuperscript{35}
Tungsten(VI) aryloxide complexes of the type W(O-2,6-C₆H₃X₂)₂Cl₄ (X = Cl, Br, Ph), are known to be very active metathesis catalysts in the presence of cocatalysts like EtAlCl₂, Et₃Al₂Cl₃ or R₄M (R = methyl or butyl, M = Sn or Pb). The problem with these catalysts is their separation from products after the catalytic reaction. Addition of dendrimers or large ligands to these catalysts can address this challenge.

### 2.2.2 Ligands

The key to successful development of homogeneous catalysts has been the exploitation of the effects that ligands exert on the properties of metal complexes. By adjusting the electronic and steric properties of a catalyst, selectivities and rates can be changed. If the Cl-ligands of the WCl₆-catalyst are substituted with oxyaryl or alkoxy groups the activity of the metathesis catalyst can be drastically influenced. The presence of the aromatic ring in the aryloxide ligand enhances the possibility to change the substituents on the ring, and thus to influence the electronic as well as the steric properties of the ligands on the tungsten core.
Ligands such as NH$_3$ and H$_2$O, which have a lone pair for interaction with the metal, form classical coordination complexes with metal atoms. They are formed only by interaction of the ligand electrons with empty $d$ orbitals of the metal. Ligands including Cl$^-$, Br$^-$, I$^-$, and OH$^-$ have two or more filled orbitals which can interact with two empty $d$ metal orbitals (Figure 2.3). One of the ligand orbitals ($\rho_x$) forms a $\sigma$ bond, but the second ($\rho_y$), which must be oriented perpendicular to the metal-ligand axis, can only form a bond having no rotational symmetry; it is therefore called a $\pi$ bond.

![Figure 2.3 Back-bonding involving two filled ligand orbitals and two empty metal $d$ orbitals.](image)

The electronic structure of metal carbene alkene complexes can be described as a combination of donor–acceptor interactions between the HOMO (Highest Occupied Molecular Orbitals) of the ligand and the LUMO (Lowest Unoccupied Molecular Orbitals) of metal carbene located at the carbene carbon. The HOMO are the electron rich and interacts as nucleophiles, while the LUMO are electron deficient and interacts as electrophiles. The difference in energy between these orbitals and the overlap between them will largely determine the probability of the reaction from occurring. Recently HOMO/LUMO energies of ligands have been reported for different properties such as ionisation potentials, electron affinities and HOMO-LUMO energy gaps. In this study, the HOMO-LUMO energy gaps between tungsten complexes and different ligands will be investigated.
2.2.3 Dendritic catalysts

The term dendrimer is derived from the Greek word *dendra*, meaning a tree. Ideally, dendrimers are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture.37 Dendrimers are produced in an iterative sequence of reaction steps, in which each additional iteration leads to a higher generation material. The first example of an iterative synthetic procedure toward well-defined branched structures has been reported by Vögtle,37 who named this procedure a ‘cascade synthesis’. These molecules are chemically inert, compatible with most organometallic reagents38,39 and easy to prepare.

Dendrimers have nanoscopic dimensions and can be molecularly dissolved. In other words, dendrimers will combine the advantages of homo- and heterogeneous catalysts, when soluble dendrimers with defined catalytical sites are developed that can be removed from homogeneous reaction mixtures by simple separation techniques (i.e., ultrafiltration or dialysis).40 There are two ways in which the active species or the metal can be placed within the dendrimer, first is within the core of the dendrimer and second is at the periphery of the dendrimer. In this study, we investigate the latter case. In periphery functionalised dendrimers, the transition metal is directly available for the substrate, in contrast to core-functionalised systems in which the substrate has to penetrate the dendrimer before it is converted.

Steric crowding was reported in organometallic dendrimers with high catalytic loading.41,42 An investigation of the catalytic activity of the organometallic dendrimers by several groups has generally led to a conclusion that the performance of these systems decreases with an increase in surface congestion due to extensive branching of dendritic structure.41,42 The interactions between neighbouring metal centres in these congested scaffolds contribute significantly to the lower rates of catalysis with an increasing number of generations.41,43 For example, Van Koten et al.44 in their study with periphery functionalised silicon dendrimers with aryl nickel(II) centres capable of catalysing the Kharasch addition of perhaloalkanes to alkenes, reported that the local concentration of nickel centres resulted in an interaction between neighbouring Ni(II) and Ni(III) sites formed during the catalytic reaction.

In one of the studies on W-carbosilane dendrimers45 it was found that by increasing the reaction time, W-alkylidenes present on the carbosilane periphery react mutually by an intermolecular metathesis reaction (Scheme 2.2). Two metal complexes are deactivated due to a dismutation, resulting in a coupling between two dendrimer units. As a result, two metal complexes (one of each dendrimer branch) are eliminated from the dendrimer surfaces and an unidentified tungsten species is formed.
Scheme 2.2 Synthesis of starpolymers by dismutation.\textsuperscript{45}

One disadvantage of the metallic dendrimers is that they have a flexible skeleton.\textsuperscript{43} This means that they change size and shape in solution, and this may cause the first and second generation dendrimers to leak through the nanofiltration membrane. Even higher generation dendrimers are still not fully retained by nanofiltration membranes.\textsuperscript{43,44} This drawback can be overcome by incorporation of alicyclic molecules in the skeleton of the dendrimer, which will help maintain the dendrimer shape in solution.\textsuperscript{46}
2.2.4 Carbocyclic ‘cage’ compounds

An alicyclic compound is an organic compound that is both aliphatic and cyclic. These compounds contain one or more all-carbon rings which may be either saturated or unsaturated, but do not have aromatic character. These compounds have been the subject of various interesting investigations over the past few decades. With the exception of adamantane, most saturated alicyclic cage molecules contain considerable strain energy as evidenced by the fact that they

i. contain unusually long framework carbon-carbon $\sigma$-bonds,

ii. contain unusually C-C-C bond angles that deviate significantly from 109.5°,

iii. possess unusually negative heats of combustion, and

iv. possess unusually positive heats of formation when compared with nonstrained systems.

These properties contribute to the unusual chemical reactivity and exceptional thermal stability of these so-called “cage” or “bird-cage” compounds. In this study we focus on the pentacyclo[5.4.0.0$^2$,6.0$^3$.10.0$^5$.9]undecane-8,11-dione (8) derivative as a starting material of ligands for the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$ precatalyst. This compound is synthesised by photocyclisation of the endo-conformer of the Diels-Alder adduct 7 (Scheme 2.3).
Scheme 2.3 Synthesis route of the cage compounds.

This study will focus on the alicyclic tungsten-type pre-catalyst with 8 as a starting material. Although there are several molybdenum\textsuperscript{51} and platinum\textsuperscript{52} based alicyclic ligands 9 and 10 (Figure 2.4) reported in literature, there is no alicyclic tungsten based pre-catalyst reported in literature.

Figure 2.4 Literature catalysts containing alicyclic ligands\textsuperscript{51,52}
Recently, Kotha et al.\textsuperscript{53} showed that highly functionalised cage compounds can be prepared via cross-metathesis using a ruthenium catalyst. Some of these polycyclic compounds are highly symmetrical in nature, and possess inherent ring strain. Due to the lack of conformational mobility, their molecular architecture has generated considerable attention.\textsuperscript{53} The synthesis of ‘cage’ molecules can thus take part in catalytic metathesis reactions such as photo-thermal metathesis reactions.

\textbf{2.3 Reaction mechanism of alkene metathesis}

A variety of mechanisms were suggested during the seventies for the olefin metathesis reaction based on experimental and theoretical studies.\textsuperscript{2} The different mechanisms can be divided into two groups which are the pair-wise and non-pairwise mechanisms.

\textbf{2.3.1 Pairwise mechanism}

The ‘pairwise’ exchange between two alkenes in the coordination sphere of a metal via a weakly held cyclobutane-type complex mechanism was initially considered as the metathesis mechanism.\textsuperscript{2,22} A number of different mechanisms have been studied and the proposed intermediates (Figure 2.5) were suggested to be the quasi-cyclobutane,\textsuperscript{57} the tetramethylene metal-complex,\textsuperscript{58} or the tetra-methylene ring complex.\textsuperscript{59,60}
Although the quasi-cyclobutane mechanism indicated that the reaction involved the cleavage of the C-C double bonds and not the transfer of groups attached to the double bond,\textsuperscript{22} minimal experimental support was obtained. Therefore Pettit \textit{et al.}\textsuperscript{58} proposed a tetramethylene complex in which four methylene units are bonded to a central metal atom. In a further attempt to explain alkene metathesis, Grubbs \textit{et al.}\textsuperscript{59} proposed that the redistribution of groups around the double bonds was due to a rearranging metallacyclopentane intermediate and not a tetramethylene complex. Later, he suggested that one mode of rearrangement could lead to formation of a cyclobutane complexed to a metal carbene as illustrated in Figure 2.5.\textsuperscript{60} Grubbs’s reaction mechanism received support from studies of the metal catalysed [2+2] cycloaddition reaction e.g. valence isomerisation of cubane of syn-tricyclooctadiene,\textsuperscript{61} cycloaddition reactions of norbornadiene\textsuperscript{62} and rearrangements of exo-tricyclo[3.2.1.0.2,4]octene,\textsuperscript{63} but was eventually discarded in favour of the non-pairwise metal carbene chain mechanism (abbreviated to carbene mechanism), in which the propagating species is a metal carbene complex formed from the catalyst/substrate system.
2.3.2 Non-pairwise mechanism

In 1971, Herrison and Chauvin\textsuperscript{64} suggested that the olefin metathesis is initiated by a metal carbene. The metal carbene mechanism is the generally accepted mechanism for the alkene metathesis reaction (Scheme 2.4). The mechanism consists of successive [2+2]-cycloadditions followed by cycloreversions. This involves the coordination of the alkene to the metal centre to form a \( \pi \)-complex followed by the formation of a metallacyclobutane intermediate, which in turn can revert to a new \( \pi \)-complex to yield the products after dissociation.

