

Synthesis and modelling of imine derivatives as ligands for Grubbs type pre-catalysts

By

Mpho Princess Motoboli

BSc, Hons. BSc

Dissertation submitted in partial fulfillment of the requirements for the degree

MAGISTER SCIENTIAE

IN

CHEMISTRY

at the North West University (Potchefstroom Campus)

Supervisor: Dr JHL Jordaan

Co-supervisor: Dr G Lachmann

Potchestroom

2010

Dedicated to my parents with love

Acknowledgements

Thanks to the almighty God for his grace, power, blessing and unconditional love to carry out the study.

I would like to sincerely thank the following people who made a difference in my studies without them this study would not be possible:

- ❖ Prof Vosloo my study leader for allowing me to be part of the Synthesis and Catalysis group and always securing funds for the study.
- ❖ Dr Johan my supervisor for his shared knowledge, understanding, support, suggestions and motivation, and for always asking me for results.
- ❖ Dr Lachmann for his tremendous knowledge, whenever I had to consult him he always had something intelligent to say and was amused by his vocabulary, how he interprets my writing.
- ❖ Dr van Sittert for helping me with modeling and her support throughout the study
- ❖ Andre Joubert for NMR analysis, Lynette van der Walt, Andrew Fouche and Dr Williams for their assistance for lab ware.
- ❖ All students in the Catalysis and Synthesis group. Ronel and Justus who were always eager to help, Carlijn for helping with pre-catalyst synthesis, Sam Xaba to be my lab mate.
- ❖ Center of Excellence in Catalysis (c*change) and North West University for financial support.
- ❖ Prof Smit for initiating this study, for mentoring me and for his support.
- ❖ My parents, my sister and her husband, twin sister and brother for their motivation, love and support. They always believed in me.

Mpho Princess Motoboli

Table of Contents

Table of contents.....	i
-------------------------------	----------

List of abbreviations and structures.....	viii
--	-------------

Summary.....	xii
---------------------	------------

Opsomming.....	xiii
-----------------------	-------------

Chapter 1: *Aims and Objectives*

1.1	Introduction.....	1
1.2	Aims and Objectives.....	6
1.3	References.....	7

Chapter 2: *Literature Survey*

2.1	Introduction.....	10
2.2	Pre-catalysts.....	12
2.2.1	Homogeneous pre-catalysts.....	12
2.2.1.1	Molybdenum.....	13
2.2.1.2	Tungsten.....	15
2.2.1.3	Ruthenium.....	16
2.3	Mechanism.....	17
2.3.1	Ruthenium carbene mechanism.....	19
2.4	Ligands.....	22
2.4.1	Hemilabile ligands: chelate ligands.....	26
2.5	Molecular modeling.....	28
2.5.1	Computational study on Grubbs type pre-catalysts.....	29

2.6	Theoretical investigation on Grubbs type pre-catalyst to address the research problem.....	31
2.6.1	Electron density.....	31
2.6.2	Electrostatics.....	32
2.6.3	Fukui function.....	33
2.6.3.1	Nucleophilic.....	33
2.6.3.2	Electrophilic.....	33
2.6.4	Orbitals: HOMO/LUMO.....	33
2.6.5	Population analysis.....	34
2.7	Summary on literature survey.....	34
2.8	References.....	35

Chapter 3: *Alkene Metathesis: Theoretical investigation*

3.1	Program and properties.....	41
3.2	References.....	44

Chapter 4: *Experimental*

4.1	Reagents and solvents.....	45
4.2	Apparatus.....	45
4.3	Synthesis.....	45
4.3.1	Synthesis of Schiff base ligands.....	45
4.3.1.1	Synthesis of 1-[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol.....	47
4.3.1.2	Synthesis of 1-[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol.....	47
4.3.2	General method for the synthesis of sodium salts.....	48
4.3.3	General method for the synthesis of thallium salts.....	49
4.4	Synthesis of Grubbs type pre-catalysts.....	50
4.4.1	General method for the synthesis of substituted Grubbs type pre-catalysts using sodium salts.....	50

4.4.2	General method for the synthesis of substituted Grubbs type pre-catalysts using sodium salts.....	51
4.5	Metathesis: Experimental investigation.....	54
4.6	Analysis.....	54
4.6.1	IR.....	54
4.6.2	GC-MS.....	55
4.6.3	NMR.....	56
4.6.3.1	NMR analysis for catalyst.....	56
4.7	GC analysis for metathesis reactions.....	56
4.8	Response factor.....	58
4.9	Calculations.....	59
4.10	References.....	61

Chapter 5: *Results and discussions*

5.1	Metathesis: Theoretical investigation.....	62
5.1.1	HOMO.....	65
5.1.2	Electrostatic potential.....	66
5.1.3	Electron density with electrophilic Fukui function.....	67
5.1.4	Population analysis: atomic charge.....	68
5.2	Summary of discussions on the ligands.....	69
5.3	Discussions of the modeled pre-catalysts.....	70
5.4	Synthesis.....	79
5.5	Metathesis.....	84
5.5.1	Metathesis reaction 1 and 2 with 1-octene.....	84
5.5.2	Comparison of activity and selectivity of synthesized pre-catalysts 75 and 76 with 1 and 2	87
5.6	References.....	88

Chapter 6: *Conclusions and recommendations*

6.1	Introduction.....	90
------------	--------------------------	-----------

6.2	Molecular modeling of imine ligands and the substituted pre-catalysts.....	90
6.3	Synthesis of ligands and substituted Grubbs type pre-catalysts.....	91
6.4	Metathesis of substituted Grubbs 2 type pre-catalyst.....	92
6.5	Recommendations.....	92
6.6	References.....	93

Appendix I:	The table containing the HOMO energies of the possible Ligands.....	95
Appendix II:	MS Spectra.....	99
Appendix III:	IR Spectra.....	103
Appendix IV:	¹H NMR Spectra.....	110
Appendix V:	¹³C NMR Spectra.....	122
Appendix VI:	Maldi-Tof MS Spectra.....	129

List of Figures

Figure 1.1:	The milestone in the development of olefin metathesis.....	2
Figure 1.2:	Grubbs first and second generation pre-catalysts.....	3
Figure 1.3:	Possible Schiff base pre-catalysts.....	4
Figure 1.4:	Schiff base Grubbs type pre-catalyst.....	4
Figure 1.5:	A series of salicylideneaniline (SA) derivatives.....	5
Figure 2.1:	Activation of several types of ruthenium olefin metathesis pre-catalysts.....	24
Figure 2.2:	Schematic representation of hemilability.....	26
Figure 3.1:	Energy profile graph.....	42
Figure 4.2:	Experimental setup for metathesis reaction.....	55
Figure 4.3:	GC-MS chromatograph of 1 for the metathesis reaction with 1-octene at 60 min and 1:9000 (Ru:1-octene) molar ratio.....	57
Figure 4.4:	GC-MS chromatograph of 2 for the metathesis reaction with 1-octene at 60 min and 1:9000 (Ru:1-octene) molar ratio.....	57
Figure 4.5:	Graph for the determination of response factor.....	58

Figure 5.1:	The HOMO energy of the ligands.....	63
Figure 5.2:	The HOMO orbitals of 28 , 68 and 69	65
Figure 5.3:	The HOMO orbitals of 28 , 68 and 69 ligands after the removal of the hydrogen atom.....	66
Figure 5.4:	Electrostatic Potential of 28 , 68 and 69	67
Figure 5.5:	Electron densities with electrophilic Fukui function of 28 , 68 and 69	68
Figure 5.6:	The LUMO orbital of 1	71
Figure 5.7:	Coordination of the HOMO orbital of the ligands with the LUMO orbital of the metal centre of the pre-catalyst.....	71
Figure 5.8:	LUMO orbital of 73 and 74	73
Figure 5.9:	Energy profile for pre-catalysts 73 and 74 for the coordination of 1-octene <i>cis</i> to the carbene.....	74
Figure 5.10:	Energy profile for pre-catalysts 73 and 74 for the coordination of 1-octene <i>trans</i> to the carbene.....	75

List of Schemes

Scheme 1.1:	Olefin metathesis reaction.....	1
Scheme 1.2:	The mechanism of the catalyzed olefin metathesis.....	1
Scheme 2.1:	Several distinct olefin metathesis reactions.....	11
Scheme 2.2:	Preparation of the Schrock pre-catalyst.....	13
Scheme 2.3:	Mechanistic steps explaining kinetics of Schrock pre-catalyst.....	14
Scheme 2.4:	The first tungsten pre-catalyst for ROM.....	16
Scheme 2.5:	Preparation of Grubbs carbene complex.....	16
Scheme 2.6:	ROMP catalyzed by well-defined Ru carbene complex.....	17
Scheme 2.7:	Chauvin's mechanism, proposed in 1971, for the catalyzed olefin metathesis involving metal alkylidene and metallacyclobutane intermediates.....	18
Scheme 2.8:	Mechanism for metathesis by Grubbs-type Ru carbene complexes....	19
Scheme 2.9:	Associative and dissociative mechanisms by Grubbs-type Ru carbene complexes.....	21

Scheme 2.10: Mechanism for metathesis with catalytic systems with Schiff-base ligands.....	27
Scheme 3.1: The mechanism of the catalyzed olefin metathesis.....	42
Scheme 3.2: Activation cycle of path 1 and path 2.....	43
Scheme 5.1: Activation cycle: Reaction path 1.....	77
Scheme 5.2: Activation cycle: Reaction path 2.....	78

List of Graphs

Graph 5.1: The conversion of 1-octene and the formation of PMP with 1	85
Graph 5.2: The conversion of 1-octene and the formation of PMP with 2	85
Graph 5.3: The formation of IP during metathesis with 1 and 2	86
Graph 5.4: The formation of SMP during metathesis with 1 and 2	86
Graph 5.5: The formation of PMP, IP and SMP during metathesis with the synthesized pre-catalyst 76	87

List of Tables

Table 5.1: Ligands HOMO energies.....	63
Table 5.2: Population analysis: atomic charge on oxygen and nitrogen atoms of 28 , 68 and 69	69
Table 5.3: Dissociation energy of 1 , 73 and 74	73
Table 5.4: Selectivity of the synthesized pre-catalysts 75 and 76 in comparison to 1 and 2	88

List of Spectrum

Spectrum 1: MS spectra of ligand 68	100
Spectrum 2: MS spectra of ligand 69	101
Spectrum 3: IR spectra of ligand 68	104
Spectrum 4: IR spectra of ligand 69	105
Spectrum 5: IR spectra of pre-catalyst 75	106
Spectrum 6: IR spectra of pre-catalyst 76	107

Spectrum 7:	IR spectra of pre-catalyst 1	108
Spectrum 8:	¹ H NMR spectra of ligand 68	111
Spectrum 9:	¹ H NMR spectra of ligand 69	112
Spectrum 10:	¹ H NMR spectra of sodium salt one.....	113
Spectrum 11:	¹ H NMR spectra of thallium salt one.....	114
Spectrum 12:	¹ H NMR spectra of thallium salt two.....	115
Spectrum 13:	¹ H NMR spectra of Pre-catalyst C1Gr1_{Na}	116
Spectrum 14:	¹ H NMR spectra of Pre-catalyst 75	117
Spectrum 15:	¹ H NMR spectra of Pre-catalyst 76	118
Spectrum 16:	¹ H NMR spectra of Pre-catalyst 1	119
Spectrum 17:	¹ H NMR spectra of Pre-catalyst 2	120
Spectrum 18:	¹³ C NMR spectra of ligand 68	123
Spectrum 19:	¹³ C NMR spectra of ligand 69	124
Spectrum 20:	¹³ C NMR spectra of S1 _{Na}	125
Spectrum 21:	¹³ C NMR spectra of S1 _{Tl}	126
Spectrum 22:	¹³ C NMR spectra of S2 _{Tl}	127
Spectrum 23:	Maldi-Tof spectra of Pre-catalyst 75	130
Spectrum 24:	Maldi-Tof spectra of Pre-catalyst 76	131

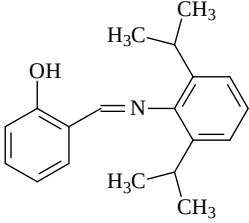
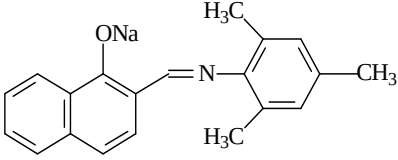
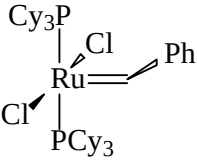
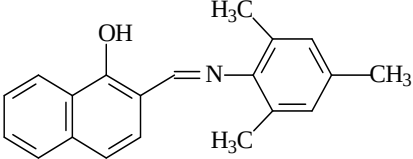
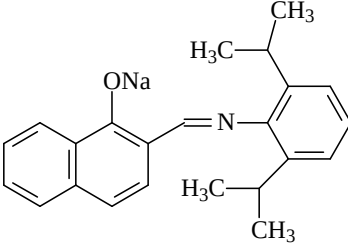
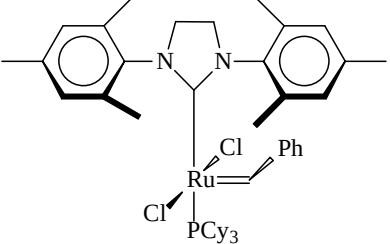
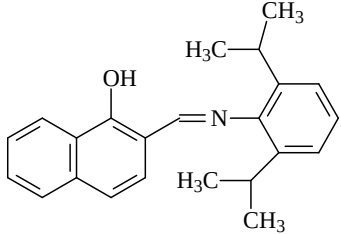
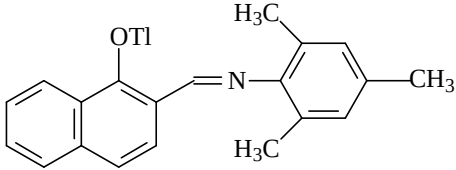
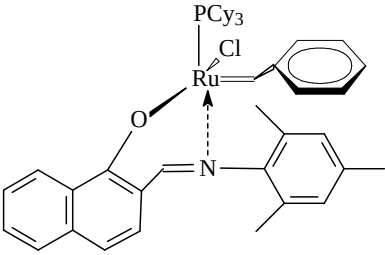
List of abbreviations and numbering of structures

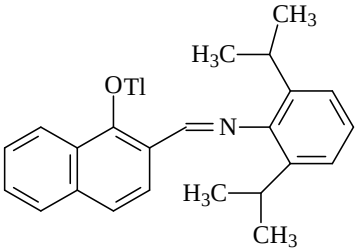
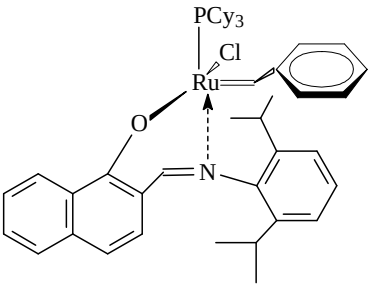
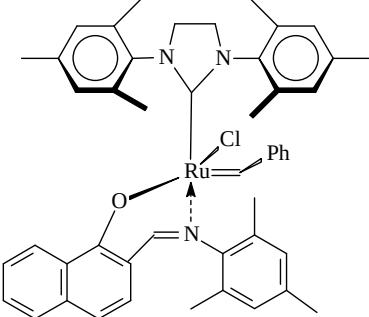
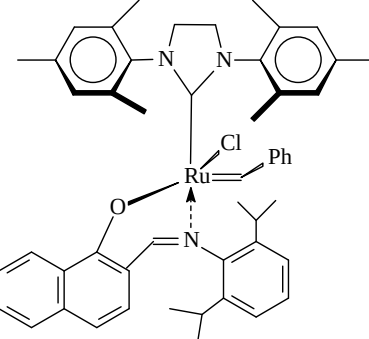
Abbreviations:

ADMET	Acyclic diene metathesis
CM	Cross metathesis
Cy	Cyclohexyl
¹³ C NMR	Carbon-13 nuclear magnetic resonance
DFT	Density functional theory
DNP	Double numeric polarized
EN	Enyne metathesis
GC	Gas chromatography
GGA	Generalized gradient approximation
HOMO	highest occupied molecular orbital
H ₂ IMes	1,3-bis-(2,4,6-trimethyl)-2-imidazolidinylidene
¹ H NMR	Proton nuclear magnetic resonance
IP	Isomerisation products
IR	Infrared spectroscopy
LUMO	Lowest unoccupied molecular orbital
M	Transition metal ion
MM	Molecular mechanics
MS	Mass Spectroscopy
NaH	Sodium hydride
NHC	N-heterocyclic carbene
PCy ₃	Tricyclohexylphosphine
PMP	Primary metathesis products
PES	Potential Energy Surface
QM	Quantum mechanics
QSPR	Quantitative structure-property relationship
QSAR	Quantitative structure-activity relationship
RCM	Ring closing metathesis
ROM	Ring opening metathesis
ROMP	Ring-opening metathesis polymerization

S	Selectivity
SA	Salicylideneaniline
SE	Semi-empirical
SCF	Self-consistent field
SMP	Secondary metathesis products
RF	Response factor
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TON	Turnover number
TS	Transition State

Numbering of structures

Ligands	Salts	Pre-catalysts
 28	 S1_{Na}	 1
 68	 S2_{Na}	 2
 69	 S1_{TI}	 Gr1C1

Salts	Pre-catalysts
 S2_{Tl}	 Gr1C2
	 75
	 76

Summary

The Grubbs type pre-catalysts are widely used for olefin metathesis. The pre-catalysts exhibit high activity and selectivity, but low stability and short lifetimes. Salicylideneanilines (SA) are Schiff bases that can be derived from the reaction of amine derivatives with salicylaldehyde and 2-hydroxy-1-naphthaldehyde. These ligands were synthesized to improve the activity, stability and lifetime of the Grubbs first and second generation pre-catalysts. In an attempt to improve on these properties both theoretical and experimental investigations were conducted.

Molecular modelling was done using Material Studio, Dmol³ (PW91/GGA/DNP) to evaluate potential imine derivative as ligands for Grubbs type pre-catalysts, for the metathesis reaction with 1-octene. Forty five ligands were chosen to investigate properties for suitable ligands. The usefulness of the HOMO energy as preliminary criteria for screening suitable ligands was investigated. The HOMO energy of possible ligands was calculated against the well defined Verpoort ligand. In this study the ligand with lower energy than that of the Verpoort's ligand was considered. Analysis of the electron density, electrostatic potential, Fukui functions, HOMO-LUMO orbitals and population analysis were used to address the research problem.

The second criteria included being found in literature, synthesis procedure as well as a high yield. The two most promising ligands were chosen to be synthesized. These ligands were used in the synthesis of new Grubbs 1 and 2 type pre-catalysts. The third criteria were the dissociation energy (Ru-N) for the new Grubbs type pre-catalysts for activation properties that may influence the hemilability. Furthermore molecular modelling helped to gain insight into the mechanism of the 1-octene metathesis reaction by using the Potential Energy Surface (PES) scan.

Both ligands were successfully synthesized according to literature methods. The ligands were characterized by MS, IR and NMR techniques. The synthesis of substituted Grubbs 1 type pre-catalysts was unsuccessful. The substituted Grubbs 2 type pre-catalysts were obtained and characterized by MALDI-TOF and NMR techniques. The two substituted Grubbs 2 type pre-catalysts were tested for metathesis activity with 1-octene. Only one substituted pre-catalyst was active for metathesis. This catalyst was less active and selective than the Grubbs first and second generation pre-catalysts but showed an increased lifetime.

Opsomming

Die Grubbs-tipe prekatalisatore word algemeen in olefinmetatese gebruik. Die katalisatore vertoon hoë aktiwiteit en selektiwiteit, maar lae stabiliteit en kort leeftye. Salisielideenanilene (SA) is Schiff basisse wat vanuit die reaksie van amienderivate met salisielaldehid en 2-hidroksie-1-naftaleenaldehyd verkry kan word. Hierdie ligande was gesintetiseer om die aktiwiteit, stabiliteit en leeftyd van die Grubbs-eerste en -tweede generasie prekatalisatore te verbeter. In 'n poging om hierdie eienskappe te verbeter is beide teoretiese en eksperimentele ondersoeke gedoen.

Molekuulmodellering is met behulp van Material Studio, Dmol³ (PW91/GGA/DNP) gedoen om die potensiële imien derivate as ligande vir Grubbs-tipe prekatalisatore te evalueer vir die metatese reaksie met 1-okteen. Vyf-en-veertig ligande is gekies om die eienskappe vir geskikte ligande te ondersoek. Die geskiktheid van die HOMO-energie as 'n voorlopige siftingskriteria vir geskikte ligande was ondersoek. Die HOMO-energie van moontlike ligande was teenoor die goed gedefinieerde Verpoort ligand bereken. In die studie was ligande met laer energieë as die van Verpoort se ligand oorweeg. Analise van die elektrondigtheid, elektrostatiese-potensiaal, Fukui-funksies, HOMO-, LUMO-orbitale en populasie analyses was gebruik om die navorsingsprobleem aan te spreek.

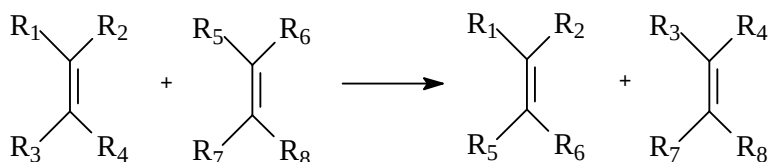
Die tweede kriteria het ingesluit dat die potensiële ligande moet bestaan, die sintese proses sowel as hoë opbrengste verkry was. Die twee mees belowende ligande was gekies om gesintetiseer te word. Die ligande is in die sintese van nuwe Grubbs 1- en 2-tipe prekatalisatore gebruik. Die derde kriteria was die dissosiasie-energie (Ru-N) vir die nuwe Grubbs-tipe prekatalisatore vir aktiveringseienskappe wat die hemilabiliteit kan beïnvloed. Verder het molekuulmodellering gehelp om 'n beter insig in die meganisme van die 1-okteenmetatese reaksie te verkry deur van die Potensiële Energie Oppervlak (PEO) skandering gebruik te maak.

Beide ligande was suksesvol volgens literatuurmetodes gesintetiseer. Die ligande was met behulp van MS, IR en KMR-tegnieke gekarakteriseer. Die sintese van die gesubstitueerde Grubbs 1-tipe prekatalisatore was onsuksesvol. Die gesubstitueerde Grubbs 2-tipe prekatalisatore was verkry en met behulp van IR, MALDI-TOF en KMR-tegnieke gekarakteriseer. Die twee gesubstitueerde Grubbs 2-tipe prekatalisatore was vir metatese aktiwiteit met 1-okteen getoets. Slegs een gesubstitueerde prekatalisator was vir metatese aktief. Hierdie katalisator was minder aktief en selektief as die Grubbs-eerste en -tweede generasie prekatalisatore, maar het 'n verhoogde leeftyd getoon.

1 INTRODUCTION AND AIMS OF THE STUDY

1.1 Introduction

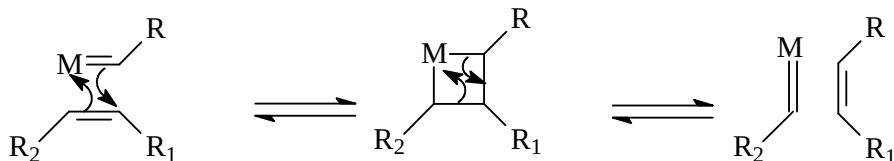
Catalysed olefin metathesis reactions represent one of the most important synthetic processes discovered in the past four decades.¹⁻⁴ Olefin metathesis is a reaction between two molecules containing double bonds shown in **Scheme 1.1**.⁵⁻⁸ This reaction describes the apparent interchange of carbon atoms between two pairs of bonds, resulting in a new olefin that contains “half” of the first olefin molecule bonded to either “half” of the second olefin.¹



Scheme 1.1 Olefin metathesis reaction.

Olefin metathesis can be conducted in several types of distinct reactions such as ring closing metathesis (RCM), ring opening metathesis (ROM), cross metathesis (CM), enyne metathesis (EN), acyclic diene metathesis (ADMET) and ring-opening metathesis polymerization (ROMP).^{5, 9}

The generally accepted mechanism that is consistent with experimental evidence was developed by Chauvin.¹⁰ Chauvin proposed that olefin metathesis involves the interconversion of an olefin and a metal alkylidene as illustrated in **Scheme 1.2**. This process is believed to occur via a metallacyclobutane intermediate by alternating [2+2] cycloaddition and cycloreversion reactions.



Scheme 1.2 The mechanism of the catalyzed olefin metathesis.

This mechanism influenced work on pre-catalyst development as shown in **Figure 1.1**.¹¹ In the late 1970s to early 1980s effort has been made to synthesize alkylidene and metallacyclobutane complexes which led to the discovery of the first single-component homogeneous pre-catalysts for olefin metathesis.¹¹ These new pre-catalysts included $(\text{CO})_5\text{W}=\text{CPh}_2$,¹² bis(cyclopentadienyl)titanocyclobutanes,¹³ tris(aryl oxide)tantalacyclobutanes,¹⁴ and various dihaloalkoxide-alkylidene complexes of tungsten.¹⁵

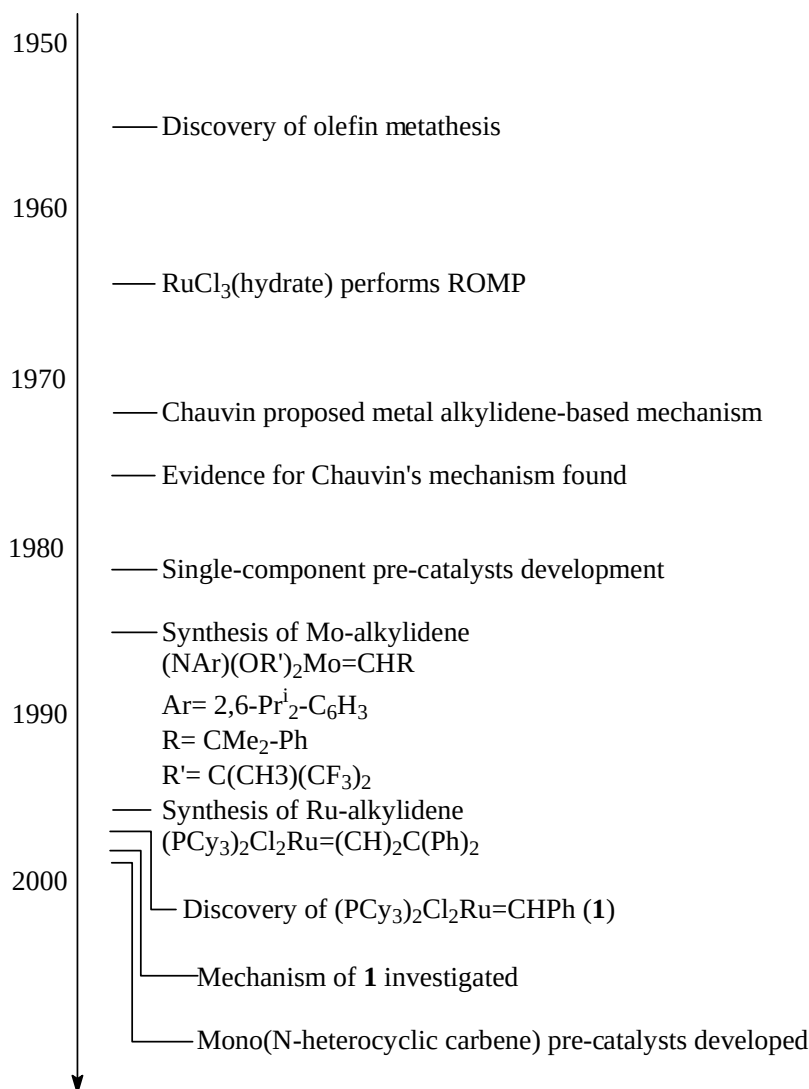


Figure 1.1 Milestones in the development of olefin metathesis.¹¹

The first pre-catalysts to be widely used are Molybdenum (Mo) and tungsten (W) alkylidenes with the general formula $(\text{NAr})(\text{OR}')_2\text{M}=\text{CHR}$, $\text{Ar} = 2,6\text{-Pr}^i_2\text{-C}_6\text{H}_3$, $\text{R} = \text{CMe}_2\text{-Ph}$, $\text{R}' = \text{C}(\text{CH}_3)(\text{CF}_3)_2$ and were reported in 1990 by Schrock et al.^{16,17} The Mo

complex has high activity which allows it to react with both terminal and internal olefins and to ROMP low strain monomers, as well as to ring-close sterically demanding and electron poor substrates.¹⁷ The limitation of this pre-catalyst is that it is extremely sensitive to oxygen, moisture and other functional groups.¹¹

Research in improving the reactivity of the pre-catalysts with various functional groups advanced.¹⁸ The new pre-catalysts that react with olefins in the presence of heteroatomic functionalities were developed, namely the ruthenium carbene complexes such as **1**, the Grubbs first generation pre-catalyst and **2** the Grubbs second generation pre-catalyst, given in **Figure 1.2**. These pre-catalysts transformed olefin metathesis into a versatile tool in organic and polymer chemistry.¹⁸⁻²¹

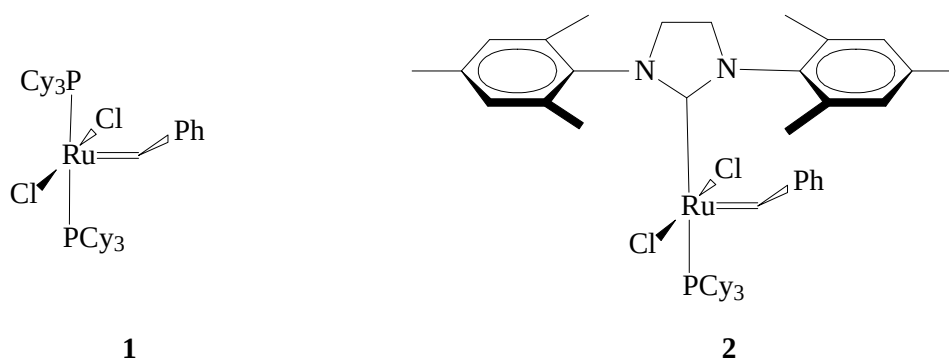
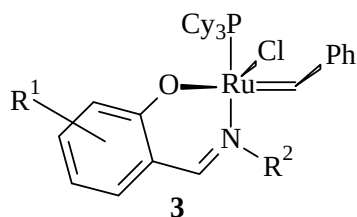


Figure 1.2 Grubbs first and second generation pre-catalysts.

The ruthenium pre-catalysts broadened the scope significantly because they operate under mild conditions and are highly tolerant towards heteroatom-containing functional groups, air and moisture.^{9, 20, 22} However **1** is thermally unstable despite its high selectivity during the metathesis of alkenes.⁶

The lifetime and the reactivity of **1** have been improved through the replacement of the phosphine ligand by a more bulky and basic N-heterocyclic carbene (NHC) ligand.^{6, 23-25} The higher activity of **2** can also be attributed to electron distribution and bulk effects that enhance the dissociation of the phosphine ligand, as well as the ratio of alkene to phosphine coordination during the catalytic cycle.^{3, 23}

Consequently, the imine- or O, N-chelate Schiff base ligands were reacted with **1** to give complexes **3** a-h in **Figure 1.3**, at room and elevated temperatures, to liberate one coordination site ‘on demand’ of a competing substrate, e.g., an alkene.^{23, 26}



- a. $R^1 = \text{H}$, $R^2 = 2,6\text{-}^i\text{PrC}_6\text{H}_3$
- b. $R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-}^i\text{PrC}_6\text{H}_3$
- c. $R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-Me-4-MeOC}_6\text{H}_2$
- d. $R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-Me-4-BrC}_6\text{H}_2$
- e. $R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-Cl-4-CF}_3\text{C}_6\text{H}_2$
- f. $R^1 = 6\text{-Me-4-NO}_2$, $R^2 = 2,6\text{-}^i\text{PrC}_6\text{H}_3$
- g. $R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-}^i\text{Pr-4-NO}_2\text{-C}_6\text{H}_3$
- h. $R^1 = 4\text{-NO}_2$, $R^2 = \text{CH}_2\text{-Ad}$

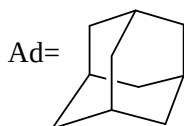


Figure 1.3 Possible Schiff base pre-catalysts.

Despite the effort to advance the pre-catalyst activity, there is still room for improvement with regard to lifetime and reactivity. The influence of the ligands on the stability and lifetime is investigated in this study. The criteria for choosing the ligands are based on the activation properties that influence **4** through salicylideneaniline Schiff bases.

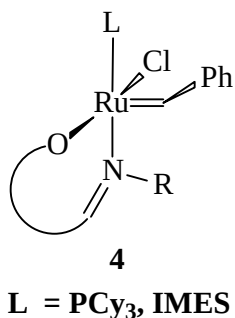


Figure 1.4 Schiff base Grubbs type pre-catalyst.

A series of salicylaldehyde-imine derivatives are formed by substituted salicylaldehyde and aniline.²⁷ 2-Hydroxy Schiff base ligands and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with amines have been extensively studied.^{28, 29}

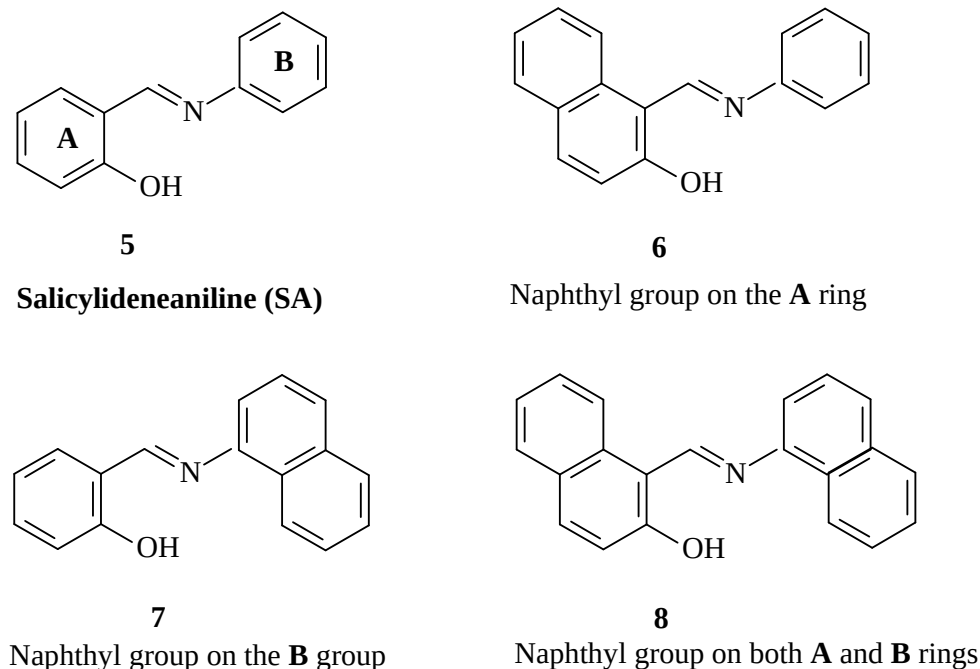


Figure 1.5 Salicylideneaniline (SA) derivatives.

Salicylideneaniline derivatives of **5** have been used as models for biological systems, in catalytic reactions; organic synthesis and coordination chemistry.²⁸⁻³¹ A series of salicylideneaniline derivatives **6-8** were synthesized to study the substituent effect on the chromic properties, namely photochromism, thermochromism, and solvatochromism in solution.³²

The considerable growth on these Schiff bases in literature is dominated by spectral, catalytic and bioactivity studies. Redox properties such as reactivity towards oxidation of organic substrates are part of the extensive literature on the Schiff bases. They offer opportunity for inducing substrate chirality, tuning metal centered electronic factors and enhancing the solubility of either homogeneous or heterogeneous pre-catalysts.³³⁻

1.2 Aims and Objectives

In literature, salicylideneaniline (SA) Schiff bases with a naphthyl group have not been mentioned as ligands for the Grubbs type pre-catalyst. Metathesis reactions with SA derivatives Schiff base ligands do not exist in literature. The aim of the study is to find naphthyl imine ligands that can be used to improve the performance of Grubbs type pre-catalysts for 1-octene metathesis. To reach the aim of the study, the following objectives are set:

1. To obtain in depth understanding of relevant imine ligands and the Grubbs derivatives by conducting a comprehensive literature study.
2. To evaluate potential imine ligands and salicylideneaniline derivatives and the catalytic reaction mechanism of the alkene metathesis where Grubbs type carbenes with these ligands are used by molecular modeling.
3. To synthesize two possible imine ligands and Grubbs type pre-catalyst with different steric and electronic properties.
4. To find factors that influence the stability and lifetime in regards to Grubbs type pre-catalysts of **1** and **2**.
5. To characterize the products using spectroscopic and other analytical methods.
6. To test for the catalytic properties of these Grubbs type pre-catalysts with 1-octene metathesis.

