

The alkene metathesis reactivity of the PUK-Grubbs 2-precatalyst

Monique Marié Loock
B.Sc, Hons. B.Sc

Dissertation submitted in partial fulfilment of the requirements for the degree
Magister Scientiae
in
Chemistry
at the North-West University (Potchefstroom Campus).

Supervisor: Dr. JHL Jordaan
Co-Supervisor: Dr. P van der Gryp

Potchefstroom
2009

*Dedicated to my parents
and late Granny*

Table of Contents:

Table of Contents:	i
List of Abbreviations and Structures:	iii
Summary:	v
Opsomming:	vii
Introduction and aims:	1
1.1 Introduction	1
1.2 Aim and objectives	3
1.3 Scope of study	3
1.4 References	4
Literature review:	5
2.1. Introduction	5
2.2. History and development	6
2.3. Alkene metathesis	7
2.4. Development of catalysts	10
2.4.1. Chelating ligands	12
2.4.2. Hemilabile ligands	14
2.5. Homogeneous alkene metathesis	16
2.6 Homogeneous precatalysts	21
2.6.1 Ruthenium precatalysts	22
2.7 Summary	25
2.8 References	25
Experimental:	31
3.1 Introduction	31
3.2 Reagents and analytical instruments	31
3.2.1 Solvents and reagents	31
3.2.2 Analytical instruments	32
3.3 Synthesis of the existing PUK-Grubbs 2-precatalyst	34
3.3.1 Standard techniques	34
3.3.2 Synthesis of 1-(2'-pyridinyl)-2,4-dimethylpentan-3-ol (46)	36
3.3.3 Synthesis of lithium diphenyl(pyridin-2-yl) methanolate (47)	37
3.3.4 Synthesis of benzylidene-chloro(1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-[1-(2'-pyridinyl)-1,1-diphenyl-methanolato]ruthenium (3)	38
3.4 Metathesis reactions	39
3.4.1. General procedures	39
3.4.2. Small scale metathesis reactions	39
3.4.3. GC method for metathesis reactions	40
3.5 NMR investigation of metathesis reactions	47
3.6 References	47

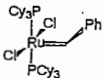
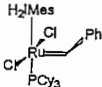
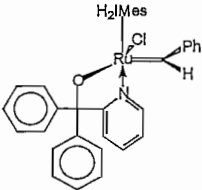
Results and Discussion:	4	49
4.1. Introduction		49
4.2 Synthesis of existing PUK-Grubbs 2-precatalyst		49
4.2.1 Ligand synthesis		49
4.2.2 Lithium salt preparation		50
4.2.3 Precatalyst (3) preparation		51
4.2.4 ESEM and EDS of precatalysts		52
4.3 Metathesis		54
4.3.1 Introduction		54
4.3.2 Reproducibility of metathesis reactions		55
4.3.3 1-Hexene metathesis reactions		56
4.3.4 1-Heptene metathesis reactions		68
4.3.5 1-Nonene metathesis reactions		78
4.3.6 1-Decene metathesis reactions		83
4.4 Comparison of 1-alkene metathesis reactions		88
4.5 Catalyst lifetime metathesis reactions		92
4.6. NMR characterization of carbene species		96
4.6.1. NMR investigation of Gr1		96
4.6.2. NMR investigation of Gr2Ph		101
4.7. Closing remarks		106
4.8. References		106
Conclusions and recommendations:	5	109
5.1 Conclusions		109
5.1.1 Introduction		109
5.1.2 Repeatability of Gr2Ph (3)		109
5.1.3 Metathesis reactions of 1-alkenes		109
5.1.4 NMR investigation of carbene species		111
5.2 Recommendations		112
5.3 References		112
Acknowledgements:		115
Appendix A:		117
Appendix B:		125

List of Abbreviations and Structures:

Abbreviations:

ADMET	Acyclic diene metathesis
CM	Cross metathesis
¹³ C-NMR	Carbon nuclear magnetic resonance spectroscopy
DSC	Differential Scanning Calorimetry
EtOH	Ethanol
ESEM	Electronic Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
¹ H-NMR	Proton nuclear magnetic resonance spectroscopy
H ₂ IMes	1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene
NHC	N-heterocyclic carbene
IP	Isomerisation product
IR	Infrared spectroscopy
NMR	Nuclear magnetic resonance
MS	Mass spectrometer
M	Transition metal atom
min	minutes
PCy ₃	Tricyclohexylphosphine
Ph	Phenyl
PMP	Primary metathesis product
³¹ P-NMR	Phosphor nuclear magnetic resonance
RCM	Ring-closing metathesis
ROMP	Ring-opening metathesis polymerisation
RF	Response factor
RT	Room temperature
S	Selectivity
SMP	Secondary metathesis product
SM	Self metathesis
TLC	Thin layer chromatography
THF	Tetrahydrofuran
TGA	Thermogravimetric analyzer
TON	Turnover numbers

Structures and abbreviations of catalysts:

Structure	Abbreviation
Benzylidene-dichloro(bis(tricyclohexylphosphine))ruthenium 	Gr1 (1)
Benzylidene-dichloro(tricyclohexylphosphine)(1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene)-ruthenium 	Gr2 (2)
Benzylidene-chloro(1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene)-[1-(2'-pyridinyl)-1,1-diphenyl-metanolato]ruthenium 	Gr2Ph (3)

Summary:

Metathesis reactions are of great value for industrial processes e.g. Shell Higher Olefin Process (SHOP) to form new alkenes. A lot of catalytic systems were developed to optimize the activity, stability and selectivity of these precatalysts. In a previous study a Grubbs 2-type precatalyst (Gr2Ph (3)) which had a N^oO hemilabile ligand with two phenyl groups coordinated to the Ru-metal was developed. This Grubbs 2-type precatalyst, known as the Puk-Grubbs 2-precatalyst (Gr2Ph (3)) was used for 1-octene metathesis reactions and showed an increase in the selectivity, thermal stability, activity and lifetime in comparison to Grubbs 1 (Gr1 (1)) and Grubbs 2 (Gr2 (2)). In order to determine if the precatalyst is of value to metathesis reactions it was used for different 1-alkenes (1-hexene, 1-heptene, 1-nonene and 1-decene) and the conditions optimized.

The Gr2Ph (3) precatalyst was successfully synthesized (43% yield) in this study and used for the metathesis reactions of the different 1-alkenes. The metathesis reactions of each 1-alkene was conducted at different temperatures, 55°C and 60°C for 1-hexene reactions, 60°C, 70°C and 80°C for 1-heptene reactions and 60°C, 80°C and 100°C for 1-decene reactions, except 1-nonene, while the Ru:1-alkene ratios were varied for 1-hexene and 1-heptene (1:7000 and 1:9000). The results of the 1-alkene metathesis reactions showed that the Gr2Ph (3) precatalyst increased the lifetime to 35 days and thermal stability when compared to Gr1 (1) (1 hour lifetime) and Gr2 (2) (3 hours lifetime). The TON, selectivity and activity is comparable to those of the Gr2 (2) reaction results, whilst an improvement on the Gr1 (1) results was obtained. The optimum conditions in terms of TON, PMP formation and selectivity for Gr2Ph (3) was found to be at 80°C with a 1:7000 Ru:1-alkene ratio for 1-heptene and 1-decene, but the ethylene accumulation in the mini reactors had an impact on the results. The ethylene accumulation resulted in the conversion of the already formed PMPs into SMPs and IPs during the course of the reaction. The optimum temperature for the 1-hexene reactions were determined to be at 60°C for Gr2Ph (3) with a Ru:1-alkene ratio of 1:7000, with a high PMP formation, selectivity and TON.

The ¹H-NMR investigation of the metathesis reactions of 1-octene and 1-hexene with Gr2Ph (3) in CDCl₃ at 30°C with a Ru:1-alkene ratio of 1:40, showed that only one carbene signal was present. Metathesis products were formed and confirmed with GC-MS and a larger amount of SMPs and IPs were formed by the competing isomerization reactions. These results indicate that metathesis does occur but that another mechanism was present or that the ligand was not hemilabile as suspected.

Opsomming:

Metatese reaksies is van groot waarde vir die produksie van nuwe alkene in industriële prosesse soos die Shell Hoër Olefin Proses (SHOP). 'n Groot hoeveelheid katalitiese sisteme is ontwikkel om die aktiwiteit, stabiliteit en selektiwiteit van hierdie pre-katalisatore te optimaliseer. In 'n vorige studie is 'n Grubbs 2-tipe pre-katalisator ontwikkel waar 'n N^o hemilabiele ligand en twee feniel groepe aan die Ru-metaal gekoördineer is. Die Grubbs 2-tipe pre-katalisator (3), bekend as die Puk-Grubbs 2 pre-katalisator (Gr2Ph (3)), is in die metatese reaksies met 1-okteen gebruik. Tydens die studie is daar gevind dat die katalisator 'n toename in selektiwiteit, termiese stabiliteit, aktiwiteit en leeftyd in vergelyking met pre-katalisatore soos Grubbs 1 (Gr1 (1)) en Grubbs 2 (Gr2 (2)) getoon het. Om die waarde van die pre-katalisator 3 ten opsigte van metatese reaksies vas te stel is verskillende 1-alkene (1-hekseen, 1-hepteen, 1-nonen en 1-deseen) bestudeer en die reaksie kondisies geoptimaliseer.