\[
\begin{align*}
\text{R}_1\text{R}_2\text{R}_1\text{R}_2 & \quad \text{[M]} \quad \text{R}_1\text{R}_2\text{R}_1\text{R}_2 & \quad \text{[M]} \quad \text{R}_1\text{R}_2\text{R}_1\text{R}_2 & \quad \text{[M]} \quad \text{R}_1\text{R}_2\text{R}_1\text{R}_2 & \quad \text{[M]} \quad \text{R}_1\text{R}_2\text{R}_1\text{R}_2
\end{align*}
\]

Scheme 2.4 Chauvin's metallacyclobutane mechanism.\textsuperscript{64}

Initially this proposal received little support, but by 1975 the evidence in its favour became so compelling that the pairwise mechanism was discarded.\textsuperscript{22} For example, labelling experiments (Scheme 2.5) revealed that the kinetic product of the metathesis of 1,7-octadiene derivatives is a statistical distribution (1:2:1) of \( d_0 \)-, \( d_2 \)- and \( d_4 \)-labelled ethene and not a non-statistical distribution (1:1.6:1) as predicted by the pairwise mechanism.\textsuperscript{65-67}

\[
\begin{align*}
\text{CH}_2\text{CH}_2 & \quad + \quad \text{CD}_2\text{CD}_2 & \quad \text{catalyst} & \quad \text{CH}_2\text{CH}_2 & \quad + \quad \text{CD}_2\text{CD}_2
\end{align*}
\]

Scheme 2.5 Labelling experiment to confirm the Chauvin mechanism for the alkene metathesis reaction.
With the discovery of well-defined carbene complexes of Ta, Mo, W, Re and Ru which would act as initiators without the need for activation by heat, light or cocatalyst, spectroscopic techniques could be used to detect the propagating metal-carbene and intermediate metallacyclobutane complexes in some of these systems. This provided additional support for the Chauvin mechanism.

2.4 Molecular modelling in alkene metathesis reactions

One of the main questions or aims of a computational study has to be the exploration of the mechanism of a given reaction, and in our case that of the alkene metathesis reaction. Molecular modelling can be used to investigate reactions in which the active species either has a very short lifetime, or is present in very low concentrations, so that it cannot be easily isolated. Through the construction of a potential energy surface (PES), viz. a plot of energy vs. reaction coordinate, a number of quantities which are of interest in molecular modelling, inter alia equilibrium and transition state (TS) geometries and energies, can be directly obtained. Although it is possible to derive TS energies experimentally from the kinetic data relative to reactants and/or products, only a qualitative idea of the TS structure can be obtained. This is mainly due to the fact that the techniques available for structure elucidation are either too slow or not sensitive enough. Molecular modelling or theoretical methods can therefore be used to describe TS structures, conformer analysis, frontier orbitals and can also be applied to the design of new catalytic systems.
The energy minima and maxima points on the PES are usually referred to as stationary points. The energy minima, also referred to as local minima, correspond to stable molecules (reactants and products), and while energy maxima correspond to transition states. An intermediate on the PES refers to species that may be too reactive during a reaction to allow easy isolation and characterisation.

The energy minima along the PES given in Figure 2.6 correspond to equilibrium geometries with relative energies relating to thermochemical stabilities. Therefore, the overall process in Figure 2.6 is thermodynamically favoured and therefore exothermic. The position of TS’s along the reaction coordinate usually corresponds to TS geometries and their energies to kinetic or activation energies, relative to the local minima. The reaction step that involves the highest energy TS is referred to as the rate limiting step of the reaction. In this study, activation energies, transition states and intermediates will be investigated by employing the PES scans obtained from molecular mechanics and quantum mechanical calculations methods.

Although the alkene metathesis reaction is one of the most studied reaction in organometallic chemistry, there have been few reports dealing with modelling of this metal-catalysed reaction using quantum chemistry tools. Thus, Rappe reported the modelling of a metathesis reaction
catalysed by high-valent group VI metals and recently, a DFT study showed that the formation of imidotungsten(VI) complexes with similar ligands can give different products through the disproportionation of the intermediates. Experimental results of $^1$H NMR were explained in a 1-octene conversion reaction from the energy profile of the catalytic cycle by a ruthenium catalyst.

2.5 References

47. Griffin GW and Marchand AP, *Chem. Rev.*, 1989, **89**, 997
55. [http://courses.chem.psu.edu/chem210/quantum/quantum3.html#Highest](http://courses.chem.psu.edu/chem210/quantum/quantum3.html#Highest) [Date of access: 06 June 2011]

23

http://en.wikipedia.org/wiki/Molecular_modelling [Date of access: 06 May 2009]
Chapter 3. Results and Discussions

3.1 Introduction

The alkene metathesis reactions catalysed by tungsten(VI) aryloxide catalyst have been reported in literature.1-4 In this study, the 1-octene conversion by the W(O-2,6-C6H3Cl2)2Cl4/Bu4Sn catalytic system is reported and theoretical study of 1 and 2 is done.

In the metathesis of 1-octene by 4, various metathesis products can be formed which are: primary metathesis products (PMP), secondary metathesis products (SMP) and isomerisation products (IP). These products are summarised in Table 3.1.

Table 3.1 Products formed in the W(O-2,6-C6H3Cl2)2Cl4/Bu4Sn catalysed reactions of 1-octene

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Substrate*</th>
<th>Products*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Primary metathesis</td>
<td>C7=C</td>
<td>C7=C + C=C</td>
</tr>
<tr>
<td>1b Isomerisation</td>
<td>C7=C</td>
<td>C6=C2</td>
</tr>
<tr>
<td>1c Secondary metathesis</td>
<td>Cross metathesis</td>
<td>C7=C + C6=C2</td>
</tr>
<tr>
<td>1c Secondary metathesis</td>
<td>Homometathesis</td>
<td>C6=C2</td>
</tr>
<tr>
<td>1d Dimerisation</td>
<td>C7=C</td>
<td>C6=C6</td>
</tr>
<tr>
<td>2a Isomerisation</td>
<td>C6=C</td>
<td>C5=C2</td>
</tr>
<tr>
<td>2b Secondary metathesis</td>
<td>Cross metathesis</td>
<td>C6=C + C5=C2</td>
</tr>
<tr>
<td>2b Secondary metathesis</td>
<td>Homometathesis</td>
<td>C5=C2</td>
</tr>
<tr>
<td>3a Isomerisation</td>
<td>C5=C2</td>
<td>C4=C2</td>
</tr>
<tr>
<td>3b Secondary metathesis</td>
<td>Cross metathesis</td>
<td>C5=C + C4=C2</td>
</tr>
<tr>
<td>3b Secondary metathesis</td>
<td>Homometathesis</td>
<td>C4=C2</td>
</tr>
</tbody>
</table>

*Hydrogens omitted for clarity, i.e., C7=C is (CH3)6CH=CH2

Primary metathesis refers to the major metathesis reaction
Secondary metathesis refers to the metathesis side-reactions due to isomerisation
Scheme 2 refers to reactions due to C6=C formed in 1c
Scheme 3 refers to reactions due to C5=C formed in 2b
Cross-metathesis refers to the metathesis reaction between different alkenes
Homo-metathesis refers to the metathesis reaction between the same alkenes
3.2 Metathesis reactions with W(0-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system

The conversion of 1-octene to products during the metathesis reaction with the W(0-2,6-C₆H₃Cl₂)₂Cl₄/ Bu₄Sn catalytic system was followed by GC. A typical gas chromatogram of the products, which were identified spectroscopically by GC-MS, is shown in Figure 3.1. The major product that was identified is 7-tetradecene which is one of the desired PMP. Apart from the primary and secondary metathesis products, Bu₃SnCl and Bu₄Sn were also identified.

*alkenes abbreviation, eg; C₁₄ is 7-tetradecene.

Figure 3.1 Typical gas chromatogram of the reaction products that formed during the metathesis of 1-octene in the presence of a W(0-2,6-C₆H₃Cl₂)₂Cl₄/Bu₄Sn catalytic system.
Figure 3.2 shows the percentage yield of PMP’s, SMP’s and IP’s and the conversion of 1-octene over a period of 210 minutes. The PMP’s reach 63.6 %, SMP’s and IP’s reaches 2.5 % and 0.9 % respectively. 1-Octene is converted to 67 % of metathesis products in 30 minutes.

Figure 3.2 The conversion of 1-octene to PMPs, SMPs and IPs in the presence of the W(O-2,6-C₆H₃Cl₂)₂Cl₄/Bu₄Sn catalytic system. (temperature = 85 °C; Sn/W molar ratio = 3/1; alkene/W molar ratio = 100/1; activation time = 20 min; solvent = PhCl)

3.3 Theoretical investigation of alkene metathesis

Mechanistic studies using calculated frontier orbitals and reaction energy profiles of the tungsten complexes are presented.

3.3.1 W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system

We proposed a mechanism for the metathesis of 1-octene into higher alkenes in the presence of the W(O-2,6-C₆H₃Cl₂)₂Cl₄/Bu₄Sn catalytic system. This mechanism consists of three steps, namely; the formation of metal-carbene, activation step and the catalytic cycle.
Scheme 3.1 The formation of a metal carbene by the W(O-2,6-C₆H₃Cl₂)₂Cl₄/Bu₄Sn catalytic system.

Scheme 3.1 shows the first step which is the formation of the metal carbene 16 which occurs by α-elimination reaction, three moles of tetrabutyltin reacts with one mole of tungsten pre-catalyst to form the metal-carbene 16, tributyltin chloride and butane. Figure 3.3 shows the HOMO and LUMO pictures of the tungsten pre-catalyst (4) and their energies.