1.3 References

1. F. Bernard, A. Bottoni and G. P. Miscione, *Organometallics*, 2003, **22**, 940
2. P. E. Romero and W. E. Piers, *J. Am. Chem. Soc.*, 2005, **127**, 5032
3. M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.*, 2002, **123**, 6543
4. M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.*, 2002, **123**, 749
5. R. H. Grubbs, *Handbook of Metathesis*, 2003, Wiley-VCH Germany
6. M. Jordaan, *Experimental and theoretical investigation of new Grubbs-type pre-catalysts for the metathesis of alkenes*, North-West University (Potchefstroom campus) PhD Thesis, 2007
7. K. N. G. Mtshatsheni, *Metathesis of alkene using ruthenium carbene complexes*, North West University (Potchefstroom campus) MSc Thesis, 2005
8. C. Adlhart and P. Chen, *J. Am. Chem. Soc.*, 2004, **126**, 3496
9. I. Dragutan, V. Dragutan, P. Filip, *ARKIVOC*, 2005 (x), 105
10. J.-L. Hérisson and Y. Chauvin, *Makromol. Chem.* 1971, **141**, 161
11. R. H. Grubbs and T. M. Trnka, *Acc. Chem. Res.*, 2001, **34**, 18
12. T. J. Katz and T. M. Sivavec, *J. Am. Chem. Soc.*, 1985, **107**, 737
13. R. H. Grubbs and W. Tumas, *Science*, 1989, **243**, 907
14. K. C. Wallace, A. H. Liu, J. C. Dewan, R. R. Schrock, *J. Am. Chem. Soc.*, 1988, **110**, 4964
15. J. Kress, A. Agüero, J. A. Osborn, *J. Mol. Catal.*, 1986, **36**, 1
16. R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robin, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875
17. R. R. Schrock, *J. Am. Chem. Soc.*, 1999, **55**, 8141
18. W. J. van Rensburg, P. J. Steynberg, W. H. Meyer, M. M. Kirk and G. S. Forman, *J. Am. Chem. Soc.*, 2004, **126**, 14332
19. P. A. Chase, M. Lutz, A. L. Spek, G. P. M van Klink, G. van Koten, *J. Mol. Catal.*, 2006, **254**, 2
20. L. Cavallo, *J. Am. Chem. Soc.*, 2002, **124**, 8965
21. A. Furster and L. Ackermann, *Chem. Commun.*, 1999, 95
22. E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887
23. M. Jordaan and H. C. M. Vosloo, *Adv. Synth. Catal.* 2007, **349**, 184
24. J. Huang, H. J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics*, 1999, **18**, 5375

25. M. Jordaan, P. van Helden, C. G. C. E. van Sittert, H. C. M. Vosloo, *J. Mol. Catal.*, 2006, **254**, 145
26. S. Chang, L. Jones, C. Wang, L. M. Henling, and R. H. Grubbs, *Organometallics*, 1998, **17**, 3460
27. H. Zhi-Hui, L. Cheng-Rong, P. Hai-Jing, Z. De-Chung, *Chinese J. Struct. Chem.*, 2004, **23**, 755
28. M. Yildiz, Z. Kilic, T. Hökelek, *J. Mol. Struct.*, 1998, **144**, 1
29. H. Nazir, M. Yildiz, H. Yilmaz, M. N Tahir, D. Ülkü, *J. Mol. Struct.*, 2000, **524**, 241
30. J. W. Pryz, A. L. Roe, L. J. Stern, L. Que Jr., *J. Am. Chem. Soc.*, 1985, **107**, 614
31. N. E. Dixon, C. Gazzalo, J.J. Watters, R. L. Blackeley, B. Zerner, *J. Am. Chem. Soc.*, 1992, **97**, 4131
32. A. Ohshima, A. Momotake, T. Arai, *J. Photochem. and Photobiol A: Chemistry*, 2004, **162**, 473
33. K. N. Kumar, R. Ramesh, *Spectrochimica Acta Part A*. 2004, **60**, 2913
34. R. Ramesh, *Inorg. Chem. Commun.*, 2004, **7**, 274
35. F. Verpooort and B. de Clercq, *Macromolecules*, 2002, **35**, 8943

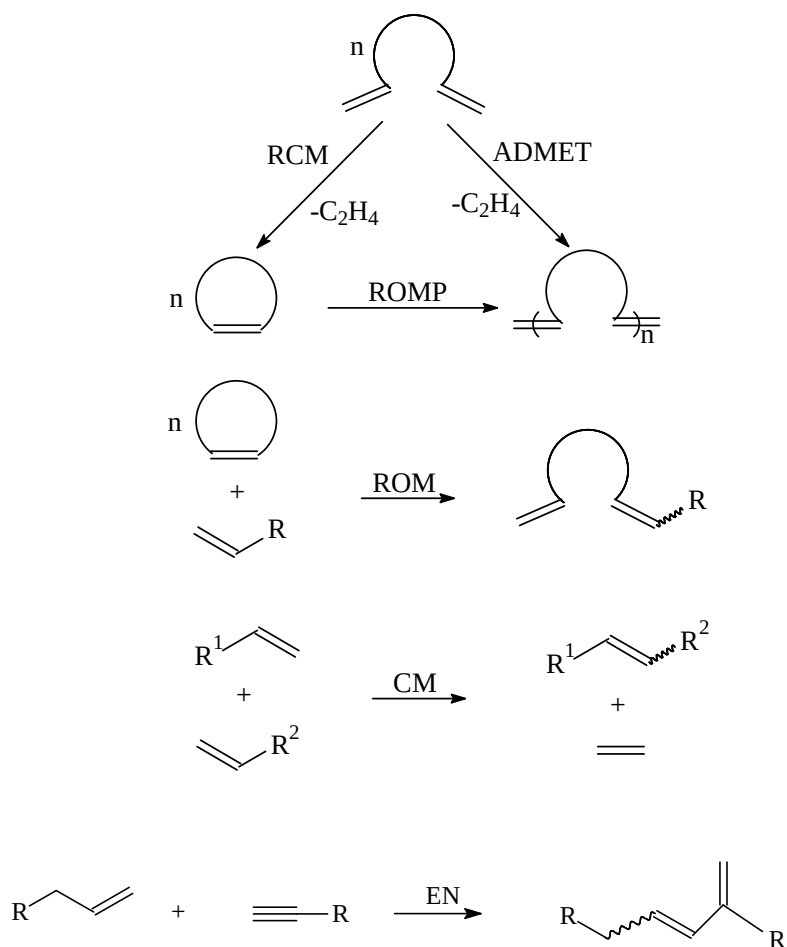
2 LITERATURE SURVEY

2.1 Introduction

The word metathesis is derived from the Greek *meta* (change) and *tithemi* (place), it refers to the interchange of atoms between two molecules.¹⁻³ In olefin metathesis it describes the interchange of carbon atoms between a pair of double bonds from the apparent molecules.^{1,2} The name metathesis was given for the first time to the reaction by Calderon in 1967.⁴ Metathesis is described by **Scheme 1.1** given in **Chapter 1**.

Like most catalytic processes olefin metathesis was discovered by accident. It was discovered as an outgrowth of a study of Ziegler polymerizations with an alternate metal system.^{1,5} The olefin metathesis can be conducted in several distinct reaction modes (illustrated in **Scheme 2.1**) such as ring closing metathesis (RCM), defined as the unimolecular condensation reaction of a diene to form a cyclic olefin and a small condensate olefin as a byproduct. The reverse reaction of RCM is ring opening metathesis (ROM) in which a cyclic olefin is reacted with an acyclic olefin to produce a new diene.⁶

Acyclic diene metathesis (ADMET) introduced by K. B. Wagener in 1991⁸ is a special type of olefin metathesis used to polymerize certain terminal dienes to polyenes. The reaction is driven by the removal of ethylene from the system which can be accomplished with a nitrogen purge. The new double bonds formed can be in *cis*- or *trans*- configurations.⁸ It is a type of step growth condensation reaction and ring-opening metathesis polymerization (ROMP) is a chain-growth polymerization. The mechanism of ROMP involves a cyclic olefin and the driving force is the relief of the ring.^{6,9} Other metathesis reactions include the cross metathesis (CM), the reaction between two acyclic olefins to form two new olefins, and enyne metathesis (EN) is a bond reorganisation of an alkene and an alkyne to produce a 1,3 diene. Katz et al. in 1985 discovered the enyne metathesis through the study of the effect of alkynes on ring opening alkene metathesis polymerization.^{6,10}



Scheme 2.1 Several distinct olefin metathesis reactions.

The metathesis reaction forms part of the development of the metal alkylidene-based mechanism. Yves Chauvin proposed a mechanism which introduced several ideas.¹¹⁻¹³ The Chauvin mechanism proposed the implication of a metal-carbene complex to initiate the catalysis of the metathesis reaction. This idea suggested the metal-alkylidene complexes can be synthesized and can react as pre-catalysts with olefins. The other important aspect of the Chauvin mechanism concerns the intermediacy of the metallacyclobutane.⁴

The olefin metathesis reaction is used in industry and research and its application has become more and more important. For the past decade, transition metal catalyzed C-C double bond formation through olefin metathesis continues to be of considerable interest and synthetic utility.¹⁴⁻¹⁶

The catalytic systems used for olefin metathesis involve almost invariably transition metal compounds. The first generation catalytic systems often require the presence of a co-pre-catalyst and sometimes a third compound (promoter) must be added to the reaction mixture. The commonly used metals for the systems are Mo, Ru, W, Re, Os or Ir. EtAlCl₂, R₃Al and R₄Sn are typical co-pre-catalysts, while oxygenates (O₂, EtOH, PhOH) can be used as promoters.¹⁵

2.2 Pre-catalysts

Pre-catalysts are substances that accelerate the rates of chemical reactions, facilitating the establishment of equilibria and are capable of greatly enhancing product selectivity.²⁰ Olefin metathesis incorporates pre-catalysts containing tungsten (W), molybdenum (Mo) and ruthenium (Ru) to induce high value olefins. The pre-catalysts can be classified in terms of type of catalysis, homogeneous and heterogeneous. The general definition of homogeneous and heterogeneous is if the pre-catalyst is in the same phase as the alkene or in the different phase, respectively.²⁰ The advantages of the homogeneous pre-catalyst are mild reaction conditions, selectivity, tenability and the ability to access all sites, whilst the advantages of the heterogeneous pre-catalyst are recyclability, amenable to high-throughput processes, easier production separation and greater stability.²¹

2.2.1 Homogeneous pre-catalysts

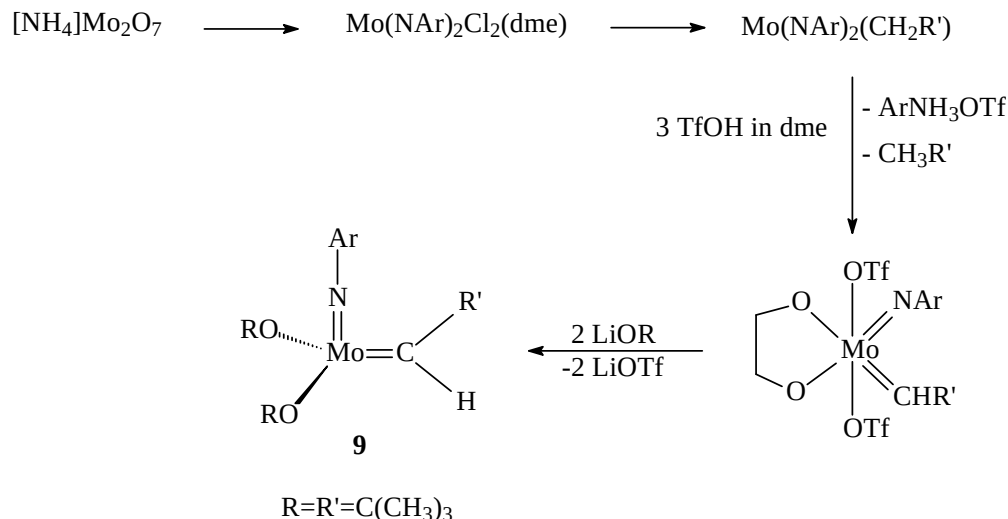
Homogeneous pre-catalysts which are structurally well-defined metal alkylidene complexes are more tolerant to common organic functional groups. The emphasis on research is on the development of mild and tolerant, but highly effective and selective pre-catalysts. Homogeneous pre-catalysts have been used in polymerization metathesis reactions.²¹ The characteristics of homogeneous catalysis by transition metal coordination compounds are:³¹

- i. Dispersion at the molecular level, i.e., the catalytically active species and the substrate molecule are in the same phase;

- ii. The pre-catalyst (or at least the pre-catalyst precursor complexes) can be unequivocally characterized by spectroscopic means and synthesized reproducibly;
- iii. Each metal center is potentially a catalytically active site; all these sites show chemical uniformity.

2.2.1.1 Molybdenum

Molybdenum (Mo), tungsten (W) and ruthenium (Ru) are three metals that are most active for metathesis of olefins in metathesis pre-catalyst systems. Molybdenum precursors where molybdenum has a high oxidation state (IV to VI) have generally been used.^{32,33} A pre-catalyst system of MoCl₅-SnMe₄ was used for co-metathesis of cycloalkene with α -alkene to generate monoene pheromone components.³⁴ This most remarkable homogeneous pre-catalyst was discovered by Schrock³⁵ in 1990, which is highly reactive and functional group tolerant and found immediate application on ROMP. The preparation of the pre-catalyst is described in **Scheme 2.2**.³⁶⁻³⁸

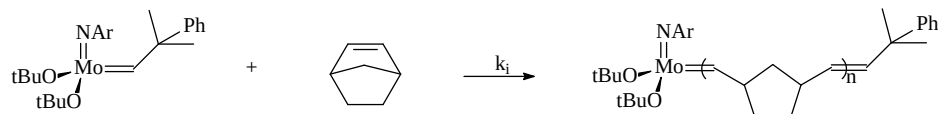


Scheme 2.2 Preparation of the Schrock pre-catalyst.

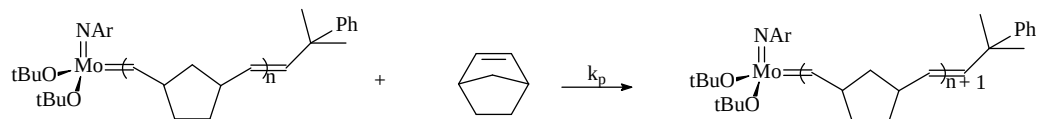
The reactive Schrock type pre-catalysts (**9**) selectivity can be achieved when the reaction time is less than the life time of the pre-catalyst.³⁹ Grubbs published an article on the kinetics and mechanism of “living” polymerization with the Schrock pre-catalyst; the mechanistic steps explaining the kinetic results are illustrated in **Scheme**

2.3.⁴⁰ The Schrock type pre-catalysts can be used in metathetic routes to produce polyesters⁴¹ or polycarbonates.⁴²

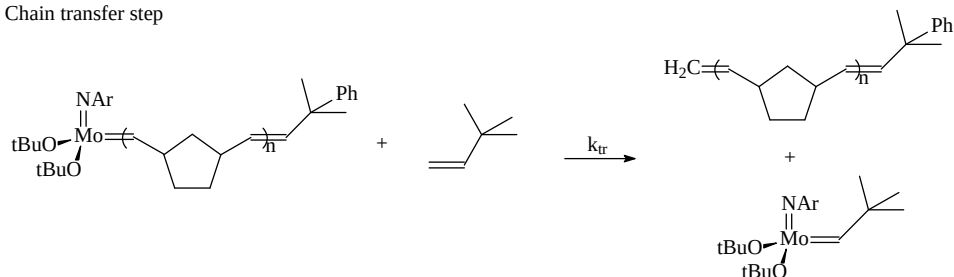
Initiation Step



Propagation Step



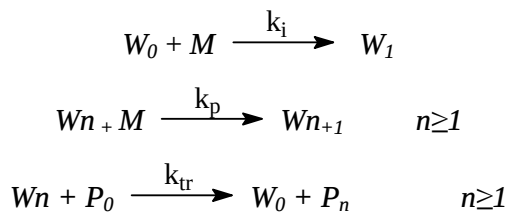
Chain transfer step



Scheme 2.3 Mechanistic steps explaining kinetics of Schrock pre-catalyst.

The following, denoted as CAT, MON and CTA, are the concentrations of pre-catalyst, monomer and chain-transfer agent, respectively, at time 0, while W_0 , M and P_0 are the concentrations of pre-catalyst, monomer and chain-transfer agent, respectively, at time t . W_n and P_n are the concentration of active and dead polymer chains containing n units of monomer, respectively at time t . k_i , k_p and k_{tr} are specific rates constants for initiation, propagation and chain transfer.

The **Scheme 2.3** can also be presented as follows:



In **Scheme 2.3**, the initiating species W_0 produced by the reaction of the chain-transfer agent P_0 with the active chain Wn has the same reactivity as the original pre-catalyst W_0 . The following kinetic equations describe the above process:

$$\frac{dM}{dt} = -k_i MW_0 - k_p M \sum_{n=1}^{\infty} W_n \quad 1$$

$$\frac{dW_0}{dt} = -k_i MW_0 + k_{tr} P_0 \sum_{n=1}^{\infty} W_n \quad 2$$

$$\frac{dW_1}{dt} = k_i MW_0 - k_p MW_1 - k_{tr} P_0 W_1 \quad 3$$

$$\frac{dW_n}{dt} = -k_p MW_n + k_p MW_{n-1} - k_{tr} P_0 W_n \quad n \geq 2 \quad 4$$

$$\frac{dP_0}{dt} = -k_{tr} P_0 \sum_{n=1}^{\infty} W_n \quad 5$$

$$\frac{dP_n}{dt} = k_{tr} P_0 W_n \quad n \geq 1 \quad 6$$

Using the conservation laws

$$MON = M + \sum_{n=0}^{\infty} (nW_n) + \sum_{n=0}^{\infty} (nP_n)$$

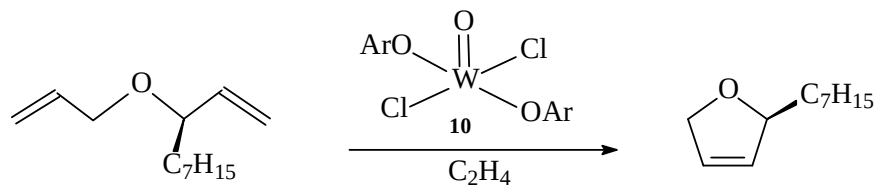
$$CAT = \sum_{n=0}^{\infty} W_n$$

$$CTA = \sum_{n=0}^{\infty} P_n$$

2.2.1.2 Tungsten

Tungsten hexachloride (WCl_6) based pre-catalysts in combination with tetramethyltin have been studied as pre-catalysts for alkene metathesis^{43,44} and the stereochemistry of ROMP of cycloalkenes.⁴⁵ Low oxidation state W(III) generates *trans* and high oxidation state W(V) generates *cis* polymers.⁴⁶⁻⁴⁸ The use of Lewis acids such as alkylaluminum halides gave predominantly *trans* double bonds in polypentylene from cyclopentene, while *cis* double bonds predominate with tetraalkyltin promoters.⁴⁹ The pre-catalyst system (**10**) shown in **Scheme 2.4** was found to be effective in the ring-closing metathesis reaction of functionalized substrates, including

those that are homochiral. This is the first tungsten pre-catalyst for ring-closing metathesis and works well even when generated *in situ*.⁵⁰

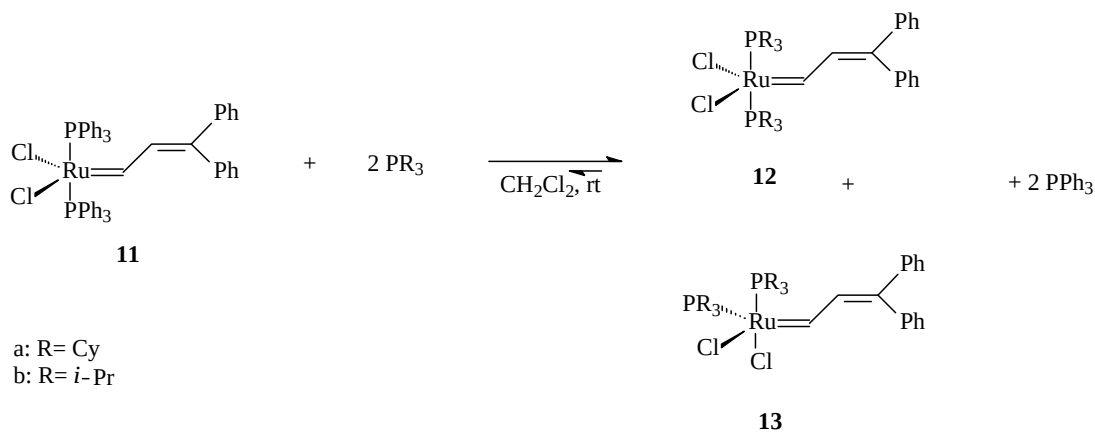


Scheme 2.4 The first tungsten pre-catalyst for RCM.

Schrock developed a tungsten carbene pre-catalyst prepared from molybdenum which was used in acyclic diene metathesis with 1,9-decadiene.⁵¹ Alkene metathesis by the Schrock carbene complex Cl₃(dme)W=CCMe₃ was found to be sensitive to alkene substituents and was inhibited by addition of internal alkynes.⁵² The metathesis and polymerization of 1-octene was studied with the RNMe₃, ClW(CO)₅/EtAlCl₂ pre-catalyst system.⁵³

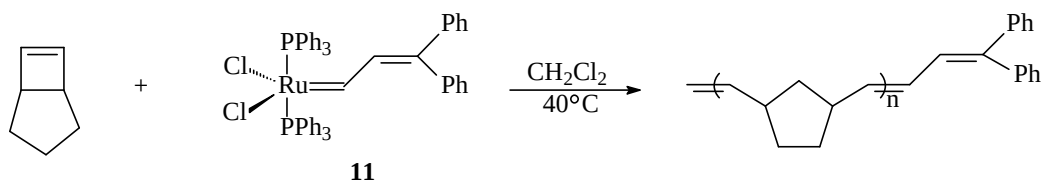
2.2.1.3 Ruthenium

Ruthenium carbene complexes have shown to be a leading class of pre-catalyst, primarily due to the extensive work of Grubbs.⁵⁴ The ease of preparation, handling, tolerance a to variety of functional groups containing O and N atoms; stability in air and water; mild condition and high selectivity lead to widespread use in organic chemistry.²¹ Since 1988 the preparation (**Scheme 2.5**) and applications of the ruthenium carbene complexes in metathesis were described.⁵⁵



Scheme 2.5 Preparation of Grubbs carbene complex.

The two types of phosphines ligands used in **Scheme 2.5** have two isomeric phosphine complexes (one where the two phosphine ligands are *trans* to each other and one where they are *cis*). The *trans* isomer is the predominant one in the product mixture. They are moderately stable to air and also in organic solvents in the presence of water, alcohol, acetic acid or a diethyl ether solution of HCl. Alkylphosphines make the pre-catalyst more soluble in organic solvents such as benzene and THF.⁵⁶ It was found that the well-defined ruthenium carbene complex (**11**) did catalyze the ROMP of bicycle[3.2.0]heptene in a ‘living’ manner.⁵⁷

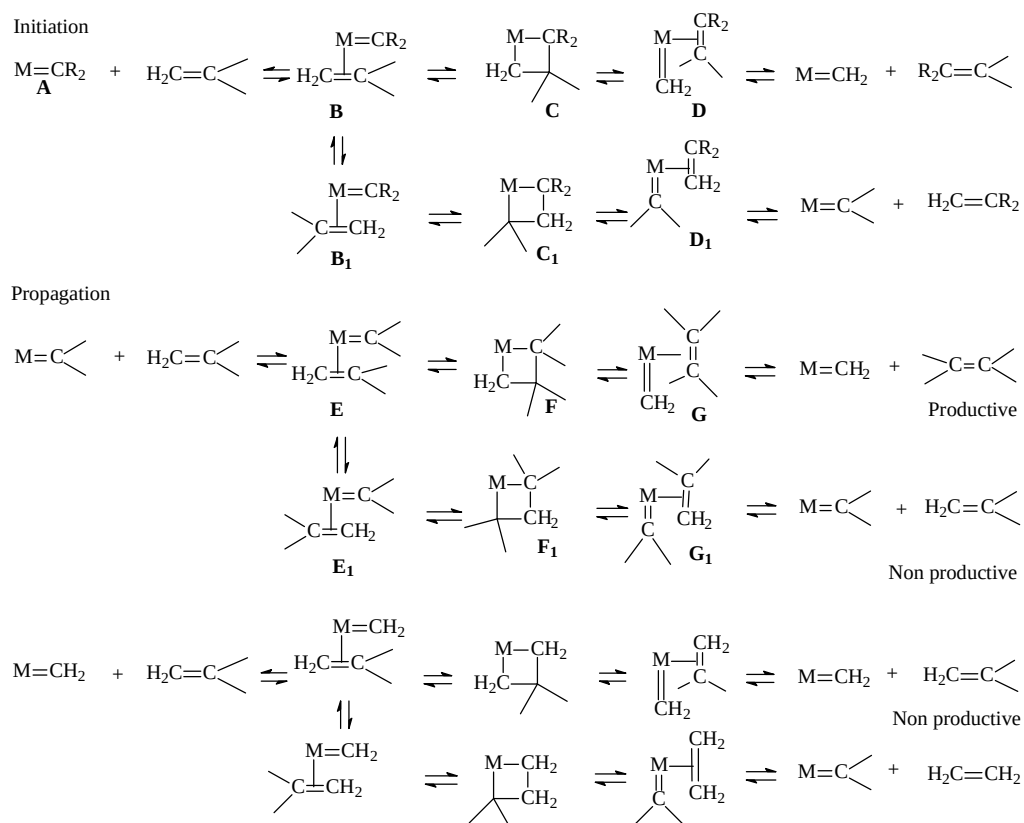


Scheme 2.6 ROMP catalyzed by well-defined Ru carbene complex.

The addition of N-heterocyclic carbene (NHC) ligands on ruthenium pre-catalysts lead to extraordinary advancement on pre-catalysts in general. The ligand is more basic than the alkylphosphine ligands and its complex is commonly known as the Grubbs second generation pre-catalyst **2**. The basicity of NHC-ligands increase the reactivity of the pre-catalyst by making it easier to push the *trans* PR₃-ligand off the metal (trans effect).⁵⁸

2.3 Mechanism

Metathesis provides a way of breaking and remaking carbon-carbon double bonds. It was first discovered in industry in the 1950s but it was not until Yves Chauvin's and his student Jean-Louis Herrison's work in 1971 that the mechanism was understood (**Scheme 2.7**).⁴



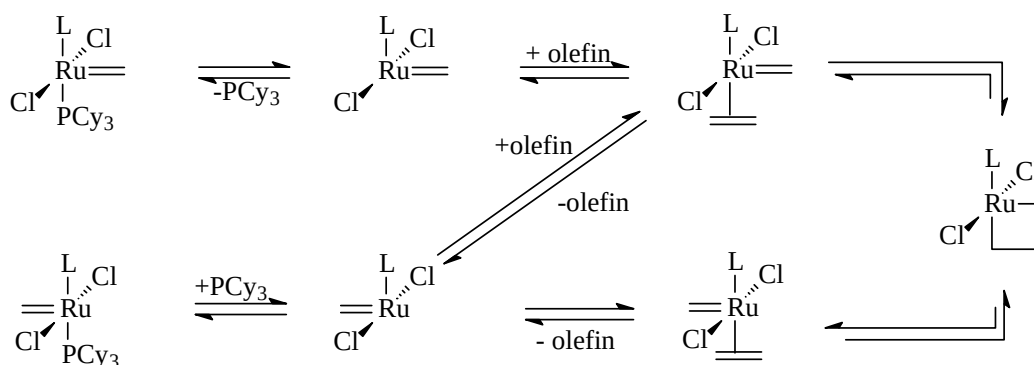
Scheme 2.7 Chauvin's mechanism, proposed in 1971, for the catalyzed olefin metathesis involving metal alkylidene and metallacyclobutane intermediates.⁴

This new olefin contains a carbene from the pre-catalyst and the other carbene from the starting olefin. The new metal-alkylidene contains one of the two carbenes of the starting olefin and it can re-enter into a catalytic cycle of the same type as the first one. Depending on the orientation of the coordinated olefin, the new catalytic cycle can give two different metallacyclobutanes (**F** and **F₁**), one leading to the symmetrical olefin and the other leading the starting olefin. The latter cycle is the degenerate olefin metathesis.

Thus the catalytic cycles alternatively involve both metal-alkylidene species resulting from the coordination of the metal with each of the two carbenes of the starting olefin. Several experiments arose from the mechanism, the reaction of a mixture of the cyclopentene and 2-pentene led to C-9, C-10 and C-11 dienes in the ratio 1:2:1 and the reaction of a mixture of cyclooctene and 2-pentene produced C-13, which was compatible with Calderon's mechanism.⁴

2.3.1 Ruthenium-carbene mechanism

Following the Herisson-Chauvin mechanism for metathesis, the study of ruthenium-catalyzed olefin metathesis reactions and mechanism has guided the development of new ligands. The principal steps of metathesis involve, according to the Chauvin⁵⁹ mechanism a transition metal carbene which forms by coordination of an olefin a *π* complex. A [2+2] cycloaddition and dissociation finally leads to the olefin product and an active metal carbene **Scheme 2.8**.



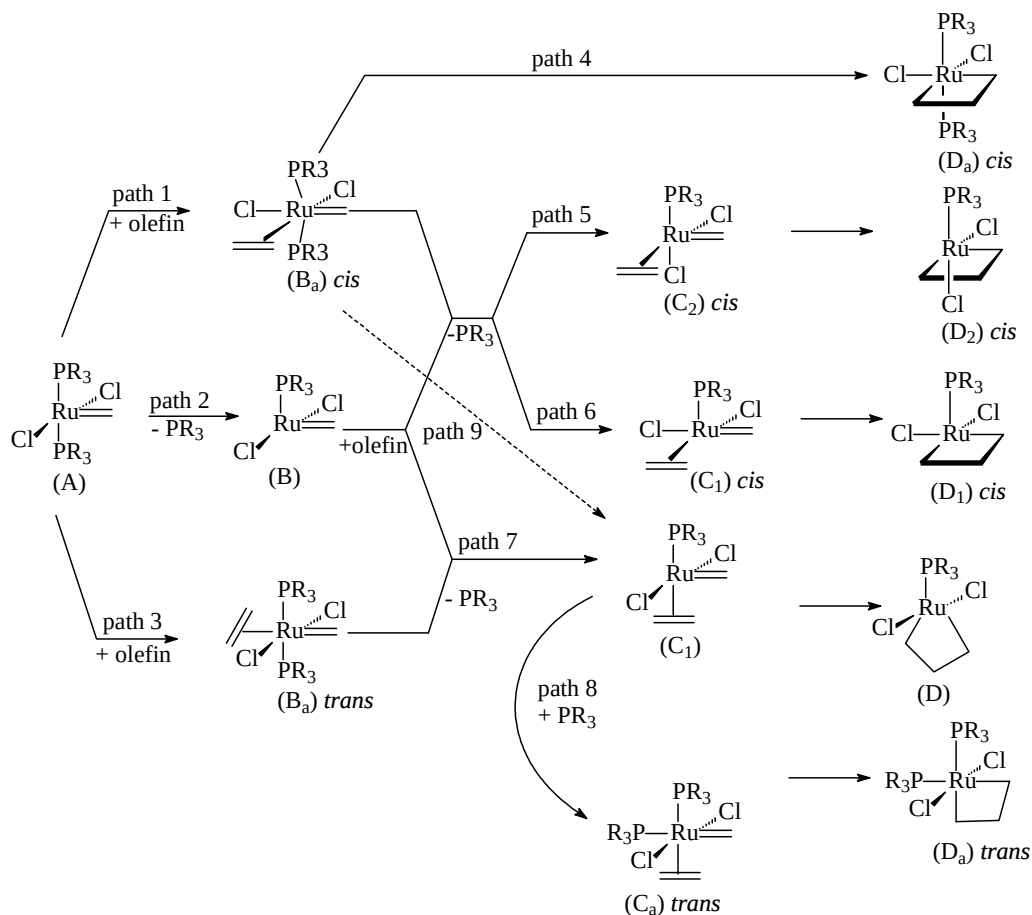
Scheme 2.8 Mechanism for metathesis by Grubbs-type Ru carbene complexes.⁶⁰

These mechanisms (as presented in the article)⁶⁰ can be divided into two classes, into associative mechanism where both phosphine ligands remain on the pre-catalyst while the olefin coordinates to the pre-catalyst to form the intermediate 18-electron olefin complex, followed by the actual metathesis steps to form the product. The dissociative mechanism; where one phosphine ligand dissociates first leaving a vacant site on the pre-catalyst to form a 14-electron complex. The vacant site is then occupied by the incoming olefin which undergoes metathesis to form a metallacyclobutane product, regenerating the pre-catalyst upon recoordination of the phosphine.⁶⁰

Although there is a general agreement for these principal steps, the detailed mechanism of olefin metathesis by ruthenium pre-catalysts carbene has been the subject of intense experimental^{61,62} and computational⁶³⁻⁶⁵ studies. The experimental studies were either performed in solution⁶⁶ or in the gas phase.⁶⁷ Most computational studies consider only a few species of the catalytic cycle⁶⁸⁻⁷⁰, focusing either on the ruthenium carbene formation process or on selected intermediates of the catalytic cycle. Others treat the complete mechanism and eventually alternative reaction pathways.⁷¹ The mechanism related to possible intermediates for olefin metathesis by Grubbs-type ruthenium carbene complexes is given in **Scheme 2.9**.⁶⁰

Some restrictions concerning possible reaction pathways are made:

- The mechanism has to be in agreement with the metallacyclobutane mechanism.⁵⁹
- The olefin has to be coordinated *cis* to the carbene before formation of the metallacyclobutane. This can be concluded from the fact that RCM works with small to moderate sized rings.⁶¹
- The principle of microscopic reversibility⁷² has to be applicable, so the reaction mechanism has to be symmetric for a degenerate reaction.
- Free rotation of the carbene ligand and the coordinated olefin is assumed, and the phosphine ligand is considered to be perfectly symmetric with respect to the coordinated olefin.
- To obtain a mechanism that can be extended to Hofmann-type and Hoveyda-type⁷³ Ru-carbenes.



Scheme 2.9 Associative and dissociative mechanisms by Grubbs-type Ru carbene complexes⁶⁰

The associative pathway assumes that the olefin simply coordinates on the pre-catalyst, forming an 18-electron olefin π complex, followed by the actual [2+2] cycloaddition and cycloreversion steps to form the product, path 1 and 4. In the associative reaction of $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CH}_2$ (**A**) with ethylene, the ethylene attacks along the bisector line of the Cl-Ru-C_{carbene} angle and thereby forces the chlorine into *cis* conformation. The 18-electron olefin complex (**B_a**) *cis* is C_s symmetric. Formation of the metallacyclobutane proceeds via approach of the methylene and ethylene carbon atoms and synchronous rotation of the methylene group. An alternative *trans* attack of the olefin to (**B_a**) *trans* cannot lead to a productive metathesis cycle, because the olefin has to coordinate *cis* to the carbene for metallacyclobutane formation, as has already been concluded by Grubbs *et al.*⁶¹

On the other hand the dissociative pathways start with the initial loss of a phosphine ligand (path 2), forming the 14-electron complex (**B**). The endothermic dissociation of PCy₃ proceeds without any enthalpy barrier beyond that due to ΔH of the reaction, although there may be an additional contribution due to entropic effects. The olefin in the five-coordinate Ru-olefin complex may be either in a *cis* (path 5 and 6) or in a *trans* position (path 7) with respect to the phosphine.

Consequently the chlorine ligands in path 5 and 6 have to be situated *cis* with respect to each other. Path 5 and 6 are distinguished from each other in the orientation of the chlorine ligands with respect to the phosphine, *cis* and *trans* in path 5 and all *cis* in path 6. Metallacyclobutane is then obtained. A variant, where the phosphine again coordinates to the olefin complex (path 8), has recently been suggested.⁴¹ Configurational fluxionality and isomerization processes at certain intermediate stages such as the isomerization of the *cis* dichloro metallacyclobutane into the *trans* dichloro isomer have been thoroughly investigated, and the activation barriers found are too high to play a significant role in the overall mechanism.

The attack of the olefin on the 14-electron complex (**B**), may occur either *cis* (path 5) along the bisector line of the Cl-Ru-C_{carbene} angle, or *trans* (path 7) to the phosphane ligand. Upon *cis* attack, the chlorine may be pushed either *trans* to the phosphane ligand (**C**₂) *cis* (path 5) or *trans* to the carbene (**C**₁) (path 6). Both steric and electronic reasons could account for the chlorine's preference for the position *trans* to the phosphine. An alternative route into the dissociative mechanism has been the associative exchange of a phosphine by the olefin. The olefin can attack either *cis* (path 1) or *trans* (path 3) to the carbene moiety and give two 18-electron intermediates which give upon loss of PCy₃ the same 16-electron olefin *pi* intermediates as found in the dissociative pathways 5 and 7, respectively. For the *cis* attack, path 1 is identical to the all-associative mechanism.⁶⁰

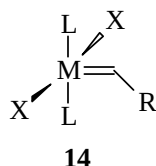
2.4 Ligands

In chemistry, a ligand is either an atom, ion, or molecule that bonds to a central metal, generally involving formal donation of one or more of its electrons. The metal-ligand bonding ranges from covalent to more ionic. Furthermore, the metal-ligand bond

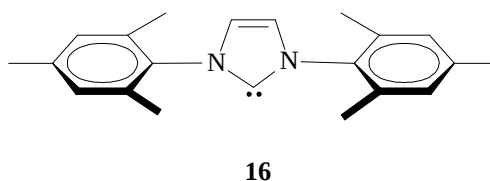
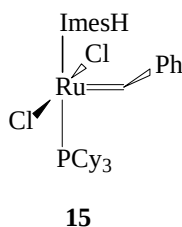
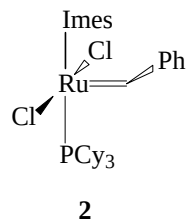
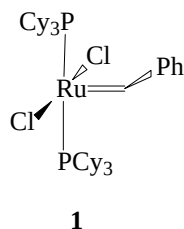
order can range from one to three.⁸⁶ There is a wide range of metal ions that can coordinate with certain ligands. The question remains - what makes certain ligands coordinate with certain metal ions? This can be explained by the hard and soft-base ligand principle, whereby hard acids tend to combine with hard bases, soft acids with soft bases. The coordination is attributed by polarisability.

Metal ions in high oxidation state tend to bind to saturated ligands such as NH_3 , H_2O and F^- which are known as hard ligands because of their low polarisability. The hard metal ions like Cr^{3+} and Al^{3+} are low in electron density and require good σ -donor ligands. In contrast low oxidation state metals, the platinum group metal, Ag^+ and Hg^+ bind to unsaturated ligands such as Br^- , I^- , PPh_3 and C_2H_4 known as soft ligands because they are polarisable. The soft metals bind soft ligands because these metals have excess electron density therefore they can form covalent bonds.

Ligands play an important role in the activity of Grubbs type pre-catalysts. The use of ligands with different electronic and steric effects was shown to optimize the pre-catalysts.⁸⁷ The structure of commonly used pre-catalyst shown to catalyze olefin metathesis is given by **14** with two dative (L type) ligand and two anionic (X type) ligands.



In the Grubbs pre-catalysts **1**, **2** and **15** the dative ligand is a hindered phosphine or N-heterocyclic carbene (**16**).



The dative ligand shields the metal from interactions with other bulky species and also plays a role in activating the pre-catalyst. In Grubbs type pre-catalyst the second dative ligand renders the pre-catalyst incapable of catalyzing metathesis. This pre-catalyst must first be activated by dissociation of one of the dative ligands to allow coordination of the olefin as shown in **Figure 2.1**

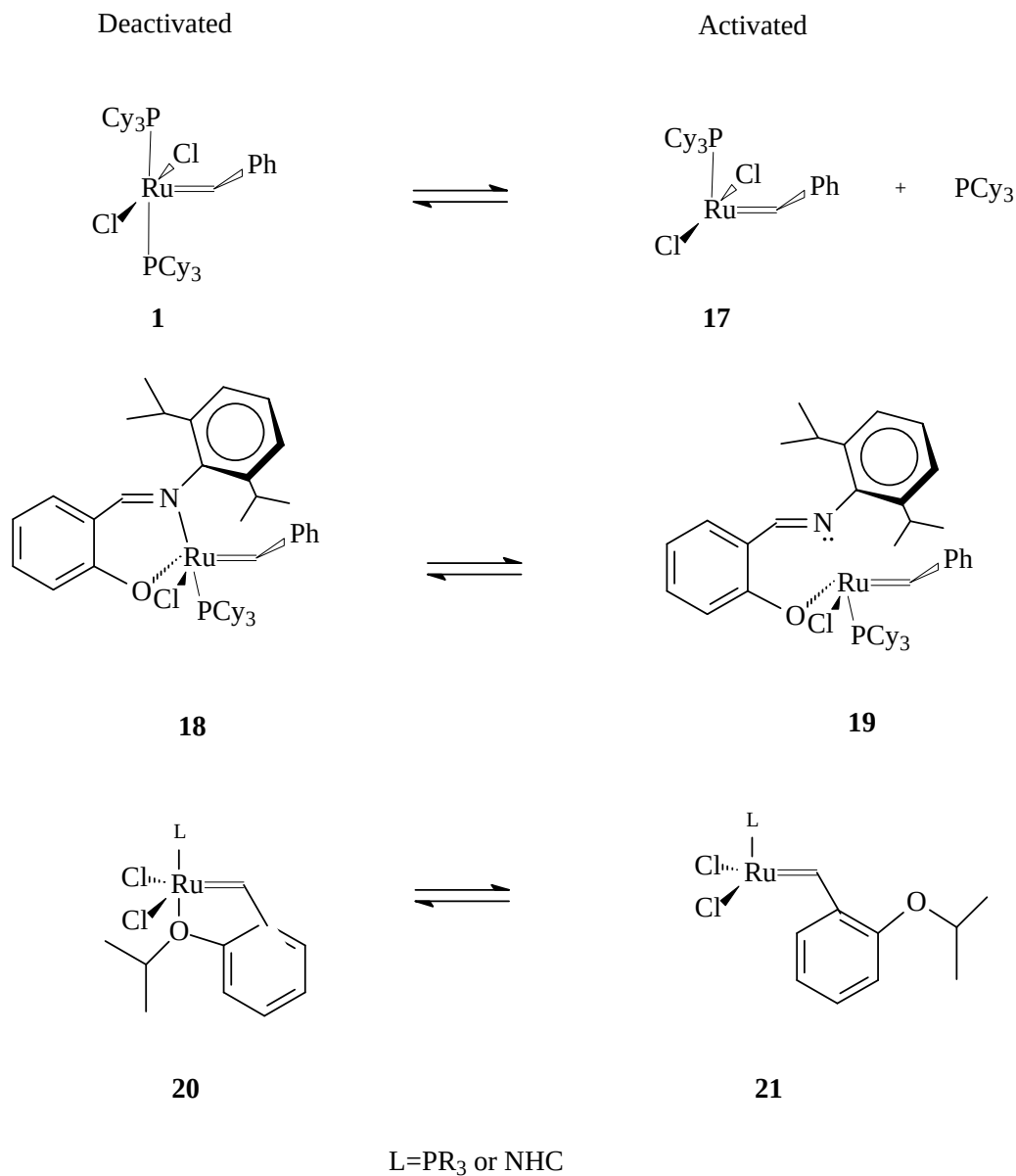
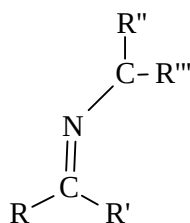


Figure 2.1 Activation of several types of ruthenium olefin metathesis pre-catalysts.