Die Gr2Ph (3) is suksesvol gesintetiseer in hierdie studie (43% opbrengs) en is vir die metatese reaksies van die verskillende 1-alkene gebruik. Die metatese reaksies vir elk van die 1-alkene is by verskillende temperature uitgevoer, 55°C en 60°C vir 1-hekseen reaksies, 60°C, 70°C en 80°C vir 1-hepteen reaksies en 60°C, 80°C en 100°C vir 1-deseen reaksies met uitsondering van 1-nonen, terwyl die Ru:1-alken verhouding vir 1-hekseen en 1-hepteen gevarieer is (1:7000 and 1:9000). Vanuit die resultate van 1-alken metatese reaksies met die Gr2Ph (3) pre-katalisator is gevind dat die leeftyd na 35 dae en termiese stabiliteit verbeter het in vergelyking met Gr1 (1) (1 uur leeftyd) en Gr2 (2) (3 ure leeftyd) resultate. Die TON, selektiwiteit en aktiwiteit van die Gr2Ph (3) metatese reaksies stem ooreen met die van die Gr2 (2) reaksies terwyl dit 'n verbetering op die Gr1 (1) resultate getoon het. 'n Reaksie temperatuur van 80°C en 'n Ru:1-alken verhouding van 1:7000 is die optimale kondisies vir die maksimale TON, PMP formasie en selektiwiteit vir Gr2Ph (3) metatese reaksies met 1-hepteen en 1-deseen. Die akkumulاسie van etileen in die klein reaktore het egter 'n impak op die resultate gehad. Die etileen akkumulاسie het veroorsaak dat die reeds gevormde PMPs omgeskakel word na SMPs en IPs gedurende die reaksie. Die optimale temperatuur vir die 1-hekseen metatese reaksie met Gr2Ph (3) was by 60°C met 'n 1:7000 Ru:1-alken verhouding, waar 'n maksimale PMP formasie, selektiwiteit en TON verkry is.

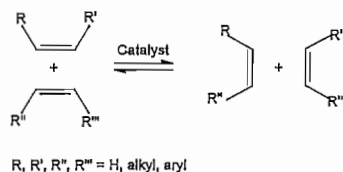
Tydens die ¹H-KMR studie van die metatese reaksies van 1-okteen en 1-hekseen met Gr2Ph (3) in CDCl₃ en 'n Ru:1-alken verhouding van 1:40 by 60°C, is slegs een karbeen seín waargeneem. Metatese produkte wat gevorm het was gekarakteriseer deur van GC-MS gebruik te maak. Die oorwegende hoeveelheid produkte (IPs en SMPs) wat gevorm het, het deur kompeterende isomerisasie reaksies gevorm. Die resultate toon dat metatese wel plaasgevind het, maar moontlik volgens 'n ander meganisme of dat die ligand nie, soos verwag, as 'n hemilabiele ligand optree nie.

Introduction and aims:

1

1.1 Introduction

The term metathesis originated from the Greek words *μετα* (change) and *τιθεμι* (place), which is an organic reaction where two alkenes exchange double bonds to be able to form two new alkenes as illustrated in **Scheme 1.1**. Furthermore the amount of double bonds of the reaction remains constant.^{1,2}



Scheme 1.1: Representation of alkene metathesis reactions.⁵

These metathesis reactions are mainly used in the industry, such as in the Shell Higher Olefins Process (SHOP), where longer hydrocarbon chains (C₁₀ and C₂₀) are formed from ethylene.³

The growing interest in the metathesis reactions was sparked when Eleuterio⁴ obtained a low yield propene-ethene copolymer from propene with the use of a molybdenum catalytic system. The catalytic systems can be divided into heterogeneous or homogeneous systems with important transition metals e.g. W, Mo, Rh and Ru. These transition metals can catalyse ring-opening metathesis polymerization (ROMP), ring opening metathesis (ROP), ring closing metathesis (RCM) and cross metathesis (CM). The catalytic systems which are the most effective are the Ru-based precatalysts.¹ The catalysts mostly used during metathesis reactions are the first generation Grubbs-precatalyst (Gr1 (1)) and second generation Grubbs-precatalysts (Gr2 (2)) as illustrated in **Figure 1.1**.⁵



Figure 1.1: The first and second generation Grubbs-precatalysts.

1. Introduction and aims

It has been shown that Grubbs 1 (**1**) indicates a high selectivity towards the metathesis of terminal alkenes, but is thermally unstable.^{6,7} The problem of thermal stability was partially solved with Grubbs 2 (**2**). During the development of the Grubbs 2 precatalyst, the thermal stability was increased by substitution of the PCy₃-group with a N-heterocyclic carbene ligand (NHC).⁸ The Grubbs 2-precatalyst however indicated a lower selectivity at higher temperatures due to the formation of secondary metathesis products. In comparison with other alkene metathesis catalysts (W and Mo), the Grubbs precatalysts (Gr1 (**1**)) have a tolerance towards a variety of functional groups that may be present on the alkenes. The catalyst is also soluble in a large variety of solvents in comparison to reactions with other transition metals.²

Hemilability was introduced by the groups of Grubbs⁹ and Verpoort¹⁰ to improve the lifetime and stability of the precatalysts. Hemilability is a class of chelating ligands, where the ligand coordinates to a catalyst by a tightly bound atom and a softly bound atom. The softly bound atom dissociates from the metal, leaving a vacant coordination site which allows the substrate, the 1-alkene, to coordinate to the metal centre, during metathesis reactions. These hemilabile ligands have the ability to place more than one donor atom with different electronic properties close to the metal atom. These ligands also have the ability to recoordinate to the vacant coordination site in the absence of other molecules. Hermann and coworkers¹¹ used a hemilabile pyridinyl alcoholate ligand to develop new precatalysts which increased the activity of metathesis reactions at higher temperatures.

Jordaan¹² synthesized a number of hemilabile ligands to coordinate onto precatalysts **1** and **2**, of which the Puk-Grubbs 2-precatalyst (**Figure 1.2**) was the most successful. It was found that N⁺O-hemilabile ligands together with aromatic groups had an influence on the activity, selectivity and lifetime of the Grubbs-2-precatalyst.

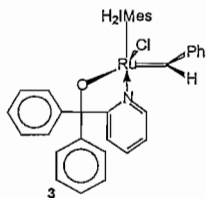


Figure 1.2: The synthesized Puk-Grubbs 2-precatalyst.

1.2 Aim and objectives

The development of these hemilabile ligands coordinated onto the Grubbs 2 precatalysts (**2**), resulted in an influence on the stability, activity and lifetime of the precatalyst as demonstrated in a previous study by Jordaan.¹² These observations were only made on the metathesis reactions of 1-octene. This study will attempt to optimize precatalyst **3** for the metathesis reactions of different linear 1-alkenes and to investigate the different active species present in the solution of the metathesis reactions.

To reach the aim of this study the following objectives were formulated:

1. An extensive literature study on the metathesis reactions in the presence of Grubbs-type precatalysts.
2. Investigate the catalytical properties of the precatalyst (**3**) with respect to the metathesis of different linear 1-alkenes (1-hexene, 1-heptene, 1-nonene and 1-decene).
3. Characterization of the precatalyst (**3**) with the help of spectrometric and other analytical methods.
4. Characterization of the active species with the help of a Nuclear Magnetic Resonance (NMR) investigation.

1.3 Scope of study

This dissertation is subdivided into five chapters, including this chapter (Chapter 1), to be able to achieve the above-mentioned objectives of this study:

In Chapter 2 a theoretical background is given into alkene metathesis reactions and the development of different precatalysts. A brief overview of the precatalyst development is described to understand why new precatalysts are constantly being developed. In addition the mechanisms of Gr1 (**1**) and the Gr2Ph (**3**) precatalyst are discussed. The chapter further elaborates on the advantages of homogeneous precatalysts. Furthermore the different effects of solvents and temperatures are also included.

In Chapter 3 the experimental setup and methods that were used during this study, are described in detail.

1. Introduction and aims

Chapter 4 focuses on the results obtained throughout this study in terms of the metathesis reactions of different 1-alkenes (1-hexene, 1-heptene, 1-nonene and 1-decene) with different precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)) and a NMR-Investigation of Gr2Ph (3).

Finally Chapter 5 summarizes the main conclusions made throughout this dissertation and gives suggestions for future work that could still be done.