For the metal-carbene 16 to be formed from 4, a co-catalyst is required which in this case is the Bu₄Sn. Figure 3.4 shows the pictures of the HOMO and LUMO of the Bu₄Sn and their energies.
Table 3.2 shows that the smallest HOMO/LUMO energy gap between the pre-catalyst 4 and the co-catalyst (Bu₄Sn) must be between the HOMO of Bu₄Sn and the LUMO of the W(O-2,6-C₆H₃Cl₂)₂Cl₄ pre-catalyst (4). The energy gap between these two interacting molecules is 0.022396 eV.

Table 3.2 Energies of the frontier orbitals of Bu₄Sn and W(O-2,6-C₆H₃Cl₂)₂Cl₄ pre-catalyst (4)

<table>
<thead>
<tr>
<th></th>
<th>Bu₄Sn HOMO vs. 4 LUMO</th>
<th>Bu₄Sn LUMO vs. 4 HOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.218114</td>
<td>0.011730</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.195718</td>
<td>-0.195718</td>
</tr>
<tr>
<td>Bu₄Sn HOMO vs. 4 LUMO E (eV)</td>
<td>-0.218114</td>
<td>0.011730</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.195718</td>
<td>-0.195718</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.022396</td>
<td>0.207448</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.022396</td>
<td>0.207448</td>
</tr>
</tbody>
</table>

The next important aspects of orbital overlap are the symmetry and orientation of the orbitals. Figure 3.5 shows how the LUMOs of 4 and HOMOs of Bu₄Sn overlaps, the symmetry of these orbitals are the same and that their orientation allows them to approach each other with minimal steric hindrance.
The second step is the activation step of the metathesis reaction. In this step, the interaction of the metal-carbene 16 and 1-octene occurs via a [2+2] cycloaddition followed by cycloreversion. In Scheme 3.2 two possible activation steps are proposed, one route leading to the heptylidene species and the other leading to the methylidene species. These routes are determined by the orientation in which the 1-octene approaches the metal carbene to form the active species.
Scheme 3.2 Two activation routes of the metathesis of 1-octene with the W(O-2,6-C₆H₃Cl₂)₂Cl₄ catalytic system.

The frontier orbitals and the energies of the metal-carbene (16) (Figure 3.5) and 1-octene (Figure 3.6) shows the overlap to be in a geometry and size proportional for the formation of the active species i.e., the heptylidene and the methylidene, 18 and 20 respectively. There is the heptylidene route 16 to 18 and the methylidene route 16 to 20 can be distinguished, each route has two transition states 16-17 and 17-18 along the heptylidene route and 16-19 and 19-20 along the methylidene route. There exist one intermediate or the metallacyclobutane for each route, 17 for the heptylidene route and 19 for the methylidene route. The heptylidene route forms 1-pentene while the methylidene route forms 4-undecene which are the metathesis products observed in Figure 3.1.
Table 3.3 shows the energies of the frontier orbitals of the metal-carbene (16) and 1-octene, the most favourable overlap is between the metal-carbene (16) LUMO and the 1-octene HOMO which have an energy gap of 0.078222 eV. This overlap is consistent with the orbitals size, shape and geometry.
Table 3.3 Energies of the frontier orbitals of 16 and 1-octene

<table>
<thead>
<tr>
<th></th>
<th>16</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>-0.204498</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO</td>
<td>-0.13904</td>
<td>-0.009538</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>16 HOMO vs. 1-octene LUMO</th>
<th>16 LUMO vs. 1-octene HOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (eV)</td>
<td>-0.204498</td>
<td>-0.139040</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.009538</td>
<td>-0.217262</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.194960</td>
<td>0.078222</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.194960</td>
<td>0.078222</td>
</tr>
</tbody>
</table>

Scheme 3.2 shows the two activation steps of 16 leading to 18 and 20, these two species are formed by the orientation in which 1-octene approaches 16. If 1-octene approaches from the butyl face of 16 therefore 18 will be formed, but if 1-octene approaches away from the butyl face of 16 then 20 will be formed (Figure 3.7). In each approach, 1-octene is oriented accordingly such that there will be symmetry on the orbitals.

![Symmetry and orientation of 16 and 1-octene](image)

Figure 3.7 Symmetry and orientation of 16 and 1-octene.

Figure 3.8 shows the energy profile of the 1-octene activation of 16. The energies of all the structures are normalised with respect to 16 and all the energy values in the profile are given in kcal/mol units. The mechanism of this reaction occurs in a manner that the bonds break and form
simultaneously suggesting an associative mechanism. The metal-carbene (16), heptylidene (18) and methylidene (20) are all 14-electron species. The electronic energy which is required to convert 16 to the metallacyclobutane 17, is the activation energy of 32.55 kcal/mol. Once 17 is formed an energy barrier of 49.12 kcal/mol is required to form 18, which has a lower energy (-8.89 kcal/mol) than its starting material 16. The methylidene species (20) is formed via a metallacyclobutane (19) when 16 goes through an activation energy of 20.39 kcal/mol. This metallacyclobutane must overcome an energy barrier of 41.23 kcal/mol to form 20, which has an energy of 1.57 kcal/mol higher than its starting material 16.

The heptylidene route is thermodynamically favoured or is exothermic and 18 is more stable than 20. The step 16→(16-17)→17 is the rate limiting step of the heptylidene route, because 16-17 is at 32.56 kcal/mol compared to 17-18 which lies at 30.18 kcal/mol. The rate limiting step of the methylidene route is 16→(16-19)→19 which has 16-19 at 20.39 kcal/mol while 19-20 lies at 11.50 kcal/mol. Therefore the methylidene route will be most favoured because of its lower activation energy.

Figure 3.8 Electronic energy profile for the activation steps of the tungsten pre-catalyst by the metathesis of 1-octene.
The third step; which is the productive catalytic cycle of the conversion of 1-octene by the metal-carbenes 18 and 20 is shown in **Scheme 3.3**, and it is the last step in the reaction mechanism. The products of this cycle are the 7-tetradecene and ethene from two moles of 1-octene. The cycle has four transition states (18-21), (21-20), (20-22) and (22-18) and two intermediates 21 and 22. The size, shape and geometry of the orbitals are, by observation and by calculations determined for the most probable overlap, which will lead to both the heptylidene and the methylidene species.

**Scheme 3.3** The productive catalytic cycle of 18 and 20 with 1-octene.

The geometry, size and shape of the frontier orbitals of the heptylidene (18) are illustrated in Figure 3.9. **Table 3.4** shows that the frontier orbitals of the heptylidene 18 and 1-octene will overlap by the heptylidene LUMO and 1-octene HOMO, which is a combination that gives the lowest energy gap of 0.073425 eV.
Table 3.4 Energies of the frontier orbitals of the heptylidene(18) and 1-octene

<table>
<thead>
<tr>
<th></th>
<th>18</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>-0.203923</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO</td>
<td>-0.143837</td>
<td>-0.009538</td>
</tr>
</tbody>
</table>

|                      | 18 HOMO vs.     | 18 LUMO vs.     |
|                      | 1-octene LUMO   | 1-octene HOMO   |
| E (eV)               | -0.203923       | -0.143837       |
| E (eV)               | -0.009538       | -0.217262       |
| Energy difference (eV)| -0.194385      | 0.073425        |
| Absolute values      | 0.194385        | 0.073425        |

Figure 3.9 HOMO and LUMO of 18.

Figure 3.10 shows how the LUMOs of 18 and HOMOs of 1-octene overlaps, the symmetry of these orbitals are the same and that their orientation allows them to approach each other without any hindrance. This interaction will lead to the methylidene (20) and 7-tetradecene as shown in Scheme 3.3.
The second half of the catalytic cycle is the interaction of the methylidene (20) and 1-octene, leading back to 18 and thus completing the cycle. The frontier orbitals energies are presented in Table 3.5 for determining the probable overlap. The HOMO and LUMO structures of 20 are shown in Figure 3.11.

Figure 3.10 Symmetry and orientation of 18 and 1-octene.

Figure 3.11 HOMO and LUMO of 20.
Table 3.5 Energies of the frontier orbitals of 20 and 1-octene

<table>
<thead>
<tr>
<th></th>
<th>20</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.209115</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.148448</td>
<td>-0.009538</td>
</tr>
<tr>
<td>20 HOMO vs. 1-octene LUMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.209115</td>
<td>-0.148448</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.009538</td>
<td>-0.217262</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.199577</td>
<td>0.068814</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.199577</td>
<td>0.068814</td>
</tr>
</tbody>
</table>

Table 3.5 shows that the frontier orbitals will overlap by the methylidene (20) LUMO and 1-octene HOMO, which is a combination that gives the lowest energy gap of 0.068814 eV. Figure 3.12 shows how the LUMO of 20 and HOMO of 1-octene overlaps, the symmetry of these orbitals are also the same and that their orientation allows them to approach each other, therefore there will be minimal steric hindrance for these two molecules to overlap. This interaction will lead back to 18 and forms ethene as shown in Scheme 3.3 and thus completing the cycle.

Figure 3.12 Symmetry and orientation of 20 and 1-octene.
The electronic energy profile of the catalytic cycle for the productive 1-octene conversion using the metal-carbenes 18 and 20 is shown in Figure 3.13. The energies of all the structures are normalised with respect to the heptylidene (18) and all the energy values in the profile are given in kcal/mol.

Figure 3.13 The energy profile of the catalytic cycle of 1-octene conversion by the metal carbenes 18 and 20.