The anionic ligands are halogens, phenoxides and alkoxides also play an important role in the activity of Grubbs type pre-catalysts. The more electron withdrawing the ligand the better the activity. The activity was found to increase in the order $X = I < Br < Cl$.⁸⁰

The most common ligands used for Grubbs type pre-catalysts are the Schiff bases (22). A Schiff base is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not the hydrogen.⁸⁰ Schiff bases proved to be another class of attractive ligands in creating new ruthenium complexes.



22

The two atoms, N and O, on chelation, provide opposite properties. The phenolate oxygen atom is a hard donor and will stabilize a higher oxidation state of the ruthenium atom, whereas the imine nitrogen atom is a softer donor and will rather stabilize the lower oxidation state of ruthenium. To capitalize on the high potential of Schiff bases, a wide range of efficient ruthenium pre-catalysts with O, N-chelated Schiff base “dangling ligands” have been prepared by Verpoort and coworkers.⁸⁷

The catalytic activity of these pre-catalysts is dependent on the steric and electronic environment of the Schiff bases.⁸⁸ The substitution of one of the phosphine ligands by a N-heterocyclic ligand like 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene has increased the pre-catalyst performance,⁹⁰⁻⁹⁶ as discussed in the previous chapter. Other efforts have been directed towards modification of the ligand sphere using halogens around the metal center in order to improve the performance characteristics of this catalytic systems.⁸⁸

2.4.1 Hemilabile ligands: chelate ligands

Chelating ligands play an important role in catalysis. Chelate, which is a Greek word, refers to *claw*, and occurs when a ligand donates lone pairs of electrons from the donor atoms to the same metal to give a ring compound.⁹⁸ The popularity of new classes of chelated ligands is due to their ability to place two or more atoms with different electronic properties to the metal atom. These classes of ligands possess different types of bonding groups (X and Y), the labile group (Y) which can be displaced from the metal center, while it remains available for recoordination.⁹⁹ The inert group (X) is firmly bonded to the metal. The reversible cleavage of the M-Y bond is referred to the “windscreen wiper” action¹⁰⁰ and is the reason that these ligands are able in inducing changes in the properties of the metal center.

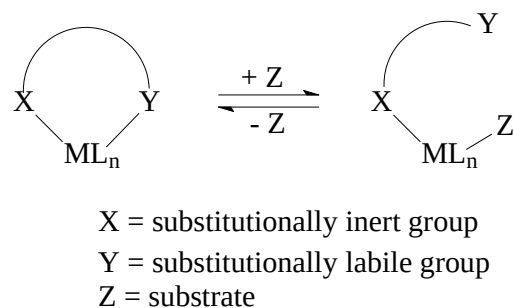
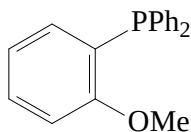
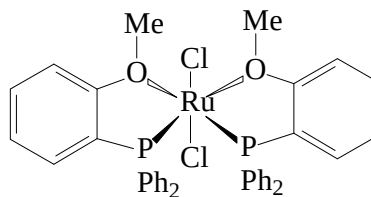


Figure 2.2 Schematic representation of hemilability

The *o*-(diphenylphosphino)anisole, which is an ether-phosphine ligand, was the first type of ligand to be termed hemilabile by Jeffrey and Rauchfuss¹⁰¹ in 1979 and was included in a Ru(II) system.



23

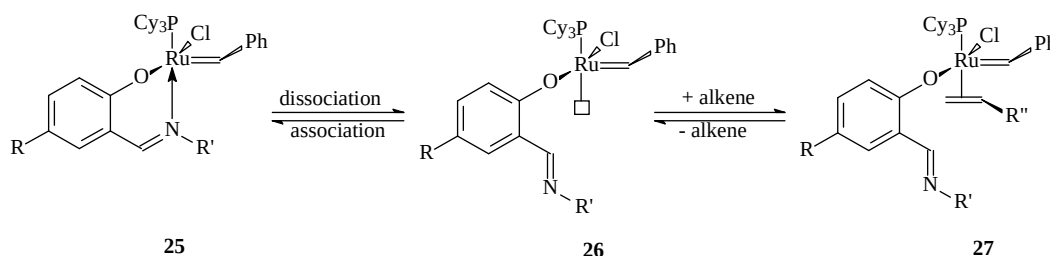


24

The reactivity and the stability of the complex increased towards a number of these ligands (**23** and **24**). These phosphine ligands are regarded to be the most versatile

ligands that can bind to the late transition metals.¹⁰² The phosphines constitute a wide range of ligands with different electronic and steric properties, namely P-O, P-N, P-Br ligands.¹⁰³ The importance in industrial applications of hemilabile phosphines are substantiated through the ability to tune the properties of the formed complex by binding different functional groups to the phosphorus atom.^{102,104,105} The complexes have been used in a range of catalytic reactions due to the hemilabile ligand being able to open a coordination site and stabilize reaction transition metal centers during the reaction.¹⁰⁶

Verpoort et al.¹⁰⁷ suggested that the Schiff base ligands act as hemilabile ligands, with the decoordination and coordination of the N-donor atom instead of the usual PCy_3 dissociation, during the metathesis reaction **Scheme 2.10**.



Scheme 2.10 Mechanism for metathesis with catalytic systems with Schiff-base ligands

The mechanism implies that the active intermediate **26** (having a vacancy for alkene coordination) is stabilized or, respectively, destabilized when the steric and electronic parameters are altered. Diminishing the electron density on the nitrogen atom stimulates the decoordination of the N-donor atom, while an increase in the steric bulk of the ligand has an opposite influence on RCM and ROMP activity of these initiators.

2.5 Molecular Modelling

Molecular modelling refers to theoretical methods and computational techniques to model or mimic the behaviour of molecules collectively.¹⁰⁸ One of the techniques used is in the fields of computational chemistry¹⁰⁹ (a branch of chemistry that uses

computers to assist in solving chemical problems) for studying molecular systems ranging from small chemical systems to large biological molecules and material assemblies.¹⁰⁸ Computational chemistry uses results of theoretical chemistry, incorporated into efficient computer programs to calculate the structures and properties of molecules and solids. All the programs are based on how the molecular Schrödinger equation associated with the molecular Hamiltonian that can be solved with different quantum-chemical methods.¹⁰⁹

Properties include structure i.e. the expected position of the constituent atoms, absolute and relative energies, electronic charge distributions, dipole and higher multipole moments, vibrational frequencies, reactivity etc. This is in contrast with quantum chemistry where electrons are considered explicitly thus more atoms are considered during simulations.¹⁰⁸

Computational chemistry is divided into two application methods:

- Computational studies can be carried out in order to understand and explain experimental data such as the position and source of spectroscopic peaks.
- Computational studies can be used to predict the possibility of entirely unknown molecules or to explore reaction mechanisms that are not readily studied by experimental means.

Several major areas may be distinguished within computational chemistry:

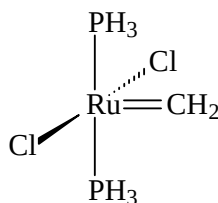
- The prediction of the molecular structure of molecules by the use of the simulation of forces, or more accurate quantum chemical methods, to find minima on the energy surface as the position of the nuclei is varied.
- Identifying correlations between chemicals structures and properties (Quantitative structure-property relationship, QSPR and Quantitative structure-activity relationship, QSAR).
- Computational approaches to help in the efficient synthesis of compounds.
- Computational approaches to design molecules that interact in specific ways with other molecules (e.g. drug design and catalysis).¹⁰⁹

Various methods may be employed in calculating approximated properties like: total energy, electron density, electrostatics, Fukui functions, orbitals and population analysis. Some of the commonly used methods are:¹⁰⁹

- *Ab initio*
- Density functional theory (DFT)
- Semi-empirical (SE)
- Molecular mechanics (MM)
- Methods for solids
- Chemical dynamics

2.5.1 Computational study on Grubbs type pre-catalysts

Having stated the properties mainly used in molecular modelling, many of these were employed in exploring metathesis reactions of 1-alkenes with Grubbs type pre-catalysts. These include a Car-Parrinello *ab initio* molecular dynamics study of the behaviour of complex **27** and its reaction with ethylene at various temperatures;⁶⁵ DFT studies^{65, 70, 110} and QM/MM studies by Adlhart and Chen.⁶⁰



27

The most common aims of the studies are:

- i. Exploring the applicability of rapid and readily accessible MM and SE methods in modeling ruthenium complexes;
- ii. The use of DFT methods to evaluate the reliability of the MM and SE approaches;
- iii. Demonstrating the application of the density functional package, Dmol³, in determining ligand dissociation energies for **1** and **2**.

In a first ab initio molecular dynamic study on **27**, Meier and co-workers found that dissociation of one of the phosphines was facile and would lead to an active species.⁷¹ This was in good qualitative agreement with prior experimental studies, which established that phosphine dissociation was indeed mandatory to achieve high catalytic activity.⁶¹ Subsequently, Hofmann and co-workers studied model compounds with *cis*- and *trans*-phosphane ligands as a preliminary analysis to the synthesis of diphosphanymethane complexes, and concluded that a small bite angle was needed to achieve relative *cis* geometry of the coordinating P-atoms.¹¹¹

A detailed study of the complete reaction profile (from the biphosphane pre-catalyst to the metallacycle) was performed by Chen and co-workers.⁶⁴ Using **27** as a model, they gave the first estimate of the energy required to dissociate one of the phosphines, the olefin uptake energy and the energy barrier for the metathesis reaction. Herrmann and co-workers¹¹² executed the first comparison between different pre-catalysts, since they calculated the binding energy of the different ligands in biphosphanes and heteroleptic pre-catalysts with NHC ligands.¹¹² In agreement with experiments, they found that the NHC ligands have a higher binding energy than phosphane ligands, and the binding energies they calculated are in valuable quantitative agreement with the experimental data.¹⁶

Cavallo did a DFT study on the phosphine dissociation of **1**, **2** and **27** systems which can be considered to correspond to the activation step according to the dissociative mechanism. Furthermore he reported on the metathesis reaction of the olefin coordination step (with ethene as probe olefin) followed by the formation of the metallacycle. He then highlighted the role of Cy, Mes and *t*-Bu groups in metathesis reaction. The conclusions are summarized as follows:¹¹⁰

- The binding energies calculated for coordination of phosphines to Ru in the different pre-catalysts show a reasonable correlation with the experimental activation ΔH and ΔG of phosphine exchange.
- The binding energies calculated for coordination of ethene to Ru in the different pre-catalysts follow the same trend observed for phosphines. The difference between the binding energy of the phosphines and that of the olefin depends on the pre-catalyst considered. In particular, smaller energy differences have been calculated for the NHC-based systems. The higher

tendency of the NHC-based pre-catalyst to bind the olefin is also confirmed by the shorter Ru-olefin distances, and the longer C=C ethene bond in the olefin adduct.

- Solvent effects reduce the absolute binding energies of the phosphines and of the NHC ligands, whereas they scarcely modify the binding energy of apolar ethene. This results in a smaller preference for phosphine coordination in solution and, in agreement with the experimental results, in higher initiation rates. Of course, the higher the polarity of the solvent the higher the effect.
- The major role played by the bulky Mes substituents in the NHC-based system is to exert a strong steric pressure on the alkylidene moiety. This steric pressure destabilizes in a remarkable manner the phosphine and olefin free intermediate, consequently they do not promote phosphine dissociation, and hence slow pre-catalyst initiation. However, they also promote olefin coordination, lower the metathesis reaction barrier, and stabilize the metallacycle intermediate. For this reason, they accelerate overall activity.

2.6 Theoretical investigation on Grubbs type pre-catalysts to address the research problem

In this study molecular modelling is used to investigate the structural properties of possible imine ligands to be synthesized, the ligand coordination (hemilability on Ru complexes to be synthesized) to the Grubbs pre-catalysts and to gain insight on the catalytic reaction mechanism of 1-octene metathesis with Grubbs type pre-catalysts. Analysis on electron density, electrostatics, Fukui functions, orbitals and population analysis were used to address the research problem.

2.6.1 Electron density

The electronic density is used to represent the probability of an electron being present at a specific location.¹¹³ The electron density was usually found around the atom and its bonds and it covered the whole region. In the delocalized or conjugated systems such as phenol and benzene the electron density covers an entire region, that is in benzene it is found above and below the planar ring.¹¹³

In multiple ring systems which are interconnected, like naphthalene, this is no longer accurate.¹¹³ The properties of molecules and intermolecular interactions may be understood by analysis of the solutions of the Schrödinger equation which yields two important parts of information: A set of complicated functions each of which describes a different distribution of all the electrons, and the discrete energy of the electrons with that distribution. The lowest energy corresponds to the ground state of the molecule. Higher energy is those of electronically excited states. The interest is in the electron density associated with the ground state because that is the state in which most molecules exist and this is sufficient to understand the structure of each molecule, most of the interactions between them and most chemical reactions.¹¹⁴

2.6.2 Electrostatics

Electrostatic potential arise from the forces that electric charges exert on each other. Such forces are described by Coulomb's law which states: the magnitude of the electrostatic force between two point electric charges is directly proportional to the product of the magnitudes of each charge and inversely proportional to the square of the distance between the charges Q_1 and Q_2 given in the **Equation 4.1**.¹¹⁵

$$F = \frac{Q_1 Q_2}{4 \epsilon_0 r^2} \quad 4.1$$

ϵ_0 is a constant called permittivity of free space, a defined value:

$$\epsilon_0 = \frac{1}{4 \pi c_0^2} = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$$

This value is many times the strength of an average chemical bond. The energies involved are so large that one may generalize to say that, in any medium of low dielectric constant, charged species in solution are always paired with oppositely charged species surrounded by neutral dipolar species. Electrostatic effects cannot be ignored whenever a process takes place that changes the number of charged species. Reactions of charged species with neutral but dipolar species will be driven by electrostatic effects.¹¹⁴

2.6.3 Fukui functions

Fukui functions are used to assess the reactivity of a chemical molecule from electronic properties like electron density, Mulliken population etc. Frontier orbital theory of Fukui relates the reactivity of a molecule with respect to electrophilic and nucleophilic attack to the charge density. Fukui functions are a qualitative way of measuring and displaying the reactivity of regions of a molecule.¹¹⁶

2.6.3.1 Nucleophilic

A nucleophile is a reagent that forms a chemical bond to its reaction partner by donating both bonding electrons.¹¹⁷ All molecules or ions with a free pair of electrons can act as nucleophiles. A nucleophile is an electron-rich chemical reactant that forms low energy combination with electron deficient compounds.¹¹⁷

2.6.3.2 Electrophilic

An electrophile is a reagent attracted to electrons that participate in a chemical reaction by accepting an electron pair in order to bond to a nucleophile. Most electrophiles are positively charged or have an atom which carries a partial positive charge.¹¹⁸

2.6.4 Orbitals: HOMO/LUMO

The HOMO; highest occupied molecular orbital represents the distribution and energy of the least held electron in the molecule. The lowest unoccupied molecular orbital describes the easiest route to the addition of more electrons to the system. The energy of the HOMO is a good approximation to the lowest ionization potential of the molecule, but the energy of the LUMO is a poor approximation to the molecule's electron affinity. A molecule that does not have a large HOMO-LUMO energy gap is chemically reactive.¹¹⁹

2.6.5 Population analysis

The population analysis complemented it by giving the electron density of the ligand; it divides the density between the atoms to give an estimate of the atomic charge.¹¹⁴

With the specific atomic charge the reactivity of the molecule can be correlated with:

- Fukui functions which can give the nucleophilicity and/or electrophilicity of a molecule
- HOMO/LUMO where the HOMO indicates the electron rich region of the molecule and the LUMO indicates the electron poor region of the molecule
- Electron density which gives the probability of the electron being present at a specific location
- Electrostatics give the strength of a chemical bond by measuring the force that electric charge exerts on each other

2.7 Summary on literature survey

Olefin metathesis is one of the great interventions discovered to date. It is used industrially and in research and has various applications. Olefin metathesis studies include pre-catalysts, which are classified in terms of homogeneous and heterogeneous. The well known Grubbs pre-catalysts, the first and second generation made history in the early 90's. This changed the scope of metathesis. The metal catalyzed olefin metathesis opened a wide range of research investigating, the mechanism involving metal alkylidene and metallacyclobutane intermediates, Chauvin and Herisson worked out an understandable mechanism.

After the Herisson-Chauvin mechanism for metathesis, the study of Ru-catalyzed olefin metathesis reaction and mechanism has guided the development of new ligands. Schiff base ligands became an interesting class to create new Ru complexes. Verpoort and co-workers prepared a wide range of efficient Ru pre-catalysts with O, N-chelated Schiff base hemilabile ligands.

Nevertheless, more is still to be done to improve the Grubbs pre-catalysts' lifetime and efficiency which are the limiting factors. With the new development of various techniques, molecular modelling is a tool to minimize and/or confirm experimental

findings. The next chapter will show how to go about addressing the aims set for this study (given in chapter one), with a guide of theoretical and experimental methods used.

2.8 References

1. K. J. Ivin and J. C. Mol, *Olefin metathesis and metathesis polymerization*, 1997, San Diego: Academic Press
2. M. Jordaan, *Experimental and theoretical investigation of new Grubbs-type pre-catalysts for the metathesis of alkenes*, North-West University (Potchefstroom campus) PhD Thesis, 2007
3. K. N. G. Mtshatsheni, *Metathesis of alkene using ruthenium carbene complexes*, North-West University (Potchefstroom campus) MSc Thesis, 2005
4. a) D. Astruc, *New. J. Chem.*, 2005, **29**, 42 b) N. Calderon, *Tetrahedron Lett.*, 1967, **34**, 3327 c) N. Calderon, *Acc. Chem. Res.*, 1972, **5**, 127
5. R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7117
6. R. H. Grubbs, *Handbook of Metathesis*, 2003, Wiley-VCH Germany
7. J. C. Mol, *J. Mol. Catal.*, 2004, **213**, 39
8. [http://: www.en.wikipedia.org/wiki/Acyclic diene metathesis](http://www.en.wikipedia.org/wiki/Acyclic_diene_metathesis), (15/10/2008)
9. V. Dragutan, P. Dragutan, Filip, *ARKIVOC*, 2005 (x), 105
10. S. T. Diver and A. J. Giessert, *Chem. Rev.*, 2004, **104**, 1317
11. R. H. Grubbs, D. D. Carr, C. Haoppin, P. L. Burk, *J. Am. Chem. Soc.*, 1976, **98**, 3478
12. T. J. Katz, J. McGinnis, *J. Am. Chem. Soc.*, 1975, **97**, 1592
13. T. J. Katz, R. Rothchild, *J. Am. Chem. Soc.*, 1976, **98**, 2519
14. F. Bernard, A. Bottoni and G. P. Miscione, *Organometallics*, 2003, **22**, 940
15. P. E. Romero and W. E. Piers, *J. Am. Chem. Soc.*, 2005, **127**, 5032
16. M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.*, 2002, **123**, 6543
17. S. Kahn and N. J. Rutherford, US Patent 3,538,182, 1970
18. R. E. Reusser, US Patent 3,729,524, 1973
19. M. B. Dinger, J. C. Mol, *Organometallics*, 2003, **22**, 1089
20. F. A Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 1999, John Wiley & Sons, Inc.

21. C. Pariya, K. N. Jayaprakash, A. Sarkar, *Coordination Chem. Rev.*, 1998, **168**, 1
22. B. N. Shelimov, I. V. Elev, V. B. Kazansky, *J. Mol. Catal.*, 1988, **46**, 187
23. K. A. Vikulov, B. N. Shelimov, V. B. Kazansky, *J. Mol. Catal.*, 1991, **65**, 393
24. I. V. Elev, B. N. Shelimov, V. B. Kazansky, M. Y. Berezin, G. A. Usacheva, P. S. Belov, *Kinet. Katal.* 1989, **30**, 1101
25. A. Frantisek, J. Novansky, *Ropa Uhlie*, 1988, **30**, 77
26. B. Liu, S. Pan, Zhejiang Daxue Xuebao-Ziran Kexueban, 1990, **24**, 189
27. K. Prandova, J. Novansky, P. Hudec, *Ropa Uhlie*, 1991, **33**, 206
28. J. Hietala, P. Knuuttila, A. Kytokivi, Finn. FI 87891, 1992
29. P. Knuuttila, J. Hietala, A. Linna, Finn. Pat. 86 298, 1992
30. K. Weiss, W. Guthmann, S. Maisuls, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 275
31. T. M. Trnka, J. P.. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 2546
32. L. Bencze, Magy, *Kem. Foly.*, 1994, **100**, 409
33. J. G. Hamilton, J.J. Rooney, *J. Chem. Soc. Chem. Commun.*, 1992, 370
34. V. I. Bykov, T. A. Butenko, E.Sh Finkel'shtein, P. T. Henderson, *J. Mol. Catal.*, 1990, **90**, 111
35. R. R. Schrock, *Acc. Chem. Res.*, 1990, **23**, 158
36. H. H. Fox, J. K. Lee, L. Y. Park, R. R. Schrock, *Organometallics*, 1993, **12**, 759
37. H. H. Fox, K. B. Yap, J. Robins, S. Cai, R. R. Schrock, *Inorg. Chem.*, 1992, **31**, 2287
38. J. H. Oskam, H. H. Fox, K. B. Yap, D. H. McConville, R. O'Dell, B. J. Lichtenstein, R. R. Schrock, *J. Organomet. Chem.* 1993, **459**, 185
39. E. Thron-Csanyi, J. Dehmel, H. D. Liginland, J.U. Zilles, *J. Mol. Catal.*, 1997, **115**, 29
40. A. D. Benedicto, J. P. Claverie, R. H. Grubbs, *Macromolecules*, 1995, **28**, 500
41. J. T. Patton, J. M. Boncella, K. B. Wagener, *Macromolecules*, 1992, **25**, 3862
42. K. B. Wagener, J. T. Patton, *Macromolecules*, 1993, **26**, 250
43. H. Hockev, *J. Mol. Catal.*, 1991, **65**, 95
44. J. C. Mol, *J. Mol. Catal.*, 1982, **15**, 35
45. H. Cramail, M. Fontanille, A. Soum, *J. Mol. Catal.*, 1991, **65**, 193

46. E. Ceausecu, A. Cornilescu, E. Nicolescu, M. Popescu, S. Coca, M. Cuzmici, M. Dimonie, V. Dragutan, *J. Mol. Catal.*, 1988, **46**, 415
47. E. Ceausecu, A. Cornilescu, E. Nicolescu, M. Popescu, S. Coca, M. Cuzmici, C. Oprescu, M. Dimonie, G. H. Hubca, M. Teodorescu, V. Dragutan, V. Chipara, *J. Mol. Catal.*, 1988, **46**, 405
48. M. Dimonie, S. Coca, M. Teodorescu, L. Popescu, M. Chipara, V. Dragutan, *J. Mol. Catal.*, 1994, **90**, 117
49. M. Dimonie, S. Coca, V. Dragutan, *J. Mol. Catal.*, 1992, **76**, 79
50. W. A. Nugent, J. Feldman, J. C. Calabrese, *J. Am. Chem. Soc.*, 1995, **117**, 8992
51. K. B. Wagener, J. M. Boncella, G. J. Nel, *Macromolecules*, 1991, **24**, 2649
52. K. Weiss, R. Gollar, G. Loessel, *J. Mol. Catal.* 1988, **46**, 267
53. J. A. K. Du-Plessis, T. J. Pienaar, H. C. M. Vosloo, *J. Mol. Catal.*, 1988, **46**, 287
54. R. H. Grubbs, S. T. Miller, G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446
55. S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 9858
56. M. A. Hillmyer, W. R. Laredo, R. H. Grubbs, *Macromolecules*, 1995, **28**, 6311
57. Z. Wu, A. D. Benedicto, R. H. Grubbs, *Macromolecules*, 1993, **26**, 4975
58. M. Jordaan and H. C. M. Vosloo, *Adv. Synth. Catal.* 2007, **349**, 184
59. Y. Chauvin, J. Herrison. *Makromol. Chem.*, 1971, **141**, 161
60. C. Adlhart, P. Chen, *J. Am. Chem. Soc.*, 2004, **126**, 3496
61. E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887
62. M. Ulman, R. H. Grubbs, *Organometallics*, 1998, **17**, 2484
63. M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, **123**, 749
64. C. Adlhart, C. Hinderling, H. Baumann, P. Chen, *J. Am. Chem. Soc.*, 2000, **122**, 8204
65. F. Bernardi, A. Bottoni, G. P. Miscione, *Organometallics*, 2003, **22**, 940
66. K. Basu, J. A. Cabral, L. A. Paquette, *Tetrahedron Lett.*, 2002, **43**, 5453
67. G. J. Spivak, J. N. Coalter, *Organometallics*, 1998, **17**, 999, 1001
68. J. N. Coalter, G. J. Spivak, H. Grard, E. Clot, E. R. Davidson, O. Eisenstein, C. K. G., *J. Am. Chem. Soc.*, 1998, **120**, 9388
69. G. Ferrando-Miguel, J. N. Coalter, H. Gerard, J. C. Huffman, O. Eisenstein, K. G. Caulton, *New J. Chem.* 2002, **26**, 687

70. S. Fomine, V. S. Martinez, M. A. Tlenkopatchev, *Organometallics*, 2003, **22**, 93
71. O. M. Aagaard, R. J. Meier, F. Buda, *J. Am. Chem. Soc.*, 1998, **120**, 7174
72. K. J. Laidler, *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987
73. S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168
74. R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875
75. G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas, W. M. Davis, *J. Am. Chem. Soc.*, 1990, **112**, 8378
76. G. C. Bazan, J. H. Oskam, H.-N. Cho, L. Y. Park, R. R. Schrock, *J. Am. Chem. Soc.*, 1991, **113**, 6899
77. R. H. Grubbs, S. Chang, *Tetrahedron*, 1998, **54**, 4413
78. J. H. Oskam, R. R. Schrock, *J. Am. Chem. Soc.*, 1993, **115**(25), 11831
79. R. R. Schrock, W. E. Crowe, G. C. Bazan, M. DiMare, M. B. O'Regan, M. H. Schofield, *Organometallics*, 1991, **10**, 1832
80. J. Kress, J. A. Osborn, *J. Am. Chem. Soc.*, 1987, **109**, 3953
81. R. R. Schrock, L. W. Messerle, C. D. Wood, L. J. Guggenberger, *J. Am. Chem. Soc.*, 1978, **100**, 3793
82. R. Toreki, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.*, 1992, **114**, 3367
83. R. R. Schrock, *J. Mol. Catal.*, 2004, **213**, 21
84. O. Fujimura, F. J. de la Mata, R. H. Grubbs, *Organometallics*, 1996, **15**, 1865
85. O. Fujimura, R. H. Grubbs, *J. Am. Chem. Soc.*, 1996, **118**, 2499
86. F. A Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley and Sons: New York, 1988 ISBN 9780471199575
87. S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3974
88. B. de Clercq, F. Verpoort, *J. Mol. Catal. A-Chem.*, 2002, **180**, 67.
89. B. de Clercq, F. Verpoort, *Tetrahedron Lett.*, 2002, **43**, 9101
90. J. Huang, E. D. Stevens, S. P. Peterson, *J. Am. Chem. Soc.*, 1999, **121**, 2674
91. J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics*, 1999, **18**, 5375
92. M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.*, 1999, **40**, 2247

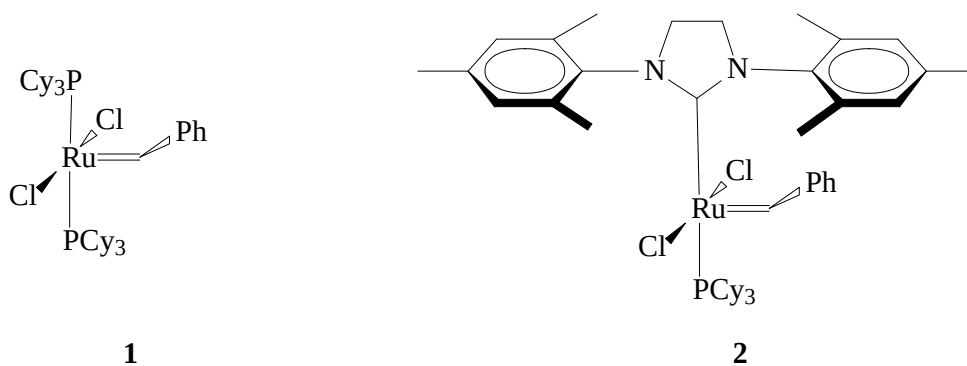
93. M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953
94. A. K. Chatterjee, R. H. Grubbs, *Org. Lett.*, 1999, **1**, 1751
95. A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, **122**, 3783
96. L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett.*, 1999, **40**, 4787
97. E. Lindner, S. Pautz, M. Haustein, *Coord. Chem. Rev.*, 1996, **155**, 145
98. G. T. Morgan, H. D. K. Drew, *J. Chem. Soc., Trans.*, 1920, **117**, 1456
99. C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233
100. L. Horner, G. Simons, *Naturforsch, B: Anorg. Chem. Org. Chem.* 1984, **39**, 497
101. J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658
102. E. Valls, J. Suades, *Organometallics*, 1999, **18**, 5475
103. C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313
104. C. W. Rages, M. O. Wolf, *Chem. Commun.*, 1999, 2297
105. E. Lindner, J. Wald, K. Eichele, R. Fawzi, *J. Orgmet. Chem.* 2000, **601**, 220
106. R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2134
107. B. de Clercq, F. Verpoort, *Adv. Synth. Catal.*, 2002, **344**, 639
108. http://en.wikipedia.org/wiki/Molecular_modelling, 23/01/2009
109. http://en.wikipedia.org/wiki/Computational_chemistry, 23/01/2009
110. L. Cavallo, *J. Am. Chem. Soc.*, 2004, **124**, 8965
111. S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisentrager, P. Hofmann, *Angew. Chem. Int. Ed. Engl.* 1999, **38**, 1373
112. T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* 1999, **38**, 2416
113. http://en.wikipedia.org/wiki/Electron_density, 20/05/2010
114. A. Rauk, *Orbital interaction theory of organic chemistry*, 2nd edition, 2001
115. <http://en.wikipedia.org/wiki/Electrostatics>, 20/05/2010
116. <http://www.accelrys.com> 04/06/2010
117. <http://en.wikipedia.org/wiki/Nucleophilic>, 20/05/2010
118. <http://en.wikipedia.org/wiki/Electrophilic>, 20/05/2010
119. J. McMurry, *Organic chemistry*, Belmont, CA: Thomson-Brooks/Cole, 2004

3 Alkene Metathesis: Theoretical investigation

3.1 Program and properties

Dmol³, a DFT modelling program, was used for all calculations.¹ The program is implemented in Accelrys Material Studio 4.2 version.² The geometry optimization used was the generalized gradient approximation (GGA) functional by Perdew and Wang (PW91)³ with the convergence tolerance values of 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å for energy, maximum force and displacement respectively. The electronic options included self-consistent field (SCF) value of 1×10^{-5} Ha with the double numeric polarized (DNP) basis set. Analysis on electron density, electrostatics, Fukui functions, HOMO, LUMO orbitals and population analysis were used to address the research problem.

Amongst the properties, orbital analysis can be a useful property, for example, the HOMO energy, as a preliminary selection criterion for screening and predicting suitable imine ligands. Other criteria included their existence, synthesis procedure and yields of the Schiff base ligands. The two most promising ligands were used to design and synthesize new Grubbs type pre-catalysts from **1** and **2**.



Molecular modeling will help gain insight into the mechanism of 1-octene metathesis reaction by using the Potential Energy Surface (PES) scan illustrated in **Figure 3.1**. The PES scan is the plot of energy the against reaction coordinate whereby the Transition State (TS) can be obtained.

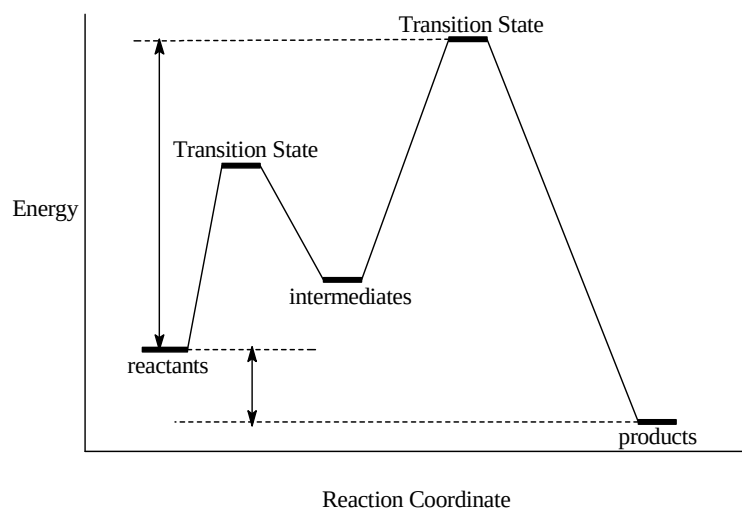
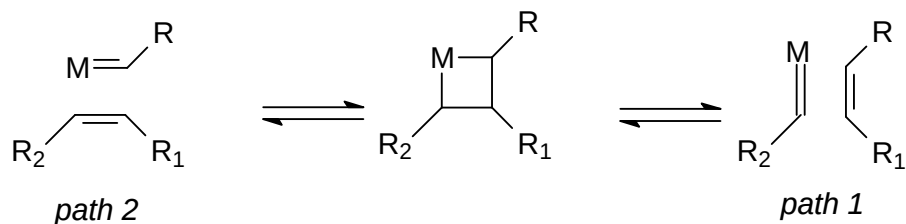


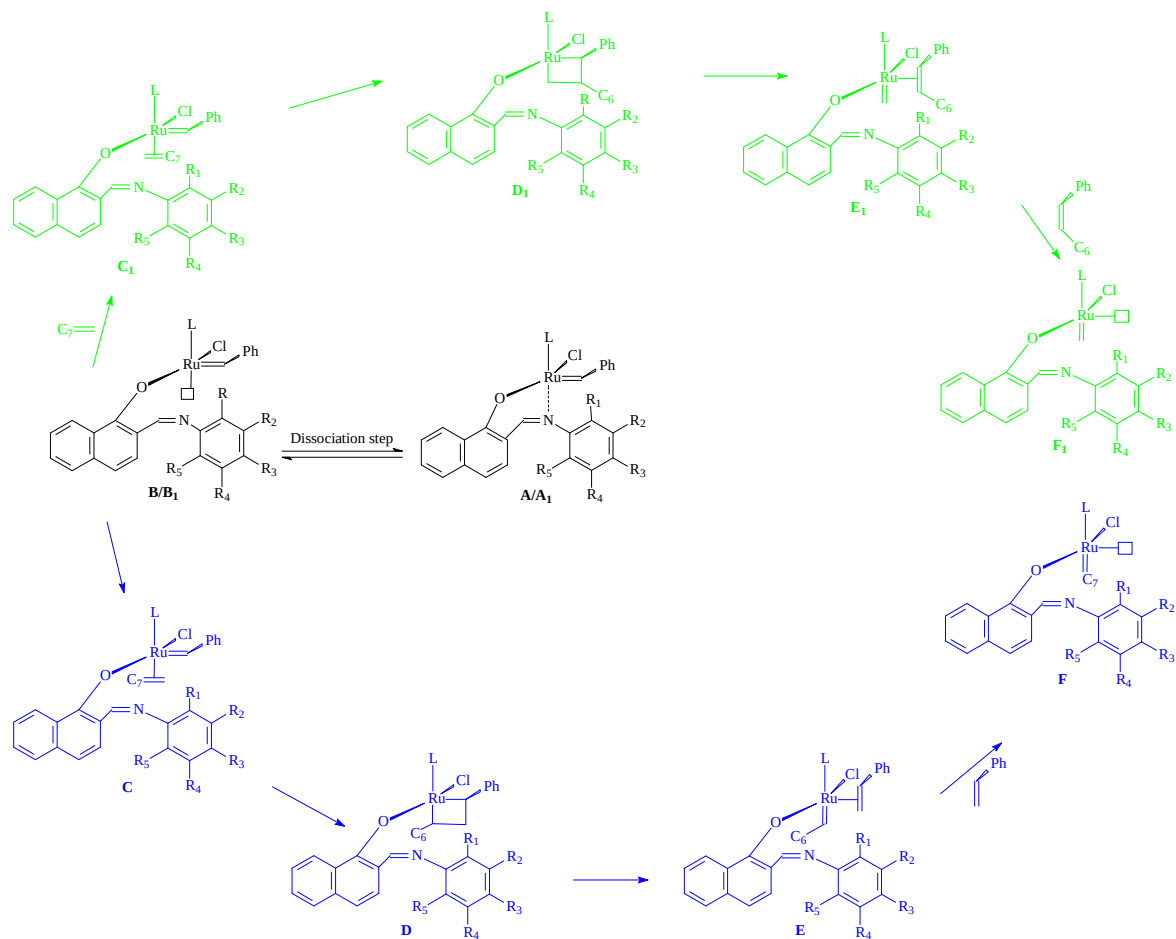
Figure 3.1 Energy profile graph.

The PES scan is meant to resemble the Chauvin mechanism, **Scheme 3.1**.



Scheme 3.1 The mechanism of the catalyzed olefin metathesis.