1.4 References

1. Ivin, K.J. and Mol, J.C., *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997
2. Grubbs, R.H., *Handbook of Metathesis*, Wiley-VCH, Germany, 2003
3. Mol, J.C., *J. Mol. Catal. A: Chem.*, 2004, **213**, 39
4. Eleuterio, H.S., *J. Mol. Catal.*, 1991, **65**, 55
5. Yao, Q. and Motta, A.R., *Tetrahedron Lett.*, 2004, **45**, 2447
6. Randl, S., *Synth. Lett.*, 2001, **3**, 430
7. Maechling, S., Zaja, M. and Blechert, S., *Adv. Synth. Catal.*, 2005, **347**, 1413
8. Haung, J., Schanz, H.-J., Stevens, E.D. and Nolan, S.P., *Organometallics*, 1999, **18**, 2370
9. Chang, S., Jones II, L., Wang, C., Henling, L.M. and Grubbs, R.H., *Organometallics*, 1998, **17**, 3460
10. De Clercq, B. and Verpoort, F., *J. Mol. Catal. A: Chem.*, 2002, **180**, 67
11. Denk, K., Friedgen, J. and Herrmann, W.A., *Adv. Synth. Catal.*, 2002, **344**, 666
12. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007

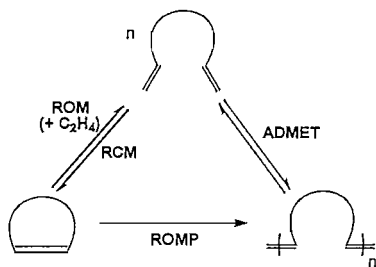
Literature review:

2

2.1. Introduction

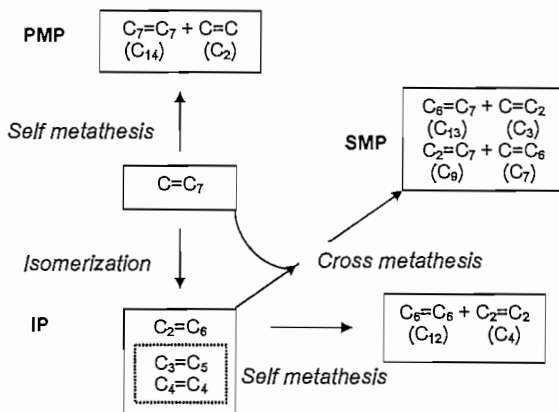
In 1967 the disproportion of alkenes were introduced by Calderon¹ as alkene metathesis. Alkene metathesis can be described as a catalytic reaction where alkenes are converted to form new products, via simultaneous breaking and reforming of the C-C double bonds.² This reaction of disproportion is shown in **Scheme 1.1**.

The metathesis reaction, as demonstrated in **Scheme 1.1**, is an example of cross metathesis reaction (CM) of linear alkenes. An additional five types of alkene metathesis reactions can be identified, e.g. ring-closing metathesis (RCM), ring-opening metathesis (ROM), ring-opening metathesis polymerisation (ROMP) and acyclic diens metathesis (ADMET), summarized in **Scheme 2.1** and self metathesis (SM).³⁻⁵



Scheme 2.1: Types of alkene metathesis reactions.³

The metathesis of 1-alkenes can occur through cross metathesis (two different 1-alkenes reacting), self metathesis (two of the same 1-alkenes reacting) and isomerization reactions (a reaction where the products formed are the isomers of the original 1-alkene) as illustrated in **Scheme 2.2**.



Scheme 2.2: The metathesis reactions for 1-octene.⁶

During the SM reactions of the 1-alkene (C_8), the primary metathesis products (PMP) C_{14} and C_2 are formed. Simultaneous isomerization of the 1-alkene can occur where the position of the double bond is changed to form Isomerization products (IP), which are internal alkenes. The IPs can undergo cross- and self metathesis to form secondary metathesis products (SMPs).

2.2. History and development

The non-catalytic metathesis reaction of propene molecules to form ethene and butene products was reported to have been observed by Schneider and Fröhlich⁷ in 1931. They described the reaction as a reaction where larger hydrocarbons can be composed from the lower ones. Generally it was thought that Banks and Bailey⁸ discovered metathesis reactions during 1964, but it was already patented by Eleuterio⁹ in 1957. The metathesis reaction was described as a reaction where linear alkenes were converted into carbon chains of shorter and longer length in relation to the original alkene. Propene was disproportioned into ethene and n-butenes with the molar ratio of the shorter and longer carbon chains approximately equal.⁸

Alkene disproportion was a term used for alkene metathesis until 1967. The change was at the same time that the first homogeneous catalytic system ($WCl_6/EtOH/EtAlCl_2$), which produced metathesis and polymerization products, was discovered.¹

In Figure 2.1 the time line for alkene metathesis and catalytical development is summarized. This summary shows the development and increasing use of the ruthenium-type precatalysts.

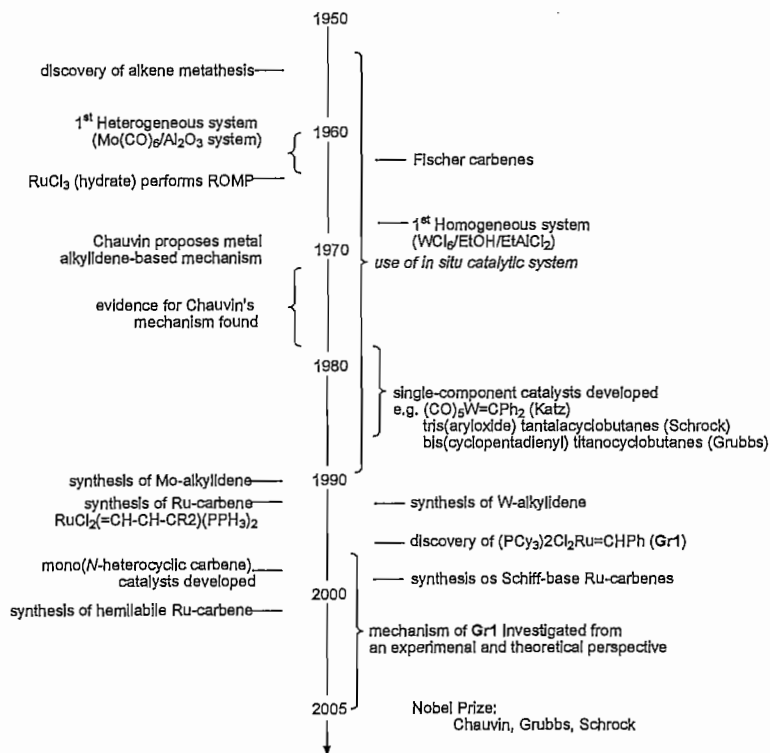


Figure 2.1: Time line of milestones in the alkene metathesis precatalyst development.^{3,10}

2.3. Alkene metathesis

- Cross Metathesis (CM)

Cross metathesis reactions take place between different linear alkenes as illustrated in Scheme 1.1. An example of such a cross metathesis reaction is the formation of propene as a result of a reaction between ethene and *n*-butene.

2. Literature review

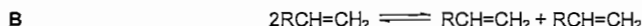
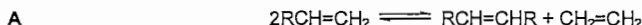
The CM reaction is of great interest for industrial applications for the formation of large organic molecules to produce important petrochemicals and polymers.¹¹ An industrial application that uses the CM reaction is SHOP (Shell-higher-olefins process) which produces C₁₀ to C₂₀ alkenes from ethylene.¹² CM reactions involve different alkene substrates which can either be acyclic compounds, the reaction then commonly known as acyclic cross metathesis, or both cyclic and acyclic compounds.^{12,13} An example of acyclic cross metathesis shown in **Scheme 2.3**, is the reaction between ethene and 2-butene to form propene.



Scheme 2.3: An example of acyclic cross metathesis.

- Self-metathesis (SM)

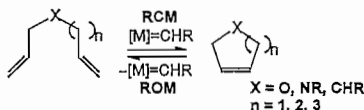
Self metathesis is defined as a reaction between two of the same alkenes. These types of reactions can be divided into productive and non-productive metathesis reactions. The productive metathesis reactions result in the formation of new linear alkene products, while with non-productive reactions no new products are formed (**Scheme 2.4**). Studies have shown that in reactions with terminal alkenes the non-productive metathesis reactions are generally faster than the productive metathesis reactions.¹³



Scheme 2.4: The productive (**A**) and non-productive (**B**) product formation during SM reactions.

- Ring Closing Metathesis (RCM)

The first example of RCM as shown in **Scheme 2.5**, was reported in 1980 by Tsuji¹⁴ and has emerged as a prominent field in alkene metathesis. This reaction is one of the most reliable methods for the formation of different sized ring compounds.



Scheme 2.5: Ring closing metathesis (RCM) and ring opening metathesis (ROM).