The formation of the metallacyclobutane (21) requires an activation energy of 37.95 kcal/mol and for this intermediate to form the methyldiene 20, 16.20 kcal/mol of energy barrier must be overcome and the first PMP, 7-tetradecene will be formed. The second metallacyclobutane (22) requires 32.3 kcal/mol of energy to be formed and to convert this intermediate back to the heptylidene (18), an energy barrier of 0.56 kcal/mol is required and the second PMP is formed namely ethene. The rate limiting step of the catalytic cycle is 18→(18-21)→21 which has the highest electronic energy of 37.95 kcal/mol. The catalytic cycle will be more possible to start at 20 which is also the more favoured route in the catalytic cycle, but as soon as the concentration of 18 is higher, the heptylidene route will then follow.
3.3.2 Beerens catalyst

The Beerens catalyst (1) is synthesised by the cross metathesis of four moles of the metal-carbene 16 and one mole of tetraallylsilane (23) (Scheme 3.4) and producing 1-pentene as a by-product.\(^5\)

Scheme 3.4 Synthesis of the Beerens Catalyst 1\(^5\).

The frontier orbitals of 23 are shown in Figure 3.14 and that of the metal-carbene (16) are shown in Figure 3.5. The smallest energy gap between the metal-carbene (16) LUMO and the tetraallylsilane (23) HOMO is indicated in Table 3.6 as 0.068322 eV.

Figure 3.14 HOMO and LUMO of the tetraallylsilane 23.
Table 3.6 Energies of the frontier orbitals of the metal-carbene (16) and tetraallylsilane (23)

<table>
<thead>
<tr>
<th></th>
<th>16</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>-0.204498</td>
<td>-0.207362</td>
</tr>
<tr>
<td>LUMO</td>
<td>-0.139040</td>
<td>-0.034566</td>
</tr>
<tr>
<td>16 HOMO vs. 23 LUMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.204498</td>
<td>-0.139040</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.034566</td>
<td>-0.207362</td>
</tr>
<tr>
<td>Energy difference E (eV)</td>
<td>-0.169932</td>
<td>0.068322</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.169932</td>
<td>0.068322</td>
</tr>
</tbody>
</table>

Figure 3.15 shows how the orbitals of 16 and 23 will overlap to form 1 and 4 molecules of 1-pentene. The symmetry of the orbitals are the same allowing the orbitals to overlap and the approach of tetraallylsilane is direct onto the orbitals of the metal-carbene (16).

The metathesis mechanism of the Basset’s and Beerens’s catalyst differ only in terms of the activation steps, the catalytic cycle is the same since the silane dendrimer/ligand of 1 is removed from the catalyst, leaving the catalyst to convert the 1-octene to PMPs, SMPs and IPs, as shown in Figure 3.2.

The two activation steps proposed for 1 are shown in Scheme 3.5 below. 1 has four peripheries in which it can interact with 1-octene, in this study we only investigated the interaction of one arm/periphery of the catalyst (1) because of calculation time and method constraints.
The frontier orbitals of 1 are shown in Figure 3.16 and in Table 3.7 the energies of the frontier orbitals of 1 and 1-octene are tabulated. From this table it is shown that the LUMO of 1 and HOMO
of 1-octene which has the smallest energy gap of 0.067778 eV, will overlap for the catalytic conversion.

Figure 3.16 HOMO and LUMO of 1.

Table 3.7 Energies of the frontier orbitals of 1 and 1-octene

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.197119</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.149484</td>
<td>-0.009538</td>
</tr>
</tbody>
</table>

Figure 3.17 shows how the frontier orbitals of 1 and 1-octene will overlap in the activation step, 1-octene can approach from the chlorine side of 1 or from the side that is between one arm of 1 and butyl side. The first approach will lead to the heptylidene (18) and 25 and the latter will lead to the methylidene (20) and 27. The HOMO and LUMO of 1 and 1-octene have the same symmetry and thus allow them to overlap with minimal steric hindrance.
Figure 3.17 Symmetry and orientation of 1 and 1-octene.

The energy profile of 1-octene activation of 1 is shown in Figure 3.18. Both the heptylidene (18) and the methylidene (20) are presented in this profile and the energy values in this graph are normalised to the energy of 1 and the units are in kcal/mol.

Figure 3.18 The energy profile of the activation steps of 1 by 1-octene.
The 1-octene activation of 1 requires 114.1 kcal/mol energy to form the metallacyclobutane (24). 25 and 18 will be formed by 24 overcoming an energy barrier of 99.13 kcal/mol. The methylidene route has the metallacyclobutane 26 which will be formed by activation energy of 86.73 kcal/mol. The methylidene species (20 and 27) will be formed by overcoming an energy barrier of 105.72 kcal/mol. The two activation steps are thermodynamically favoured since, the products (18 and 25) and (20 and 27) are lower in energy than their starting material 1. The rate limiting step for the heptylidene route is 1→1-24→24 and for the methylidene route is 26→26-27→20+27. The methylidene route will be most favoured because of its lower activation energy.

The energy profiles of both 1 in (Figure 3.18) and 16 in (Figure 3.7) shows that the methylidene route has lower activation energy. The energy of the intermediate (19) of the methylidene route in 16 is lower in energy than the intermediate (17) of the heptylidene route, while in 1, the energy of the intermediate (24) of the heptylidene route is lower in energy than the intermediate (26) of the methylidene route. The heptylidene (18) is lower in energy than the methylidene (20) energy, making 20 the more stable active species in both the activation steps of 1 and 16.
3.3.3 The G0-W$_2$ catalyst.

Scheme 3.6 shows the synthesis of 2, four moles of 4 reacts with one mole of tetrallylsilane in chlorobenzene to give the intermediate (28). The intermediate reacts with 12 moles of tetrabutyltin and forms 2, tributyltin chloride and butane.$^6$

![Scheme 3.6 Synthesis of 2.$^6$](image)

The frontier orbitals of 4 and 23 are shown in Figure 3.3 and Figure 3.14 respectively. From Table 3.8 the formation of 28 will occur from the overlap of 4 LUMO and 23 HOMO which have an energy gap of 0.011644 eV.
### Table 3.8 Energies of the frontier orbitals of 4 and 23

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.233568</td>
<td>-0.207362</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.195718</td>
<td>-0.034566</td>
</tr>
<tr>
<td><strong>4 HOMO vs. 23 LUMO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.233568</td>
<td>-0.195718</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.034566</td>
<td>-0.207362</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.199002</td>
<td>0.011644</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.199002</td>
<td>0.011644</td>
</tr>
<tr>
<td><strong>4 LUMO vs. 23 HOMO</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.18** shows the cross sectional view of the LUMOs of 4 and HOMOs of 23, the symmetry of these orbitals are the same and that their orientation allows them to approach each other and overlap with minimal steric hindrance.

**Figure 3.19** shows the frontier orbitals of 28 and that of tetrabutyltin are shown in **Figure 3.4**. **Table 3.9** shows the energies of the frontier orbitals of 28 and the tetrabutyltin, and the overlap will occur between 28 LUMO and the tetrabutyltin (23) HOMO which have energy gap of 0.037636 eV.
**Figure 3.19** HOMO and LUMO of the 28 pre-catalyst.

**Table 3.9** Energies of the frontier orbitals of tungsten pre-catalyst 28 and tetrabutyltin

<table>
<thead>
<tr>
<th></th>
<th>28</th>
<th>Bu₄Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.219944</td>
<td>-0.218114</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.180478</td>
<td>0.01173</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>28 HOMO vs. Bu₄Sn LUMO</th>
<th>28 LUMO vs. Bu₄Sn HOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (eV)</td>
<td>-0.219944</td>
<td>-0.180478</td>
</tr>
<tr>
<td>E (eV)</td>
<td>0.01173</td>
<td>-0.218114</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.231674</td>
<td>0.037636</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.231674</td>
<td>0.037636</td>
</tr>
</tbody>
</table>

**Figure 3.20** shows the LUMOs of 28 and HOMOs of Bu₄Sn, the symmetry of these orbitals are also the same and that their orientation allows them to approach each other, and therefore there will be no hindrance for these two molecules to overlap. This interaction will lead to the formation of 2, tributyltin chloride and butane (Scheme 3.6).
Figure 3.20 Symmetry and orientation of 28 and Bu₄Sn.

The mechanism of the 1-octene activation of 2 can be formulated as in Scheme 3.7. This activation leads to both the heptylidene (30) and the methyldiene (32) species. In Figure 3.21 is the two frontier orbitals of 2 with its orbital energies in eV.

![Figure 3.21 HOMO and LUMO of 2.](image)

HOMO

E = -0.160319 eV

LUMO

E = -0.143185 eV
Table 3.10 shows that the most probable overlap between the frontier orbitals of 2 and 1-octene are the LUMO of 2 and the HOMO of 1-octene, with an energy gap of 0.074077 eV.
Table 3.10 Energies of the frontier orbitals of 2 and 1-octene.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.160319</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.143185</td>
<td>-0.009538</td>
</tr>
<tr>
<td><strong>2 HOMO vs. 1-octene LUMO</strong></td>
<td><strong>2 LUMO vs. 1-octene HOMO</strong></td>
<td></td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.160319</td>
<td>-0.143185</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.009538</td>
<td>-0.217262</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.150781</td>
<td>0.074077</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.150781</td>
<td>0.074077</td>
</tr>
</tbody>
</table>

Figure 3.22 shows the symmetry and orientation of 2 and 1-octene frontier orbitals, 1-octene can approach from the chlorine side of 2 or from the side that is between one arm of 2 and the butyl side. The first approach will lead to the heptylidene (30) and the latter will lead to the methylidene (32). The HOMOs and LUMOs of 2 and 1-octene have the same symmetry and thus allow them to overlap without any hindrance.

Figure 3.22 Symmetry and orientation of 2 and 1-octene.

Molecular modelling of 2, specifically the PES scans were also done on one arm/periphery of the complex only because of computing time and method constrains. Figure 3.23 gives the energy profile of the two activation steps involved in the productive metathesis of 1-octene with 2, all the energies are normalised with respect to 2 and the units are given in kcal/mol.
Figure 3.23 Energy profile of the activation steps of 2.