The energy profile plotted can either result in the products in *path 1* or *path 2*. Both reaction paths were investigated. Detailed mechanisms of the two paths are given in **Scheme 3.2**



Scheme 3.2 Activation cycle of **path 1** and **path 2**

The mechanism of the substituted ruthenium complex starts at **A/A₁** with the dissociation of the hemilabile ligand and result in **B/B₁**. The incoming 1-octene coordinates with **B/B₁** to form **C/C₁**. The double bonds are then changed and a metallocyclobutane is obtained **D₁**. The activated pre-catalyst with a bulky olefin leaving the coordination results in a vacant site **F₁**.

The 1-octene can also coordinate to the pre-catalyst *trans* to the phenyl of the carbene, **D**. The activated pre-catalyst with a bulky olefin leaving the coordination results in a vacant site **F**. The activation mechanism for path 1 and 2 will be investigated in this study.

Now that **F** and **F₁** are activated they continue with the propagation cycle where they will again react with 1-octene. It was shown from previous studies that when **F** reacts with 1-octene in the same direction as the phenyl it results in **F₁**. When **F** reacts with 1-octene in a different direction as the phenyl it result in **F** thus it is called an unproductive reaction. The same unproductive reaction was found in **F₁** when entering the catalytic cycle.⁴ The primary metathesis products 1-phenyl-1-nonene and styrene were obtained in the activation steps.

3.2 References

1. B. Delley, *J. Chem. Phys.*, 1990, 92, 508
2. <http://www.accelrys.com>, 16/11/2009
3. J. Langlet, J. Berges, P. Reinhardt, *Chem. Phys. Lett.*, 2004, 396, 10
4. C. A. A. Huijsmans, *Modelling and synthesis of Grubbs type complexes with hemilabile ligands*, North-West University (Potchefstroom campus), MSc Dissertation, 2009

4 EXPERIMENTAL

4.1 Reagents and solvents

Compounds **1** and **2** (Aldrich) were used as obtained. 2,6-diisopropylaniline, 2,4,6-trimethylaniline and 2-hydroxy-1-naphthaldehyde (Aldrich) were used as obtained. THF, pentane benzene and toluene were dried under argon. Other solvents including ethanol, methanol, formic acid, diethyl ether, 1-octene and nonane were used without further purification.

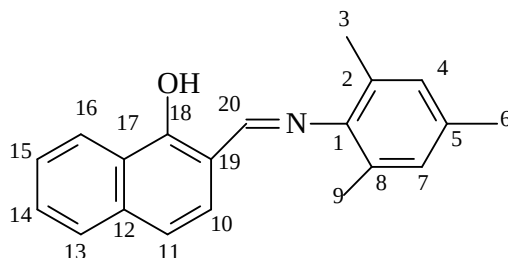
4.2 Apparatus

All glassware, including Schlenk flasks was thoroughly washed and dried in an oven at 100 °C before use. Hamilton GASTIGHT[®] syringes were used to measure some of the reagents. A hot plate with a magnetic stirrer was used for reflux. Melting points were determined on a BUCHI B-540 melting point apparatus. All melting points were uncorrected. A rotary evaporator was used to remove solvents from the ligands.

4.3 Synthesis

4.3.1 Synthesis of Schiff base ligands

4.3.1.1 Synthesis of 1-[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol[L1]¹



2,4,6-Trimethylaniline (0.34 g, 2.5 mmol) in ethanol (10 ml) was added slowly over 30 minutes into a stirred solution of 2-hydroxy-1-naphthaldehyde (0.43 g, 2.5 mmol)

in ethanol (10 ml) at ambient temperature. The solution was heated at reflux for 4 hours. Upon cooling to room temperature, the solvent was removed with a rotary evaporator, and then chilled to 0 °C to give a yellow solid.

Yield: 0.549 g, 83.5%

MS (EI): 289.14 m/z

Molecular mass: 289.38g/mol

Melting point: 86-87 °C

IR $\nu_{\max}$:^a 3443 (OH), 2989-2800 (C-H, aromatic), 1620 (C=N), 1575 (C=C), 1476 (C-N), 1328 (CH₃), below 500 (C-C)

¹H NMR δ_{H} :^b 2.1 (s, C₃), 2.2 (s, C₉), 3.7 (s, C₆), 6.9 (d, H₁₆), 7-7.25 (m, H₁₅), 7.34-7.45 (m, H₁₄), 7.7 (d, H₁₃), 7.8 (d, H₁₁), 7.92 (d, H₁₀), 9.0 (s, HC=N), 15.2 (s, OH) ppm

¹³C NMR δ_{C} :^c 22.24 (Q, C₃), 18.63 (Q, C₉), 14.08 (Q, C₆), 118.6 (D, C₂₀), 122.1-123.3 (T, C₁₄₊₁₅), 127.18 (D, C₁₃₊₁₆), 128.08 (S, C₁₂₊₁₇), 129.34 (D, C₁₁), 129.80 (D, C₁₀), 133.32 (S, C₅), 135.47 (D, C₄₊₇), 136.23 (s, C₂₊₇), 142.49 (S, C₁₈), 160.70 (S, C₁₉), 169.51 (S, C₁) ppm

a: IR with KBr

s/S: singlet

b: ¹H NMR 600 MHz

d/D: doublet

c: ¹³C NMR 600 MHz

dd: doublets of doublets

e: small letter indicate H-H coupling

t/T: triplet

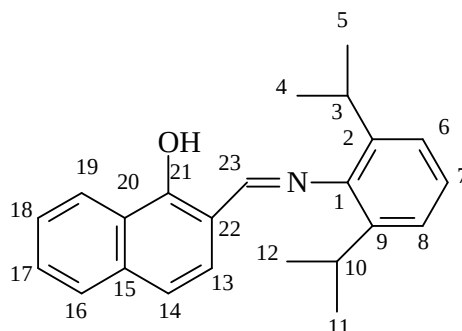
d: capital letters indicate C-H coupling

m/M: multiplet

f: solvent CDCl₃

q/Q: quartets

4.3.1.2 Synthesis of 1-[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol[L2]²



2,6-Diisopropylaniline (0.425g, 2.4 mmol) and 2-hydroxy-1-naphthaldehyde (0.3 g, 2 mmol) were dissolved in methanol (10 ml). Formic acid (0.2 ml) was added and the reaction mixture was stirred for 30 minutes. The resulting precipitate was collected on a frit and washed with methanol (10 ml). The product was then dissolved in diethyl ether (15 ml) and was stirred for 3 hours. The solution was filtered through a frit and the solvent was removed under vacuum to give a yellow microcrystals.

Yield: 0.144 g, 24%

MS (EI): 331.192 m/z

Molecular mass: 331.46

Melting point: 149.2 °C

IR $\nu_{\max}$:^a 3400 (OH), 3100-2800 (C-H, aromatic), 1627 (C=N), 1580 (C=C), 1463 (C-N), 1400 (C-H, aliphatic), 1340 (CH₃), below 500 (C-C)

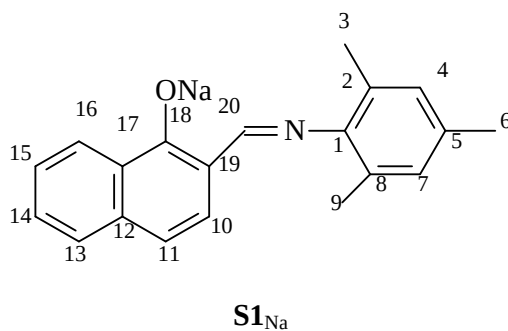
¹H NMR:^b δ_{H} 1.2 (s, H₄₊₁₂), 2.1 (d, H₃₊₁₀), 3.1 (s, H₅₊₁₁), 7.1 (d, H₁₆₊₁₉), 7.2 (t, H₇), 7.3 (t, H₁₈), 7.45 (t, H₁₇), 7.7 (d, H₁₄), 7.8 (d, H₁₃), 7.98 (d, H₆₊₈), 9.05 (s, HC=N), 15.3 (s, OH) ppm

¹³C NMR:^c δ_{C} 23.7 (Q, C₄₊₁₂), 28.3 (Q, C₅₊₁₁), 118.7 (D, C₂₃), 121.43 (T, C₁₇₊₁₈), 123.44 (D, C₁₆₊₁₉), 123.53 (S, C₁₅₊₂₀), 126.26 (D, C₁₄), 128.11 (D, C₁₃), 129.33 (D, C₃₊₁₀), 133.18 (D, C₆₊₈), 135.92 (T, C₇), 140.30 (S, C₄₊₉), 143.88 (S, C₂₂), 161.5 (S, C₁) ppm

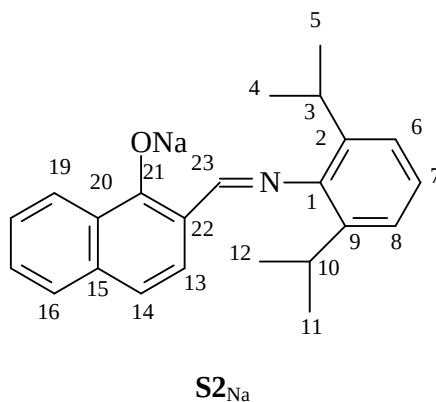
a: IR with KBr	s/S: singlet
b: ^1H NMR 600 MHz	d/D: doublet
c: ^{13}C NMR 600 MHz	dd: doublets of doublets
e: small letter indicate H-H coupling	t/T: triplet
d: capital letters indicate C-H coupling	m/M: multiplet
f: solvent CDCl_3	q/Q: quartets

4.3.2 General method for the synthesis of sodium salts

The ligand (2 mmol) was dissolved in 5 ml THF under argon. NaH (48 mg, 2 mmol) was slowly added to the solution and the reaction was stirred for 12 hours. The solution was filtered under argon atmosphere, then the solvent was removed to yield the desired salt.³ Due to the sensitivity to moisture of the sodium salts, they were used without further purification and the analysis for the S2_{Na} was not successful.



Yield: 66.4%

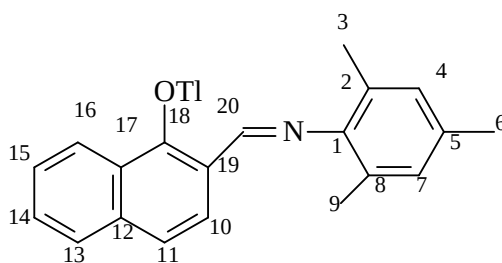


Yield: 73.1%

The difference in characterization for the salts and the ligands is the OH peak. In the NMR analysis no OH resonance signal was observed. The ^1H NMR and the ^{13}C NMR spectra of the salts are given in Appendices IV and V respectively.

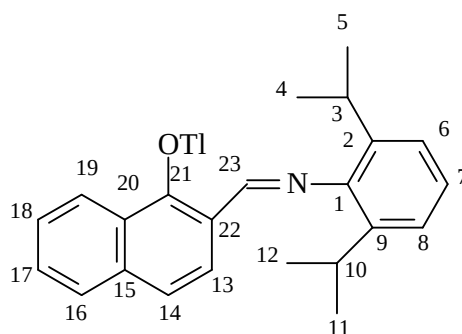
4.3.3 General method for the synthesis of thallium salts

A solution of thallium ethoxide (0.05 mmol) in THF (5 ml) was added dropwise to a solution of the Schiff base (2 mmol) in THF (10 ml) at room temperature. The reaction mixture was stirred for 2 hours. Filtration of the solution under argon atmosphere gave the respective thallium salt which was immediately used in the next step without further purification.⁴



S1_{Tl}

Yield: 70%



S2_{Tl}

Yield: 78%

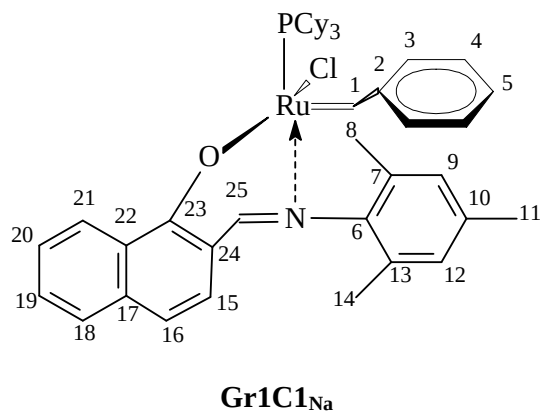
The salt where not analyzed by IR due to decomposition in air. The ^1H NMR and the ^{13}C NMR spectra of the salts are given in Appendices IV and V respectively.

4.4. Synthesis of substituted Grubbs pre-catalysts

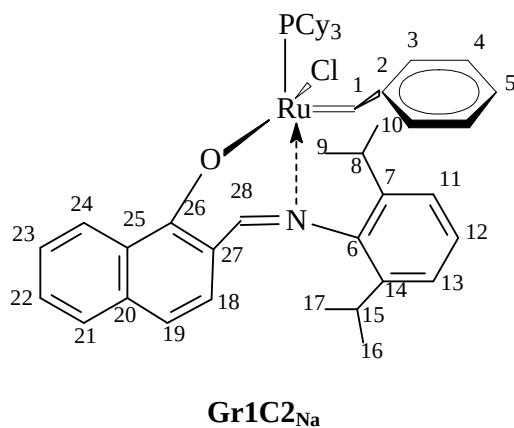
4.4.1 General method for the synthesis of substituted Grubbs type pre-catalysts using sodium salts

The synthesis of substituted Grubbs type pre-catalysts was carried out under inert atmosphere (Ar) due to instability of the pre-catalysts in solution. The sodium salt (0.5 mmol) and **2** (0.5 mmol) were placed in a Schlenk tube and were flushed with argon gas. THF (20 ml) was added. The reaction mixture was stirred for 3 days at approximately 30 °C. The reaction was monitored with TLC which showed a large brownish speck on formation of the complex. When the reaction was complete THF was removed under vacuum. The brown residue was dissolved in toluene (10 ml) and the solution was filtered to a second Schlenk tube to remove sodium chloride formed. After the toluene was removed under vacuum the brown solid was dissolved in THF (1 ml) and pentane (20 ml). The Schlenk tube was placed in an ultrasonic bath for about 10 minutes to remove any sodium chloride that might still be there after which the solvent was removed. The substituted Grubbs type pre-catalyst was washed with pentane (50 ml) to yield a product as a brown solid which was dried under vacuum.⁵

In all the attempts to synthesize the substituted Grubbs type pre-catalyst, **2** was synthesized first. If the carbene was obtained with **2** then **1** would be synthesized. This was done because of the stability of **2**. In this instance the carbene peak was not obtained for the Grubbs two type synthesis. The carbene peak for Grubbs two type pre-catalyst is normally obtained between 17-19 ppm in ¹H NMR spectra. Further investigations for the synthesis of Grubbs one type were not carried out. The synthesized pre-catalyst could not be tested for metathesis because of the absence of the carbene peaks. The NMR spectra are given in Appendix IV.



Yield: 68%

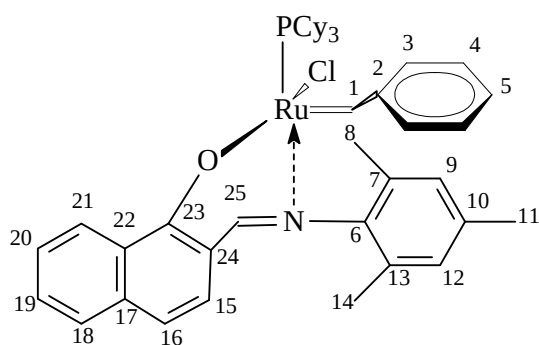


Yield: 65%

4.4.2 General method for the synthesis of substituted Grubbs type pre-catalysts using thallium salts

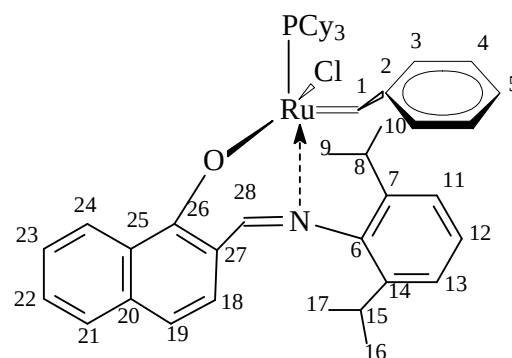
The solution of thallium salt was added to a solution of either **1** or **2** (0.5 mmol) in THF (10 ml). The reaction mixture was stirred at room temperature for 4 hours. After evaporation of the solvent, the residue was dissolved in a minimal amount of benzene and cooled to 0 °C. The thallium chloride was removed by filtration. The Schlenk tube was placed in an ultrasonic bath for about 10 minutes to remove any thallium chloride that might still be there then the solvent was removed. After evaporating benzene the substituted Grubbs pre-catalyst was washed with pentane (50 ml) and the desired product, obtained as a brown solid, was dried under vacuum.⁴

In this instance the carbene peak was obtained for the Grubbs two type synthesis, which is normally obtained between 17-19 ppm in the ^1H NMR. Therefore further investigations for the synthesis of Grubbs one type were carried out. The carbene peak was not obtained for both Grubbs one type synthesis. The synthesized Grubbs two type pre-catalyst were tested for metathesis and Grubbs one type pre-catalysts could not be tested for metathesis because of the absence of the carbene peaks. All the NMR spectra are given in Appendix IV.



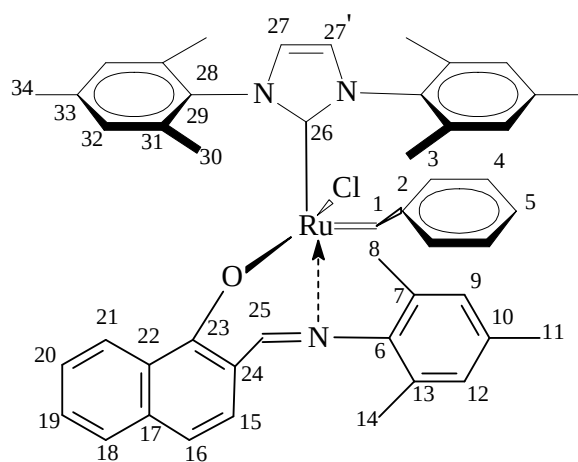
Gr1C1_{Ti}

Yield: 69%



Gr1C2_{Ti}

Yield: 71%



Gr2C1_{Ti}

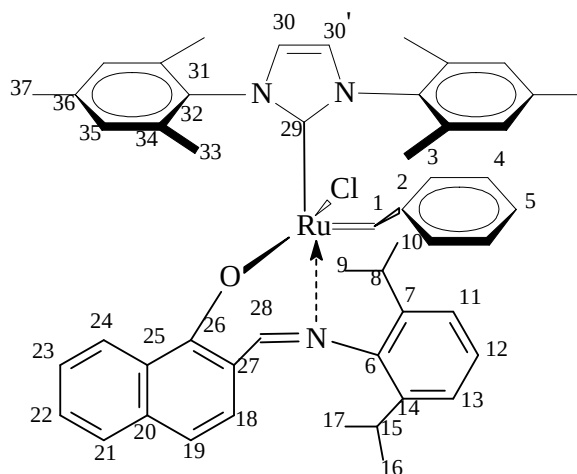
Yield: 47%

IR: 3450 (OH), 2987-2802 (C-H), 1625 (C=N), 1580 (C=C), 1491 (C-N), 1341-1325 (CH₃)

^1H NMR: 17.45 (s, H_1), 9.03 (s, $\text{HC}=\text{N}$), 7.95 (d, H_{15}), 7.8 (d, H_{16}), 7.78 (d, H_{18}), 7.79-7.6 (dd, H_{19}), 7.4-7.5 (m, H_{20}), 7.3 (d, H_{21}), 6.8-6.97 (m, $\text{H}_{31+31'}$), 4.5 (d, H_3), 3.9-4.0 (m, $\text{H}_{27+27'}$), 3.8 (m, H_4), 3.1 (d, H_5), 2.1-2.8 (m, 18H), 1.1, 1.0 and 0.8-0.9 (m, C_8 , C_{11} and C_{14}) ppm

^{31}P NMR: No visible peaks

a: IR with KBr	s: singlet
b: ^1H NMR 600 MHz	d: doublet
c: ^{31}P NMR:	dd: doublets of doublets
d: small letter indicate H-H coupling	t/T: triplet
e: solvent CDCl_3	m/M: multiplet
	q/Q: quartets



Gr2C2Ti

Yield: 31%

IR: 3468 (OH), 2900-2700 (C-H, aromatic), 1592 ($\text{C}=\text{N}$), 1580 ($\text{C}=\text{C}$), 1490 ($\text{C}-\text{N}$), 1340-1280 (CH_3)

^1H NMR 17.45 (s, H_1), 9.03 (s, $\text{HC}=\text{N}$), 7.98 (d, H_{10+12}), 7.8 (d, H_{17}), 7.7 (d, H_{18}), 7.6 (dd, H_{21}), 7.45 (t, H_{22}), 7.1 (t, H_{11}), 7.09 (d, H_{20+23}), 6.8-6.97 (m, $\text{H}_{33+33'}$), 4.2 (dd, H_3), 3.6-4.0 (m, $\text{H}_{27+27'}$), 3.5 (m, H_4), 3.2 (dd, H_5), 2.1-2.7 (m, 18H), 1.0 (d, H_{3+10}), 0.7-0.9 (m, C_4 , C_5 , C_{11} and C_{12}) ppm

^{31}P NMR: No visible peaks

a: IR with KBr	s: singlet
b: ^1H NMR 600 MHz	d: doublet
c: ^{31}P NMR:	dd: doublets of doublets
d: small letter indicate H-H coupling	t/T: triplet
e: solvent CDCl_3	m/M: multiplet
	q/Q: quartets

4.5 Metathesis: Experimental investigation

The activity and selectivity of Grubbs substituted pre-catalysts were investigated through the metathesis reactions with 1-octene. The metathesis setup is illustrated in **Figure 3.2**. The Grubbs type pre-catalyst (0.015 mmol) was added to a solution of 1-octene (20 ml, 0.127 mmol) and nonane (1 ml, as an internal standard) that was preheated to 30 °C. The progress of the metathesis reaction was monitored by adding 0.3 ml of the samples to a GC vial from 0 to 60 minutes at 10 minutes intervals. The GC vial contains 0.3 ml of toluene to make up the volume of the sample and 2 drops of tert-butyl hydrogen peroxide to quench the reaction.⁵

4.6 Analysis

4.6.1 IR

A Nicolet FTIR 550 spectrophotometer was used at a scan range of 4000-500 cm^{-1} . About 2 mg of sample was mixed with approximately 300 mg dried KBr and pressed into a pellet.

4.6.2 GC-MS

Samples were prepared for an Agilent Technologies 6890N GC-MS equipped with ZB-1 100% methyl siloxane capillary column (30 m x 320 μm x 1.0 μm) connected to the Agilent 5973 mass selective detector (MSD).

MSD parameters: MS source 230 °C, Quadrupole analyzer 150 °C

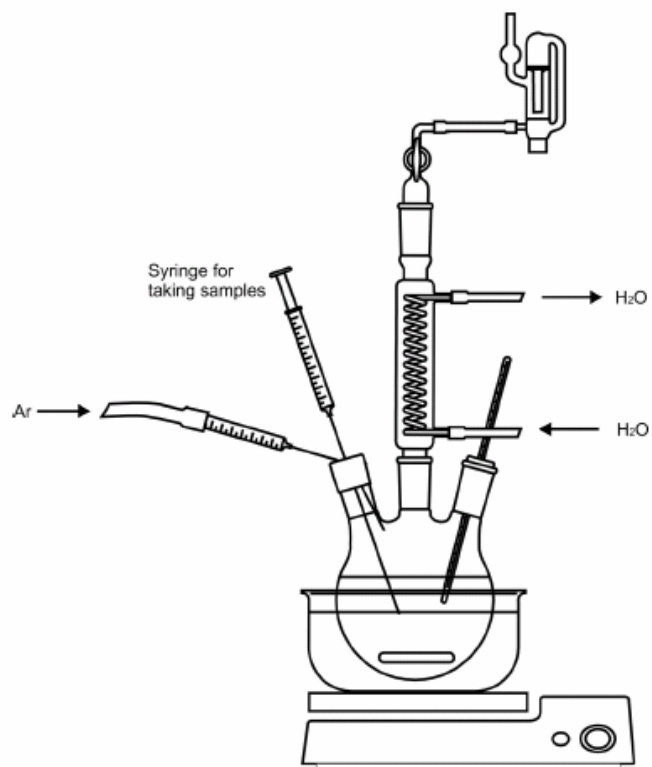


Figure 4.1 Experimental setup for metathesis reaction.

The method that was adapted is as follows:

Injection volume	: 0.2 μ l
Split ratio	: 50.5: 1
Inlet temperature	: 200°C
He carrier gas flow	: 1.4 ml min ⁻¹
He flow rate	: 40 ml min ⁻¹
Air flow rate	: 450 ml min ⁻¹
Oven programming	: 60 °C to 110 °C at 25 °C min ⁻¹ 110 °C for 16 min 110 °C to 300 °C at 25 °C min ⁻¹ 300 °C for 5min
Detector temperature	: 300°C

4.6.3 NMR

The NMR spectra (^1H and ^{13}C) were obtained by a BRUKER 600 MHz spectrometer. NMR samples were prepared by dissolving 40 mg of sample in CDCl_3 . The thallium salts were analyzed in deuterated THF.

3.6.3.1 NMR analysis for pre-catalyst

The Schlenk tube was flushed with argon gas and weighed. 40-60 mg of the pre-catalyst was weighed using the Schlenk. A 0.7 ml of CDCl_3 was added to the Schlenk tube while the NMR tube was flushed with argon gas. Then the mixture from the Schlenk tube was transferred to the NMR tube.

4.7 GC analysis for metathesis reactions

The metathesis reactions were monitored with Agilent Technologies 6850N GC-FID equipped with a HP-1 100% methyl siloxane column (30m x 0.32mm x 0.25 μm) and an Agilent Technologies 7683 series autoinjector. The following settings were adapted:

Injection volume	: 0.2 μl
Split ratio	: 50.5: 1
Inlet temperature	: 200 $^{\circ}\text{C}$
N_2 carrier gas flow	: 1.4 ml min^{-1}
H_2 flow rate	: 40 ml min^{-1}
Air flow rate	: 450 ml min^{-1}
Oven programming	: 60 $^{\circ}\text{C}$ to 110 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ 110 $^{\circ}\text{C}$ for 16 min 110 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ 300 $^{\circ}\text{C}$ for 5min
Detector temperature	: 300 $^{\circ}\text{C}$

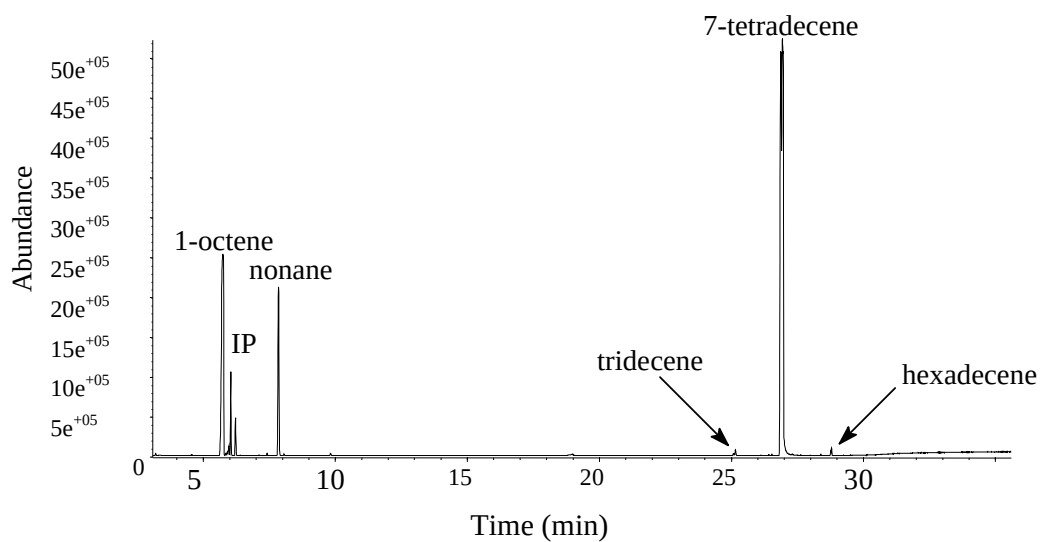


Figure 4.2 GC-MS chromatograph of **1** for the metathesis reaction with 1-octene at 60 min and 1:9000 (Ru:1-octene) molar ratio.

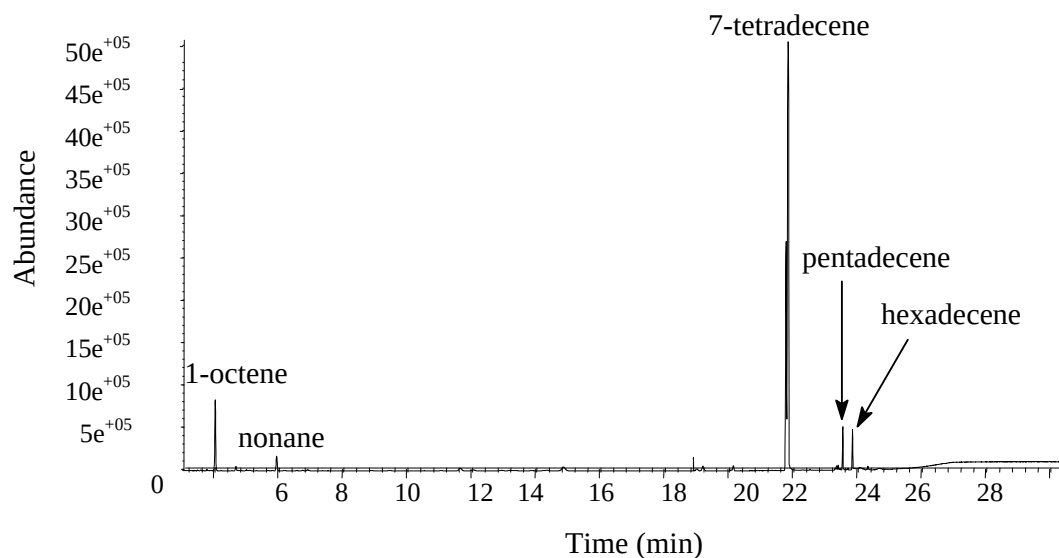


Figure 4.3 GC-MS chromatograph of **2** for the metathesis reaction with 1-octene at 60 min and 1:9000 (Ru:1-octene) molar ratio.

4.8 Response factor

An instrument calibration must be done to calculate the response factor given by equation (1).

$$\frac{A_{\text{nonane}}}{A_{\text{1-octene}}} = Rf \times \frac{V_{\text{1-octene}}}{V_{\text{nonane}}} \quad (1)$$

where Rf = response factor

$V_{\text{1-octene}}$ = volume of 1-octene

V_{nonane} = volume of nonane

A_{nonane} = area of nonane

$A_{\text{1-octene}}$ = area of 1-octene

A response factor was calculated from a calibration curve obtained by a plot of

$\frac{A_{\text{nonane}}}{A_{\text{1-octene}}}$ against $\frac{V_{\text{nonane}}}{V_{\text{1-octene}}}$ for solutions with different ratios of nonane and 1-octene.

The nonane was kept constant. The solutions were prepared as follows:

0.25 ml nonane: 1.00 ml 1-octene

0.25 ml nonane: 0.75 ml 1-octene

0.25 ml nonane: 0.50 ml 1-octene

0.25 ml nonane: 0.25 ml 1-octene

A response factor of 0.9795 for 1-octene was calculated from the gradient of the calibration curve. The calibration results obtained are shown in **Figure 4.2**.

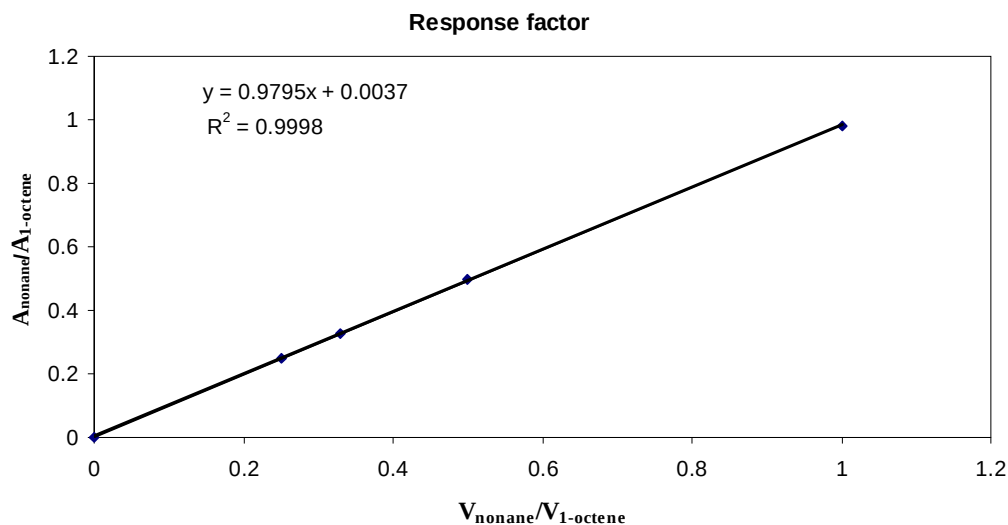


Figure 4.4 Graph for the determination of response factor.

4.9 Calculations

During the metathesis reactions the 1-octene decreases as the other alkenes are formed. The formed alkenes are thus called the primary metathesis products (PMP), the secondary metathesis products (SMP) and the isomerisation products (IP). The following equations determine the increase in the formation of products as well as the decrease in 1-octene.

Equation 2: Determination of the mole percentage of 1-octene

$$\text{mol}\%C_8 = 100 \times rf \times \frac{V_{is}}{V_{C_8}} \times \frac{A_{C_8}}{A_{is}} \quad (2)$$

- C_8 = 1-octene
- rf = GC response factor
- V_{is} = volume of the internal standard at $t=0$
- V_{C_8} = volume of 1-octene at $t=0$
- A_{C_8} = area of 1-octene
- A_{is} = area of internal standard

Equation 3: Determination of the mole percentage of PMP, SMP, IP

$$mol\%C_n = 2 \times Rf \times \left(V_{is} \frac{A_{c_n}}{A_{is}} \right) \times \frac{p_{c_n}}{M_{c_n}} \times \left(\frac{M_{C_8}}{p_{c_8} \times V_{c_n}} \right) \times 100 \quad (3)$$

C_n	=	alkene
rf	=	GC response factor
V_{is}	=	volume of the internal standard at t=0
V_{C_8}	=	volume of 1-octene at t=0
A_{C_n}	=	area of alkene
A_{is}	=	area of internal standard
M_{C_n}	=	molecular mass of alkene
M_{C_8}	=	molecular mass of 1-octene
p_{C_n}	=	density of alkene
p_{C_8}	=	density of 1-octene

Equation 4: Determination of selectivity

$$\%selectivity = \frac{\%PMP}{\%PMP + \%SMP} \quad (4)$$

Equation 5: Determination of turnover number

$$TON = \%PMP * \left(\frac{1 - octene}{catalyst} \right) \div 100\% \quad (5)$$

4.10 References

1. F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song, W-H. Sun, *J. Org. Chem.*, 2004, **689**, 936
2. L. K. Johnson, M. A. Bennett, S. D. Simpson, J. Feldman, E. B. Coughlin, PCT Int. Appl. WO 9830609
3. M. Jordaan, *Experimental and theoretical investigation of new Grubbs-type pre-catalysts for the metathesis of alkenes*, North-West University (Potchefstroom campus) PhD Thesis, 2007
4. B. de Clercq, F. Verpoort, *Adv. Synth. Catal.*, 2002, **344**, 639
5. C. A. A. Huijsmans, *Modelling and synthesis of Grubbs type complexes with hemilabile ligands*, North-West University (Potchefstroom campus), MSc Dissertation, 2009

5 RESULTS AND DISCUSSIONS

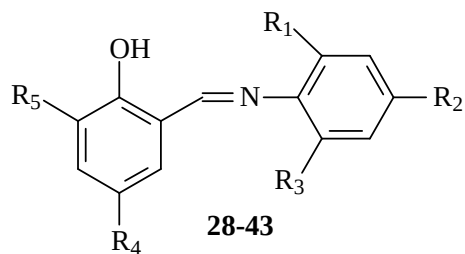
5.1 Metathesis: Theoretical investigation

In molecular modeling, the molecular structure needs to be refined to bring it to a stable geometry. The refinement is known as geometry optimization. The ligands were optimized and the following properties were calculated using a DFT modeling program mentioned in **3.1**:

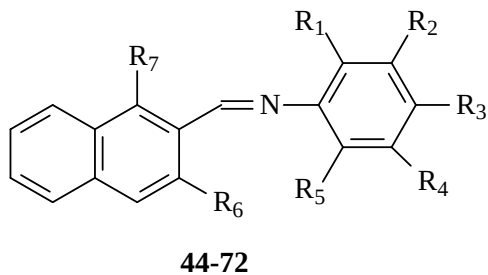
- Electron density
- Electrostatics
- Fukui function
- Orbitals: HOMO/LUMO
- Population analysis

45 ligands were initially chosen to investigate properties for suitable ligands (See Appendix I).

- 16 of these ligands are salicylideneanilines derivatives



- 29 of them are naphthalene derivatives



The most significant properties calculated were the Fukui functions, HOMO and LUMO orbitals used as a tool to predict the most suitable ligands. The Fukui function shows that the electron rich position of the molecule is usually where the HOMO orbital is the largest, whilst electron deficient position of the molecule is usually where the LUMO orbital is large. The coordination of the ligand to the pre-catalyst is obtained by an overlap of the HOMO orbital of the ligand around the oxygen atom or the nitrogen atom with the LUMO orbital of the pre-catalyst on the ruthenium metal. If the oxygen atom or the nitrogen atom is shown to be electron rich, it will be possible for the ligand to form bonds with Grubbs pre-catalysts. The usefulness of the HOMO energy as preliminary criteria for screening suitable ligands was investigated. The two most promising ligands thus found will be used to design and synthesize a new Grubbs type pre-catalyst from **1** and **2**.

Figure 5.1 shows the HOMO energy of possible ligands calculated against the well defined Verpoort ligand labeled as **28**.¹ In this study the ligand with the lower energy than that of Verpoort is considered. **Table 5.1** shows the calculated HOMO energies of two ligands that suited the preliminary criterion. Ligands **68** and **69** showed the lowest energies therefore were selected.