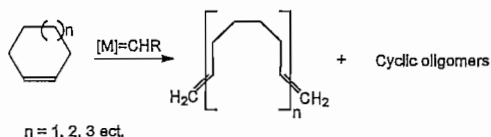
Studies done recently showed that the ADMET products that are found during the RCM reactions may be intermediates, while the ring opening metathesis (ROM) reactions are the inverse of the RCM reactions.¹⁵

- Ring Opening Metathesis (ROM)

The example for this metathesis reaction is shown in **Scheme 2.5**. The ring strain of cycloalkenes is the driving force for the releasing of strain for ring-opening metathesis or ring-opening metathesis polymerization to take place.^{16,17}

- Ring Opening Metathesis Polymerisation (ROMP)

A typical ROMP reaction where linear polymers and cyclic oligomers are formed as products is illustrated in **Scheme 2.6**.⁴

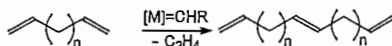


Scheme 2.6: Ring opening metathesis polymerisation.

These types of reactions need cyclic alkenes (norbornene) and the reactions are thermodynamically controlled.¹⁸ Alkenes such as cyclohexene with low ring strain energy cannot be polymerised as there is no driving force for this reaction to take place.^{11,18,19} The change in the monomer/catalyst ratio can affect the chain growth, thus the addition of more monomers will result in further chain growth.¹⁵ This is known as living polymerisation, because there is no termination of these chains as long as there are enough monomers present. When a mixture of monomers is used the more reactive monomer will react first followed by the less reactive monomer. The result of this reaction is a perfect block polymer or tapered block copolymer.¹⁵

- Acyclic Diene Metathesis (ADMET)

The acyclic cross metathesis reaction applied to dialkenes is described as ADMET reactions (**Scheme 2.7**).⁵ The metathesis reaction of the terminal diene results in polymers of high molecular weight.¹⁵ These diene compounds can react to form trienes, pentaenes etc.¹²



Scheme 2.7: ADMET reaction.

As with the RCM reactions, the driving force for the reaction is the release of ethylene and can be accelerated by the addition of N_2 to the reaction.¹¹ The N_2 is added to the reaction mixture to remove the ethylene from the reaction and to shift the equilibrium towards the formation of products according to Le Chatelier's principle.

2.4. Development of catalysts

There are numerous amounts of catalytic systems that can initiate alkene metathesis reactions. During earlier work in alkene metathesis ill-defined multicomponent precatalyst systems were used. These systems have active species that cannot be easily identified.¹⁵ In more recent years well-defined metal carbene complexes were discovered and used.⁴ The well-defined precatalysts that are mostly used are the molybdenum complex **4** and the ruthenium complexes **5** and **1** (Figure 2.2).⁴

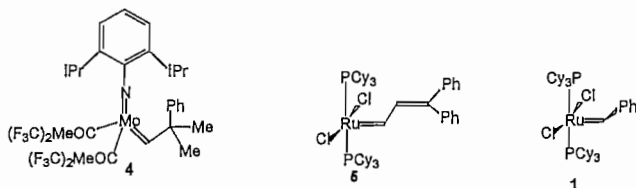


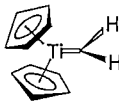
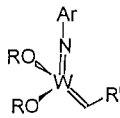
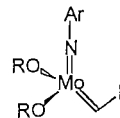
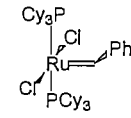
Figure 2.2: The well-defined catalysts commonly used for alkene metathesis.

The molybdenum-based alkylidene (**4**) was one of the first Schrock-type carbenes that were commonly used.²⁰ The $\text{Mo(CHR')}(NAr)(OR)_2$ (**4**) precatalysts have certain advantages such as a greater tolerance for functional groups than tungsten precatalysts, but is extremely sensitive towards O_2 , H_2O and other polar functional groups as shown in Table 2.1. These disadvantages can lead to a greater tendency of lower activity during reactions.²¹

The search for a precatalyst with less sensitivity to moisture and air was a ruthenium precatalyst. The Ru precatalysts showed a remarkable tolerance towards a variety of organic functional groups but also have a high reactivity in many different reactions such as ROMP, RCM and CM, under mild conditions.

These precatalysts have high activity for alkene metathesis and are tolerant towards oxygen, water and solvent impurities.⁴ This well-defined ruthenium precatalyst (**5**) was developed and it was found to be reactive for ROMP but also displayed activities for RCM.²¹

Table 2.1: Functional group tolerance of the different alkene metathesis precatalysts.^{10,22,23}

 Titanium  Tungsten  Molybdenum  Ruthenium				↑ Increasing reactivity
Acids	Acids	Acids	<u>Alkenes</u>	
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids	
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water	
Ketones	Ketones	<u>Alkenes</u>	Aldehydes	
Esters, Amides	<u>Alkenes</u>	Ketones	Ketones	
<u>Alkenes</u>	Esters, Amides	Esters, Amides	Esters, Amides	

→ Increase in the reactivity of the metal-carbene complexes with different functional groups

The discovery and improvement of the Grubbs metal carbenes, based on ruthenium, led to the development of Grubbs first (**1**) and second generation (**2**) precatalysts. Precatalyst **1** was synthesized from $\text{RuCl}_2(\text{PPh}_3)_3$, tricyclohexylphosphine and phenyldiazomethane and this catalyst was easier to handle due to its stability to air and moisture than the Mo-based precatalysts.²⁴ Further investigation of the catalyst showed that the PCy_3 -ligand suffers from P-C degradation at increased temperatures, which then limits the lifetime of the precatalyst.^{25,26}

Imidazolylidene ligands were investigated, because the ligand can mimic the behaviour of the phosphine but with an improvement in stability at high temperatures. A NHC-ligand was developed which slowed the decomposition of the precatalyst and resulted in a more stable precatalyst.²⁷ The one PCy_3 -ligand was then substituted by a NHC-ligand to improve the precatalysts stability at higher temperatures and this led to the synthesis of a new generation precatalyst, Gr2 (**2**) as illustrated in Figure 2.3.^{24,25}

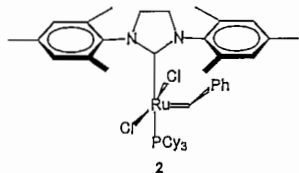


Figure 2.3: The second generation Grubbs precatalyst.

Different research groups started to change the ligands attached to the Gr1 (1) and Gr2 (2) precatalysts, resulting in the investigation of chelating ligands (§ 2.3.1).^{2,28,29} These chelating ligands can exhibit hemilability as a property (§ 2.3.2).

2.4.1. Chelating ligands

A ligand can be defined as any element or a combination of elements which can form bonds with a transition metal.¹⁰ The metal can have a specific function but the properties can be altered or completely changed by the variation of the ligands. The molecules or ions (ligands) that are coordinated to the metal are the reason for the property change. A ligand must have an electron density available to be able to donate to an empty metal orbital to coordinate to the metal. The coordination ability of a ligand can be changed by changing the donor atom as well as the properties of the precatalyst formed.³⁰ By keeping the donor atom constant and changing the substituents the electronic, steric and solubility properties of the ligand and precatalyst can be influenced. Transition metals can form bonds with almost all the elements of the periodic table and therefore it is used as catalysts. Some of these ligands possess more than one donor atom that attaches to the metal centre, which is then called chelating ligands.³⁰ Different types of ligands can be identified e.g. monodentate, bidentate and multidentate. Bidentate and multidentate ligands are illustrated in Figure 2.4.

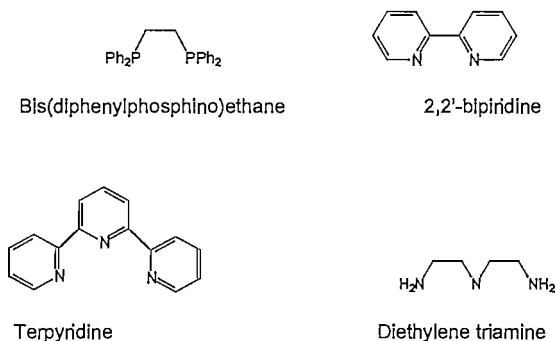


Figure 2.4: Examples of chelating ligands.¹⁰

Hoveyda²⁸ replaced a PCy₃-ligand of Gr1 (1) with a chelating ligand and this complex was called the first generation Hoveyda-Grubbs precatalyst (6) illustrated in **Figure 2.5**. This ligand was attached to the Ru-metal but also to the phenyl of the carbene group. This change resulted in the increased stability towards air and moisture. The second generation Hoveyda-Grubbs precatalyst (7) was introduced by Blechert *et al.*³¹

Here the PCy₃-ligand of the first generation Hoveyda-Grubbs was replaced by a NHC-ligand. Although an improvement towards the stability was observed, the precatalysts showed a lower initiation activity than for Gr 1 (1) and Gr 2 (2) precatalysts. The Hoveyda-Grubbs precatalysts (6 and 7) showed an improved activity towards alkenes that are electron deficient e.g. acrylonitriles and fluorinated alkenes.³²

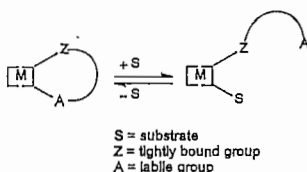


Figure 2.5: Hoveyda-Grubbs first and second generation precatalysts.