In the heptylidene route, 2 requires an activation energy of 21.81 kcal/mol to form the metallacyclobutane (29). This metallacyclobutane has to overcome 25.71 kcal/mol of energy in order to form the heptylidene (30), which lies at 8.96 kcal/mol. 2 requires an activation energy of 32.35 kcal/mol to form the metallacyclobutane (31), this metallacyclobutane will have to overcome 42.76 kcal/mol of energy to form the methylidene (32), which lies at -5.58 kcal/mol. The methylidene route is thermodynamically favoured since their product 32 is lower in energy than its starting material 2 and the heptylidene is thermodynamically unfavoured. The rate limiting step of the heptylidene route is the step 2→(2-29)→29 and for the methylidene route is the step 31→(31-32)→32, therefore the heptylidene route will be most favoured because of its lower activation energy.
The heptylidene route in the activation step of 2 has a lower activation energy than the methylidene route, but the metallacyclobutane (31) of the methylidene route is lower in energy than the metallacyclobutane (29) of the heptylidene route. 32 is lower in energy than 30, which makes the methylidene species (30) to be more stable than the heptylidene species (32). The methylidene route has a higher probability to take place than the heptylidene route because of its lower activation energy.

The activation steps of the three catalytic systems considered namely; 16, 1 and 2 are compared. The activation steps of 16 and 1 are similar because both have the methylidene route with the least activation energy, and that their heptylidene products (18) and (18 + 25) respectively are lower in energy than their methylidene products (20) and (20 + 27). The difference in these two energy profiles is their intermediates; the intermediate (19) of the methylidene route in 16 is lower in energy than the intermediate (17) of the heptylidene route. The intermediate (24) of the heptylidene route in 1 is lower in energy than the intermediate (26) of the methylidene route. The energy profile of 2 is similar with the energy profile of 16 only in their intermediates, because the intermediates (19) and (31) for the methylidene route are lower in energy than the intermediates (17) and (29) of the heptylidene route. However, the energy profile of 2 has the methylidene species (32) lower in energy than the heptylidene species (30).

Scheme 3.8 shows the catalytic cycle of 2 with 1-octene using only one arm of the dendritic periphery. The catalytic cycle has four transition states (30-33), (33-32), (32-34) and (34-30) and two intermediates (33) and (34). One half of the cycle leads to the methylidene (32) and produces the 7-tetradecene, the other half leads to the heptylidene (30) and produces ethene.
Scheme 3.8 The productive catalytic cycle of 2.

Figure 3.24 shows the HOMO and LUMO of 30 which will overlap with 1-octene frontier orbitals shown in Figure 3.6. The orbitals’s size, shape and geometry of these molecules will overlap to produce 7-tetradecene and 32. This fact is in agreement with the frontier orbital energies given in Table 3.11, which indicates that the smallest energy gap is 0.085338 eV between the heptylidene (30) LUMO and 1-octene HOMO.
Table 3.11 Energies of the frontier orbitals of 30 and 1-octene.

<table>
<thead>
<tr>
<th></th>
<th>30</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.183131</td>
<td>-0.217262</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.131924</td>
<td>-0.009538</td>
</tr>
<tr>
<td>30 HOMO vs. 1-octene LUMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.183131</td>
<td>-0.131924</td>
</tr>
<tr>
<td>E (eV)</td>
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<td>-0.217262</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
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<td>0.085338</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.173593</td>
<td>0.085338</td>
</tr>
</tbody>
</table>

Figure 3.25 shows the LUMOs of 30 and HOMOs of 1-octene, the symmetry of these orbitals are the same and their orientation allows them to approach each other, there will be minimal steric hindrance for these two molecules to overlap. This interaction will lead to 32 and forming 7-tetradecene as shown in Scheme 3.8.
Examination of the frontier orbitals of 32 shown in Figure 3.26 and those of 1-octene in Figure 3.6, the orbitals will overlap by 32 LUMOs and the 1-octene HOMOs. Table 3.12 shows the energies of the frontier orbitals of 32 and 1-octene, the smallest energy gap of 0.066495 eV, for 32 LUMO and 1-octene HOMO are the most probable orbitals to overlap for this interaction.

Figure 3.25 Symmetry and orientation of 30 and 1-octene.
Table 3.12 Energies of the frontier orbitals of 32 and 1-octene.

<table>
<thead>
<tr>
<th></th>
<th>32</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
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<td>-0.217262</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.150767</td>
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<td>E (eV)</td>
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<td>-0.150767</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.162954</td>
<td>0.066495</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.162954</td>
<td>0.066495</td>
</tr>
</tbody>
</table>

Figure 3.27 shows the LUMOs of 32 and HOMOs of 1-octene, the symmetry of these orbitals are the same and their orientation allows them to approach each other, there will be no hindrance for these two molecules to overlap. This interaction will lead to 30 and forming ethene as shown in Scheme 3.8.
The electronic energy profile of the catalytic cycle for the productive 1-octene conversion using the metal-carbenes (30) and (32) is shown in Figure 3.28. The energies of all the structures are normalised with respect to the 30 and all the energy values in the profile are given in kcal/mol units.
Figure 3.28 Energy profile of the catalytic cycle of 30 and 32.

The formation of the metallacyclobutane (33) requires an activation energy of 55.0 kcal/mol, and for this intermediate to form 32 an energy barrier of 58.56 kcal/mol must be overcome and the first PMP, 7-tetradecene is formed. The second metallacyclobutane (34) requires 73.40 kcal/mol of activation energy to form and to convert this intermediate back to 30, an energy barrier of 57.12 kcal/mol must be overcome and the second PMP is generated, namely ethene. This cycle is thermodynamically favoured and 32 is more stable for it is lower in energy than 30, and the rate limiting step is $32 \rightarrow (32-34) \rightarrow 34$ which has the highest energy of 63.75 kcal/mol.
3.4 The carbocyclic ‘cage’ catalysts

In this study a method was used to attempt the synthesis of ‘cage’ carbocyclic catalysts 15 (Scheme 5.2) with the carbene on the outside (i.e., W between 3 and carbene). This meant that the W-complex will not dissociate from the dendrimers during metathesis reaction and that would make the recycling of the dendritic catalyst by nanomembrane process possible. The coordination of 12 or 3 to the W(O-2,6-C₆H₃Cl₂)₂Cl₄ system could not be achieved.

3.4.1 3,5-divinyl-4-oxahexacyclo[5.4.1.0₂,6.0₃,10.0⁵,9.0⁸,11]dodecane catalytic system

The step of the synthesis of the ‘cage’ catalyst bearing 12 as ligand is shown in Scheme 3.9. Examining the frontier orbitals of these interacting compounds i.e., 12 and 4, the most probable overlap must occur between the LUMO of 4 and the HOMO of 12 which have the energy gap of 0.008457 eV (Figure 3.29 and Table 3.13).

![Scheme 3.9 Synthesis of the cage divinyl ether catalyst.](image-url)
Table 3.13 Energies of the frontier orbitals of 12 and 4.

<table>
<thead>
<tr>
<th></th>
<th>12</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.204175</td>
<td>-0.233568</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.013281</td>
<td>-0.195718</td>
</tr>
<tr>
<td>12 HOMO vs 4 LUMO</td>
<td>-0.008457</td>
<td>0.220287</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.204175</td>
<td>-0.013281</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.195718</td>
<td>-0.233568</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.008457</td>
<td>0.220287</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.008457</td>
<td>0.220287</td>
</tr>
</tbody>
</table>

The frontier orbitals have energy values associated with them and energy gaps could be calculated. However, the symmetry and orientation of the orbitals must also match for a coordination to occur between two compounds. Figure 3.30 shows the symmetry and orientation of 4 and 12, the orbitals size and shape of these two compounds does not match. The part of the orbitals responsible for overlap are distributed along two carbon atoms in the double bond of 12 and those of 4 are on one chlorine atom only. The shapes of the orbitals on 12 are oval in shape and those in 4 are spherical and the sizes of the two different orbitals on 4 and on 12 are not equal to permit an overlap and therefore no reaction takes place.
3.4.2 3,5-diallyl-4-oxahexacyclo[5.4.1.0².⁶.0³.¹⁰.0⁵.⁹.0⁸.¹¹]dodecane catalytic system

The frontier orbitals of 3 are shown in Figure 3.31 with their energies, and Table 3.14 shows that the LUMO of 4 and HOMO of 3 must overlap with energy gap of 0.008867 eV to form a coordination.
Table 3.14 Energies of the frontier orbitals of 3 and 4.

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (eV)</td>
<td>-0.204585</td>
<td>-0.233568</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-0.009307</td>
<td>-0.195718</td>
</tr>
<tr>
<td>3 HOMO vs 4 LUMO</td>
<td>-0.008867</td>
<td>0.224261</td>
</tr>
<tr>
<td>3 LUMO vs 4 HOMO</td>
<td>-0.204585</td>
<td>-0.009307</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.195718</td>
<td>-0.233568</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-0.204585</td>
<td>-0.009307</td>
</tr>
<tr>
<td>Energy difference (eV)</td>
<td>-0.008867</td>
<td>0.224261</td>
</tr>
<tr>
<td>Absolute values</td>
<td>0.008867</td>
<td>0.224261</td>
</tr>
</tbody>
</table>

Compound 3 showed a different interaction with 4, the reaction was a chlorine addition reaction or electrophilic addition of the chlorine atoms on the double bonds of 3 instead of coupling to form the catalytic complex 14 which was the desired product (Scheme 3.10). The addition reaction lead to three identified chlorine compounds 35, 36 and 37. This result can be attributed to minute quantities of water present in the reaction mixture, since 3 was obtained as an oil instead of a powder or crystals in § 5.3.5.

Scheme 3.10 Reaction of 3 and 4.
Figure 3.32 shows the GC chromatogram of the products formed 35, 36 and 37 (Scheme 3.10) during the synthesis of 14. The most prominent peak at about 5.8 minutes is the internal standard chlorobenzene and the second dominating species is the 2,6-dichlorophenol. The peaks of 35, 36 and 37 can all be read at 21.3, 23.3 and 26.5 minutes respectively with their mass per charge.
Another peak of the unreacted 3 can be read at 18.4 minutes. One last unidentified compound appears at 20.8 minutes with a mass to charge ratio of 241. The GC-MS spectra of these identified compounds are listed in the appendices section.