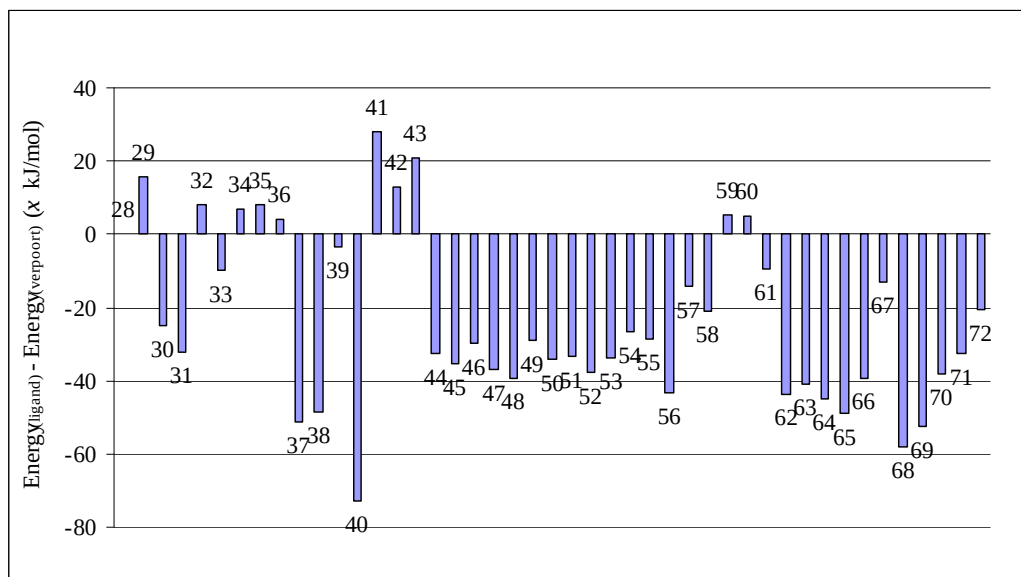
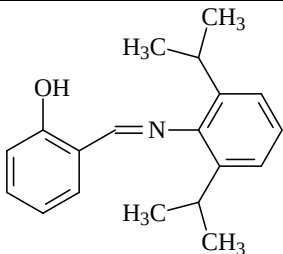
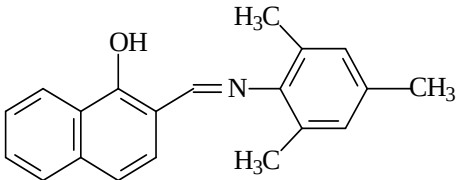
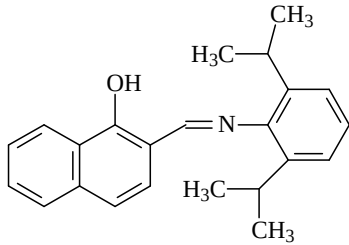


Figure 5.1 The HOMO energy of possible ligands.

The ligands studied were selected to reflect the influence of resonance and steric effects on the conformational stability of imine ligand containing naphthalene group. Ligands **28** to **43** are salicylideneanilines derivatives and ligands **44** to **72** are naphthalene derivatives. Ligand **40** was not chosen because it does not contain the naphthalene group. The table containing the HOMO energies of possible ligands as shown in **Figure 5.1** is found in Appendix I.

Table 5.1 Ligands HOMO energies.

Ligand	Ligand name	HOMO kJ/mol
 28	1-[[2,6-diisopropylphenyl]imino]methylene-2-phenol	-514.437
 68	1-[[2,4,6-trimethylphenyl]imino]methylene-2-naphthalenol	-461.932
 69	1-[[2,6-diisopropylphenyl]imino]methylene-2-naphthalenol	-456.229

The two selected ligands are discussed fully with their respective modeling results with calculated properties: HOMO, electron density with electrophilic Fukui function, electrostatic potential and the population analysis: atomic charge. The Verpoort ligand¹ (**28**) was chosen as a reference because it has been proved to be very active in

the metathesis reactions when coordinated to **1** and its molecular structure is similar to ligand **68** and **69** except for the naphthalene group.^{1,2}

5.1.1 HOMO

The importance of the HOMO orbital around the nitrogen and oxygen atoms of the ligand is to overlap with the LUMO orbital around the metal of the pre-catalyst during the coordination to form a bond. The comparison of the HOMO orbital of **28** with the HOMO orbital of naphthalene ligands **68** and **69** is shown in **Figure 4.2**.

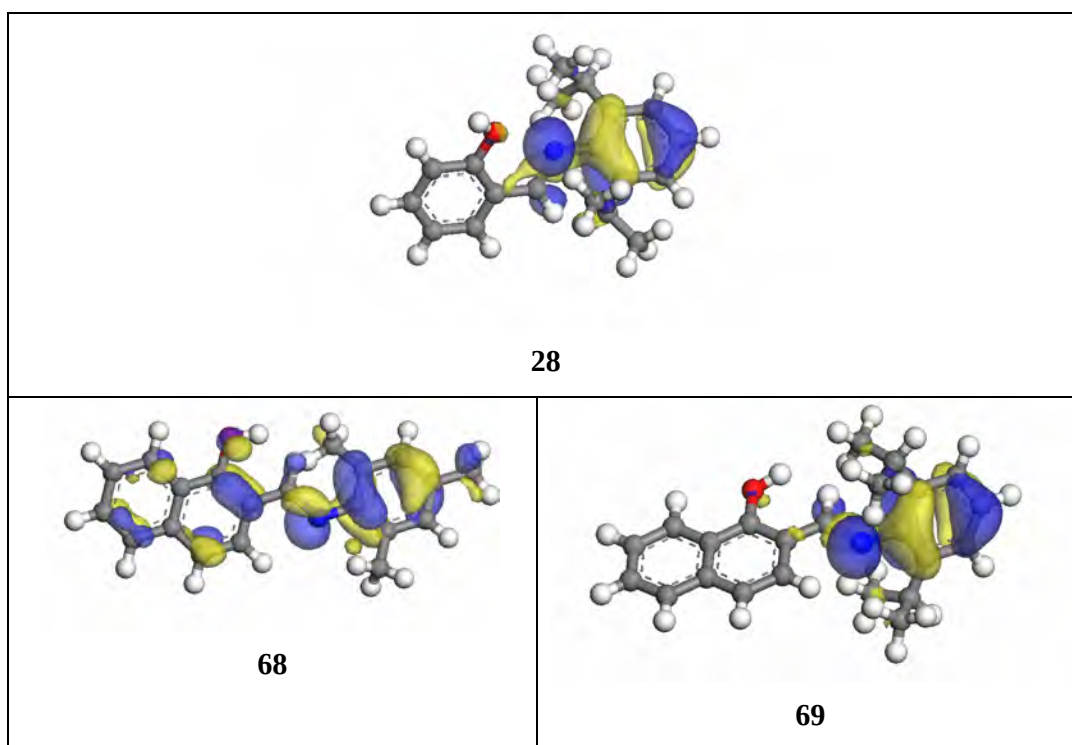


Figure 5.2 The HOMO orbitals of **28**, **68** and **69**.

The HOMO orbital around the nitrogen atom is similar for all three ligands; **28**, **68** and **69**. The HOMO orbital around the oxygen atom in **69** and **28** is quite small, it is barely visible but in **68** the orbital is visible.

However the coordination of the ligand to **1** is made up of two steps: the removal of the hydrogen atom from the oxygen atom so that a negatively charged oxygen atom is

obtained. The removal of the hydrogen atom is done by the addition of sodium hydride or thallium ethoxide to the ligand to produce the respective metal salt. The removal changes the HOMO orbital around the oxygen atom, **Figure 5.3**. Then **1** is added and a strong bond is formed between the ruthenium and the oxygen atom while a weaker bond forms between the ruthenium and nitrogen, so that hemilability is achieved. When the hydrogen atom is removed, the orbital around the oxygen atom is visible in all three ligands.

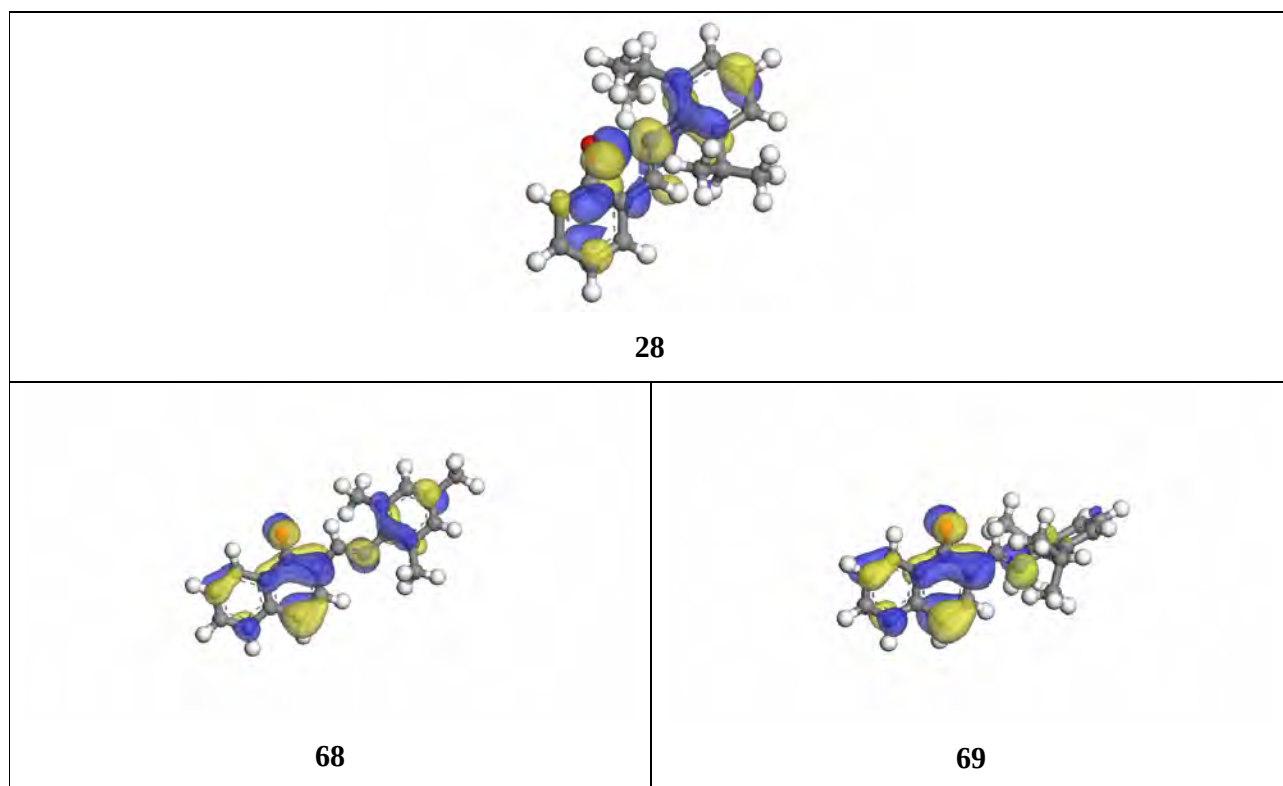


Figure 5.3 The HOMO orbitals of **28**, **68** and **69** ligands after the removal of the hydrogen atom.

5.1.2 Electrostatic Potential

Electrostatic potential arises from the forces that electric charges exert on each other.³ It measures the strength of a chemical bond.⁴ The electrostatic potential map is shown in **Figure 5.4**.

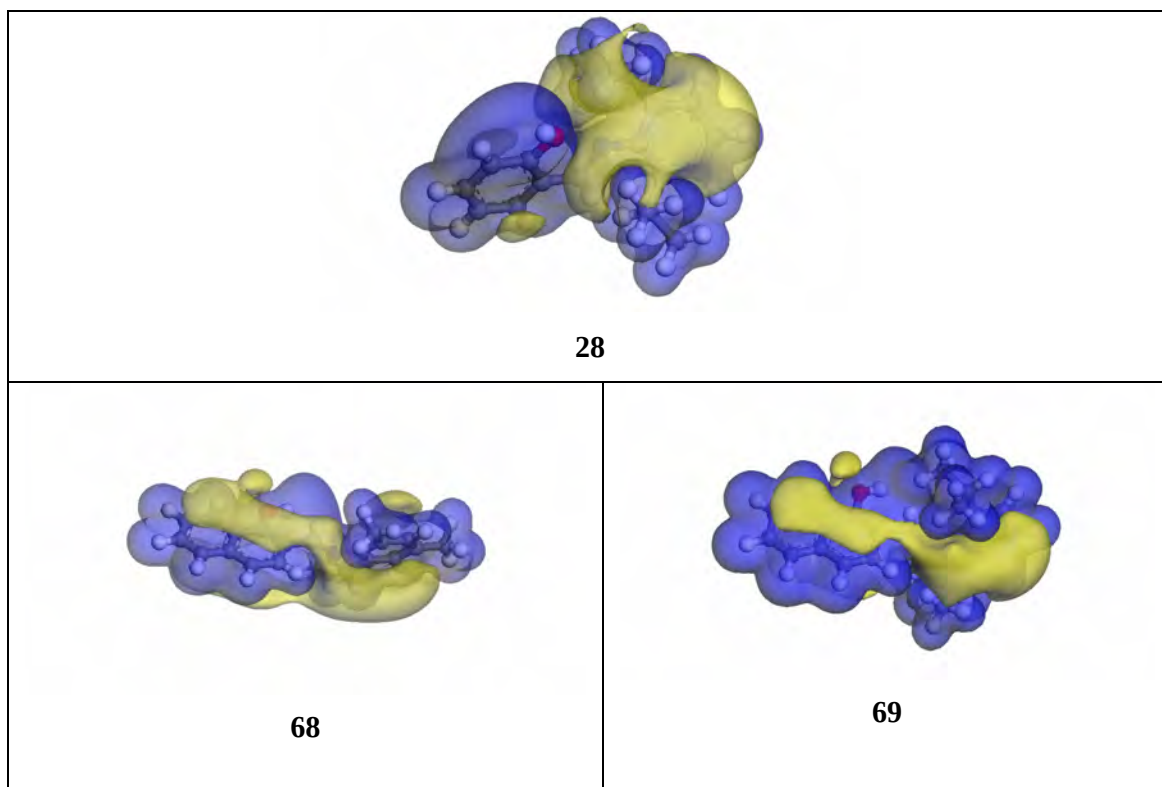


Figure 5.4 Electrostatic Potential of **28**, **68** and **69**.

The electrostatic potential map on **28** is large on the benzene with the isopropyl group substituted at 2 and 6 positions as compared to benzene with no substituent. The similarities of this electrostatic potential map can be seen in **68** and **69**. Ligand **68** has three methyl groups substituted at 2, 4 and 6 positions, with **69** the same as for **28**. The naphthalene group in **68** and **69** has smaller electrostatic potential maps than that of benzene. Both the naphthalene group in **68** and **69** has no substituent attached to it. It can be concluded that a strong chemical bond is on the benzene ring.

5.1.3 Electron density with electrophilic Fukui function

A Fukui function is used to assess the reactivity of a chemical molecule from electronic properties like electron density.³ The electronic density was used to measure the probability of an electron being present at a specific location. A Fukui function relates the reactivity of a molecule with respect to electrophilic and nucleophilic attack as shown in **Figure 5.5**.

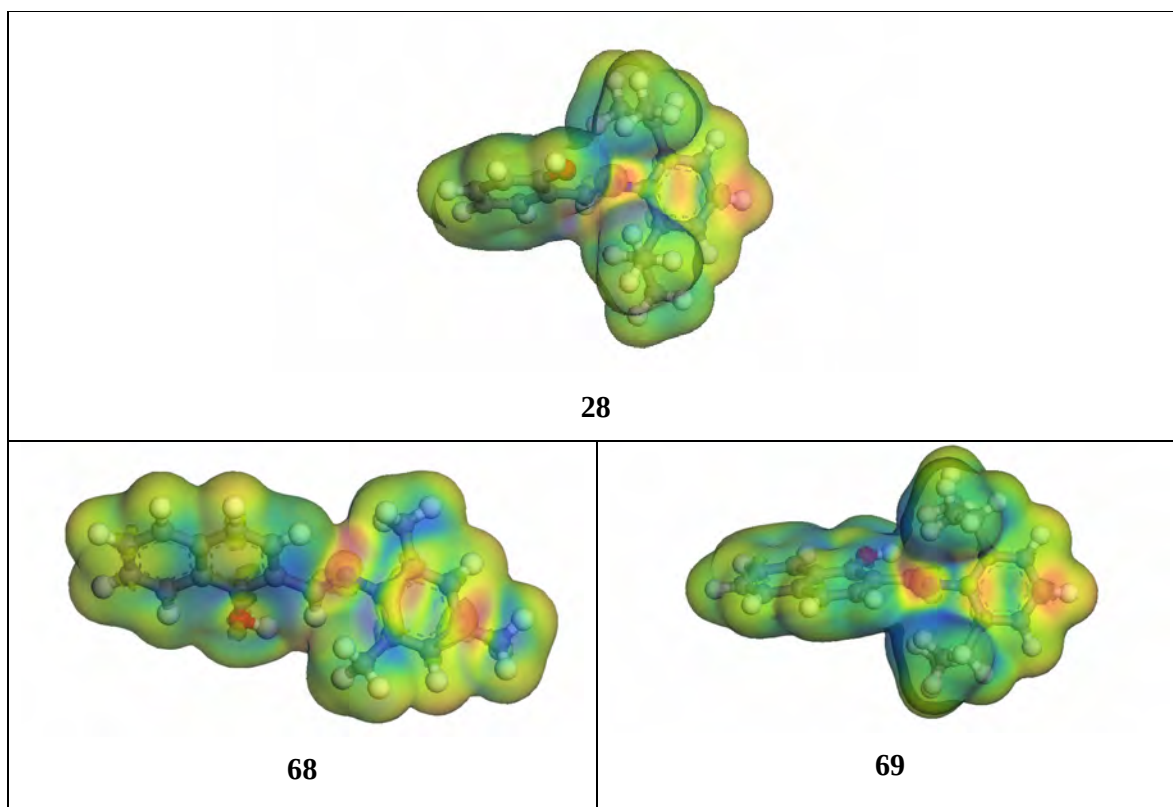


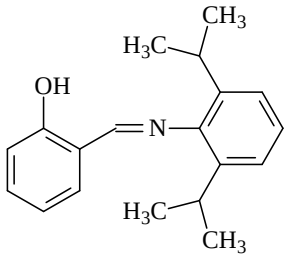
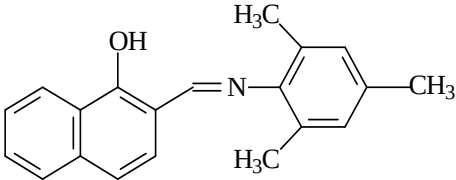
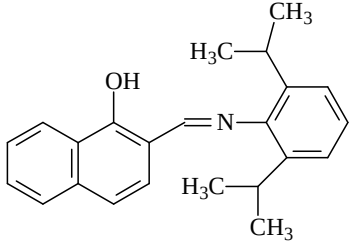
Figure 5.5 Electron densities with electrophilic Fukui function of **28**, **68** and **69**.

In all three ligands the most electron rich part, as shown by the electron density map with the electrophilic Fukui function, is the nitrogen atom (red spot) and a less electron rich part was around the oxygen (yellow spot), while the rest of the molecule is neutral (blue, green and light yellow).

5.1.4 Population analysis: atomic charge

The population analysis gives the electron density of the ligand; it divides the density between the atoms to give an estimate of the atomic charge.³ In **Table 5.2** the nitrogen atom in all the ligands is more negatively charged than that of oxygen atom. In **28** the nitrogen atom is -0.289 and the oxygen atom is -0.412. Ligand **68** has -0.307 on the nitrogen atom and -0.456 on the oxygen atom. The nitrogen atom on **69** is -0.316 and the oxygen atom is -0.452.

Table 5.2 Population analysis: atomic charge on oxygen and nitrogen atoms of **28**, **68** and **69**.

Ligand	Nitrogen atom charge	Oxygen atom charge
 28	-0.289	-0.412
 68	-0.307	-0.456
 69	-0.316	-0.452

5.2 Summary of discussions of modeling results for **28**, **68** and **69**

In the screening process, ligands **68** and **69** were chosen as ligands because of their HOMO energies were lower than that of **28**. The difference between ligands **68** and **69** to **28** is the naphthalene group. The R group on the benzene ring is the only difference between **68** and **69**. It has been shown from the previous studies that the more sterically hindered the nitrogen and the oxygen atoms are, the more difficult for the ligand to coordinate to **1**.⁵ When a bulky pre-catalyst is tested for metathesis reaction, the bulky R group can either cause steric hindrance around the carbene,

which can make it more difficult for the 1-octene to react with the carbene or the bulky R group can guide the 1-octene to the active site.⁵

Between the two chosen ligands, **69** is the most bulky ligand with the isopropyl group on the benzene ring. The similarity of **69** and **28** is the isopropyl group, whereas **68** has methyl group on the benzene ring. Ligand **69** is most likely to behave the same way as **28**.

All the properties calculated have proven that the regions around the nitrogen and oxygen atoms are subject to electrophilic attack, with the HOMO orbital delineating the areas which are more electron rich. Electrostatic potential maps serve to outline the location of the highest energy electrons. The map also shows where the electrostatic potential is more negative, for example, above and the below plane on the benzene ring with substituent, **Figure 5.4**.

The colour schemes in electron density with the electrophilic Fukui function were used to identify the electron rich part of the molecule. Red is more electron rich than yellow. Green, blue and light yellow represent neutral regions of the molecule. Population analysis confirmed the results with the specific charges on the atoms which relate to the electron rich part of the molecule. Both nitrogen and oxygen atoms have proven to be electron rich.

5.3 Discussions of the modeled pre-catalysts

Only the Grubbs 1 type pre-catalyst was modeled to be later used for synthesis. **1** was modelled to test how it is going to coordinate with the ligands. **Figure 4.6** shows the LUMO orbital of **1**.

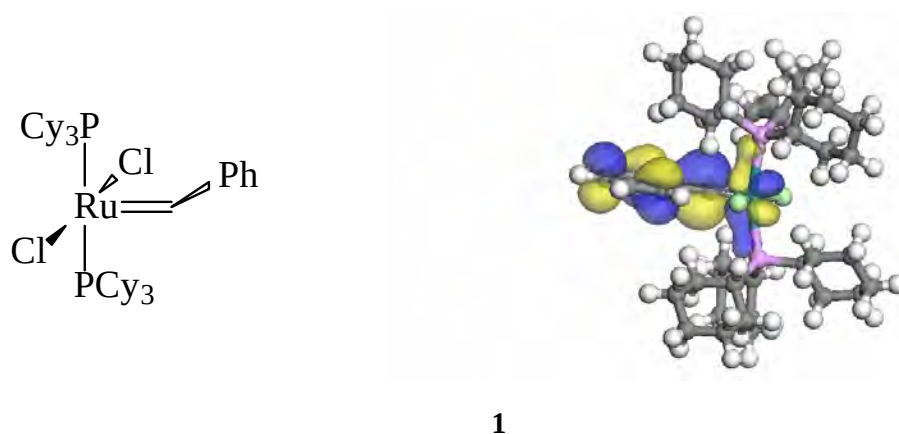


Figure 5.6 The LUMO orbital of **1**

For the pre-catalyst to form a bond with a ligand the LUMO orbital on the metal must correspond to that of the HOMO orbital of the ligand as shown in **Figure 4.7**, meaning the size and the orientation of the orbitals must be the same. From the observations, it is possible for the pre-catalyst to coordinate with the ligands.

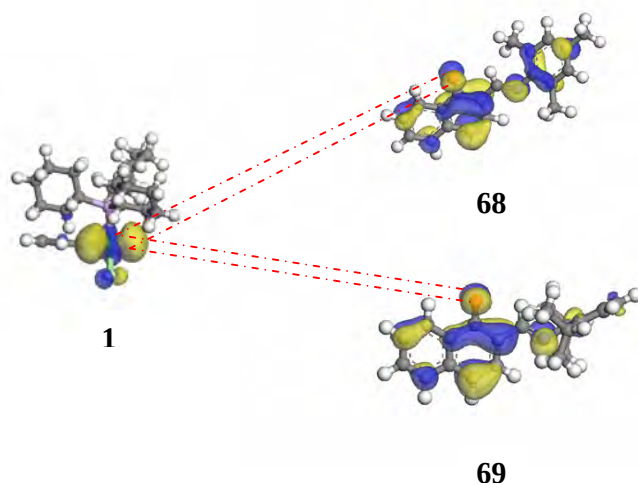
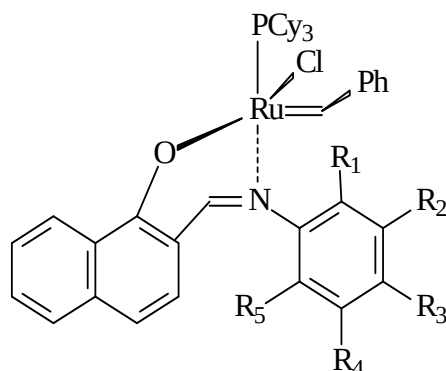


Figure 5.7 Coordination of the HOMO orbital of the ligands with the LUMO orbital on the metal centre of the pre-catalysts

The substituted pre-catalysts were also modelled. As discussed in **Chapter 3**, the molecular modelling will help gain insight to the mechanism of the 1-octene metathesis reaction. If the dissociative mechanism is assumed in the 1-octene metathesis reaction and the ligand will react as a hemilabile ligand, an active coordination site can be formed, followed by the coordination of 1-octene to the active coordination site on the ruthenium atom of the pre-catalyst, **Scheme 3.2**.

The HOMO orbital of the 1-octene overlaps with the LUMO orbital of the carbene to form the metallacyclobutane intermediate. This means that the form and orientation of the LUMO orbital in the pre-catalyst is important together with the HOMO orbital of the 1-octene. To undergo a metathesis reaction therefore the substituted pre-catalysts were modelled, **Figure 5.8**, with the same optimizing method used with the properties listed in **4.1**.



73: R₁= R₃= R₅= methyl, R₂=R₄=hydrogen

74: R₁= R₅= isopropyl, R₂=R₃=R₄=hydrogen

The LUMO orbital around the carbene and the ruthenium for both **73** and **74** were not the same and also the orientation of the orbital did not look the same. The LUMO orbital around the carbon atom of the carbene in **74** is larger than that in **73**. This was also observed for the LUMO orbital around the ruthenium. Since the metathesis reaction occurs at the ruthenium carbene group, the modelling results can be used as prediction tools to the activity the two pre-catalysts.

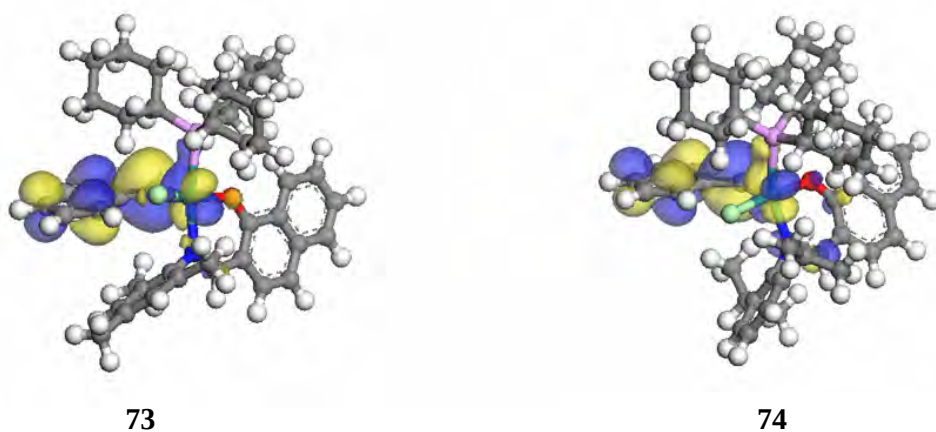


Figure 5.8 LUMO orbitals of **73** and **74**

Furthermore the dissociation energy of the new pre-catalysts were modelled to show how difficult or easy it is for the pre-catalyst to dissociate to form an active coordination site and later on recoordinate again. In this way hemilability is obtained. **Table 5.3** shows the dissociation energies of the pre-catalysts **1**, **73** and **74**.

Table 5.3 Dissociation energies of **1**, **73** and **74**

Pre-catalyst	Dissociation energy / kcal.mol ⁻¹	ΔE / kcal.mol ⁻¹
1	21.89	0
73	20.01	-1.88
74	24.88	2.99

The dissociation energy of **74** is the highest in all three pre-catalysts, followed by **73** relative to **1**. There is more energy needed to dissociate **74** from the metal atom to form an active coordination site. The two possible activation reaction paths for metathesis were modelled as shown in **Schemes 5.1** and **5.2** for **73** and **74**. The energies calculated are electronic energies and no transition energies were calculated. The first step (**A**→**B**) is the dissociation step of the nitrogen atom from the ruthenium

atom to form an active coordination site. From **B**→**C** is the second step where an incoming 1-octene coordinates to the ruthenium atom. The next is the formation of the metallocyclobutane intermediate given by **C**→**D**. In **D**→**E** the activated pre-catalyst with a bulky olefin leaving the coordination site is obtained. From **E**→**F** the bulky olefin leaves the coordination and results in either a methyldiene **G**₁ or **G** heptylydene. The primary metathesis products 1-phenyl-1-nonene and styrene were obtained in the activation steps. The nitrogen atom can re-coordinate to the ruthenium atom given by **F**→**G**. The energy profiles for the catalyzed olefin metathesis for the two possible reaction paths are given in **Figure 5.9** for the formation of methyldiene **G**₁ and **Figure 5.10** for the formation of heptylydene **G**.

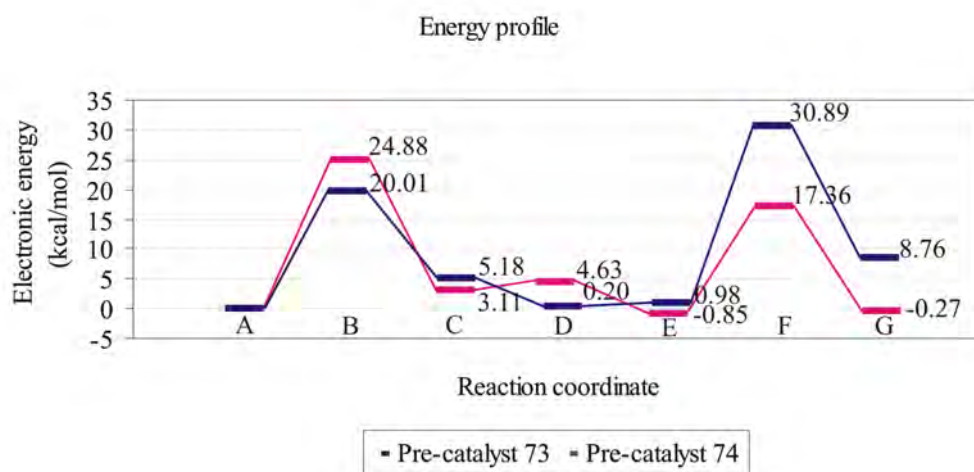


Figure 5.9 Energy profile for pre-catalysts **73** and **74** for the coordination of 1-octene *cis* to the carbene

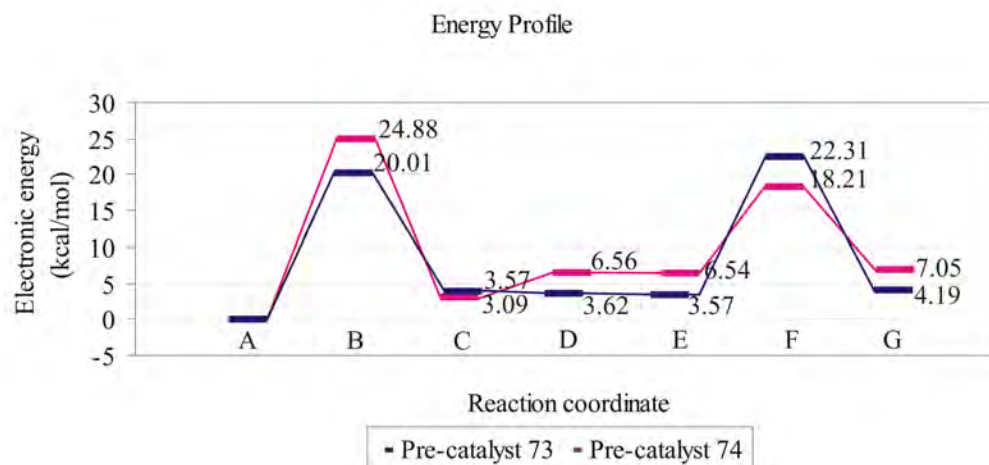


Figure 5.10 Energy profile for pre-catalysts **73** and **74** for the coordination of 1-octene *trans* to the carbene

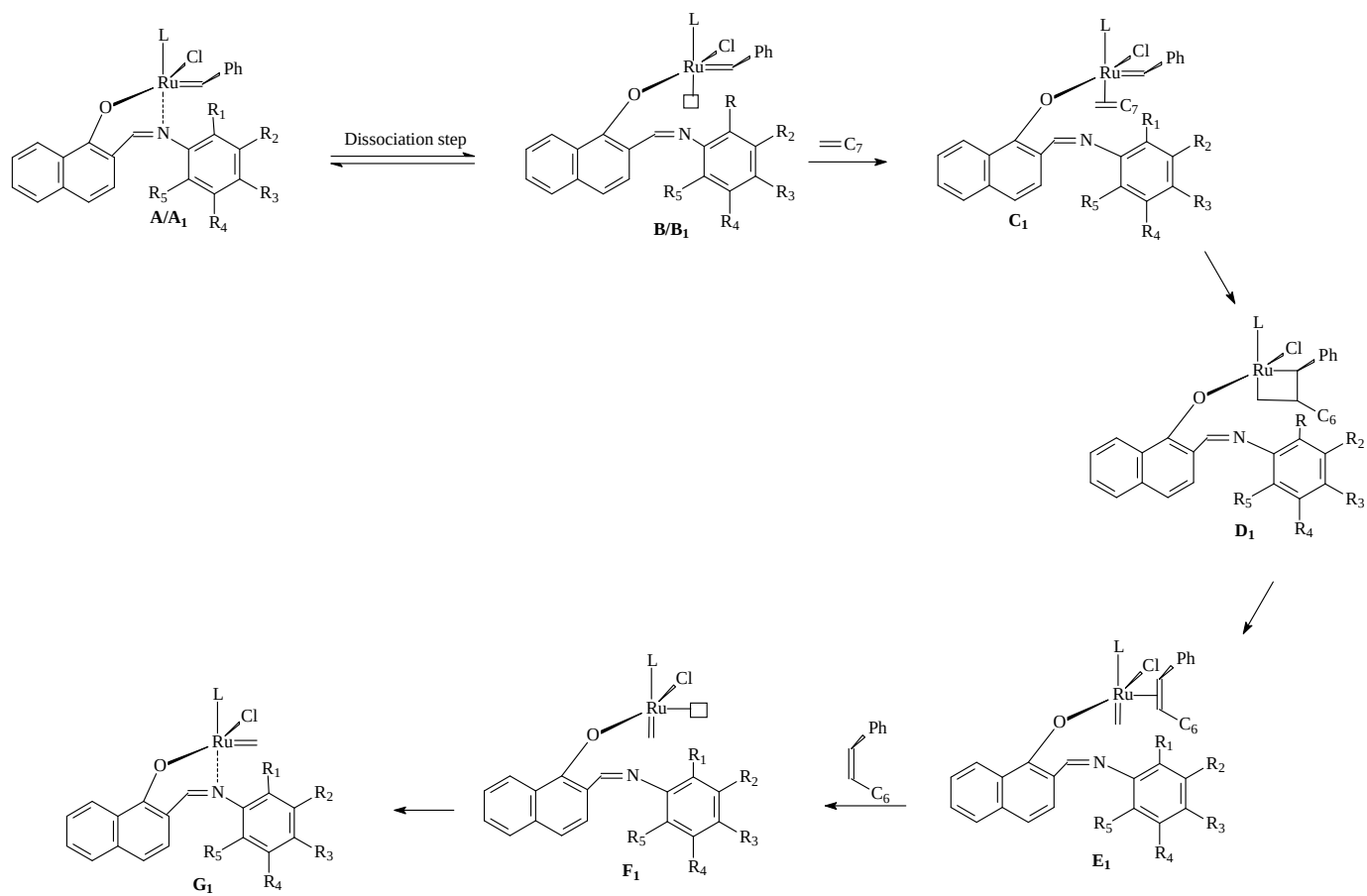
The activation cycle for the metathesis reaction of 1-octene with Grubbs type pre-catalyst with ligands **68** and **69** were evaluated. Both *trans* and *cis* positions of the 1-octene in respect to the carbene were modelled. As discussed above, the dissociation of the nitrogen atom in **74** (**B**, $\Delta E=24.88$ kcal/mol) was calculated to be 4 kcal/mol less favourable than the dissociation of the nitrogen atom in **73** (**B**, $\Delta E=20.01$ kcal/mol). After the dissociation, 1-octene coordinates to the ruthenium metal.

In **Figure 5.9**, where the 1-octene is *cis* to the carbene, the pre-catalyst **74** (**C**, $\Delta E=3.11$ kcal/mol) was calculated to be -2.09 kcal/mol more favourable to coordinate with the 1-octene than pre-catalyst **73** (**C**, $\Delta E=5.18$ kcal/mol). The same trend can be observed where the coordination of 1-octene is *trans* to the carbene shown in **Figure 5.10**. The pre-catalyst **74** (**C**, $\Delta E=3.09$ kcal/mol) was calculated to be -0.48 kcal/mol more favourable to coordinate with the 1-octene than pre-catalyst **73** (**C**, $\Delta E=3.57$ kcal/mol).

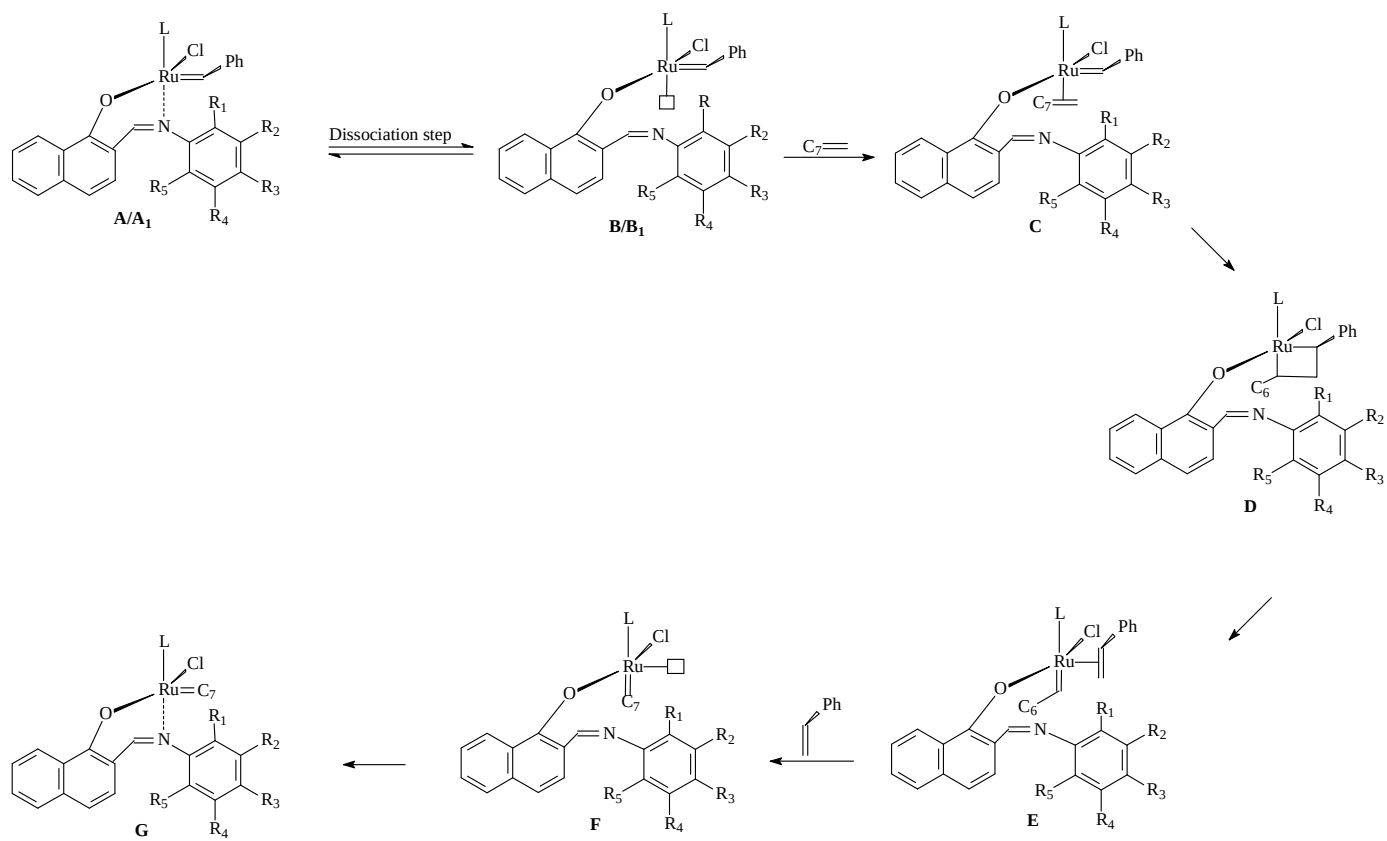
The metallocyclobutane intermediate is then obtained denoted as **D** in both **Figures 5.9** and **5.10**. The most stable intermediate was observed in pre-catalyst **74** with energies of 4.63 kcal/mol and 6.56 kcal/mol in **Figures 5.9** and **5.10** respectively. The

formation of the product 1-phenyl-1-nonene (**F**) in **Figure 5.9** was less favourable in pre-catalyst **73** ($\Delta E=30.89$ kcal/mol) and was calculated to be -13.53 kcal/mol and the formation of the product methyldene (**F**) in **Figure 5.10** was calculated to be -4.1 kcal/mol less favourable in pre-catalyst **73**.