2.4.2. Hemilabile ligands

The incorporation of hemilabile ligands by Grubbs³³, Verpoort³⁴ and Hermann²⁹ led to the improvement of the precatalysts properties. Due to the change in catalytic properties e.g. increase in lifetime, stability, activity and selectivity further research was conducted on these types of precatalysts.

Chelating ligands were investigated by a few research groups, as it seemed to increase the stability of the catalysts.^{2,28,29} Chelating ligands are ligands that can be attached to the metal atom (M) with two or more bonds. Hemilabile ligands are a kind of chelating ligand, thus having the ability to place two or more donor atoms close to the metal atom (M). These donor atoms have different electronic properties, for the formation of tightly (Z) and softly (A) bound donor atoms (Scheme 2.8). The reason for this is that they can create and/or occupy a vacant coordination site at the metal centre on-demand, when there are competing substrates like alkenes in a reaction.³⁵ During the reaction the soft bond of the labile group (A) will break and create a free coordination site. The tightly bound Z group will keep the ligand bound to the metal centre, thus meaning that in the presence of a substrate the labile portion A will dissociate and allow a metal-substrate complex with an open coordination site to form.³⁶ The hard donor atom will stabilize the higher oxidation state of the metal centre upon chelating. The soft donor atom will then stabilize the lower oxidation state of the metal centre.³⁷ This action of the ligand leads to higher activity of the complex.^{2,29}



Scheme 2.8: Schematic representation of hemilability.¹⁰

Once chelating has occurred it can be followed by re-coordinating or another substrate can coordinate in the place of A.³⁰ Hemilability leads to the balance between high activity and sufficient stability of the precatalysts. These properties are important for organometallic catalysts as well as selectivity.³⁵

A variety of transition metal complexes with hemilabile N,N-^{38,39}, O,N-^{29,40,41}, O,O-^{42,43}, P,N-⁴⁴, P,O-⁴⁵, P,P-⁴⁶ and S,O-ligands^{35,42} have been synthesised. The catalytic activity of the catalytic system can be changed if the electronic and steric properties of the ligands were altered.

Herrmann *et al.*²⁹ developed precatalysts (**8a** to **d**) where hemilabile pyridinyl alcoholate ligands were coordinated to **2** to form Grubbs 2 type precatalysts (Figure 2.6). During alkene metathesis reactions at higher temperatures, an increase in activity was observed.²⁹ Jordaan¹⁰ used these hemilabile ligands and developed a Grubbs 2 type precatalyst where a N⁺O-hemilabile ligand with two phenyl groups were coordinated unto **2**.

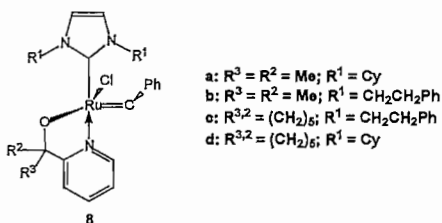


Figure 2.6: Different hemilabile ligands coordinated to a Grubbs 2 precatalyst.

These newly synthesized precatalysts (**8a** to **d**) were tested for ROMP metathesis reactions of norbornene and cyclo-octene at room temperature and 60°C.²⁹ The yields obtained at the higher temperatures were better than for lower temperatures, and could be compared to other precatalysts. The yields for the norbornene reactions were $\geq 98\%$ and for the cyclo-octene it was $\geq 72\%$ for the 60°C reactions. The yields at the room temperature were low due to the stabilization of the hemilabile ligand.²⁹

The two Grubbs type precatalysts **9** and **10** (Figure 2.7) with hemilabile ligands coordinated to the metal centre was compared in a previous study with Gr1 (**1**) and Gr2 (**2**).¹⁰

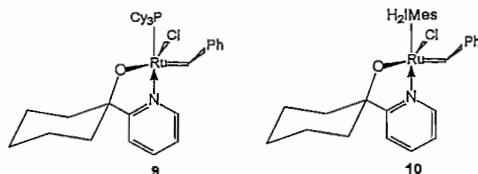


Figure 2.7: Grubbs type precatalysts **9** and **10**.

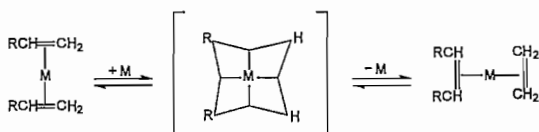
During the metathesis reactions of 1-octene with precatalysts **9** and **10** it was found that the yields (PMP formations) increased at higher temperatures (60°C to 80°C), while the selectivity compared well to the Gr1 (**1**) and Gr2 (**2**) reactions at room temperature.

2. Literature review

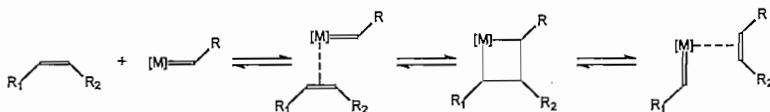
During the metathesis reactions of **9** and **10** with 1-octene the activity was lower at 35°C than reactions with **1** and **2**, due to the stabilization of the hemilabile ligand.¹⁰ An increase in temperature resulted in an increase in the activity and stability of **9** and **10** towards the PMP formation relative to the results of **1** and **2** reactions. This indicates that the addition of a pyridinyl alcoholate ligand to **1** and **2** stabilized the precatalyst at higher temperatures.¹⁰

2.5. Homogeneous alkene metathesis

The alkene metathesis reaction mechanisms can be divided into two different groups e.g. pairwise (Scheme 2.9) and non-pairwise (Scheme 2.10) mechanisms. Before Chauvin *et al.*,⁴⁷ proposed the non-pairwise mechanism in the 1970's it was believed that the mechanism followed, was the pairwise mechanism.¹³ During the pairwise alkene metathesis reaction, the orbitals of the two double bonds and the transition metal overlapped and formed a weak cyclobutane intermediate.^{13,48,49}



Scheme 2.9: An alkene metathesis reaction via a pairwise mechanism.^{10,49,50}

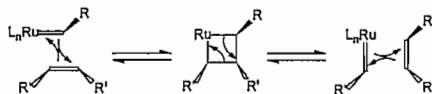


Scheme 2.10: An alkene metathesis reaction via a non-pairwise mechanism.⁴⁹

Certain terms will be defined at this point such as metal carbene complex, benzylidene, alkylidene and methylidene. The term metal carbene complex refers to a general type $\text{L}_n\text{M}=\text{CRR}'$ compound, where the L_n represents the different ligands coordinated to the metal (M). The carbene is the $=\text{CRR}'$ ligand (alkylidene) coordinated to the M .

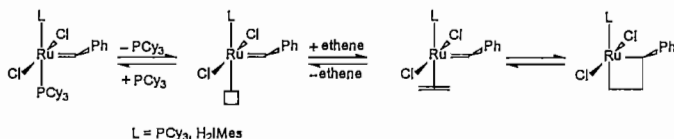
The generally accepted mechanisms for cyclic and acyclic alkene metathesis reactions are through a series of metallacyclobutanes and carbene complexes. The stability of the carbenes and metallacyclobutanes can be changed due to changes in the reaction conditions, alkene substitutions and the catalyst composition.⁴

Benzylidene refers to a $=CRR'$ ligand where the $R'=Ph$ and $R=H$, while if $R=R'=H$ the carbene ligand is referred to as a methylidene. This indicates that the R' -group determines the name of the alkylidene. The general mechanism for alkene metathesis reactions was proposed by Chauvin, which was proved by NMR-studies done by Schrock^{51,52} and Kress.⁵³⁻⁵⁶ The mechanism consists of a [2+2] cycloaddition reaction between an alkylidene complex and an alkene to form a metallacyclobutane ring intermediate (Scheme 2.11).^{13,57} The metallacyclobutane dissociation and [2+2] cyclo-reversion follow by forming a new alkylidene and alkene.^{13,57,58} By repetition of the reaction an equilibrium mixture of alkenes will be obtained.



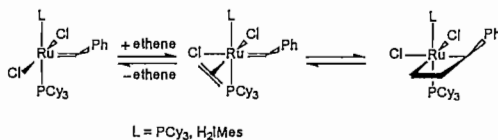
Scheme 2.11: [2+2] cycloaddition reaction of the Chauvin mechanism.

Research by Sanford *et al.*⁵⁹ was done on the mechanism of homogeneous metathesis reactions with ruthenium alkylidene species, to determine if it is a dissociative (Scheme 2.12) or associative mechanism (Scheme 2.13). Studies⁵⁹ showed that the homogeneous metathesis reactions will take place via the dissociative mechanism, meaning that firstly a vacant site will be created on the metal by means of the removal of a soft bonded ligand. This is followed by the coordination of an alkene substrate molecule to the metal at the vacant site.