The energy gap between the frontier orbitals of 3 and 4 shows also that the two compounds can overlap. However, the orbital’s size and shape of these two compounds does not match and does not allow them to coordinate. The orbitals are both round and are concentrated on only one atom in each compound. The part of the orbitals in 3 and in 4 that must overlap can only react to add chlorine atoms on the double bonds of 3 (Figure 3.33). The orbitals of both 3 and 4 are symmetrical and their orientation does allow them to interact but not to form a coordinate.

![Figure 3.33 Symmetry and orientation of 4 and 3.](image)

Synthesis of 15 (Scheme 5.2) was unsuccessful; the next step was to test if there was activity when the reaction is run in-situ. The reaction was performed as discussed in § 5.4.2. The GC chromatogram of the in situ 1-octene metathesis reaction between 3 and 4 (Scheme 5.3) at 210 minutes is given Figure 3.34. In this chromatogram, the most prominent peak is the internal standard which is chlorobenzene, followed by 1-octene, tetrabutyltin 2,6 dichlorophenol, and unreacted 3 peak can be read at 16.7 minutes. The reaction was monitored in 30 minutes intervals for 12 hours and no metathesis products were observed at any given time of the reaction.
Figure 3.34 GC Chromatogram of the *in-situ* reaction between 3 and 4.
3.5 References

Chapter 4. Conclusions

4.1 Introduction

The aim of this study was to investigate, theoretically and experimentally the W(O-2,6-C6H3Cl2)2Cl4 catalyst and to synthesise ‘cage’ alicyclic ligands that will help retain the catalyst during the membrane separation process. Experimental work was done on the W-carbosilane dendritic catalysts 1 and 2.1,2 These catalysts have shown good activity, but their mode of formation and their reaction energy profiles have been unknown and inconclusive.1,2 Synthesis of ‘cage’ carbocyclic catalysts was attempted and the results were negative.

4.2 Theoretical and experimental investigation of W(O-2,6-C6H3Cl2)2Cl4

The conversion of 1-octene into PMPs, SMPs and IPs over a period of 210 minutes was in good comparison with literature results.3 The PMP’s reached 63.6 %, SMP’s and IP’s reaches 2.5 % and 0.9 % respectively, 1-octene was converted to 67 % of metathesis products in 30 minutes.

The coordination of the co-catalyst (Bu4Sn) to the W(O-2,6-C6H3Cl2)2Cl4 pre-catalyst to form the metal-carbene (16) occurs through an overlap of the pre-catalyst LUMO and the co-catalyst HOMO. The activation step via the methylidene route is more favoured because of its low activation energy, compared to that of the heptylidene route which is higher. However, the heptylidene route is thermodynamically favoured and 18 is a more stable species than 20. The catalytic cycle is thermodynamically favoured since the methylidene (20) is lower in energy than the heptylidene (18). The orbitals symmetry and orientations of all the metal-carbenes and ligand/1-octene are in an accessible position for reactions to occur.

4.3 W-carbosilane dendritic catalysts

Compound 1 is formed through cross metathesis, from the overlap of the LUMO of the metal-carbene (16) and the HOMO of tetraallylsilane (23). The LUMO of 1 overlaps with the HOMO of 1-octene in the activation step and forms the heptylidene (18) and the methylidene (20), together with two silane by-products 25 and 27. The HOMO and LUMO of 1 and 1-octene have the same symmetry and thus allow them to overlap without any steric hindrance. The two activation steps are thermodynamically favoured since, the products (18 and 25) and (20 and 27) are lower in energy than their starting material 1; the methylidene route will be a much preferred route in the activation step because of its low activation energy. However, the heptylidene (18) and its by-product 25 are more stable.
Compound 2 is formed in two steps; the LUMO of \( W(\text{O}-2,6-\text{C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}_4 \) overlaps with the HOMO of tetraallylsilane (23) to give the intermediate (28), which its LUMO will overlap with the \( \text{Bu}_4\text{Sn} \) HOMO to form 2. The LUMO of 2 will undergo 1-octene activation with the HOMO of 1-octene leading to the heptylidene (30) and the methylidene (32). The orbitals’s symmetry and orientation of 2 and 1-octene indicates a good coordination without any hindrance. The heptylidene route will be more favoured than the methylidene route because of its low activation energy, however the methylidene species (32) is thermodynamically more stable than the heptylidene species (30) and it is lower in energy than its starting material 2.

4.4 Cage carbocyclic catalysts

The formation of the catalytic complexes using 12 or 3 as ligands with the \( W(\text{O}-2,6-\text{C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}_4 \) system could not be obtained. Compound 3 reacts with 4, and the reaction is a chlorine addition reaction or electrophilic addition of the chlorine atoms on the double bonds of the ligand instead of coupling to form the catalytic complex 14 which was the desired product. The orbitals of 12 are distributed along the double bonds and do not permit a coordination to occur. The formation of 35 and 36 are attributed to minute quantities of water present in the starting material. No metathesis products were observed in the \textit{in-situ} reaction of 3 or 12 with \( W(\text{O}-2,6-\text{C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}_4 \) as catalyst using 1-octene.

4.5 Recommendations

To fully and eloquently describe the theoretical metathesis behaviour of 1 and 2, a PES scan method must be developed to comprehend all the four arms/peripheries of the catalysts. Experimental results of the 1-octene metathesis must be performed to compare properties such as kinetics and thermodynamics with the theoretical results. Synthesis of 3 and 12 and the \textit{in-situ} metathesis reactions must be performed in an inert atmosphere such as glove boxes to prevent any presence of water in the products.

4.6 References

Chapter 5. Experimental

5.1 Solvents and reagents

5.1.1 Solvents

Chlorobenzene (Merck) and chloroform (Merck) were dried with calcium chloride and stored over 4Å molecular sieves, benzene (Holpro), ethanol (Saarchem), dichloromethane (Labchem), hexane (Labchem), methanol (Merck), ethyl acetate (Saarchem), n-hexane (Labchem) were all used as obtained from the supplier. Tetrahydrofuran (Saarchem) was distilled under nitrogen from sodium with benzophenone as indicator before use and was stored over 4Å mol sieves.

5.1.2 Reagents

The alkene, 1-octene (Aldrich), was passed through a neutral alumina column for purification and was stored under a nitrogen atmosphere. Dicyclopentadiene (Fluka) was distilled and used immediately. p-Benzoquinone (Riedel-de Haën), allyl magnesium bromide (Aldrich), vinyl magnesium bromide (Aldrich), tetraallylsilane (Fluka), toluene-4-sulfonic acid (BDH), magnesium sulfate (Saarchem) were used as obtained from the supplier. Bu₄Sn (Aldrich), the phenolic compound 2,6-dichloro-phenol (Aldrich) was used as obtained from the supplier. All the gasses used for purification and drying of solvents were supplied by Afrox.

5.2 Apparatus

An experimental setup (Figure 5.1) was used for the synthesis of the 2,6-disubstituted aryloxide tungsten(VI) pre-catalyst 4.
The metathesis reactions were carried out by small scale setup shown in Figure 5.2. 5 mL glass mini reactors with plastic screw tops that have a small opening on top for the syringe needle (the screw tops can be turned open and close by a stop cock) and Hamilton-gastight syringes were used for the reactions. The mini reactor containing a small magnet insulated with plastic was heated in an aluminium block on a hot plate with 4, Bu₄Sn, 1-octene and PhCl as an internal standard.
5.3 Experimental procedure

The synthesis of 3 and 12 ligands is shown in Scheme 2.3. The procedure involves a reaction of a 1:1 mole ratio of cyclopentadiene with p-Benzquinone to give the adduct 7, upon irradiation of 7 in methanol compound 8 is formed. Compound 8 was reacted with an excess of vinylmagnesium bromide or allylmagnesium bromide in THF to form 11 or 13 respectively. Both 11 and 13 were reacted with dilute hydrochloric acid to give the expected 12 and 3. All the spectra of the synthesised compounds can be found in the appendices section.

5.3.1 Synthesis of pentacyclo[5.4.0.02,6.03,10.05,9]undecane-8,11-dione (8)
Equivalent molar amounts of cyclopentadiene and p-benzoquinone were used. Cyclopentadiene (11 mL) was added slowly (10 mL per min) into a solution of p-benzoquinone (18 g) in 150 mL benzene. The reaction was stirred for 12 hours in the dark, covered with aluminium foil. The reaction was monitored with TLC, with benzene-chloroform-diethylether (1:2:1) as eluent to make sure that all the p-benzoquinone is used up in the reaction. The reaction solution was concentrated in vacuo and the residue was recrystallised from petroleum ether, light yellow adduct was obtained (18.5 g, 81%). A solution of the adduct (3.08 g; 0.23 mol) in 300 mL ethyl acetate was irradiated for 12 hours with a Hanovia medium-pressure Hg lamp (Pyrex filter). The solution was concentrated, whereupon ‘cage’ dione crystallized as a white, microcrystalline solid (2.95 g, 78%).

Melting point : 236-237°C.