The energies for the recoordination of the nitrogen atom to the ruthenium metal of the pre-catalysts are 22.13 kcal/mol for **73** and 17.16 kcal/mol for **74** in methyldene; **Figure 5.9** and 18.12 kcal/mol for **73** and 11.16 kcal/mol in **74** for heptylindene shown in **Figure 5.10**. In both cases the recoordination of the nitrogen atom is favourable in **74**, but overall the recoordination of the nitrogen in heptylindene is most favourable with less energy required.



Scheme 5.1 Activation cycle reaction path 1

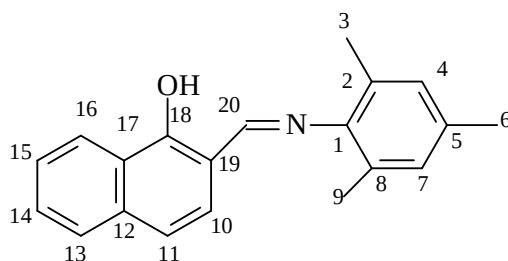


Scheme 5.2 Activation cycle reaction path 2

5.4 Synthesis

After modelling the ligands, the two most promising ligands **68** and **69** were synthesized followed by the synthesis of their corresponding salts and lastly the substituted pre-catalysts **75** and **76**. The ligands and complexes were characterized by MS, IR, ^1H NMR and ^{13}C NMR. The results are discussed below:

❖ Ligand **68**



The MS spectrum shows a molecular ion (M^+) of 289 m/z which indicates the molecular mass of **68** which is in correspondence with that found in literature.⁵

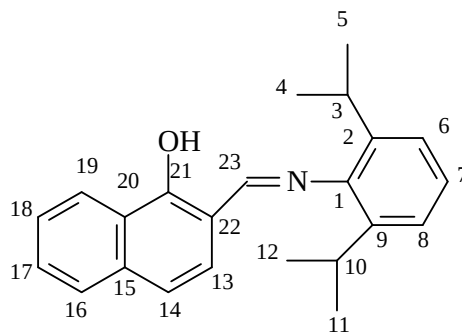
The IR spectrum shows an OH stretch at 3443 cm^{-1} , a C-H stretch between $2989\text{--}2800\text{ cm}^{-1}$, a C=N stretch at 1620 cm^{-1} , a C-N stretch at 1476 cm^{-1} , a stretch of C=C at 1575 cm^{-1} and a CH_3 bending at 1328 cm^{-1} and a C-C absorption bend below 500 cm^{-1} .

The ^1H -NMR spectrum showed a singlet at 15.2 ppm for the OH group. Another singlet was found at 9.0 ppm for the HC=N group. A doublet signal from the H_{10} -atom was found at 7.92 ppm due to coupling of this atom with the H_{11} -atom. The H_{11} -atom showed a doublet at 7.8 ppm due to coupling with the H_{10} -atom. A doublet from H_{13} -atom was found at 7.7 ppm due to coupling with the H_{14} -atom. The H_{14} -atom showed a multiplet between 7.34–7.47 ppm due to coupling with the H_{13} and H_{15} -atoms. Between 7–7.25 ppm a multiplet was found for the H_{15} -atom due to coupling with the H_{14} and H_{16} atoms. The H_{16} -atom showed a doublet at 6.9 ppm due to coupling with the H_{15} -atom. The nine H-atoms of the C_3 , C_6 and C_9 methyl groups were found as singlets at 2.1, 3.7 and 2.2 ppm.

The ^{13}C NMR spectrum showed a singlet at 169.51 ppm for the C_1 atom which was not coupled to any H-atoms. Another singlet signal was found at 160.70 ppm for the C_{19} -atom which was not coupled with any H-atoms. At 142.49 ppm a singlet was found for the C_{18} atom. At 136.23 ppm a singlet was found for the C_{2+8} atoms due to no coupling. A doublet for the C_{4+7} atoms was found at 135.47 ppm due to coupling to one H-atom. Due to no coupling a singlet was found at 133.32 ppm for the C_5 atom. C_{10} and C_{11} atoms showed doublets at 129.80 ppm and 129.34 ppm. A singlet at 128.08 ppm for the C_{12+17} atoms was found due to no coupling. At 127.18 ppm a doublet was found for the C_{13+16} atoms. Between 123.34-122.16 ppm a triplet was found for the C_{14} and C_{15} atoms due to coupling with two H atoms. A doublet was found at 118.62 ppm for the C_{20} atom due to coupling with one H atom. Quartets were found at 22.24, 18.63 and 14.08 ppm for the C_3 , C_6 and C_9 atoms due to coupling with the three H atoms. The singlets and doublets are C-H resonances which were confirmed with Dept ^{13}C NMR.

From all the data obtained, together with the melting point which is similar to the melting point mentioned in literature,⁵ it can be concluded that the correct product **68** was obtained. The yield of the ligand **68** is 83.5%, which also correspond to that in literature.

❖ Ligand **69**



The MS spectrum showed a molecular ion (M^+) of 330 m/z which indicates the molecular mass of **69** which is in correspondence with that found in literature.⁶

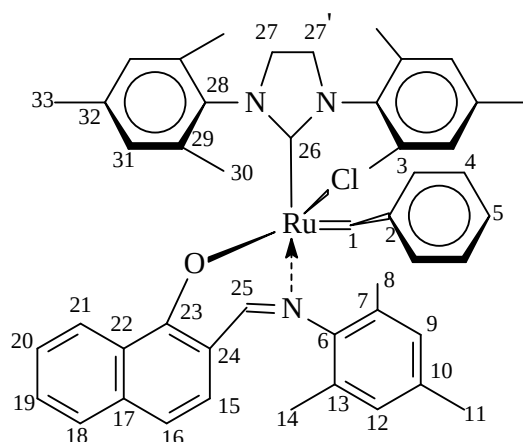
The IR spectrum showed an OH stretch at 3400 cm^{-1} , a C-H stretch between $3100\text{--}2800\text{ cm}^{-1}$, a C=N stretch at 1627 cm^{-1} , a stretch of C=C at 1580 cm^{-1} a C-N stretch at 1467 cm^{-1} , a CH_3 absorption bend at 1328 cm^{-1} and C-C bend below 500 cm^{-1} .

The ^1H -NMR spectrum showed a singlet at 15.3 ppm for the OH group. Another singlet was found at 9.15 ppm for the HC=N group. A doublet signal from the H_{6+8} atoms was found at 7.98 ppm due to coupling of this atom with the H_7 atom. The H_{13} atom showed a doublet at 7.8 ppm due to coupling with the H_{14} atom. A doublet from H_{14} was found at 7.7 ppm due to coupling with the H_{13} atom. The H_{17} atom showed a triplet at 7.45 ppm due to coupling with the H_{16} and H_{19} atoms. At 7.3 ppm a triplet was found for the H_{18} atom due to coupling with the H_{17} and H_{19} atoms. At 7.2 ppm a triplet for the H_7 atom was found. The H_{16+19} atoms showed a doublet at 7.1 ppm. A doublet was found at 2.1 ppm for the H_{3+10} atoms. The twelve H atoms of the C_4 , C_5 , C_{11} and C_{12} methyl groups were found as singlets at 3.1 and 1.2 ppm.

The ^{13}C NMR spectrum showed a singlet at 161.59 ppm for the C_1 atom which was not coupled to any H atoms. Another singlet signal was found at 143.88 ppm for the C_{22} atom which was not coupled with any H atoms. At 140.30 ppm a singlet was found for the C_{4+9} atoms. At 135.92 ppm a triplet was found for the C_7 atom. At 133.18 ppm and 129.33 ppm doublets were respectively found for the C_{6+8} and C_{3+10} atoms which are coupled to one H atom. Due to coupling to one H atom doublets were found at 128.11 and 126.26 ppm for the C_{13} and C_{14} atoms. The C_{15+20} atoms showed a singlet at 123.53 ppm and at 123.44 ppm a doublet was found for the C_{16+19} atoms due to coupling with one H atom. A triplet was found at 121.43 ppm for the C_{17+18} atoms and at 118.75 ppm a doublet was found for the C_{23} atom. Quartets were found at 28.30 and 23.70 ppm for the C_{4+12} and C_{5+11} atoms due to coupling with the three H atoms. The singlets and doublets are C-H resonances which were confirmed with Dept ^{13}C NMR.

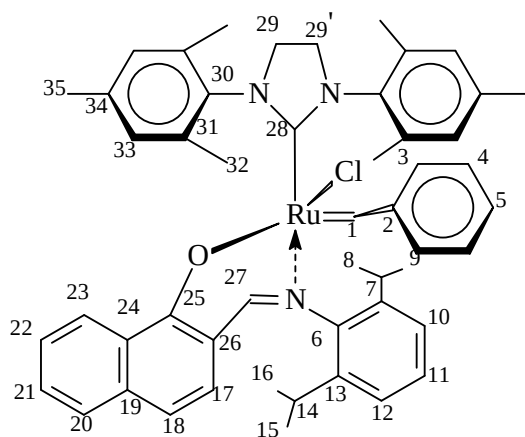
From all the data obtained, together with the melting point of which is similar to the melting point mentioned in literature, it can be concluded that the correct product was obtained.⁶ The yield percentage of the ligand is 24% which does not correspond to that in literature.

❖ Pre-catalyst **75**



The Maldi-Tof MS did not indicate the exact mass of **75**. The pre-catalyst decomposed during sample preparation that was not under inert conditions and the instability of the pre-catalyst. Nonetheless the spectrum showed the isotopes of **75**.

The ^1H NMR spectrum showed a singlet signal from the carbene H_1 atom at 17.45 ppm. Another singlet was found at 9.03 ppm for the H of the $\text{HC}=\text{N}$ group. A doublet signal from the H_{15} atom was found at 7.95 ppm due to coupling of this atom with the H_{16} atom. The H_{16} atom showed a doublet at 7.8 ppm due to coupling with the H_{15} atom. A doublet from the H_{18} atom was found at 7.78 ppm due to coupling with the H_{19} atom. The H_{19} atom showed a doublet of doublets between 7.79-7.6 ppm due to coupling with the H_{18} and H_{20} atoms. Between 7.4-7.5 ppm a multiplet was found for the H_{20} atom due to coupling with the H_{19} and H_{21} atoms. The H_{21} atom showed a doublet at 7.3 ppm due to coupling with the H_{20} atom. A multiplet was found between 6.8-6.97 ppm for the $\text{H}_{31}+\text{H}_{31'}$ atoms. At 4.5 ppm a doublet was found for the H_3 atom due to coupling with the H_4 atom. The $\text{H}_{27}+\text{H}_{27'}$ atom showed a multiplet between 3.9-4.0 ppm. Another multiplet was found at 3.8 ppm for the H_4 atom due to coupling with the H_3 and H_5 atoms. The H_5 atom showed a doublet of doublet at 3.1 ppm due to coupling with the H_4 atom. A multiplet of the 18H atoms of the methyl groups of the NHC ligand were found between 2.1-2.8 ppm. The methyl groups of C_8 , C_{11} and C_{14} were found as doublets and multiplet at 1.1, 1.0 and between 0.8-0.9 ppm.

❖ Pre-catalyst **76**

The Maldi-Tof MS did not indicate the exact mass of **76**. The pre-catalyst decomposed during sample preparation that was not under inert conditions and the instability of the pre-catalyst. Nonetheless the spectrum showed the isotopes of **76**.

The ^1H NMR spectrum showed a singlet signal from the carbene H_1 atom at 17.45 ppm. Another singlet was found at 9.03 ppm for the H of the $\text{HC}=\text{N}$ group. A doublet signal from the H_{10+12} atoms was found at 7.98 ppm due to coupling of this atom with the H_{11} atom. The H_{17} atom showed a doublet at 7.8 ppm due to coupling with the H_{18} atom. A doublet from the H_{18} atom was found at 7.7 ppm due to coupling with the H_{17} atom. The H_{21} atom showed a doublet of doublets at 7.6 ppm due to coupling with the H_{20} and H_{22} atoms. At 7.45 ppm a triplet was found for the H_{22} atom due to coupling with the H_{21} and H_{23} atoms. At 7.1 ppm a triplet for the H_{11} atom was found due to coupling with the H_{10} and H_{12} atoms. The H_{20+23} atoms showed a doublet at 7.09 ppm. A multiplet was found between 6.8-6.97 ppm for the $\text{H}_{33+33'}$ atoms. At 4.2 ppm a doublet of doublets was found for the H_3 atom due to coupling with the H_4 atom. The $\text{H}_{27+27'}$ atoms showed a multiplet between 3.6-4.0 ppm. Another multiplet was found at 3.5 ppm for the H_4 atom due to coupling with the H_3 and H_5 atoms. The H_5 atom showed a doublet of doublet at 3.2 ppm due to coupling to H_4 atom. A multiplet of the 18H atoms of the methyl groups of the NHC ligand were found between 2.1-2.7 ppm. A doublet was found at 1.0 ppm for the H_{3+10} atom. The twelve H-atoms of the C_4 , C_5 , C_{11} and C_{12} methyl groups were found as multiplet between 0.7-0.9 ppm.

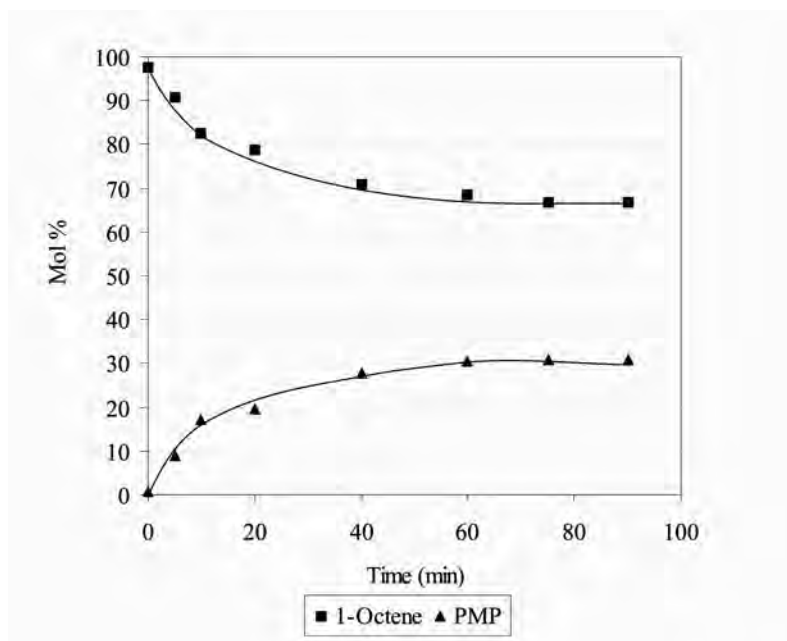
5.5 Metathesis

During the metathesis reactions the 1-octene decreases as the other alkenes are formed. The formed alkenes are thus called the primary metathesis products (PMP), the secondary metathesis products (SMP) and the isomerisation products (IP). The PMP are ethylene and 7-tetradecene, the IP are 2-octene, 3-octene and 4-octene and the SMP were nonene, decene, undecene, dodecene, tridecene, pentadecene and hexadecene. The metathesis products were identified by GC-MS. The metathesis of the two substituted Grubbs 2 type pre-catalysts **75** and **76** were compared with the metathesis of **1** and **2** and the comparison is discussed below. The activity of **75** and **76** were tested and the pre-catalysts were not optimized.

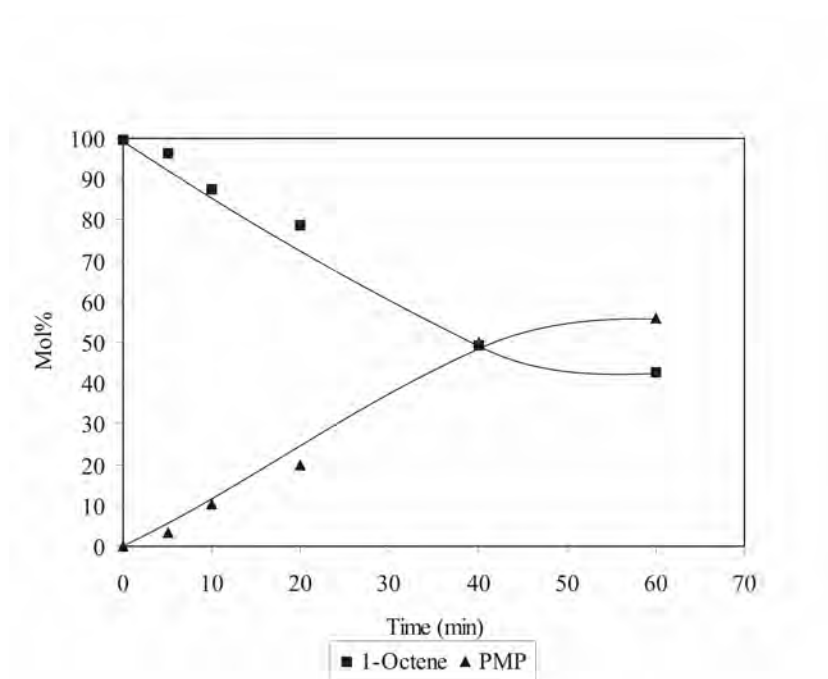
5.5.1 Metathesis reaction of **1** and **2** with 1-octene

The activity and selectivity of the Grubbs substituted pre-catalysts were investigated through the metathesis reactions with 1-octene at 60°C, with molar ratio ruthenium to 1-octene of 1: 9000. To discuss the activity and selectivity of a pre-catalyst it is important to look at the conversion of 1-octene and the formation of the PMP, IP and SMP. The graphs for the conversion of 1-octene and the formation of the PMP with **1** and **2** are shown in **Graph 5.1** and **5.2**. The formation of the IP with **1** and **2** are shown in **Graph 5.3** and the formation of the SMP with **1** and **2** are shown in **Graph 5.4** respectively. From **Graph 5.1** it was found that 30% of PMP were formed after 60 minutes while a conversion concentration of 1-octene was 68% in the reaction mixture. In **Graph 5.2** it was found that 42% of PMP were formed after 60 minutes while a conversion concentration of 1-octene was 56% in the reaction mixture.

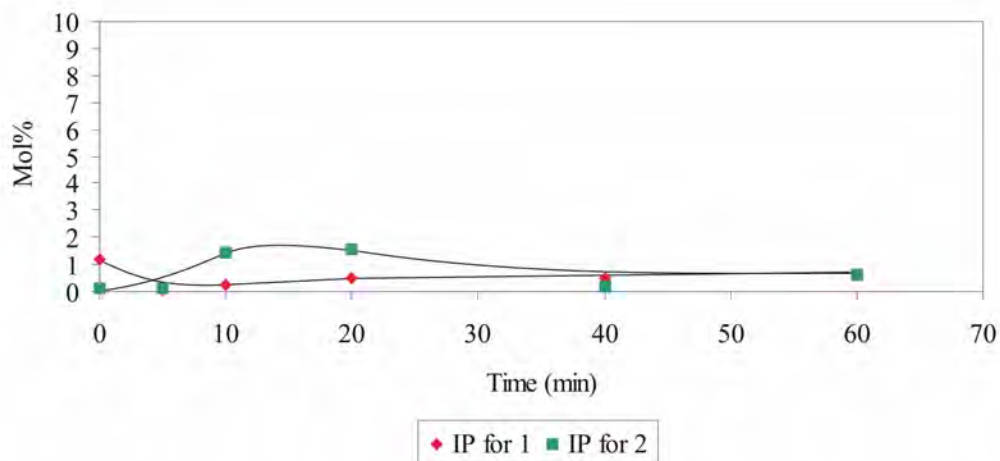
The overall efficiency of the pre-catalyst can also be described as the turnover number (TON). The TON is defined as the number of 1-alkene molecules that are converted to metathesis products by one molecule of a pre-catalyst, which was found to be 2756 for **1** and 1429 for **2**.



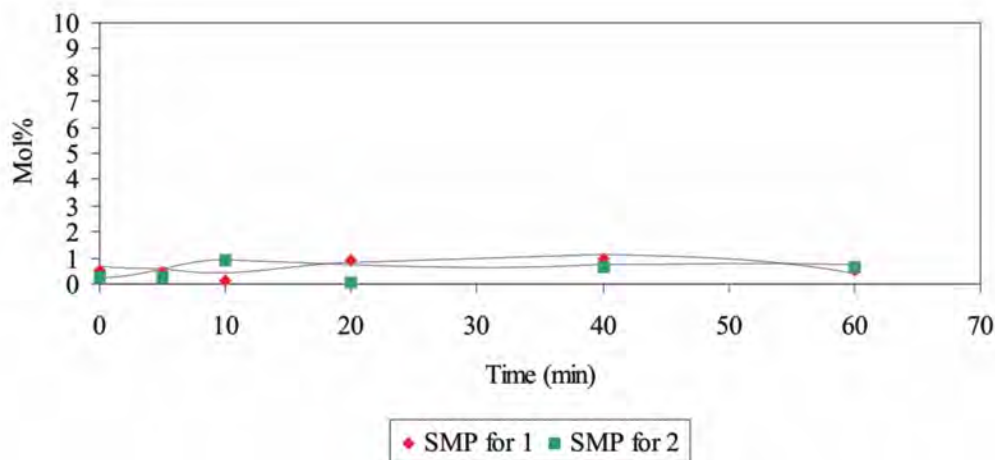
Graph 5.1 The conversion of 1-octene and the formation of PMP with 1



Graph 5.2 The conversion of 1-octene and the formation of PMP with 2



Graph 5.3 The formation of IP during metathesis with **1** and **2**

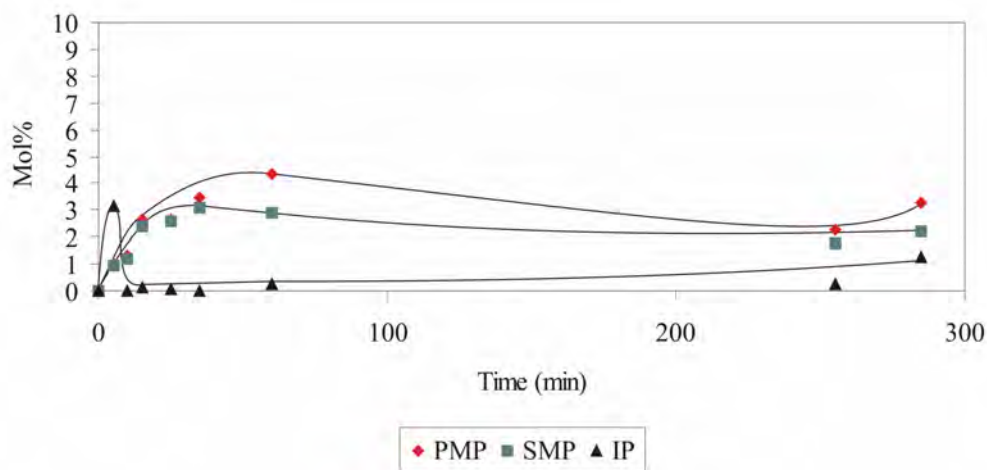


Graph 5.4 The formation of SMP during metathesis with **1** and **2**

In **Graph 5.3** the IP that formed after 60 minutes for **1** was 0.6% but at the first sample that was drawn, which is indicated as t=0, showed that there was 1.22% of IP formed. The reason for this is the 1-octene was used without further purification. The percentage of IP formed for **2** was 0.6%, but in the first 10 minutes of the reaction the IP was 1.4%, the reason for this is that the 1-octene was used without further purification. **Graph 5.4** shows the SMP formation for **1** and **2** after 60 minutes which were 0.53% and 0.6% respectively. The selectivity of both **1** and **2** were 98% after 60 minutes.

5.5.2 Comparison of activity and selectivity of synthesized pre-catalysts **75** and **76** with **1** and **2**

To be able to compare **75** and **76** to **1** and **2** the metathesis reactions of 1-octene with **75** and **76** were done under the same conditions as for **1** and **2**, **Paragraph 5.5.1**. The graph for the formation of PMP, IP and SMP is given in **Graph 5.5**.



Graph 5.5 The formation of PMP, IP and SMP during metathesis with the synthesized pre-catalyst **76**

To determine which pre-catalyst is more active, the increase of PMP within a certain time was compared. After 60 minutes, **1** formed 30% PMP, **2** formed 42% PMP and the synthesized pre-catalyst **76** formed 4.3% PMP and it converted 92.5% of 1-octene. From this it can be concluded that **2** is the most active pre-catalyst. The determination of which pre-catalyst is more selective, the **equation 4** given in **3.9** was used to calculate the selectivity towards PMP. It was found that none of the synthesized pre-catalysts showed better selectivity than **1** and **2**. The pre-catalyst **75** was not active for metathesis under these conditions. The selectivity for **76** was 55% and the summary for the metathesis reactions are given in **Table 5.4**.

Table 5.4 Selectivity of the synthesized pre-catalysts **75** and **76** in comparison to **1** and **2**

Pre-catalyst	PMP (mol%)	SMP (mol%)	IP (mol%)	TON	% Selectivity
1	30.49	0.53	0.60	2756	98
2	42.71	0.66	0.62	1429	98
75	0	0	0	0	0
76	4.33	3.52	0.27	389.7	55

The formation of IP showed a similar curve in **76** in comparison to **1** and **2**. For pre-catalyst **76** the maximum IP of 3.1% was found at about 5 minutes, while that of **1** was 1.22% at 0 minutes and that of **2** was 1.4% at about 10 minutes. The IP undergo metathesis to form SMP, the earlier the maximum IP formed the faster the formation of SMP. In conclusion the pre-catalyst **75** was not active for metathesis. The assumption for the inactivity is that the metathesis conditions were not favourable, due to either the temperature and/or molar ratio. The pre-catalyst **76** was less active and selective than both **1** and **2**, however it was more active and selective than pre-catalyst **75**.

5.6 References

1. P. Roscher, *Modelling en sintese van Grubbs-tipe komplekse met imienligande*, North-West University (Potchefstroom campus) MSc dissertation, 2010
2. S. Chang, L. Jones, C. Wang, L. M. Henling, and R. H. Grubbs, *Organometallics*, 1998, **17**, 3460
3. A. Rauk, *Orbital interaction theory of organic chemistry*, 2nd edition, 2001
4. <http://en.wikipedia.org/wiki/Electrostatics>, 20/05/2010
5. C. A. A. Huijsmans, *Modelling and synthesis of Grubbs type complexes with hemilabile ligands*, North-West University (Potchefstroom campus), MSc Dissertation, 2009
6. F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song, W-H. Sun, *J. Org. Chem.*, 2004, **689**, 936
7. L. K. Johnson, M. A. Bennett, S. D. Simpson, J. Feldman, E. B. Coughlin, PCT Int. Appl. WO 9830609

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

The aim of the study was to find naphthyl imine ligands that can be used to improve the performance of Grubbs type pre-catalysts for 1-octene metathesis. The limitation of **1** and **2** is the lifetime, reactivity and activity. The lifetime and the reactivity of **1** have been improved through the replacement of the phosphine ligand by a more bulky and basic N-heterocyclic carbene (NHC) ligands.¹⁻⁴ The higher activity of **2** can also be attributed to electron distribution and bulky effects that enhance the dissociation of the phosphine ligand as well as the ratio of alkene to phosphine coordination during the catalytic cycle.^{2,5}

6.2 Molecular modeling of imine ligands and the substituted pre-catalysts.

Molecular modeling was used as a screening process to choose the possible ligands to be synthesized. A series of 45 salicylaldehyde imine derivatives were modeled using Material Studio version 4.2 with a basis set of PW91/GGA/DNP.⁶ The following properties were calculated: electron density, electrostatics, Fukui functions, orbitals and population analysis to evaluate the possible imine ligand. The screening was done by visual analysis.

Initially the HOMO energy of the 45 ligands was used as the preliminary criteria of choosing the possible imine ligand. The HOMO energy of possible ligands was calculated against the well defined Verpoort⁷ ligand. In this study the ligands with lower energy than that of Verpoort⁷ was considered. Ligands **68** and **69** were chosen. The lower the energy of the ligand the more stable and the more flexible it will be, but it depends on the R substituent and their orientation. It was found that the position and the size of the substituent attached to the ligand had an influence on the size and orientation of the HOMO, electron density with Fukui function, electrostatics and population analysis.

The electron withdrawing and the electron donating groups also play a role in analyzing the calculated properties, because the most electron rich part as shown by the electron density map with electrophilic Fukui function is the nitrogen atom (red spot) and a less electron rich part was around the oxygen (yellow spot) while the rest of the molecule is neutral (blue, green and light yellow) and the HOMO around the nitrogen atom and oxygen atom is large. This will result in an overlap with Grubbs type pre-catalysts; therefore the substituted Grubbs 1 type pre-catalysts were modeled. From the observations, it will be possible for the Grubbs 1 type pre-catalyst to coordinate with the ligands.

The dissociation energy of the substituted Grubbs 1 type pre-catalysts, **73** and **74**, showed that it will be easier for the pre-catalyst **73** to be dissociated than pre-catalyst **74**. Furthermore molecular modeling helped gain insight into the mechanism of the 1-octene metathesis reaction by using the Potential Energy Surface (PES) scan and the two possible reaction paths for metathesis were investigated. From the PES results it is concluded that the pre-catalyst **74** is more favourable to coordinate with 1-octene than pre-catalyst **73** for both *cis* and *trans* 1-octene positions to the carbene. In both cases the recoordination of the nitrogen atom is favourable in **74**, but overall the recoordination of the nitrogen in heptylidene is most favourable with less energy required.

6.3 Synthesis of ligands and substituted Grubbs type pre-catalysts

Both ligands **68**⁸ and **69**⁹ were successfully synthesized according to preparation methods in literature. Ligand **68** was obtained in 83.5% yield and ligand **69** in 24% yield.

The synthesis of the substituted Grubbs 1 type pre-catalysts was not successful. Because of the instability of **1** it decomposed during the washing process. The synthesis of the substituted Grubbs 1 type pre-catalysts does not correlate to the modeling results. Molecular modeling showed that the coordination of the ligands with **1** was possible. The substituted Grubbs 2 type pre-catalyst **75** and **76** were successfully obtained and were tested for metathesis.

6.4 Metathesis of substituted Grubbs 2 type pre-catalyst

The metathesis of pre-catalysts **75** and **76** were carried out under the following conditions: at 60°C and with a ruthenium: 1-octene molar ratio of 1: 9000. The pre-catalyst **75** was not active for metathesis. The assumption for the inactivity is that the metathesis conditions were not favourable. The pre-catalyst **76** was less active and selective than both **1** and **2**, however it was found to be long lasting, which means that this pre-catalyst will convert more 1-octene into PMP.

6.5 Recommendations

- ❖ There are various imine ligands with naphthyl group that can also be investigated.
- ❖ The PES scan results for this study were unsatisfactory; the electronic energies were used to investigating the mechanism. It would be advisable to refine the model and then re-do the PES scans.
- ❖ The transition states (TS) of **75** and **76** for the two possible mechanisms were not investigated in this study, so it would be useful to do this for the next study.
- ❖ The Grubbs 2 type pre-catalysts were not modelled, it would be interesting to investigate them to see whether they agree with experimental work.
- ❖ Since the substituted Grubbs 1 type pre-catalysts were not obtained due to the decomposition during the washing process, the use of other purification methods, solvents and synthesis procedures must be investigated.
- ❖ The optimization of the substituted pre-catalysts was not covered in this study; therefore it would be interesting to see how the substituted pre-catalysts would behave under different conditions.
- ❖ It would be useful to study the kinetics for the substituted pre-catalysts and correlate it with the modeling results.
- ❖ The ¹H NMR spectra of the substituted pre-catalysts showed the possibility of more than one carbene peak. The NMR studies to investigate what kind of carbenes are formed and how many carbenes would be interesting.
- ❖ Since the substituted pre-catalysts were only tested for 1-octene metathesis reactions, it would be interesting to test other alkenes and other metathesis

reaction modes like ROMP, RCM, etc. experimentally as well as through molecular modeling.

6.6 References

1. M. Jordaan, *Experimental and theoretical investigation of new Grubbs-type catalysts for the metathesis of alkenes*, North-West University (Potchefstroom campus) PhD Thesis, 2007
2. M. Jordaan and H. C. M. Vosloo, *Adv. Synth. Catal.* 2007, **349**, 184
3. J. Huang, H. J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics*, 1999, **18**, 5375
4. M. Jordaan, P. van Helden, C. G. C. E. van Sittert, H. C. M. Vosloo, *J. Mol. Catal.*, 2006, **254**, 145
5. M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.*, 2002, **123**, 6543
6. <http://www.accelrys.com>, 07/07/2008
7. P. Roscher, *Modellering en sintese van Grubbs-tipe komplekse met imienligande*, North-West University (Potchefstroom campus) MSc dissertation, 2010
8. F. Chang et al. *J. Org. Chem.*, 2004, **689**, 936
9. L. K. Johnson, M. A. Bennett, S. D. Simpson, J. Feldman, E. B. Coughlin, PCT Int. Appl. WO 9830609

Appendix I

The table containing the HOMO energies
of the possible ligands

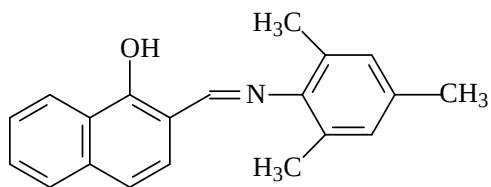
	Name	HOMO Hartree	HOMO kcal/mol	HOMO kJ/mol
1	Verpoort	-0.19592	-122.9535144	-514.4375042
2	N-(3,5-diiodosalicylidene)-2,6-diethylaniline	-0.201944	-126.7339961	-530.2550396
3	N-(3,5-diiodosalicylidene)-2,6-dimethylaniline	-0.186413	-116.9872064	-489.4744716
4	N-salicylideneaniline	-0.183736	-115.3072015	-482.4453312
5	N-3,5-dichlorosalicylideneaniline	-0.198998	-124.8851749	-522.5195716
6	N-salicylidene-2,4,6-trichloroaniline	-0.192203	-120.6208367	-504.6775808
7	N-(3,5-dichlorosalicylidene)-2,4,6-trichloroaniline	-0.198575	-124.6197128	-521.4088781
8	N-3,5-dibromosalicylideneaniline	-0.19898	-124.8738786	-522.4723081
9	N-(3,5-diiodosalicylidene)-2,4,6-trichloroaniline	-0.197456	-123.9174619	-518.4706607
10	N-(3,5-dichlorosalicylidene)-2,4,6-trimethylaniline	-0.176322	-110.6543975	-462.9779993
11	N-3,5-diisopropylsalicylideneaniline	-0.177512	-111.4012058	-466.1026452
12	N-salicylidene-2,4,6-triiodoaniline	-0.19466	-122.1627762	-511.1290556
13	N-(3,5-di-tertbutylsalicylidene)-2,4,6-tri-tertbutylaniline	-0.168117	-105.5051857	-441.4336969
14	N-3,5-diiodosalicylideneaniline	-0.206656	-129.6911059	-542.6275872
15	N-(3,5-dibromosalicylidene)-2,4,6-tribromoaniline	-0.200884	-126.0687719	-527.4717415
16	N-salicylidene-2,4,6-tribromoaniline	-0.203863	-127.9383029	-535.2938594
17	1-phenyliminomethyl-10-naphthalenol	-0.183551	-115.1911011	-481.9595669
18	1-[(2-isopropylphenyl) imino] methylenyl]-10-naphthalenol	-0.182513	-114.5396834	-479.2340354
19	1-[(2-ethylphenyl) imino] methylenyl]-10-naphthalenol	-0.184525	-115.8023543	-484.5170502
20	1-[(2,5-dimethylphenyl) imino] methylenyl]-10-naphthalenol	-0.181793	-114.087833	-477.3434933
21	1-[(2,6-dimethylphenyl) imino] methylenyl]-10-naphthalenol	-0.180945	-113.5556537	-475.1168549
22	1-phenyliminomethyl-2-naphthalenol	-0.184887	-116.0295346	-485.4675727

23	1-[(2-isopropylphenyl) imino] methylenyl]-2-naphthalenol	-0.182844	-114.7474091	-480.1031596
24	1-[(2-ethylphenyl) imino] methylenyl]-2-naphthalenol	-0.183162	-114.9469763	-480.938149
25	1-[(2,5-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.181531	-113.9234097	-476.6555461
26	1-[(2,6-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.183002	-114.8465651	-480.5180285
27	1-[(4-bromo-2,6-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.185861	-116.6407878	-488.025056
28	1-[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol	-0.185095	-116.1600692	-486.0137293
29	1-[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.179451	-112.6180641	-471.1939801
30	1-[(2-fluorophenyl) imino] methylenyl]-2-naphthalenol	-0.190464	-119.5294925	-500.1113965
31	1-[(2,6-difluorophenyl) imino] methylenyl]-2-naphthalenol	-0.187873	-117.9034586	-493.3080708
32	1-[(2,3,4-trifluorophenyl) imino] methylenyl]-2-naphthalenol	-0.197949	-124.2268539	-519.7651568
33	1-[(2,3,6-trifluorophenyl) imino] methylenyl]-2-naphthalenol	-0.197722	-124.0843955	-519.1691109
34	1-[(2,4,5-trifluorophenyl) imino] methylenyl]-2-naphthalenol	-0.19235	-120.7130895	-505.0635665
35	1-phenyliminomethyl-2-naphthalenol	-0.179337	-112.5465211	-470.8946442
36	1-[(2-isopropylphenyl) imino] methylenyl]-2-naphthalenol	-0.180277	-113.1364369	-473.3628519
37	1-[(2-ethylphenyl) imino] methylenyl]-2-naphthalenol	-0.178774	-112.1931992	-469.4163454
38	1-[(2,5-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.177245	-111.2336447	-465.4015692
39	1-[(2,6-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.180939	-113.5518882	-475.1011004
40	1-[(4-bromo-2,6-dimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.190983	-119.8552013	-501.4741623
41	1-[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol	-0.173752	-109.0415426	-456.2298144
42	1-[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol	-0.175924	-110.4046247	-461.9329497
43	1-[(2-fluorophenyl) imino] methylenyl]-2-naphthalenol	-0.181404	-113.8437083	-476.3220754
44	1-[(2,6-difluorophenyl) imino] methylenyl]-2-naphthalenol	-0.183541	-115.1848254	-481.9333093
45	1-[(2,3,4-trifluorophenyl) imino] methylenyl]-2-naphthalenol	-0.18803	-118.0019871	-493.720314