Scheme 2.12: The dissociative alkene metathesis mechanism.

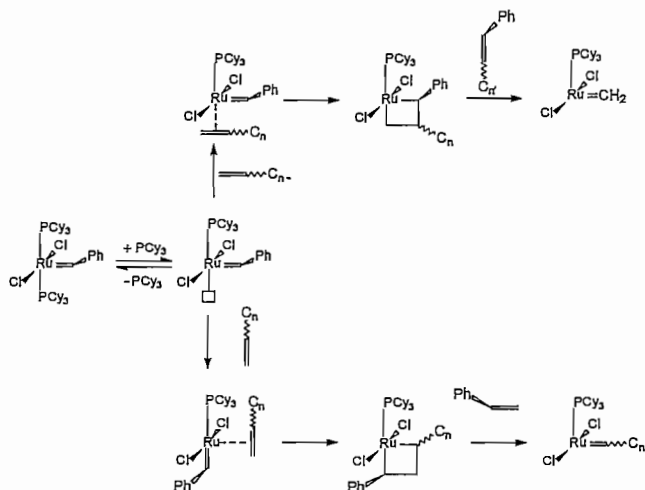
During the associative mechanism the alkene substrate coordinates to the metal first before dissociation takes place.



Scheme 2.13: The associative alkene metathesis mechanism.

2. Literature review

The coordination of the alkene can differ as illustrated in **Scheme 2.14**.

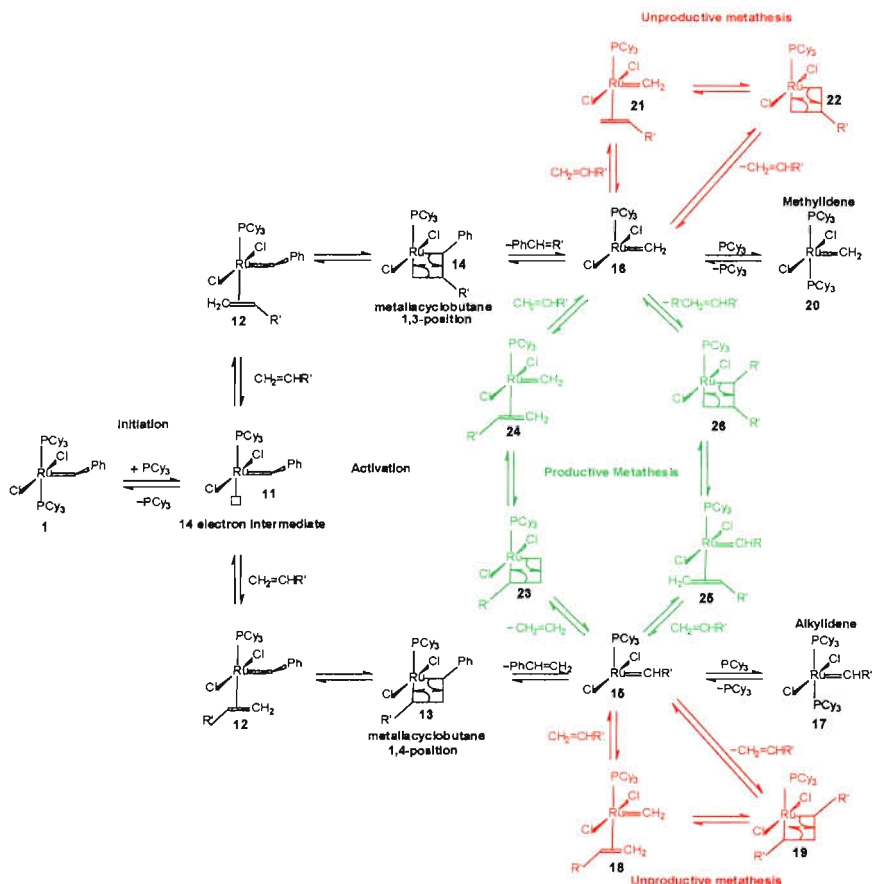


Scheme 2.14: Illustration of different alkene coordinations unto the vacant site.

For the purpose of this study only the general coordination, parallel coordination of the alkene to the metal carbene, will be discussed.

The catalytic cycle for Grubbs **1** (**1**) is shown in **Scheme 2.15**. Firstly the dissociation of one of the phosphine ligands (activation step), from the 16 electron benzylidene complex **1**, takes place to form the highly reactive 14 electron intermediate (**11**).⁶⁰ This 14 electron intermediate can then re-coordinate with the phosphine which then removes it from the catalytic cycle or coordinate with the alkene, to the metal complex to form (**12**). The formation of the ruthenium metallacyclobutane ring (16 electron intermediate) then takes place (**13** and **14**) due to the 2+2 cycloaddition.⁶⁰ Afterwards the metallacyclobutane dissociates ([2+2] cycloreversion) to form the alkene product and the 14 electron ruthenium species (**15** and **16**). These two active species can then coordinate to a phosphine and form two 18 electron species, alkylidene (**17**) and methylidene (**20**). When coordinating to the original alkene, the metathesis reaction can be productive (steps **23** to **26** shown in green), to form a new alkene and metal complex. When an unproductive reaction (steps **18**, **19**, **21** and **22** shown in red) occurs, the regeneration of the original alkene and complex is formed.^{15,23,58,61}

A NMR-investigation conducted on precatalyst **1** with 1-octene in CDCl_3 at 30°C and 50°C , revealed the presence of three carbene species, e.g. benzylidene, methylidene and heptylidene. During the course of the metathesis reaction it was observed that the benzylidene concentration reduces while being converted into methylidene and heptylidene. Decreases in the methylidene and heptylidene species was observed later in the reaction.^{8,10}

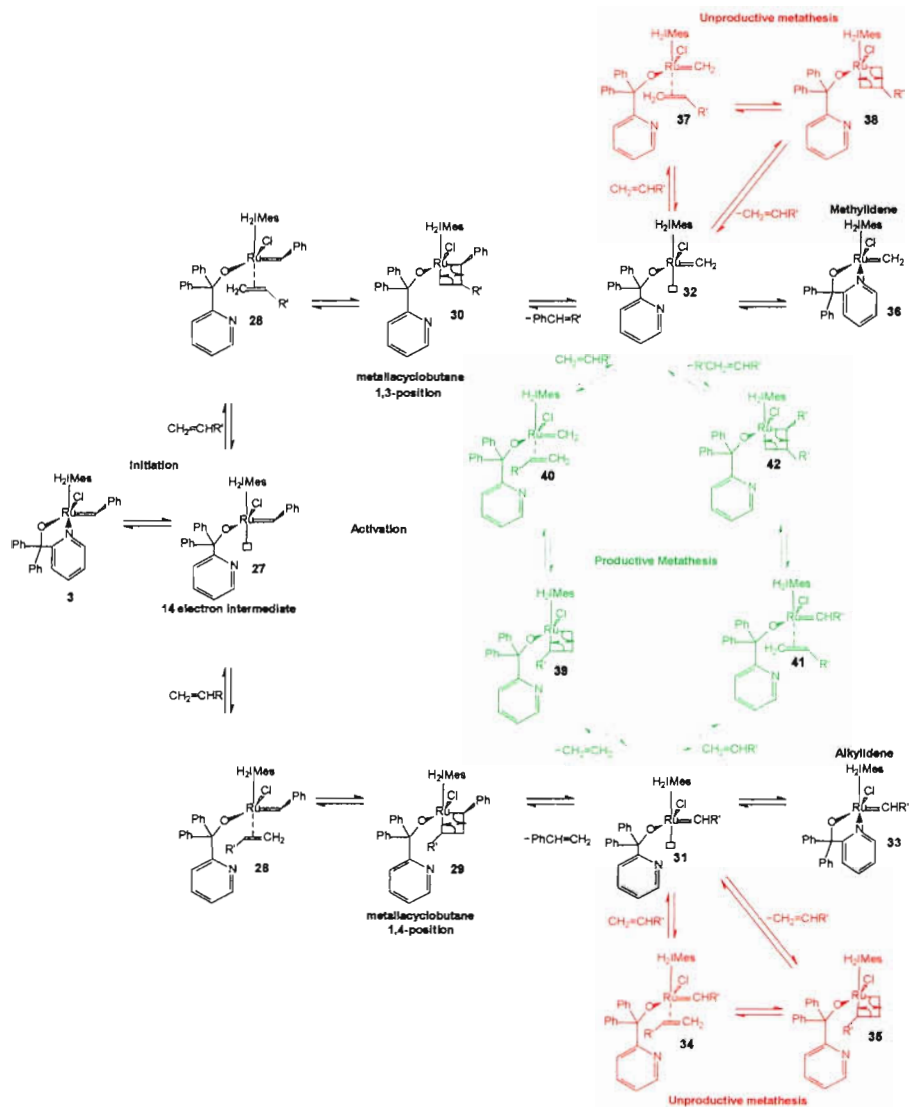


Scheme 2.15: The activation of the catalytic cycle for precatalyst **1**.