Infrared spectrum : $\nu_{\text{max}}$ 3 000, 1 756, 1 068 cm$^{-1}$

Mass spectrum : m/z 174 (M$^+$)

$^1$H NMR spectrum : (CDCl$_3$, 600 MHz) $\delta$H 1.95 ppm (d, 2 x H), 2.79 ppm (s, 2 x H), 3.15 ppm (q, 2 x H), 2.91 ppm (q, 2 x H), 2.68 ppm (d, 2 x H)

$^{13}$C NMR spectrum : (CDCl$_3$, 600 MHz) $\delta$C 38.7 ppm (2 x C$_2$,6), 43.8 ppm (2 x C$_1$,7), 44.6 ppm (2 x C$_3$,5), 40.5 ppm (1 x C$_4$), 212.1 ppm (2 x C$_9$,11), 54.7 ppm (2 x C$_9$,10)

5.3.2 Synthesis of exo-8-exo-11-divinylpentacyclo[5.4.0.0$^2$,6.0$^3$.10.0$^5$.9]undecane-endo-8-endo-11-diol (11)$^2$

To a solution of 8 (Scheme 2.3) (1.00 g, 5.74 mmol) in dry THF (10 mL) under nitrogen was added with stirring a 1 molar solution vinylmagnesium bromide in dry THF (22.9 mL, 22.9 mmol). The resulting solution was stirred at ambient temperature for 3 h and then it was heated to 50 °C and was stirred at that temperature for an additional 12 h. The reaction mixture was cooled to 0 °C via application of an external ice-water bath, and the reaction was quenched via addition of cold
saturated aqueous NH₄Cl (10 mL). The resulting aqueous suspension was extracted with EtOAc (3 x 30 mL), and the combined organic layers were washed with water (10 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated in vacuo. Dark brown oil was obtained (0.74 g, 59 %).

Infrared spectrum : ν\text{max} 2969, 1412, 1271, 1116, 1069, 989, 915, 672 cm⁻¹

Mass spectrum : m/z 207 (M⁺)

¹H NMR spectrum : (CDCl₃, 600 MHz) δH 2.44 ppm (d, 2 x H), 2.45 ppm (t, 2 x H), 2.36 ppm (q, 2 x H), 1.07 ppm (t, 2 x H), 2.15 ppm (d, 2 x H), 1.97-2.24 ppm (d, 2 x H), 5.90 ppm (t, 2 x H), 5.01 ppm (d, 2 x H), 5.30 ppm (s, 2 x OH)

¹³C NMR spectrum : (CDCl₃, 600 MHz) δC 40.0 ppm (2 x C₂,6), 42.8 ppm (2 x C₁,7), 44.0 ppm (2 x C₃,₅), 33.9 ppm (1 x C₄), 72.2 ppm (1 x C₈), 49.1 ppm (2 x C₉,₁₀), 77.2 ppm (1 x C₁₁), 44.0 ppm (2 x C₁'), 133.8 ppm (2 x C₂')

5.3.3 Synthesis of 3,5-divinyl-4-oxahexacyclo[5.4.1.0²,6.0³,10.0⁵,9.0⁸,11]dodecane (12)

The diol 11 (1.00 g) was refluxed in dilute HCl for one hour. The solution was allowed to cool to ambient temperature and it was extracted with diethyl-ether. The extract was neutralised with sodium bicarbonate solution and dried with sodium sulphate. The solution was concentrated in vacuo and a light brown oil was obtained (0.56 g, 66 %).

Infrared spectrum : ν\text{max} 2968, 1412, 1271, 1068, 915, 672 cm⁻¹

Mass spectrum : m/z 212 (M⁺)

¹H NMR spectrum : (CDCl₃, 600 MHz) δH 2.44 ppm (d, 2 x H), 2.45 ppm (t, 2 x H), 2.36 ppm (q, 2 x H), 1.07 ppm (t, 2 x H), 2.15 ppm (d, 2 x H), 1.97-2.24 ppm (d, 2 x H), 5.90 ppm (t, 2 x H), 5.01 ppm (d, 2 x H)
A mechanically stirred suspension of allyl-magnesium bromide (15 mL of a 0.392 $M$ solution in dry THF, excess) was cooled to 0 °C using an external ice bath. To this suspension, 8 (1.10 g; 336 mmol) in 75 mL dry THF was added dropwise with vigorous stirring at 0 °C over a period of 2 hours. After the addition of 8 had been completed, the external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring under nitrogen for 24 hours. The reaction was quenched by dropwise addition of saturated aqueous NH$_4$Cl solution until a pH of ca. 6-7 was reached. The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic extracts were dried with MgSO$_4$ and filtered, and the filtrate was concentrated in vacuo. The residue was recrystallized from hexane, thereby affording 13 as a brown oil, (0.44 g, 51 %).

**Infrared spectrum**: $\nu_{\text{max}}$ 3071, 2955, 1639, 1436, 1282, 1154, 1050, 911 cm$^{-1}$

**Mass spectrum**: m/z 217 (M$^+$)

$^1$H NMR spectrum: (CDCl$_3$, 600 MHz) $\delta_H$ 2.44 ppm (d, 2 x H), 2.45 ppm (t, 2 x H), 2.36 ppm (q, 2 x H), 1.07 ppm (t, 2 x H), 2.15 ppm (d, 2 x H), 1.97-2.24 ppm (d, 2 x H), 5.90 ppm (t, 2 x H), 5.01 ppm (d, 2 x H), 5.30 ppm (s, 2 x OH)

$^{13}$C NMR spectrum: (CDCl$_3$, 600 MHz) $\delta_C$ 40.0 ppm (2 x C$_{2,6}$), 42.8 ppm (2 x C$_{1,7}$), 44.0 ppm (2 x C$_{3,5}$), 33.9 ppm (1 x C$_4$), 72.2 ppm (1 x C$_8$), 49.1 ppm (2 x C$_{9,10}$), 77.2 ppm (1 x C$_{11}$), 44.0 ppm (2 x C$_{1'}$), 133.8 ppm (2 x C$_{2'}$), 117.9 ppm (2 x C$_3'$)
5.3.5 Synthesis of 3,5-diallyl-4-oxahexacyclo[5.4.1.0².⁶.0³.⁰.⁹.⁰^8.¹¹]dodecane (3)

The diol 13 (1.00 g) was refluxed in dilute HCl for one hour. The solution was allowed to cool to ambient temperature and it was extracted with diethyl-ether. The extract was neutralised with NaHCO₃ solution and dried with Na₂SO₄. The solution was concentrated in vacuo and a light brown oil was obtained 3 (0.49 g, 55 %).

Infrared spectrum : \( \nu_{\text{max}} 2959, 1639, 1437, 1293, 993, 908 \text{ cm}^{-1} \)

Mass spectrum : m/z 240 (M⁺)

\(^1\text{H NMR spectrum} : (\text{CDCl}_3, 600 \text{ MHz}) \ \delta_\text{H} 2.44 \text{ ppm (d, 2 x H)}, 2.45 \text{ ppm (t, 2 x H)}, 2.36 \text{ ppm (q, 2 x H)}, 1.07 \text{ ppm (t, 2 x H)}, 2.15 \text{ ppm (d, 2 x H)}, 1.97-2.24 \text{ ppm (d, 2 x H)}, 5.90 \text{ ppm (t, 2 x H)}, 5.01 \text{ ppm (d, 2 x H)}

\(^{13}\text{C NMR spectrum} : (\text{CDCl}_3, 600 \text{ MHz}) \ \delta_\text{C} 40.0 \text{ ppm (2 x C}_2,6\text{), 42.8 ppm (2 x C}_1,7\text{), 44.0 ppm (2 x C}_3,5\text{), 33.9 ppm (1 x C}_4\text{), 72.2 ppm (1 x C}_8\text{), 49.1 ppm (2 x C}_9,10\text{), 77.2 ppm (1 x C}_11\text{), 44.0 ppm (2 x C}_1\text{), 133.8 ppm (2 x C}_2\text{), 117.9 ppm (2 x C}_3\text{)}

5.3.6 Purification of WCl₆

WCl₆ was transferred into a round bottom flask under N₂. It was then heated at a temperature of 250 °C, and tungsten oxide compounds (yellowish-red) which have a sublimation temperature lower than that of WCl₆ were removed by a constant nitrogen flow. WCl₆ was heated under N₂ until all tungsten oxides have been removed; dark-purple crystals of WCl₆ remained in the flask. WCl₆ was stored under argon to avoid oxidation indicated by colour change from dark-purple to yellow. The crystals were used in the preparation of W(O-2,6-C₆H₃Cl₂)₂Cl₄ complex.
5.3.7 Synthesis of W(O-2,6-C₆H₃Cl₂)₂Cl₄⁴

A solution of HO-2,6-C₆H₃Cl₂ (0.839 g; 5.1 mmol) in 20 mL chloroform was added to a solution of WCl₆ (1.02 g; 2.56 mmol) suspended in 20 mL of chloroform in a round bottom flask. The reaction mixture was stirred under reflux for 4 hours. During the reaction, the reaction mixture turned from red to dark red. Filtration of the mixture followed by recrystallisation from ethanol gave W(O-2,6-C₆H₃Cl₂)₂Cl₄ (1.4 g; 85%) as black microcrystals with a green lusture. The synthesis was carried out under inert environment.

Infrared spectrum : νₘₐₓ 1 556, 1 436, 1 246, 1 099, 915, 777 cm⁻¹

5.3.8 Synthesis of ‘cage’ compound catalysts⁶

W(O-2,6-C₆H₃Cl₂)₂Cl₄ complex (0.30 g; 3.08 x 10⁻⁴ mol) was added into a mini reactor (1, 2 and 3 in Figure 5.2) under nitrogen. Dry chlorobenzene (0.3 mL) was added as a solvent to the complex, using a Hamilton-gastight syringe (4 and 5 in Figure 5.2). The reaction mixture was heated at 85°C for 10 minutes (6 in Figure 5.2). ‘Cage’ diallyl ether ligand 3 (0.074 g; 3.08 x 10⁻⁴ mol) dissolved in chlorobenzene (0.3 mL) was added to the mixture (4 and 5 in Figure 5.2). The solution was heated and stirred for 90 minutes under nitrogen (6 in Figure 5.2). Scheme 5.2 shows the synthetic route of the cage diallyl ether catalyst 15, the coordination of 3 and 4 to produce 14 that will be alkylated with Bu₄Sn to 15 could not be obtained.