Appendix II

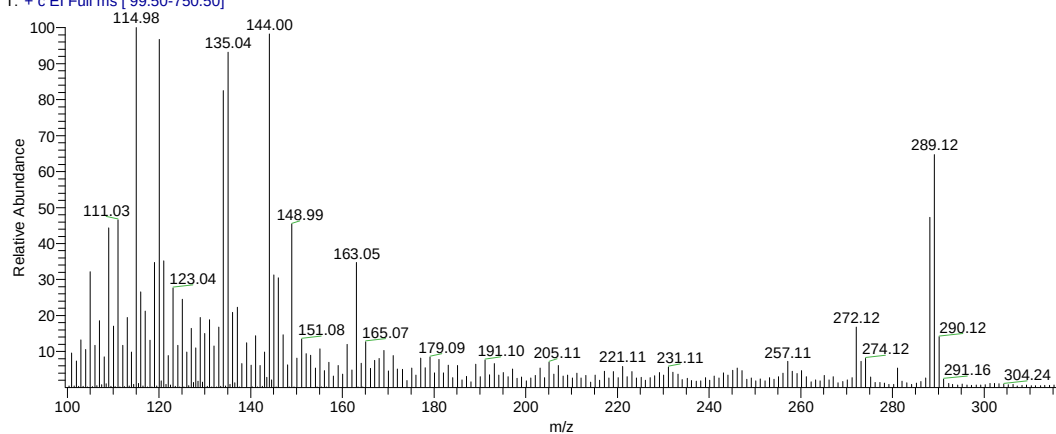
MS Spectra

❖ Ligand **68**: 1-[[[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol



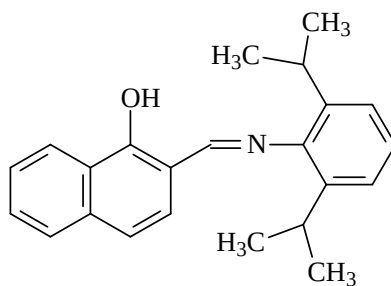
M_w=289.12 m/z

LIGAND 1_LR #49 RT: 0.90 AV: 1 NL: 2.59E7
T: + c EI Full ms [99.50-750.50]



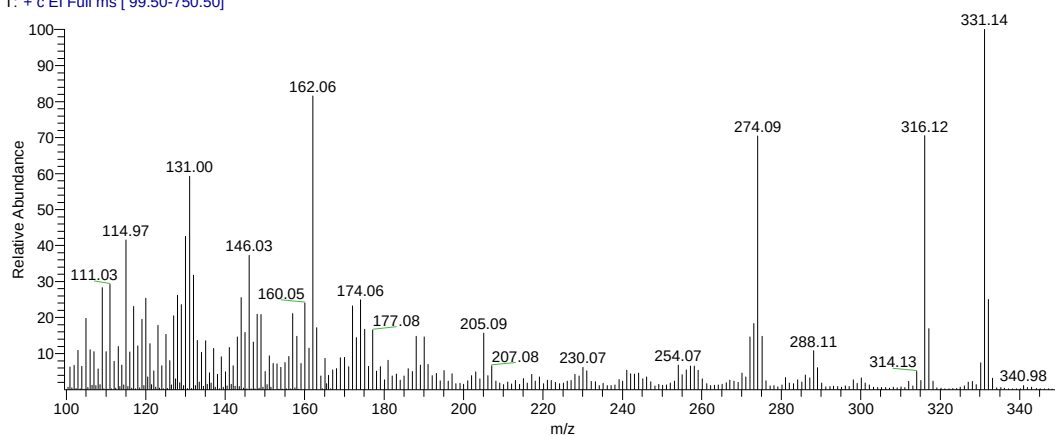
Spectrum **1** MS spectra of ligand **68**

❖ Ligand **69**: 1-[[[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol



M_w=331.14 m/z

LIGAND 2_LR #45 RT: 0.83 AV: 1 NL: 1.42E7
T: + c EI Full ms [99.50-750.50]

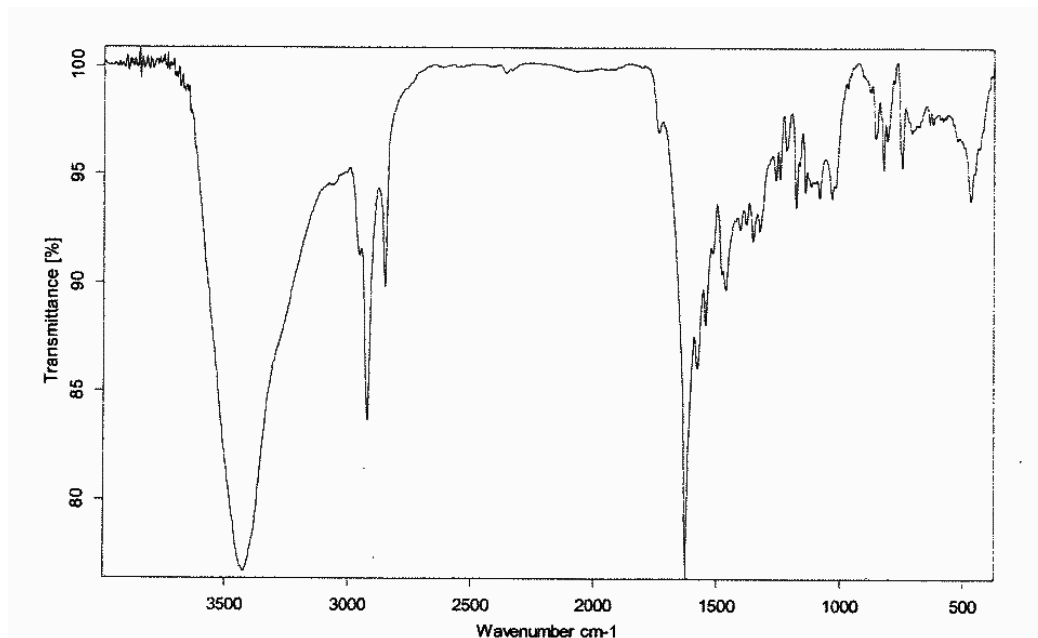
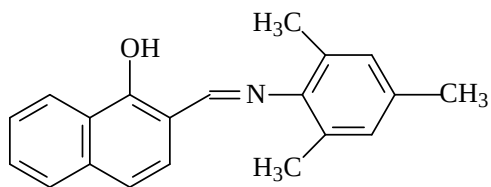


Spectrum 2 MS spectra of ligand **69**

Appendix III

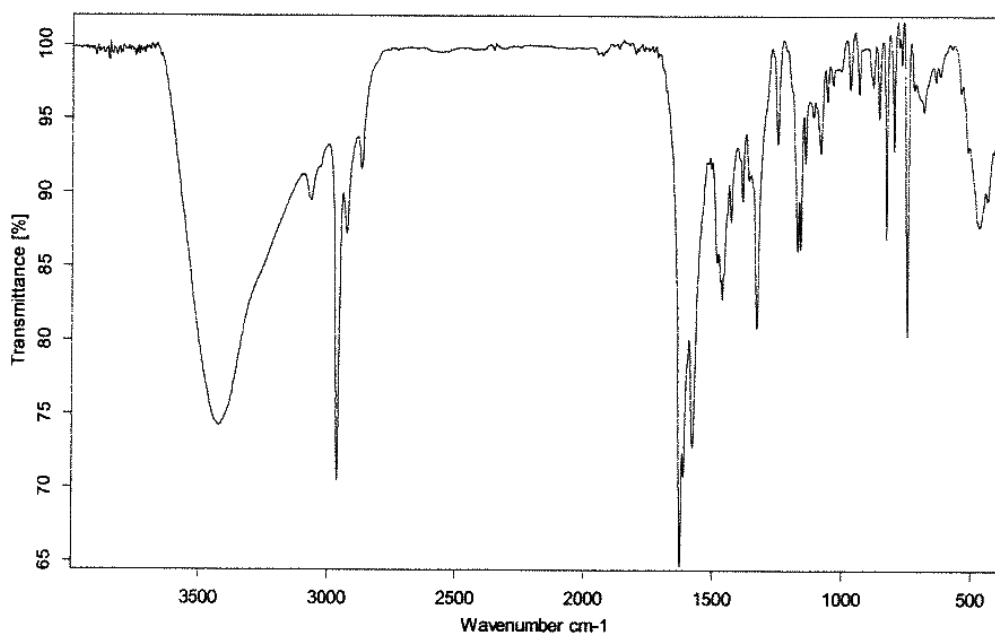
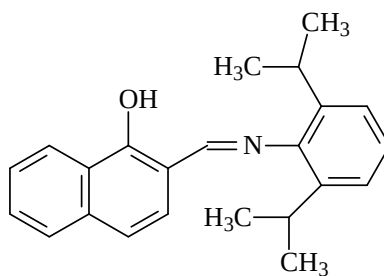
IR Spectra

❖ Ligand **68**: 1-[[[(2,4,6-trimethylphenyl) imino] methylenyl]-2-naphthalenol



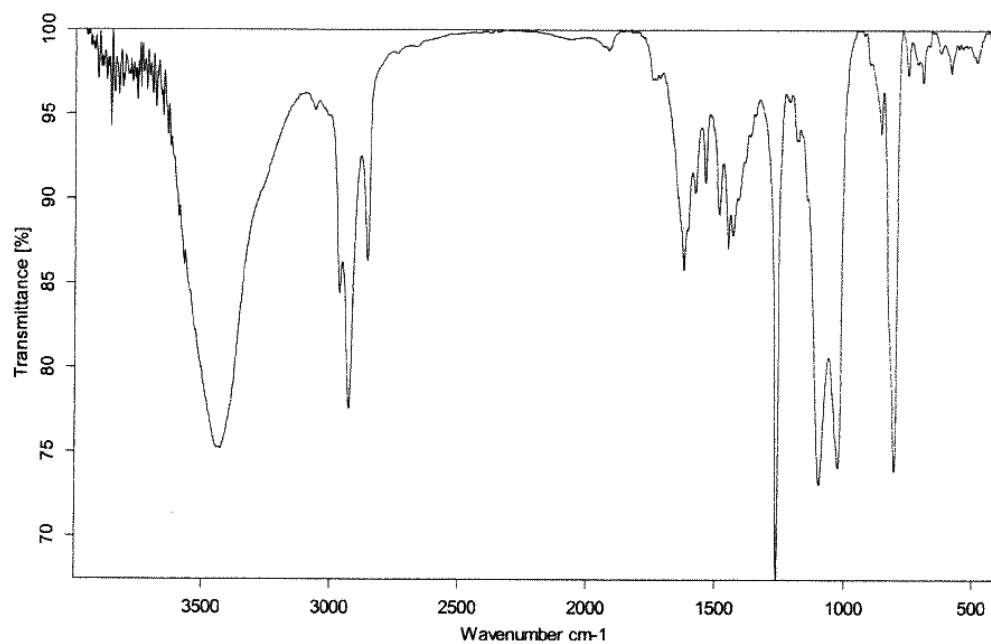
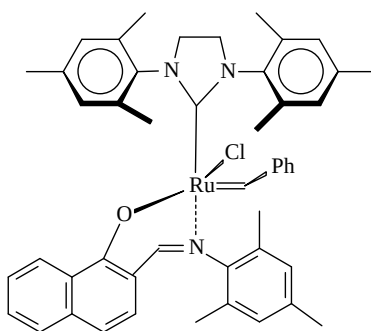
Spectrum 3 IR spectra of ligand **68**

❖ Ligand **69**: 1-[[[(2,6-diisopropylphenyl) imino] methylenyl]-2-naphthalenol



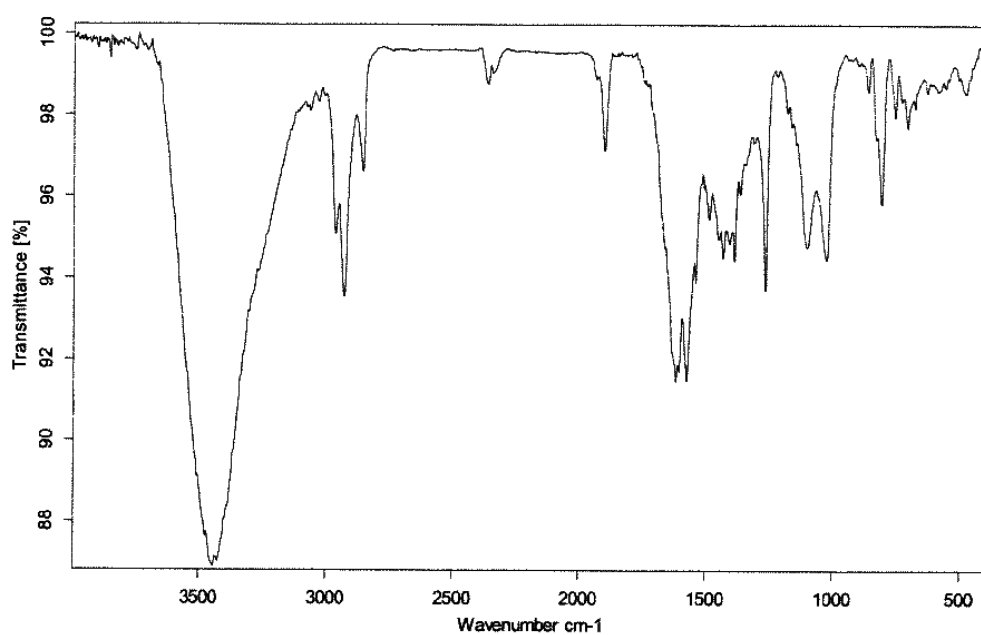
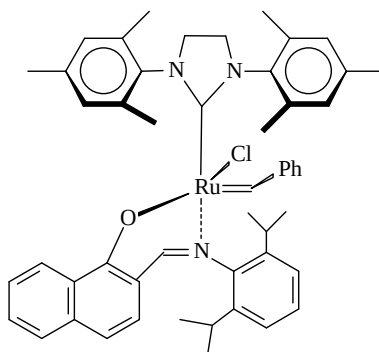
Spectrum 4 IR spectra of ligand **69**

❖ Pre-catalyst 75



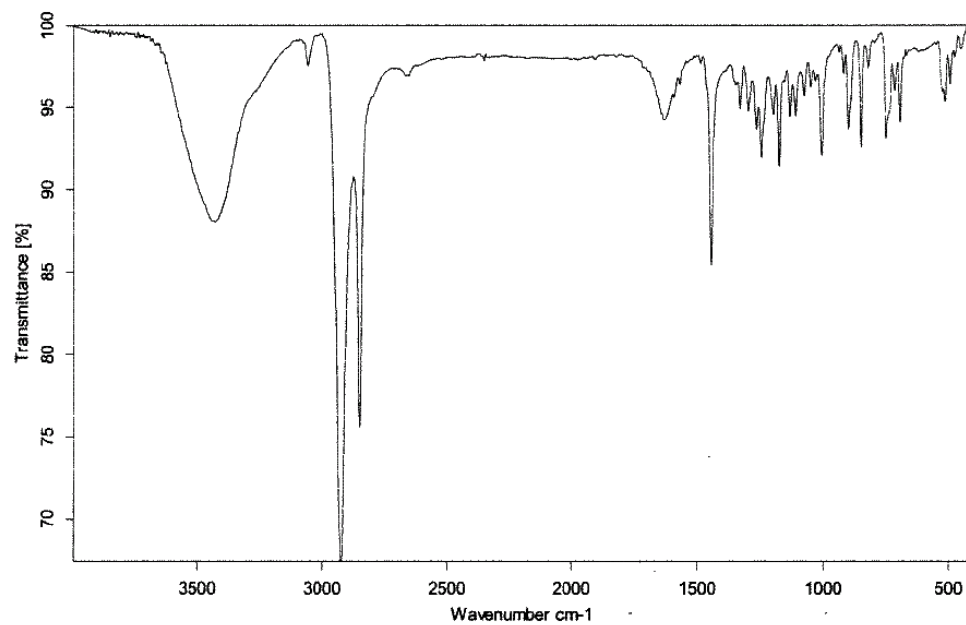
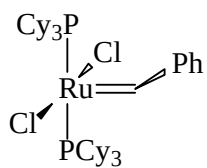
Spectrum 5 IR spectra of pre-catalyst 75

❖ Pre-catalyst **76**



Spectrum **6** IR spectra of Pre-catalyst **76**

❖ Pre-catalyst **1**

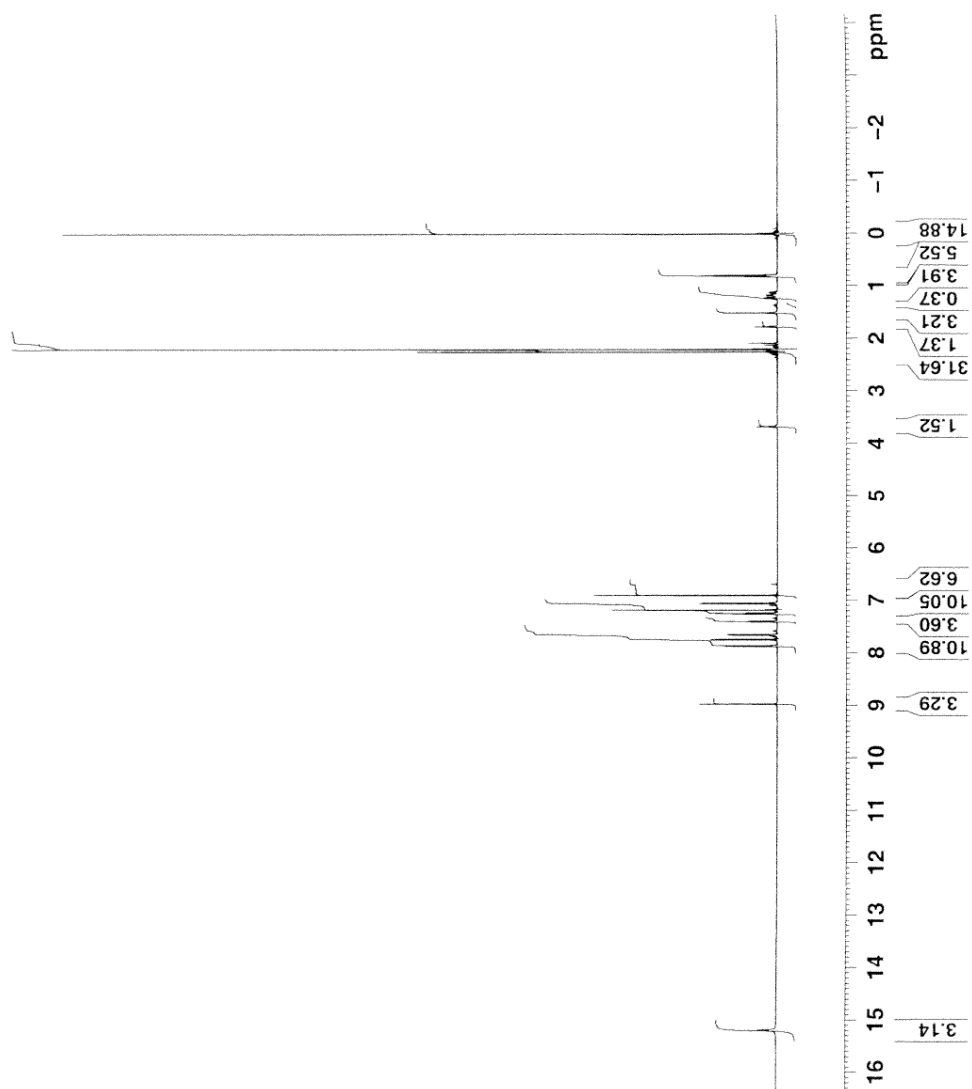


Spectrum 7 IR spectra of Grubbs one type pre-catalyst

Appendix IV

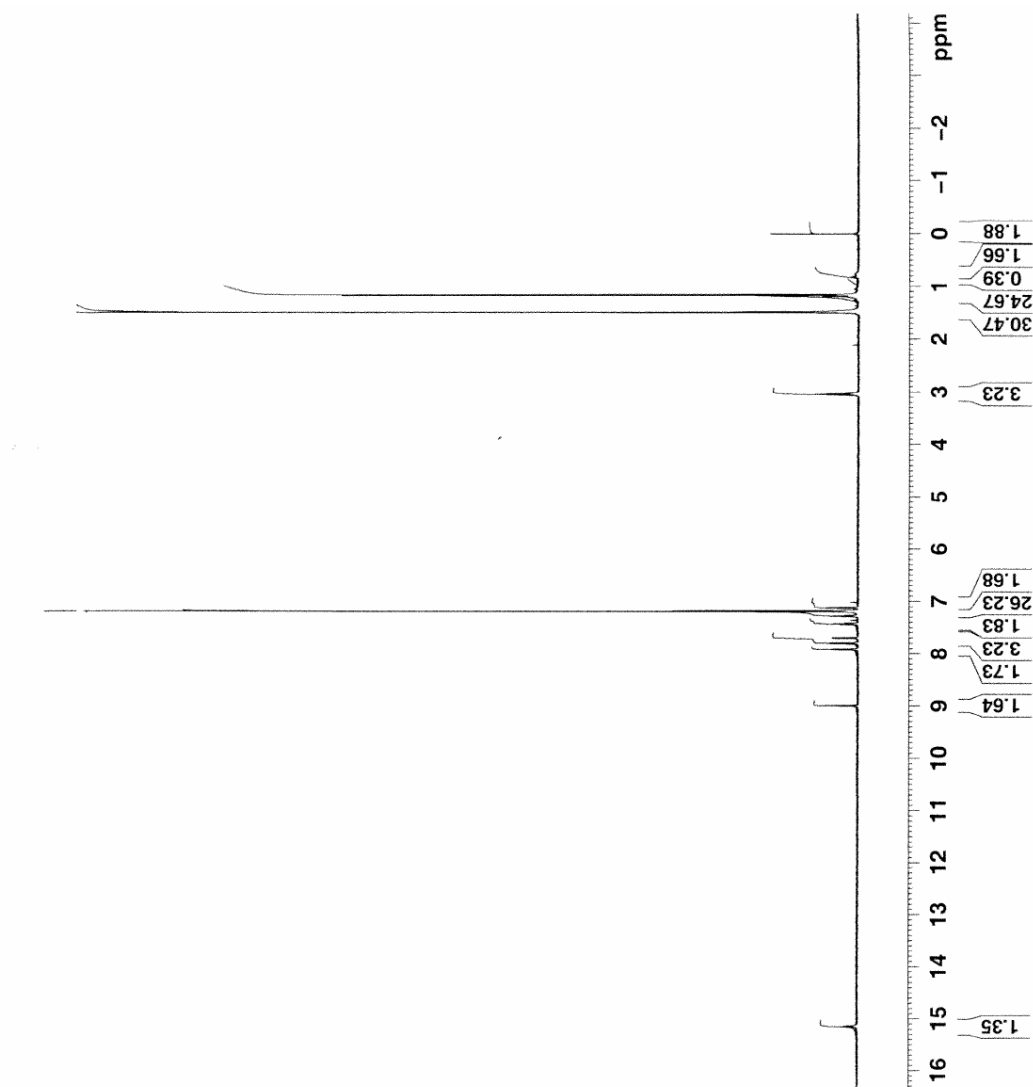
^1H NMR Spectra

❖ Ligand **68**: 1-[[[(2,4,6-trimethylphenyl) imino] methylene]-2-naphthalenol



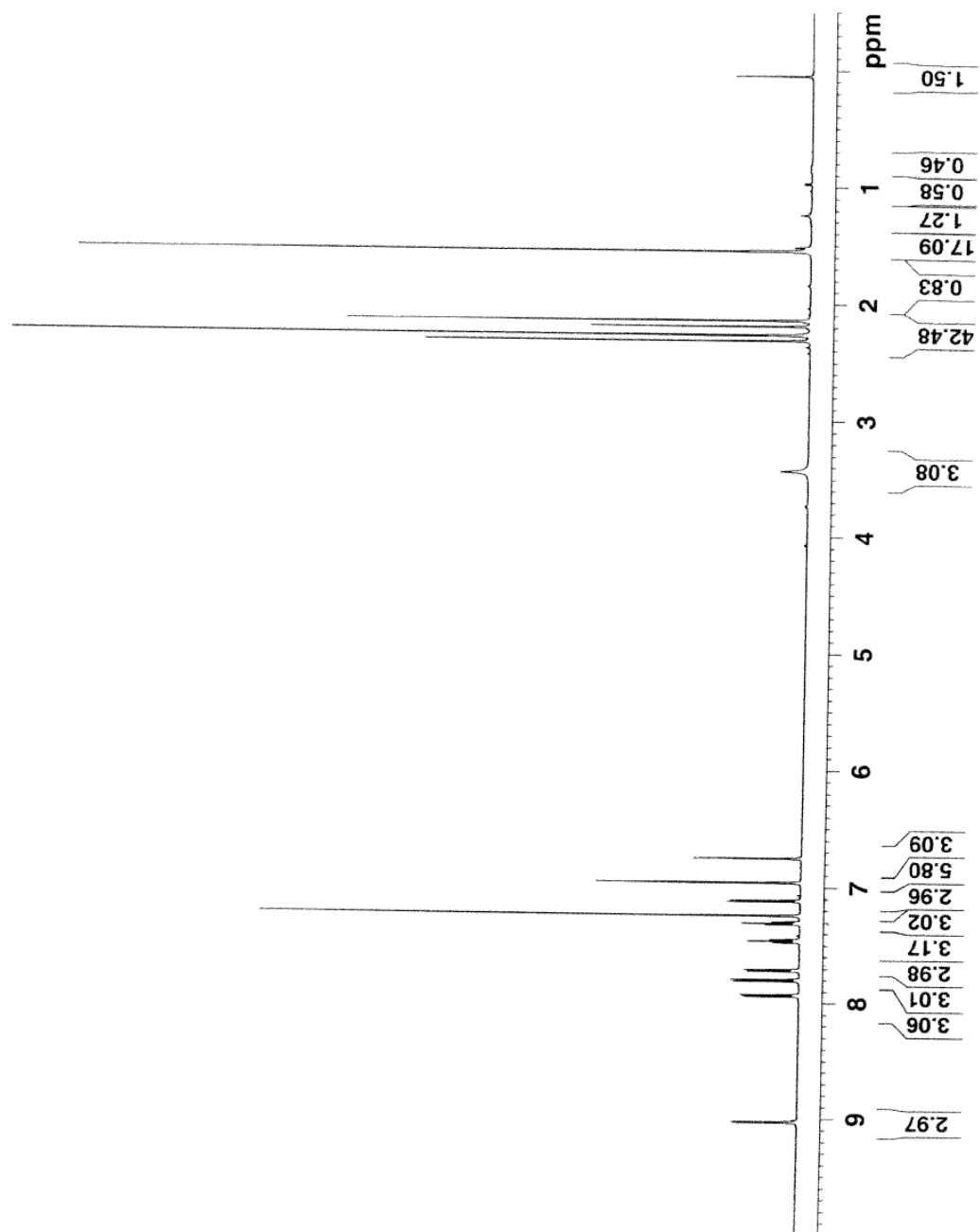
Spectrum **8** ¹H NMR spectra of ligand **68**

- ❖ Ligand **69**: 1-[[[(2,6-diisopropylphenyl) imino] methylene]-2-naphthalenol

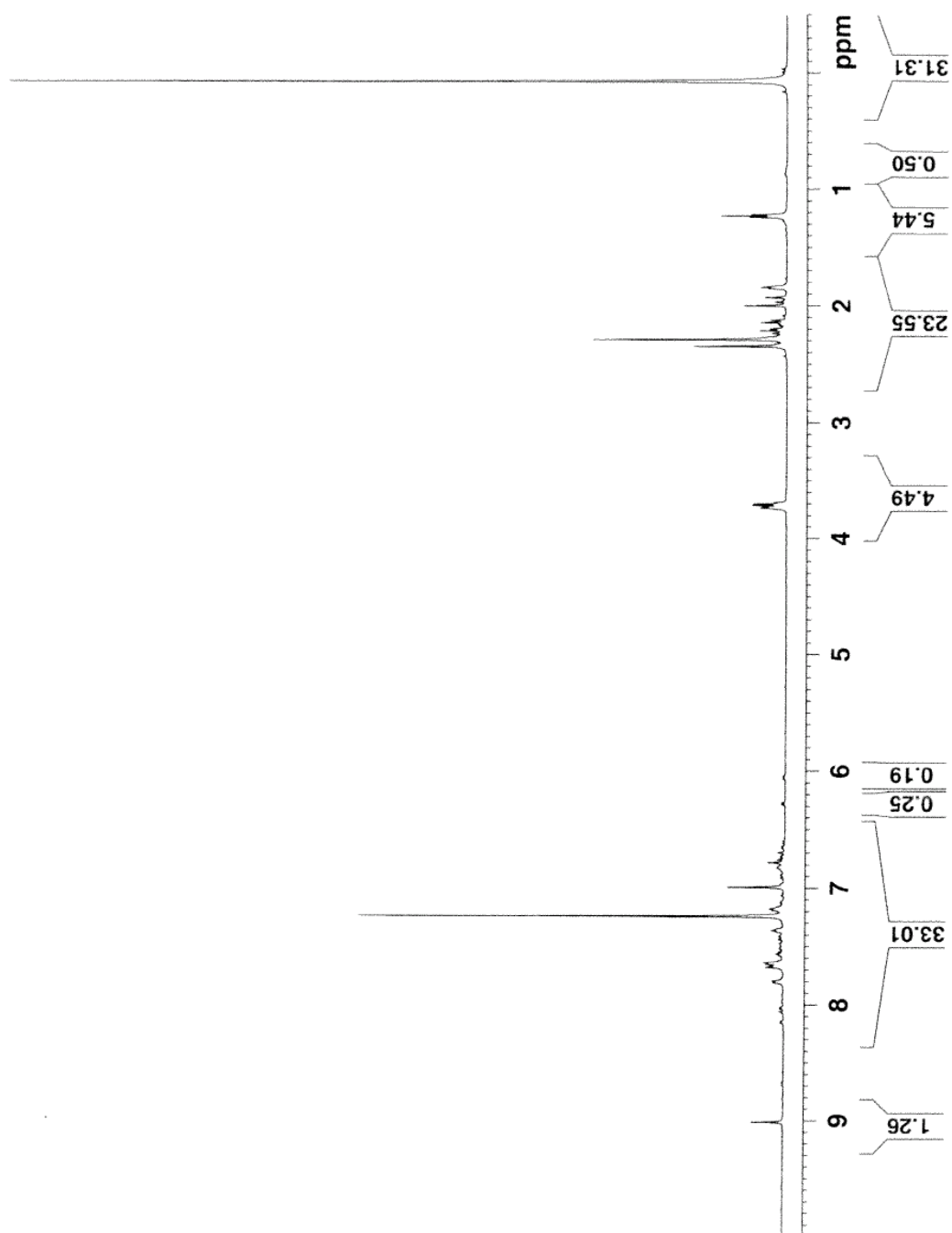


Spectrum **9** ¹H NMR spectra of ligand **69**

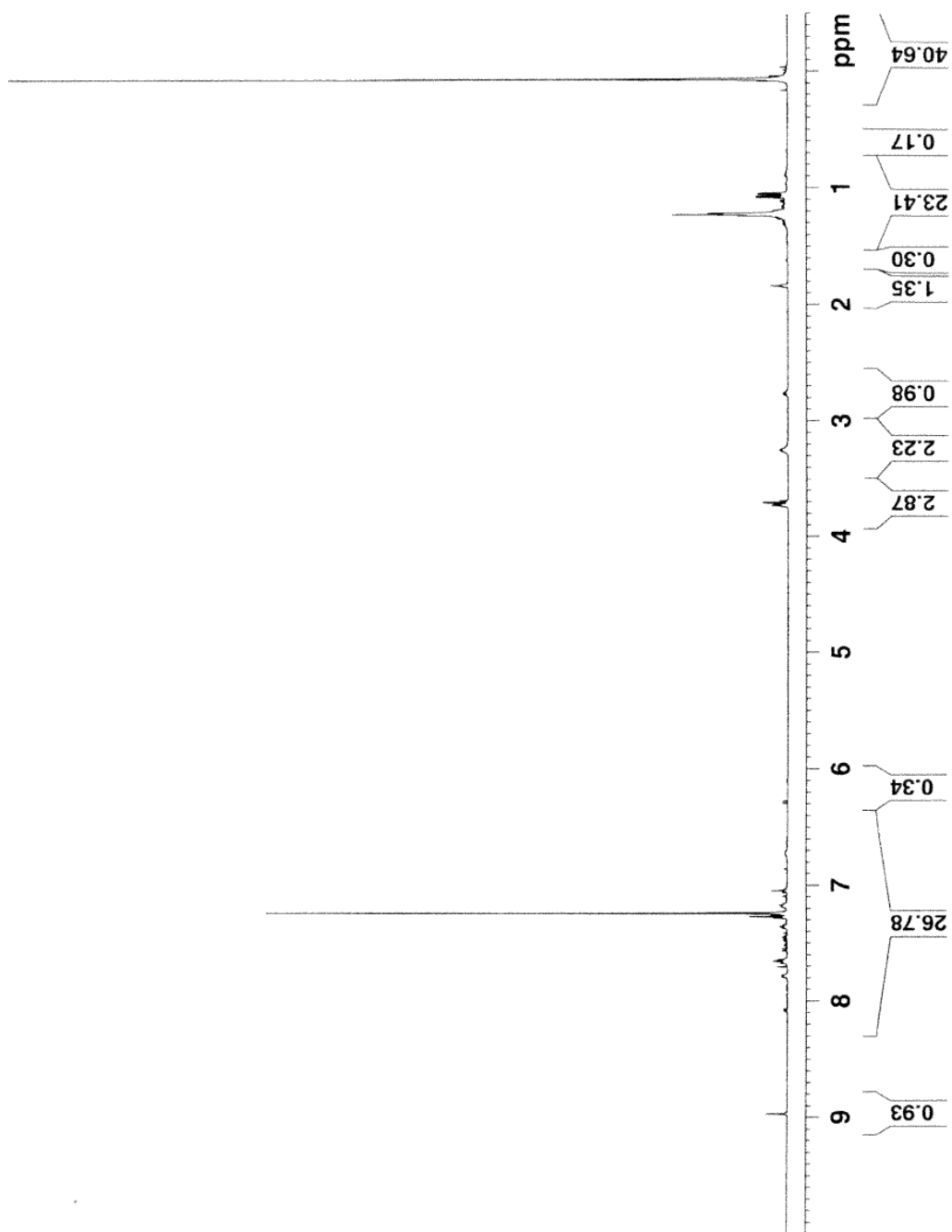
❖ S1_{Na}



Spectrum **10** ¹H NMR spectra of sodium salt one

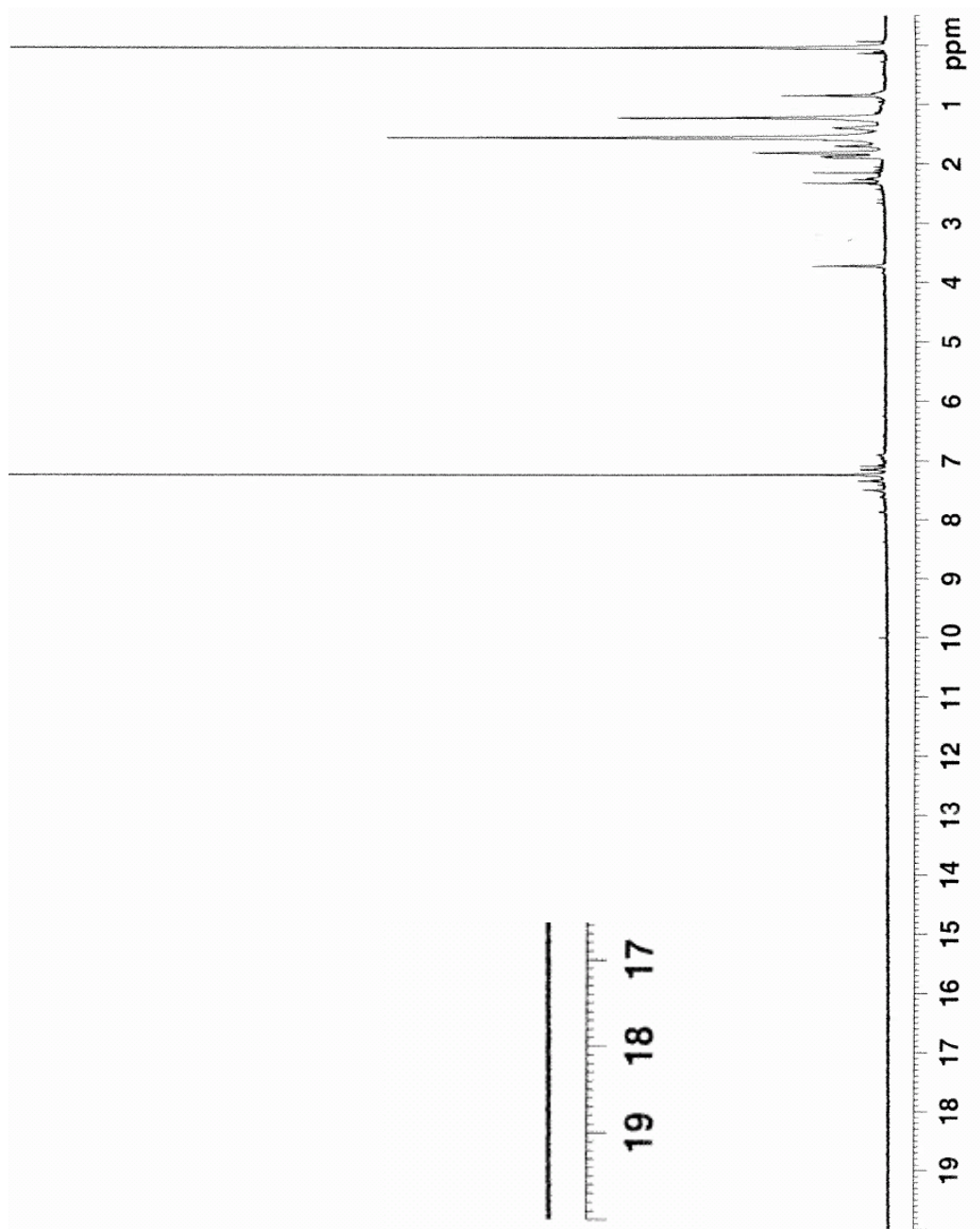
Spectrum 11 ¹H NMR spectra of thallium salt one