The rate determining step of the metathesis mechanism is believed to be the formation of the metallacyclobutane.⁵⁸

2. Literature review

During a previous study precatalyst (**3**) was synthesized to improve on the Ru-catalysts.¹⁰ This catalyst has a hemilabile ligand attached to it and in the study a dissociative mechanism was proposed. The proposed mechanism is shown in **Scheme 2.16**.



Scheme 2.16: A proposed mechanism for the activation of the catalytic cycle for precatalyst **3**.

Firstly the N-atom of the hemilabile ligand dissociates, from the benzyldiene specie (**3**), to accommodate the coordination of the alkene to the ruthenium (initiation step). This leads to the formation of a reactive 14 electron intermediate (**27**). This 14 electron intermediate (**27**) can then re-coordinate with the N-atom of the hemilabile ligand, which removes it from the catalytic cycle or coordinate with the alkene to form **28**. The formation of the ruthenium metallacyclobutane ring (16 electron intermediate) then takes place (**29** and **30**) due to the 2+2 cycloaddition.⁶⁰ Afterwards the metallacyclobutane dissociates ([2+2] cycloreversion) to form the alkene product and 14 electron ruthenium species **31** and **32**. These two active species can then re-coordinate to the hemilabile ligand to form two 18 electron species, alkylidene (**33**) and methyldiene (**36**). The reactions where **33** and **36** coordinates with the original alkene are the propagation of the catalytic cycle.

When coordinating to the original alkene, the metathesis reaction can be productive (steps **39** to **42** shown in green), to form a new alkene and metal complex. When an unproductive reaction (steps **34**, **35**, **37** and **38** shown in red) occurs, the original alkene and catalyst is formed.

2.6 Homogeneous precatalysts

A large number of precatalysts can initiate alkene metathesis reactions. These precatalysts can be divided into two main groups e.g. heterogeneous and homogeneous catalysts. A variety of transition metal compounds (W, Mo, Re and Ru are the most important metals) are capable of catalyzing metathesis reactions (Table 2.1).¹³

Table 2.1: Transition metals for alkene metathesis initiation.¹³

IVA	VA	VIA	VIIA	VIII
Ti	V	Cr		
Zr	Nb	Mo		Ru, Rh
Hf	Ta	W	Re	Os, Ir

Homogeneous catalysis is defined as catalytic reactions where the precatalysts and substrates are in one phase e.g. liquid phase.⁶² Meaning that the catalysts are dissolved in the medium where in the reaction take place. In Table 2.2 a few illustrative examples of homogeneous catalyst systems are given. These types of catalytic systems have the ability to give high yields of pure products and repeatable results for alkene metathesis.

2. Literature review

Table 2.2: W-, Mo-, Re- and Ru-based homogeneous metathesis catalysts.¹³

Alkenes	Catalyst	Temperature (°C)
Mo-based		
2-pentene	MoCl ₅ /SnPh ₄	20
2-pentene	MoCl ₃ (NO)EtAlCl ₂	20
2-pentene	MoCl ₃ (OPPh ₃) ₂ N/EtAlCl ₂	20
W-based		
2-pentene, 2-butene	WCl ₆ /EtAlCl ₂ /EtOH	20
2-pentene	WCl ₆ /BuLi	20
2-pentene	WCl ₆ /SnMe ₄	20
2-pentene	W(=CHCMe)Br ₂ (OCH ₂ CMe ₃) ₂ /GaBr ₃	-
1-hexene	WCl ₆ /SnBu ₄	60
Re-based		
Norbornene	ReCl ₅ /EtAlCl ₂	20
2-pentene	ReCl ₅ /SnBu ₄	20
2-pentene	ReCl(CO) ₅ /EtAlCl ₂	90
2-pentene	ReOCl ₃ (PPh ₃)/EtAlCl ₂	20
Ru-based		
4-nonene	Ru(=CHPh)Cl ₂ (PCy ₃) ₂	20
4-decene	Ru(=CHPh)Cl ₂ (PCy ₃) ₂	20
3-heptene	Ru(=CHPh)Cl ₂ (PCy ₃) ₂	20
Methyl oleate	Ru(=CHPh)Cl ₂ (PCy ₃) ₂	20
Methyl elaldate	Ru(=CHPh)Cl ₂ (PCy ₃) ₂	20

2.6.1 Ruthenium precatalysts

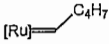
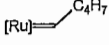
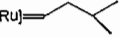
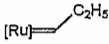
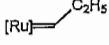
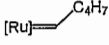
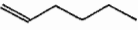
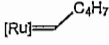
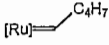
Comparing the rate of propagation of the Mo-catalyst and Ru-carbene systems, the Ru has resulted in the catalyst of choice. Only when working with sterically hindered substrates the Ru-catalysts propagation rates are slow.⁴

It was observed by Ulman *et al.*⁶¹ that when the benzylidene (3) reacts with the terminal alkenes, the alkylidene (17) was the first initial organometallic product, which was identified by ¹H NMR. After a short while the benzylidene (3) completely disappears and the methylidene (20) starts forming. The organometallic product observed at the end of the reaction is the methylidene (20). The alkylidene formed is the kinetic product and the methylidene (20) the thermodynamic product.⁶¹

Following this, it was concluded that precatalyst (1) will react rapidly with terminal alkenes to form the metallacyclobutane intermediate where the groups are arranged in a 1,3-position (14). When productive [2+2] cyclo-reversion takes place the kinetically favoured alkylidene (17) product is formed. When the reaction times are extended the complex undergoes slow reaction to form the metallacyclobutane intermediate where the groups are arranged in a 1,4-position (13).

In **Table 2.3** the different carbene activities are compared. The benzylidene has a higher activity than the methylidene during metathesis reactions with the same acyclic alkene (reactions 2 and 8). In addition the activity of the alkylidene is greater than the benzylidene (reactions 1 and 9). The type of carbene is not the only factor that determines the rate of the metathesis reactions, the steric bulk of the alkene is also important. Data from **Table 2.3** indicates that the kinetically preferred metallacyclobutane has the substituent of the alkene placed next to the metal.⁶¹

Table 2.3: Metathesis reactions with alkenes.⁶¹

	Alkene	Initiator	Product	Temp/°C	k ± SDOM ^a /L/mole*sec
1		Benzylidene		7	1.48 ± 0.04 × 10 ⁻³
2		Benzylidene		35	~ 10 ⁻²
3		Benzylidene		7	1.02 ± 0.06 × 10 ⁻³
4		Benzylidene	Ru=CH ₂	35	2.5 ± 0.2 × 10 ⁻⁴
5		Benzylidene		35	3.0 ± 0.4 × 10 ⁻⁴
6		Benzylidene		35	7.6 ± 0.8 × 10 ⁻⁴
7		Methylidene		25	1.64 ± 0.1 × 10 ⁻⁴
8		Methylidene		35	6.10 ± 0.04 × 10 ⁻⁴
9		Alkylidene		7	~ 7 × 10 ⁻³

^a SDOM = Standard Deviation of the Mean

It was further observed, that metathesis reactions with 1-octene as the substrate, with no solvents present and a variation of the alkene: Ru ratio, influences the product formation. The increase of the molar ratio of Ru:alkene (1:2000 to 1:100 000) results in a decrease of the percentage PMPs formed during the reaction. This can be attributed to the presence of more precatalyst present in the smaller ratio reactions, which can generate higher yields and reaction rates.^{10,63,64}

- Influence of solvents

The addition of solvents can have a significant effect on the metathesis reactions of alkenes. It is known that precatalyst **1** has a high activity for alkene metathesis and is tolerant towards oxygen, water and solvent impurities.^{4,65} Metathesis reactions done with 1-octene and the addition of water, butanol and acetic acid resulted in a decrease in the activity of the catalyst. These solvents have the ability to donate a H-ion that can partake in the reaction and deactivate the catalyst by means of hydrolyses.⁶⁶ The lowest product formation was with the addition of water and butanol. Reactions with chlorobenzene and diethyl ether resulted in the highest PMP formations of 63%.⁶⁶

Solvent effects on precatalysts **6** (Hoveyda-Grubbs first generation) and **7** (Hoveyda-Grubbs second generation) in **Figure 2.5** showed that most organic solvents have negative effects on the metathesis reactions.⁶⁴ Metathesis reactions of 1-octene with **6** and **7** with the addition of organic solvents (e.g. toluene, diethyl ether, acetic acid, tetrahydrofuran (THF), ethanol and dimethyl sulphoxide (DMSO)) decreased the PMP formation of the reactions.⁶⁴ Reactions with diethyl ether improved the activity of the reaction, but the SMP formation also increased thus decreasing the selectivity of the catalyst towards PMP formation.