![Scheme 5.2 Synthesis of 15.⁶]
5.4 Metathesis reactions

5.4.1 W(O-2,6-C₆H₃Cl₂)₂Cl₄ complex

The tungsten(VI) aryloxide complex 4 (0.016 g; 2.5 x 10⁻⁵ mol) was transferred under nitrogen into a 5 mL mini reactor (1, 2 and 3 in Figure 5.2). Chlorobenzene (0.3 mL) was added as a solvent to the complex, using a Hamilton-gastight syringe (4 and 5 in Figure 5.2). The mixture was heated at 85 °C for 10 minutes (6 in Figure 5.2). Bu₄Sn, the co-catalyst, (0.025 mL; 0.75 x 10⁻⁵ mol) was added (4 and 5 in Figure 5.2) to the heated mixture. The reaction mixture was heated at 85 °C for 20 minutes (6 in Figure 5.2). After 20 minutes which is the activation time, 1-octene (0.5 mL; 2.5 x 10⁻³ mol) was added (4 and 5 in Figure 5.2). The reaction mixture was stirred at 85 °C (6 in Figure 5.2) and followed with a GC for 210 minutes.

5.4.2 ‘Cage’ compound catalysts

The next step was the same reaction when it is run in situ. W(O-2,6-C₆H₃Cl₂)₂Cl₄ (0.30 g; 3.08 x 10⁻⁴ mol) was added into a mini reactor (1, 2 and 3 in Figure 5.2) under nitrogen. Dry chlorobenzene (0.3 mL) was added as a solvent to the complex, using a Hamilton-gastight syringe (4 and 5 in Figure 5.2). The reaction mixture was heated at 85 °C for 10 minutes (6 in Figure 5.2). ‘Cage’ diallyl ether, 3 ligand (0.074 g; 3.08 x 10⁻⁴ mol) dissolved in chlorobenzene (0.3 mL) was added to the mixture (4 and 5 in Figure 5.2). The solution was heated and stirred for 90 minutes under nitrogen (6 in Figure 5.2). Bu₄Sn (0.025 ml; 0.075 x 10⁻⁴ mol) was added by using a Hamilton-gastight syringe (4 and 5 in Figure 5.2) and heated for further 90 minutes. 1-Octene (0.5 ml; 2.5 x 10⁻³ mol) was added and the reaction was followed with a GC, Scheme 5.3 shows the reaction of the in situ metathesis of 3 with 1-octene.

![Scheme 5.3 in situ metathesis of the cage diallyl ether catalyst.](image)

The reactions in Scheme 5.2 and in Scheme 5.3 were also performed with 12 as a ligand using the same reaction conditions and the same results were obtained.
5.5 Analysis

5.5.1 Gas Chromatography (GC)

GC analyses were performed on an HP 6890 gas chromatography equipped with a Phenomenex 80646 (ZB-1) column (50.0 m x 250 μm x 0.50 μm) and flame ionisation detector (FID). The following temperature programme and analytical conditions were used.

Oven programme:

\[ \text{70 °C for 3 min} \rightarrow \text{10 °C min}^{-1} \rightarrow \text{250 °C for 10 min} \]

Inlet temperature: 250 °C
Detector temperature: 250 °C
N₂ carrier gas flow: 1.2 mL/min
Fuel gas flow
  H₂ flow rate: 40 mL/min
  Air flow rate: 450 mL/min
Injection volume: 0.2 μL
Split ratio: 50:1

Chlorobenzene was used as the internal standard to determine the mole percentage of 1-octene converted to the primary metathesis products, secondary metathesis products and isomerisation products. The GC response factor (Rf) was calculated from a calibration curve plotted as $A_{\text{chlorobenzene}}/A_{\text{octene}}$ against $V_{\text{chlorobenzene}}/V_{\text{octene}}$ (Figure 5.3). A response factor of 0.9933 for 1-octene was calculated from the slope of the calibration curve.
Figure 5.3 Calibration curve for determining the response factor.

Equation 5.1 was used to determine the mol percentage conversion of 1-octene to 7-tetradecene:

\[
\text{mol}\%C_8 = 100 \times R_f \times \frac{V_{is}}{V_{C8}} \times \frac{A_{C8}}{A_{is}}
\]  

(5.1)

Where

- \( C_8 \) = 1-octene
- \( R_f \) = GC response factor
- \( V_{is} \) = Volume of the internal standard at \( t = 0 \)
- \( V_{C8} \) = Volume of the 1-octene at \( t = 0 \)
- \( A_{C8} \) = Area of 1-octene
- \( A_{is} \) = Area of the internal standard

Equation 5.2 was used to determine the mol percentage of 7-tetradecene formed during the reaction:

\[
\text{mol}\%C_n = 2 \times R_f \times \left( V_{is} \frac{A_{Cn}}{A_{is}} \right) \times \frac{\rho_{Cn}}{M_{Cn}} \times \left( \frac{M_{C8}}{\rho_{C8} \times V_{C8}} \right) \times 100
\]  

(5.2)

Where
C_n  =  Alkene  
R_f  =  GC response actor  
V_{is}  =  Volume of the internal standard at t = 0  
V_{C8}  =  Volume of the 1-octene at t = 0  
A_{Cn}  =  Area of the alkene  
A_{is}  =  Area of the internal standard  
M_{Cn}  =  Molecular mass of C_n  
M_{C8}  =  Molecular mass of 1-octene  
\rho_{Cn}  =  Density of C_n  
\rho_{C8}  =  Density of 1-octene  

5.5.2 Gas Chromatography-Mass Spectrometry (GC-MS)  

MS analyses were performed on an HP 6890 GC-MS equipped with a PE-001 capillary column (60 m x 0.32 mm x 1.00 μm, Elite Methyl Siloxane) connected to an Autospec Micromass Time-of-Flight (TOF) mass spectrometer. The NIST database of the OPUS v 3.6 X software was used for characterisation of the products identified during analysis. The temperature programme and analytical conditions used were similar to those used in GC. 100 mg of the sample was weighed and dissolved in 2 mL diethyl-ether in a GC vial for analysis.  

5.5.3 Infrared spectroscopy (IR)  

The IR spectra were recorded using a FTIR Bruker Tensor 27 equipped with a diamond ATR. The software OPUS version 6.5 was used for data analysis.  

5.5.4 Nuclear Magnetic Resonance spectroscopy (NMR)  

A Bruker Advance III Ultra Shield 600 MHz Nuclear Magnetic Resonance spectrometer (NMR); for the \(^1\)H and \(^{13}\)C spectroscopy was used. TopSpin 2.1 Version 2.1.1 was used for processing commands and parameters as well as data acquisition. Approximately 40 mg of the sample was dissolved in 0.7 mL of CDCl\textsubscript{3} in an NMR tube.
5.6 Computational details

5.6.1 Hardware

There were two types of hardware used for this study:

i) 52 CPU cluster (HP Proliant CP4000 Linux Beowulf with Procurve Gb/E Interconnect on computer nodes):
   1 x Master node: HP DL385 - 2 x 2.8 MHz AMD Opteron 64, 2 GB RAM, 2 x 72 GB HDD
   12 x Compute nodes: HP DL145G2 - 2 x 2.8 MHz AMD Opteron 64, 2 GB RAM, 2 x 36 GB HDD
   Operating system on compute nodes: Redhat Enterprise Linux 4
   Cluster operating system: HPC CMU v3.0 cluster

ii) 336 CPU Cluster
   1 x Master Node: HP BL460C G6 - 2 Quad Core 2.93 GHz, 16GB RAM, 2 146 GB HDD
   40 X Compute Nodes :HP BL460C G6 - 2 Quad Core 2.93 GHz, 16GB RAM, 2 146 GB HDD, ProLiant BL2x220c G5, HP BL460C G1
   1 x HP EVA 4400 SAN 3TB
   1X Storage Server :HP BL460C G6
   Operating system on compute nodes: Scientific Linux SL release 5.3
   Cluster operating system : Rocks 5.2 - Scientific Linux SL release 5.3

5.6.2 Software

All molecular modelling calculations were performed using the Accelrys Material Studio 5.0. Geometric optimizations and determinations of properties were calculated with the Density Functional Theory (DFT) method DMol³ using the GGA functional PW91 together with the following specifications:

- A medium quality of convergence tolerance using $2 \times 10^{-5}$ Ha (Energy), 0.004 Ha/Å (Max. force) and 0.005 Å (Max. displacement)
- A medium Self Consistent Field (SCF) of $1 \times 10^{-5}$ Ha using a maximum of 1000 SCF cycles and octupole multipolar expansion
- A Double Numeric Polarized (DNP) basis set
5.7 References


7. North-West University High Performance Computer Centre
   *http://efundi.nwu.ac.za/access/wiki/site/4ba488f2-2b27-43be-b5f4f1d97148ec98/home.html*
   Year 2010 [Date of access: August 2010]
Appendices

Appendix A: IR spectra

IR spectrum of 4.
IR spectrum of 8.
IR spectrum of 11.
IR spectrum of 12.
IR spectrum of 13.
IR spectrum of 3.
Appendix B: GC-MS spectra

GC-MS spectrum of 8.
GC-MS spectrum of 11.
GC-MS spectrum of 12.
GC-MS spectrum of 13.
GC-MS spectrum of 3.
GC-MS spectrum of 35.
GC-MS spectrum of 36.
GC-MS spectrum of 37.
Appendix C: $^1$H NMR spectra

$^1$H NMR spectrum of 8.
$^1$H NMR spectrum of 11.
$^1$H NMR spectrum of 12.
$^1$H NMR spectrum of 13.
$^1$H NMR spectrum of 11.
Appendix D: $^{13}$C NMR spectra

$^{13}$C NMR spectrum of 8.
$^{13}$C NMR spectrum of 11.
$^{13}$C NMR spectrum of 12.
$^{13}\text{C}$ NMR spectrum of 13.
$^{13}$C NMR spectrum of 3.