❖ S2_{II}



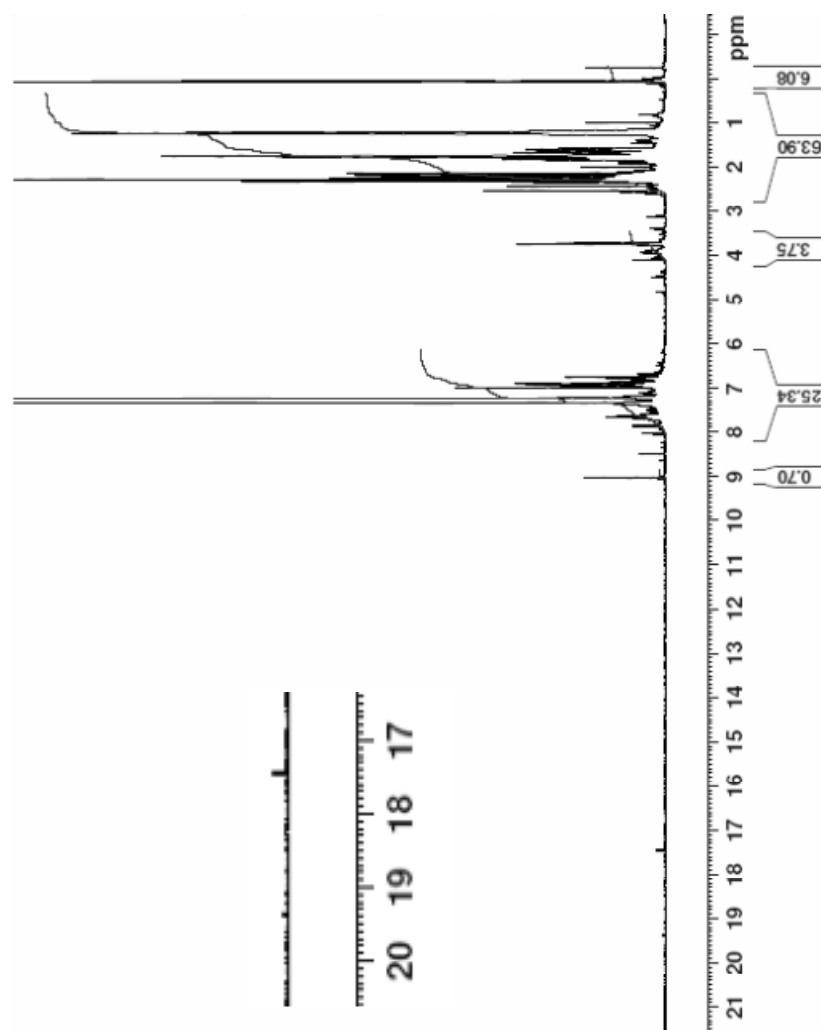
Spectrum 12 ^1H NMR spectra of thallium salt two

❖ Pre-catalyst **C1Gr1_{Na}**



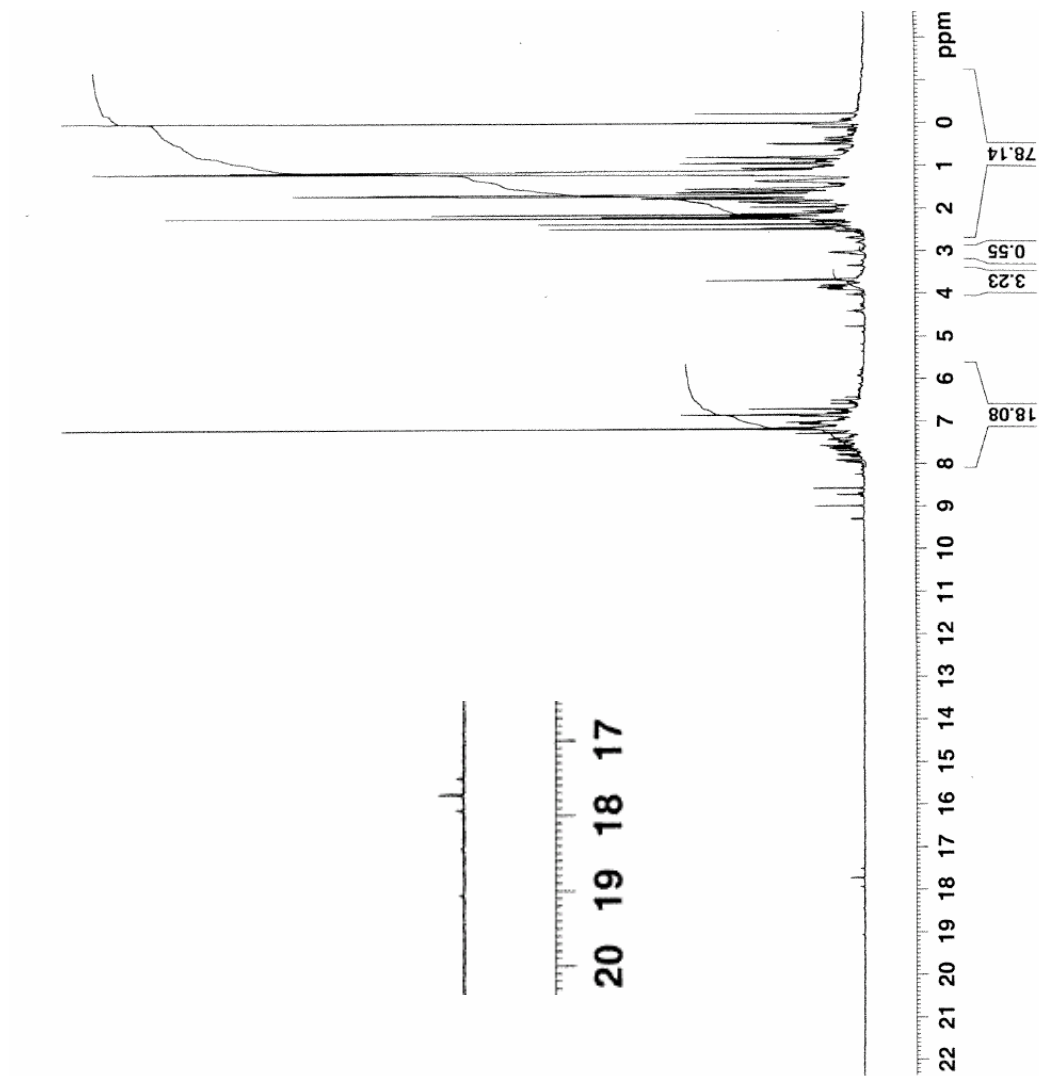
Spectrum ^1H NMR spectra of Pre-catalyst **C1Gr1_{Na}**

❖ Pre-catalyst 75



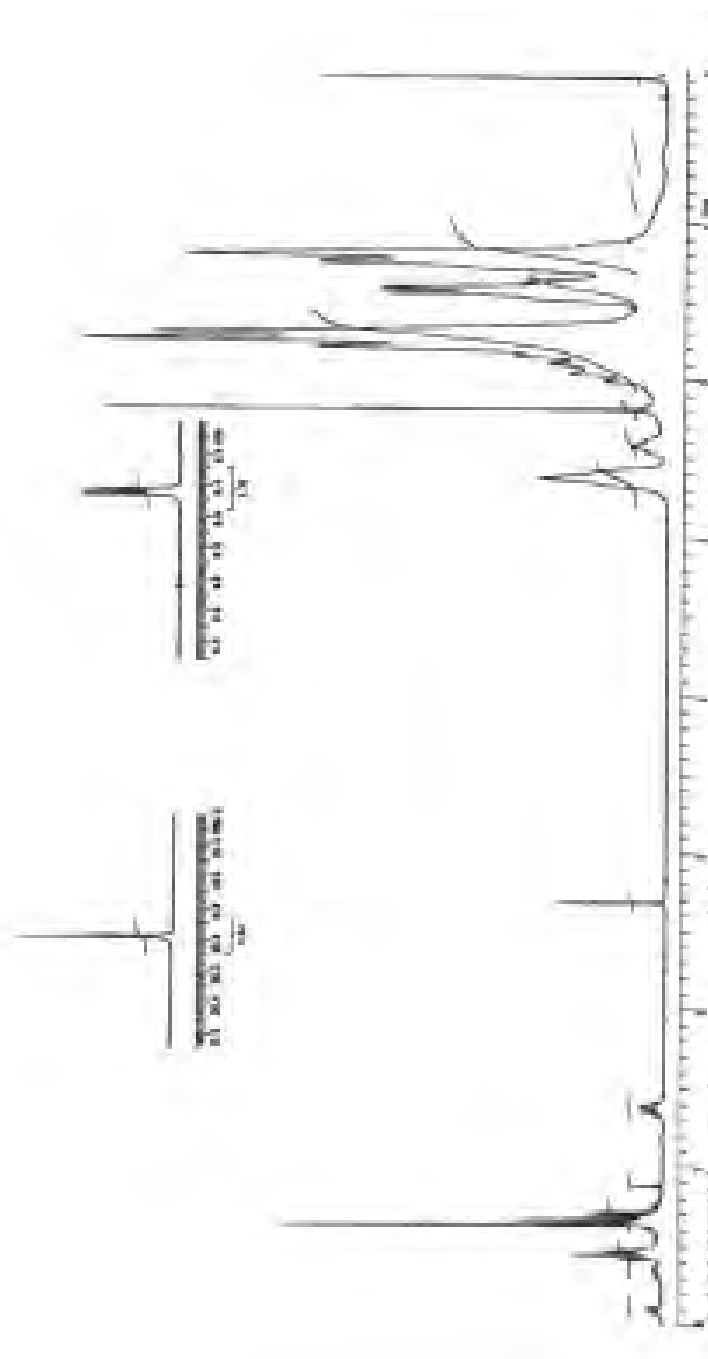
Spectrum **14** ^1H NMR spectra of Pre-catalyst **75**

❖ Pre-catalyst **76**



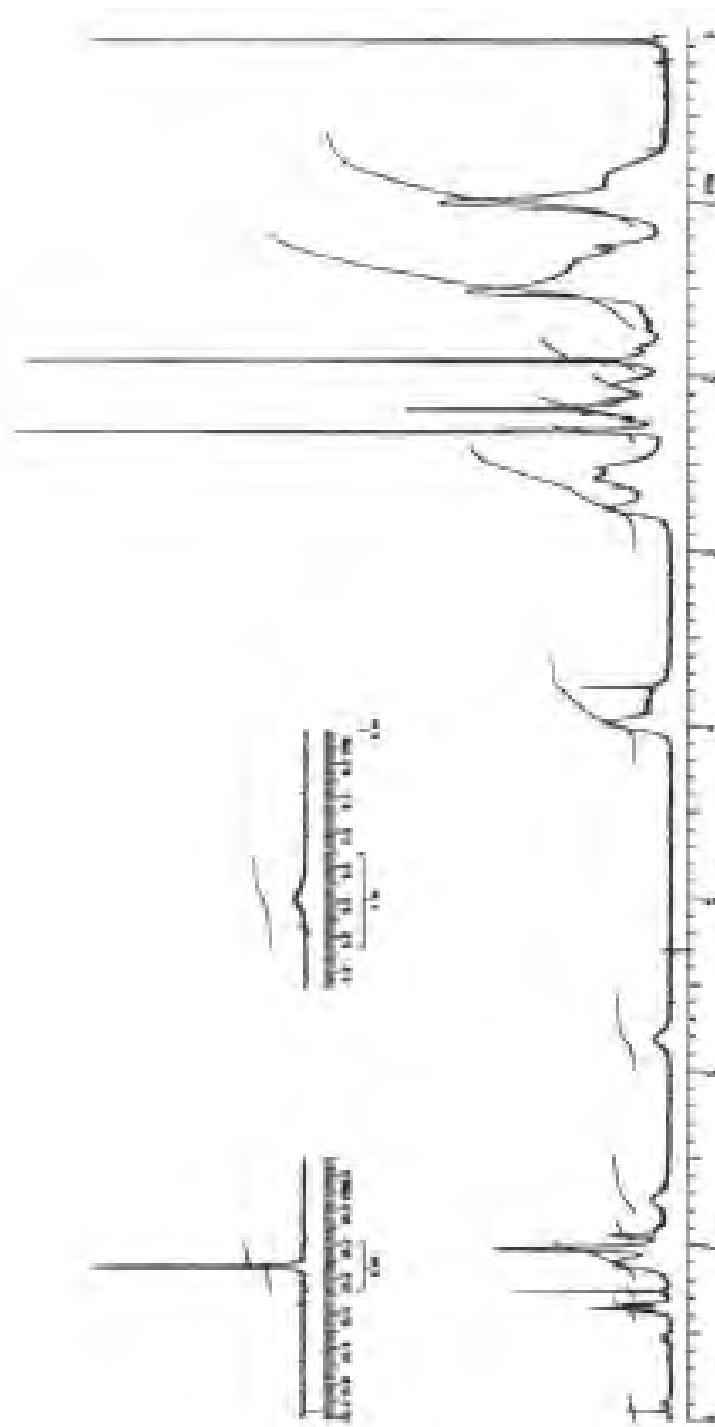
Spectrum **15** ^1H NMR spectra of Pre-catalyst **76**

❖ Pre-catalyst **1**



Spectrum **16** ^1H NMR spectra of Pre-catalyst **1**

❖ Pre-catalyst 2

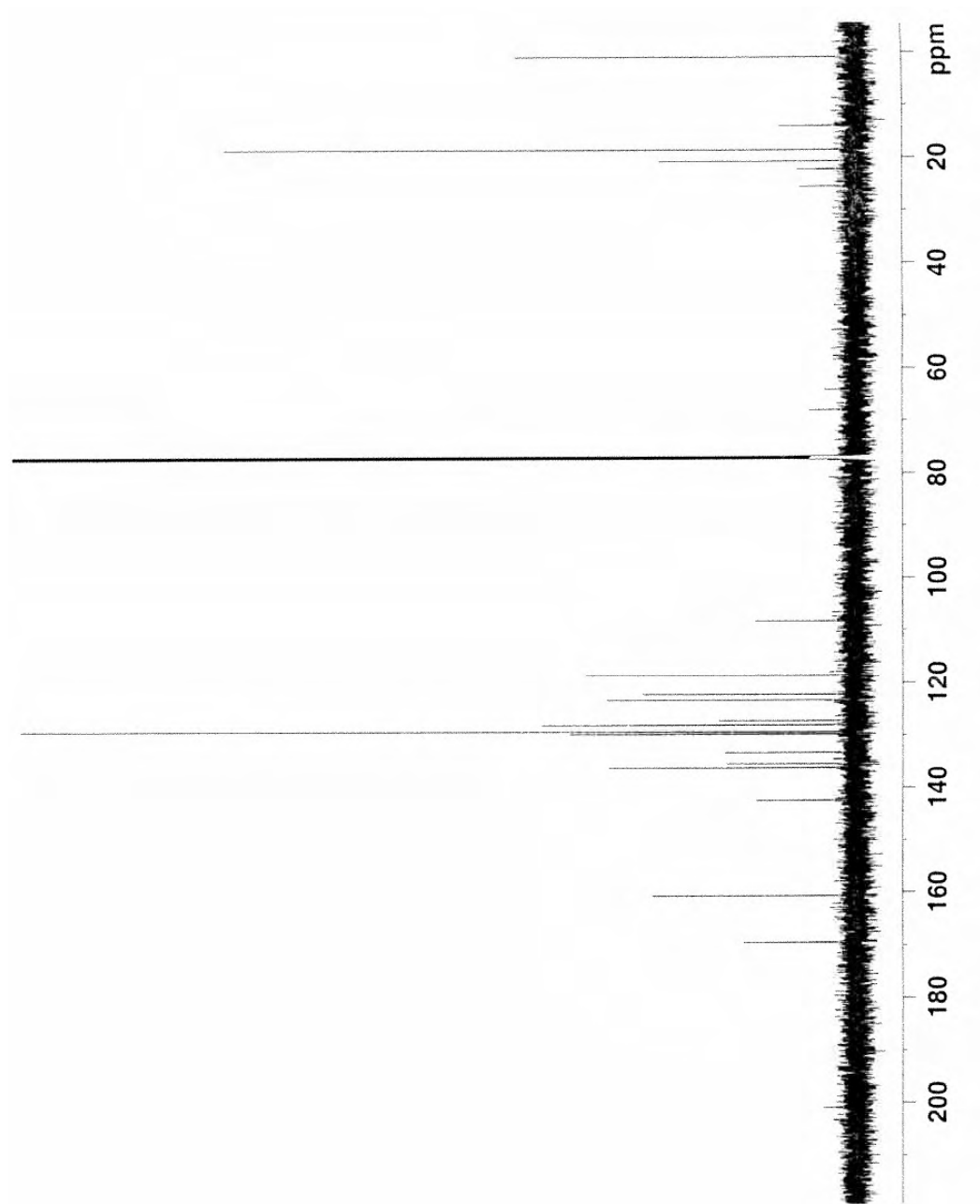


Spectrum 17 ^1H NMR spectra of Pre-catalyst 2

Appendix V

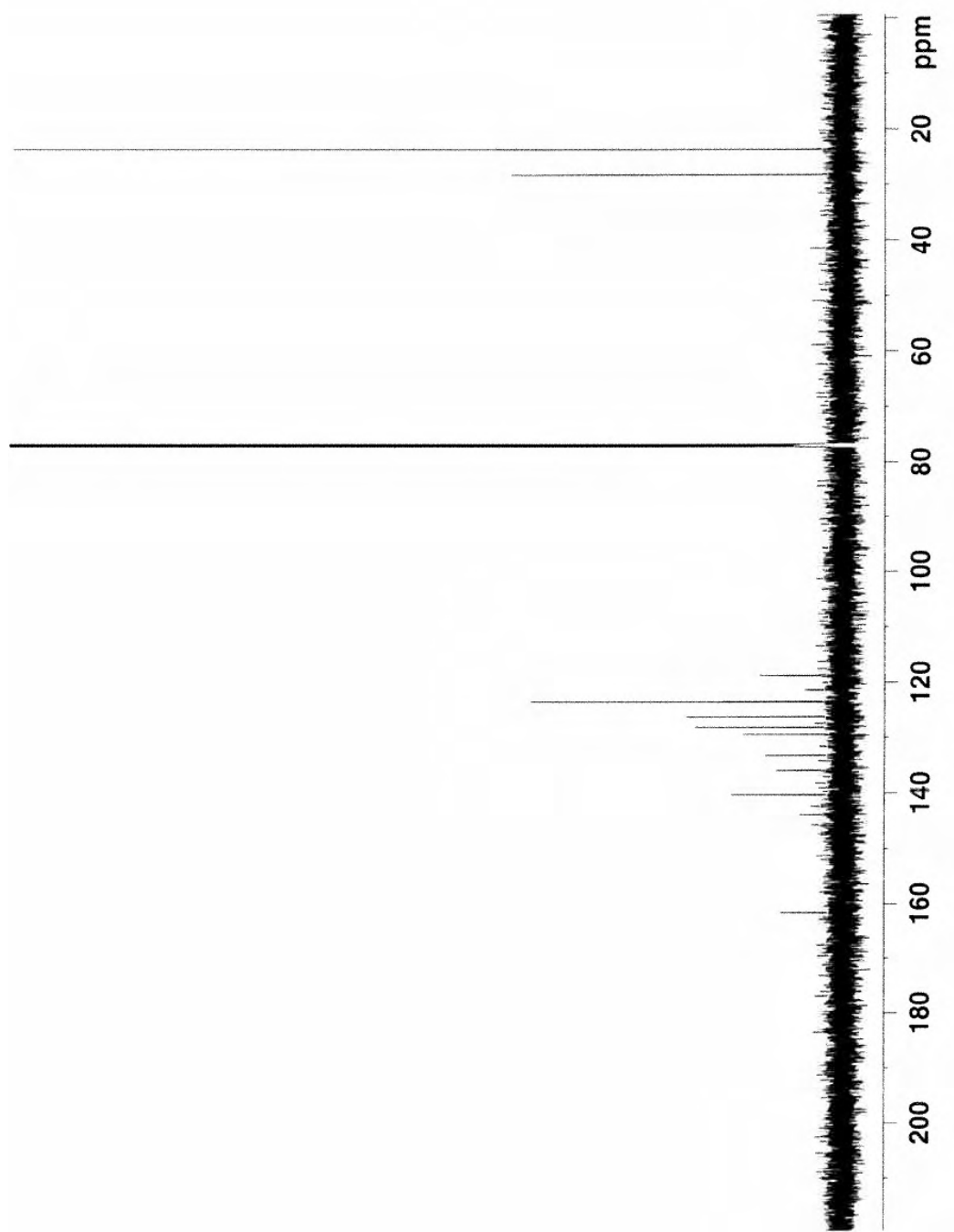
^{13}C NMR Spectra

❖ Ligand **68**



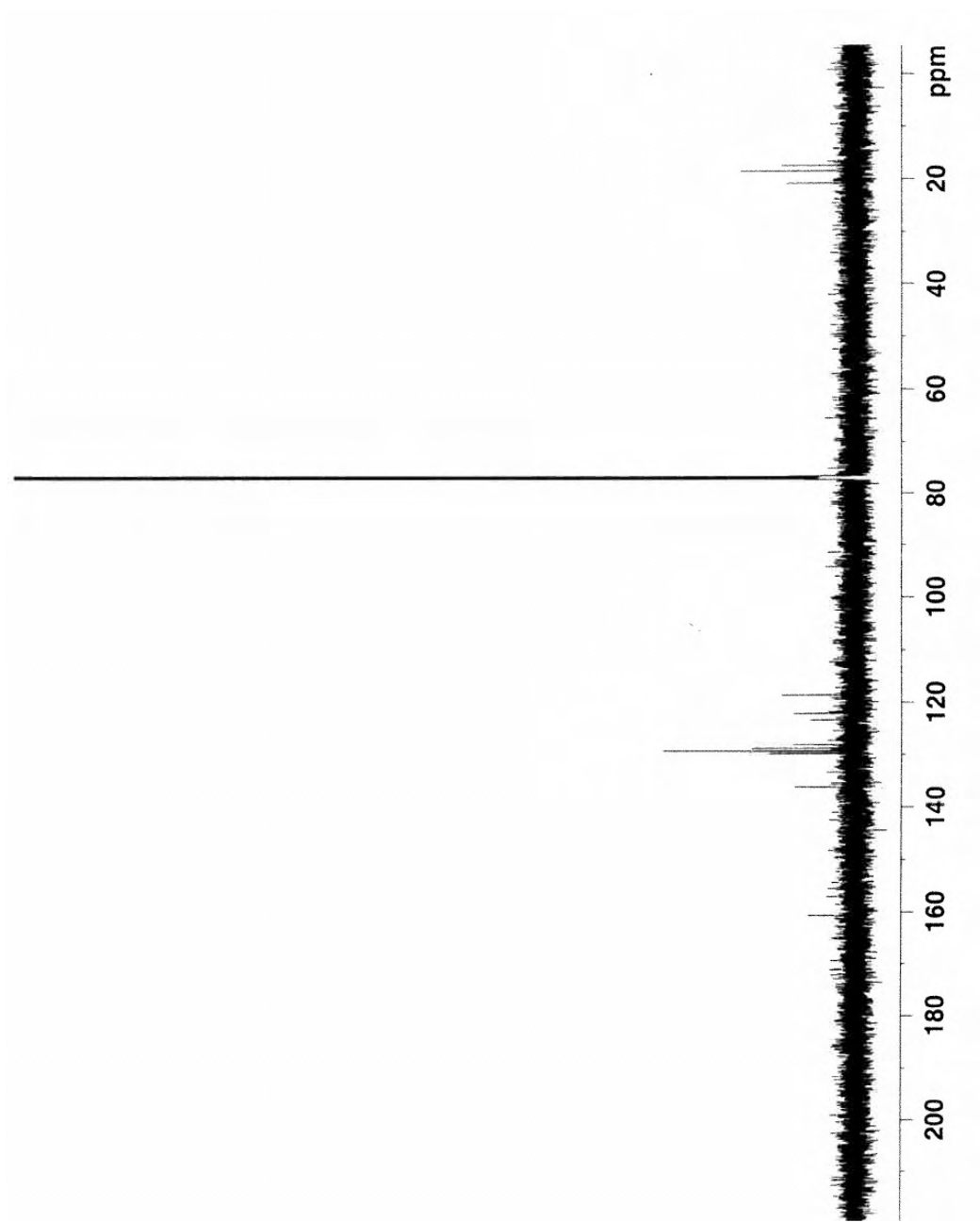
Spectrum **18** ^{13}C NMR spectra of ligand **68**

❖ Ligand **69**



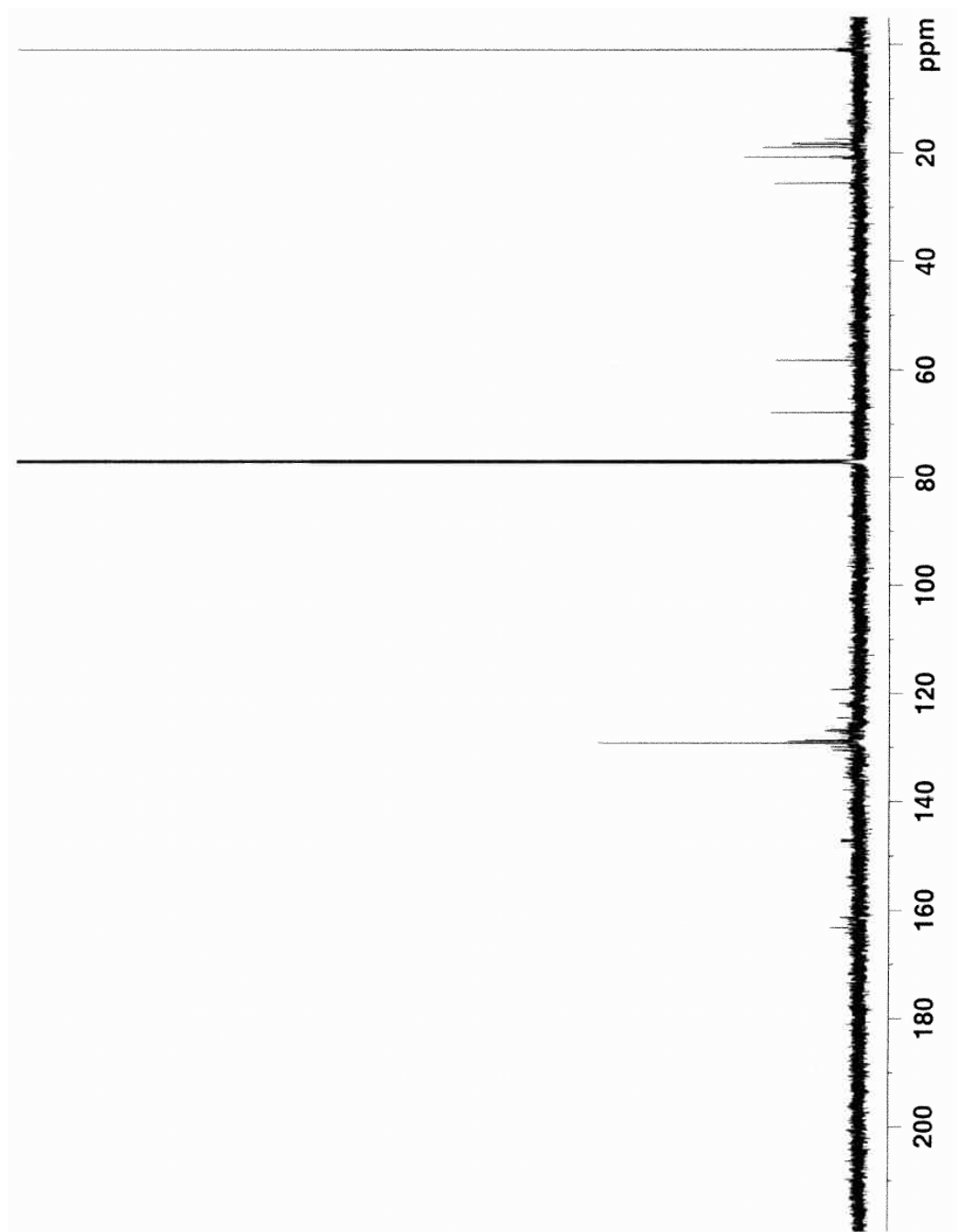
Spectrum **19** ^{13}C NMR spectra of ligand **69**

❖ $S1_{Na}$



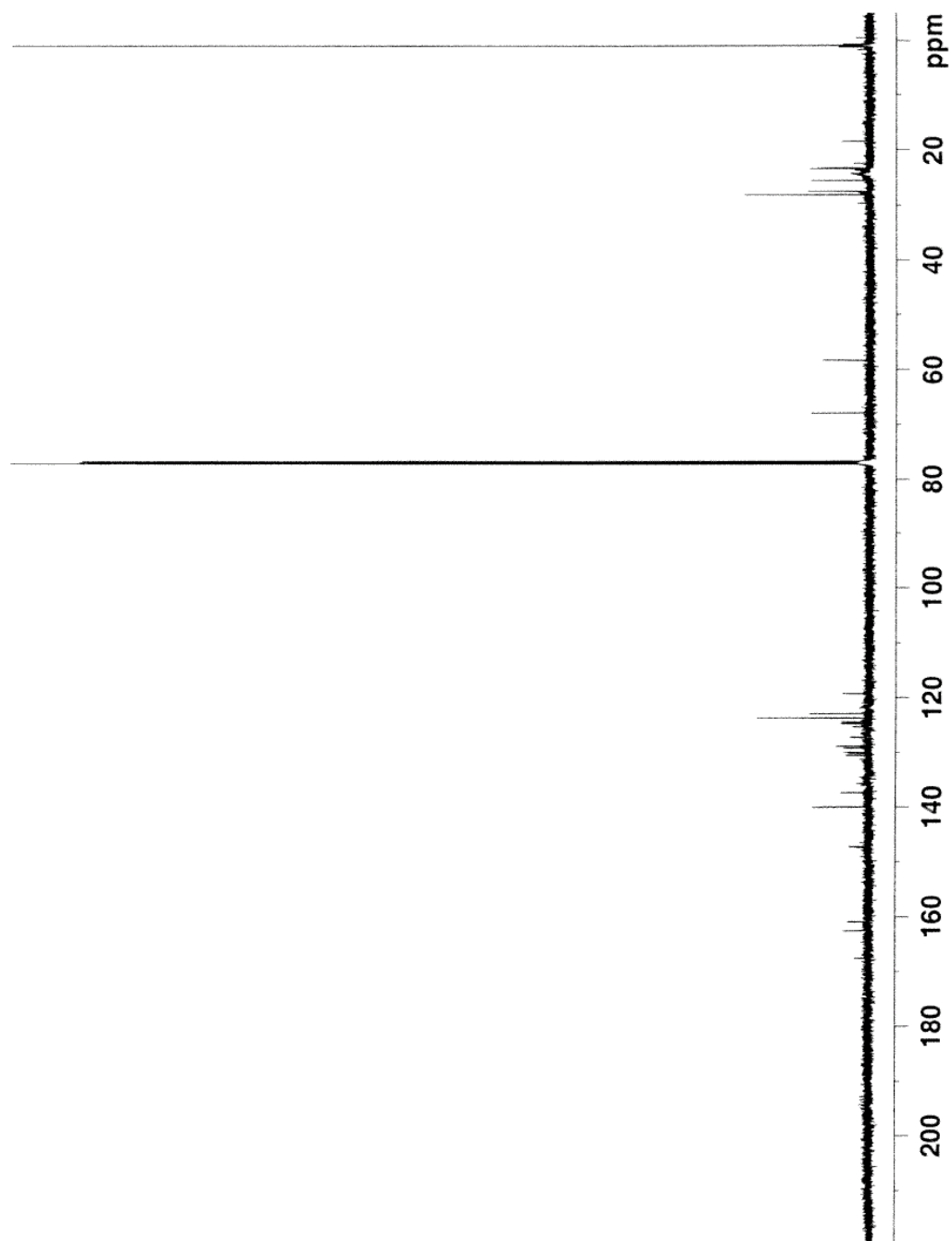
Spectrum **20** ^{13}C NMR spectra of $S1_{Na}$

❖ S1_{Tl}



Spectrum **21** ^{13}C NMR spectra of S1_{Tl}

❖ S_{2-TI}

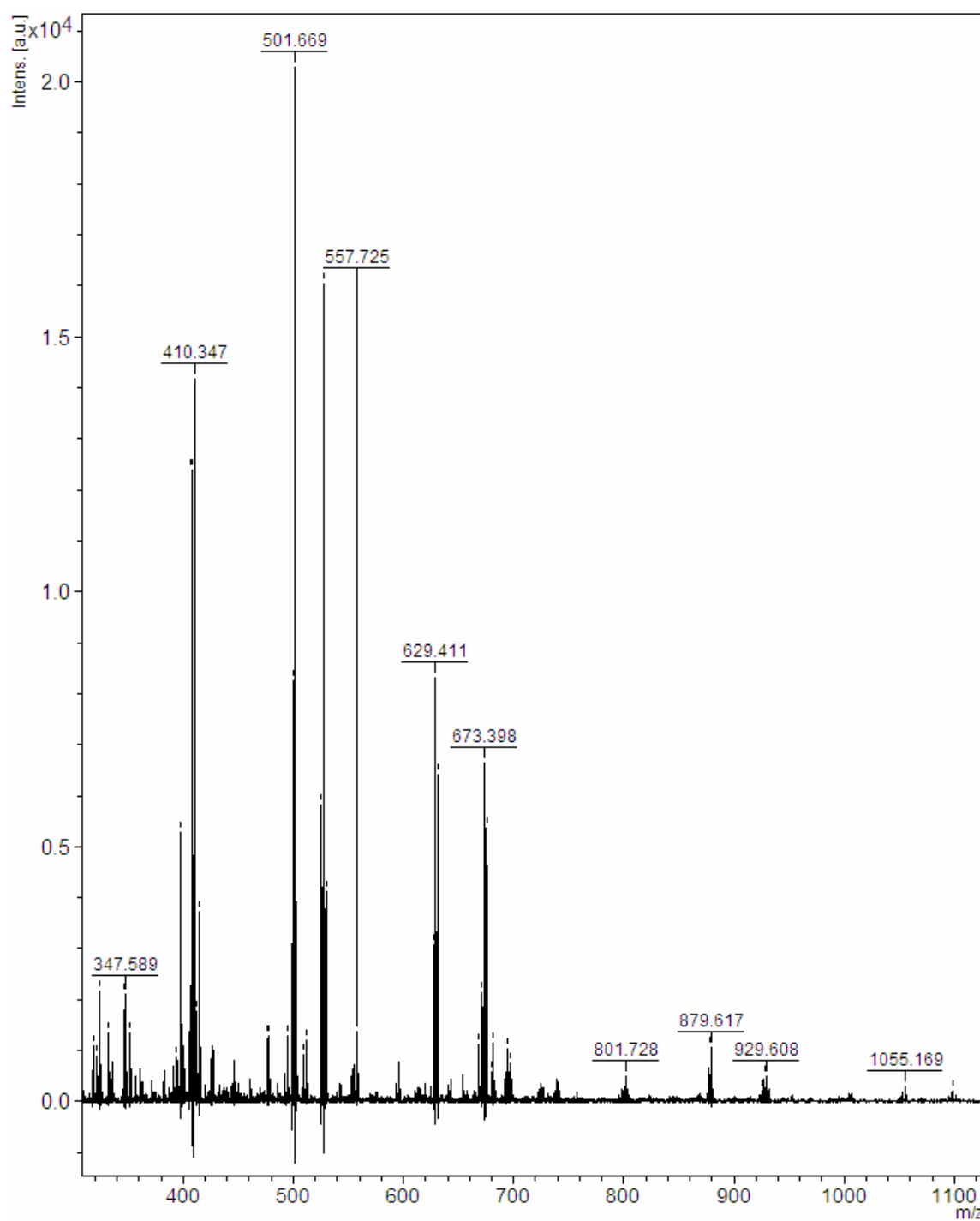


Spectrum 22 ¹³C NMR spectra of S_{2-TI}

Appendix VI

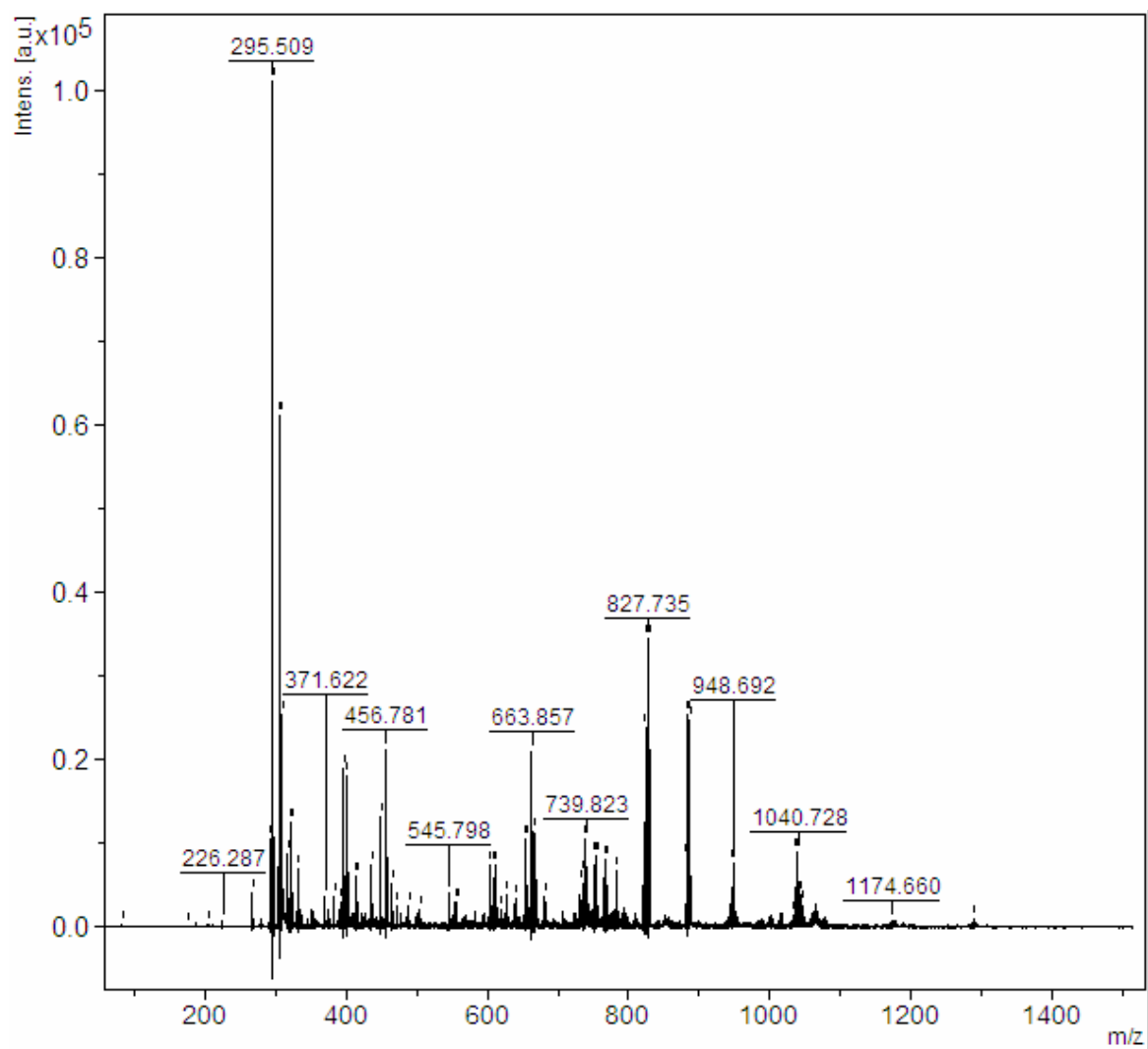
Maldi-Tof

❖ Pre-catalyst 75



Spectrum 23 Maldi-Tof spectra of Pre-catalyst 75

❖ Pre-catalyst **76**



Spectrum **24** Maldi-Tof spectra of Pre-catalyst **76**