- Influence of different hydrocarbon lengths

Metathesis reactions with precatalyst **1** and alkenes with different chain lengths were investigated by Booyen.⁶³ The 1-alkenes used during the study were 1-pentene, 1-octene and 1-decene. The formation of PMPs during the metathesis reactions was higher for the 1-pentene than for the longer chained alkenes. The difference in PMP formation for the longer chain alkenes was small.

- Influence of temperature

The reaction rate of a metathesis reaction can be altered by temperature changes, where the catalyst may decompose or alternative products can start to form.^{10,64} During the temperature increase of precatalyst **1** reactions the product formation (PMPs) decreased but with precatalyst **2** it increased.¹⁰ During the temperature increase the IP formation started to show an increase at 60°C. The TON of precatalyst **1** decreased with the increase in temperature, but precatalyst **2** had an increase in TON. The same effects were observed during the reactions of precatalysts **23** and **24**. For precatalyst **3** with the hemilabile ligand, no activity for 1-octene was observed below 50°C. The PMP formation and TON increases with a temperature increased up to 90°C.⁶⁴

- NMR Investigations

During NMR-studies conducted by Jordaan⁶⁷ and Mtshatsheni⁶ on 1-octene, three carbene species were identified for Gr1 (1) and Gr2 (2) metathesis reactions in CDCl_3 at 25°C, 30°C and 50°C. A NMR-investigation was conducted on 1-octene with precatalyst 9 and 10 (Figure 2.7) in CDCl_3 at 50°C.¹⁰ Only three carbene species were observed during the metathesis reaction of 9, but five species were observed with 10.¹⁰

These five species were identified as three species for the coordinated benzylidene, methylidene and heptylidene. The other two species observed were the decoordinated benzylidene and methylidene. The coordinated species of 10 showed similar trends than the species of Gr1 (1). The concentration of the uncoordinated methylidene specie increased rapidly during the course of the metathesis reaction.¹⁰

2.7 Summary

Metathesis is an organic reaction that is mainly used in the industry. Different kinds of metathesis reactions exist but CM and SM reactions were mainly used during this study. Numerous amounts of catalytic systems can initiate these alkene metathesis reactions. Different transition metals (W, Mo, Rh and Ru) were used for catalytic systems and the ligands attached to these metals were varied to optimize the precatalysts. The precatalyst systems that are focussed on in this study are the Ru-based systems e.g. Gr1 (1), Gr2 (2) and a precatalyst that is a variation of Gr2. Further investigations of hemilabile ligands were conducted by Jordaan¹⁰ and Huijsmans⁵⁰ to improve the stability of Ru precatalysts. The hemilabile precatalyst (3) synthesized by Jordaan¹⁰ that showed the best results during metathesis and was used by van der Gryp⁶⁴ to determine solvent effects and different Ru:1-octene ratios. This study will attempt to assess the effect of temperature, catalyst load, alkene chain length etc. as to optimize the reactive nature of precatalyst (3). The results will be subsequently compared to the results of Gr1 (1) and Gr2 (2) precatalysts. The procedures followed will be subsequently discussed in the following chapters.

2.8 References

1. Calderon, N., Chen, H.Y. and Scott, K.W., *Tetrahedron Lett.*, 1967, **8**, 3327
2. De Clercq, B. and Verpoort, F., *Tetrahedron Lett.*, 2002, **43**, 9101
3. Trnka, T.M. and Grubbs, R.H., *Acc. Chem. Res.*, 2001, **34**, 18

2. Literature review

4. Grubbs, R.H. and Chang, S., *Tetrahedron*, 1998, **54**, 4413
5. Ivin, K.J., *Olefin Metathesis*, Academic Press, London, 1983
6. Mtshatsheni, K.N.G., *Metathesis of alkenes using ruthenium carbene complexes*, M.Sc dissertation, (North-West University), 2005
7. Schneider, V. and Frollich, P.K., *Ind. Eng. Chem*, 1931, **23**, 1405
8. Banks, R.L. and Bailey, G.C., *Ind. Eng. Chem*, 1964, **3**, 170
9. Eleuterio, H.S., *J. Mol. Catal*, 1991, **65**, 55
10. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007
11. Krause, J.O., *Development of new ruthenium catalysts for homogeneous and heterogeneous olefin-metathesis*, Ph.D thesis, (Technischen Universität München), 2004
12. Mol, J.C., *J. Mol. Catal A: Chem.*, 2004, **213**, 39
13. Ivin, K.J. and Mol, J.C., *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997
14. Tsuji, J., Hashiguchi, S., *Tetrahedron Lett.*, 1980, **21**, 2955
15. Kirk, M.M., *Ruthenium based homogeneous olefin metathesis*, M.Sc dissertation, (University of the Free State), 2005
16. Fürstner, A., *Angew. Chem. Int. Ed.*, 2000, **39**, 3012
17. Connon, S.J. and Blechert, S., *Angew. Chem. Int. Ed.*, 2003, **42**, 1900
18. Fomine, S. and Tlenkopatchev, M.A., *Organometallics*, 2007, **26**, 4491
19. Bielawski, C.W., Louie, J. and Grubbs, R.H., *J. Am. Chem. Soc.*, 2000, **122**, 12872
20. Grubbs, R.H., Miller, S.J. and Fu, G.C., *Acc. Chem. Res.*, 1995, **28**, 446
21. Schrock, R.R., Murdzek, J.S., Bazan, G.C., Robbins, J., DiMare, M. and O'Regan, M., *J. Am. Chem. Soc.*, 1990, **112**, 3875
22. Grubbs, R.H., *J. Mol. Struct. - Pure Appl. Chem. A*, 1994, **11**, 1829
23. Kurosawa, H. and Yamamoto, A., *Current Methods in Inorganic Chemistry: Fundamentals of Molecular Catalysis*, Volume 3, Elsevier, Amsterdam, 2003

24. Scholl, M., Ding, S., Lee, C.W. and Grubbs, R.H., *Org. Lett.*, 1999, **1**, 953
25. Huang, J., Stevens, E.D., Nolan, S.P. and Petersen. J.L., *J. Am. Chem. Soc.*, 1999, **121**, 2674
26. Huang, J., Schanz, H.-J., Stevens, E.D. and Nolan, S.P., *Organometallics*, 1999, **18**, 2370
27. Arduengo, A.J., Harlow, R.L. and Kline, M., *J. Am. Chem. Soc.*, 1991, **113**, 361
28. Kingsbury, J.S., Harrity, J.P.A., Bonitatebus, P.J., Jr. and Hoveyda, A.H., *J. Am. Chem. Soc.*, 1999, **121**, 791
29. Denk, K., Friedgen, J. and Herrmann, W.A., *Adv. Synth. Catal.*, 2002, **344**, 666
30. Burrows, S.P., *Science Progress*, 2002, **85**, 199
31. Gessler, S., Randl, S. and Blechert, S., *Tetrahedron Lett.*, 2000, **41**, 9973
32. Michrowska, A., Bujok, R., Harutyunyan, S., Sashuk, V., Dolgonos, G. and Grela, K., *J. Am. Chem. Soc.*, 2004, **126**, 9318
33. Chang, S., Jones II, L., Wang, C., Henling, L.M. and Grubbs, R.H., *Organometallics*, 1998, **17**, 3460
34. De Clercq, B. and Verpoort, F., *J. Mol. Catal. A: Chem.*, 2002, **180**, 67
35. Meyer, W.H., Brüll, R., Raubenheimer, H.G., Thompson, C. and Kruger, G.J., *J. Organomet. Chem.*, 1998, **553**, 83
36. Slone, C.S., Weinberger, D.A. and Mirkin, C.A., *Prog. Inorg. Chem.*, 1999, **48**, 233
37. Lahiri, G.K., Bhattacharya, S., Ghosh, B.K. and Chakravorty, A., *Inorg. Chem.*, 1987, **26**, 4324
38. Baratta, W., Herdtweck, E., Slega, K., Tonlutti, M. and Rigo, P., *Organometallics*, 2005, **24**, 1660
39. Jamieson, J.Y., Schrock, R.R., Davis, W.M., Bonitatebus, P.J., Zhu, S.S. and Hoveyda, A.H., *Organometallics*, 2000, **19**, 925
40. Desjardins, S.Y., Cavell, K.J., Jin, W., Skelton, B.W. and White, A.H., *J. Organomet. Chem.*, 1996, **515**, 233
41. Hoare, J.L., Cavell, K.J., Skelton, B.W. and White, A.H., *J. Chem. Soc., Dalton Trans.*, 1996, 2197

2. Literature review

42. Britovsek, G.J.P., *J. Mol. Catal. A: Chem.*, 1996, **110**, 77
43. Schrock, R.R., Jamieson, J.Y., Dolman, S.J., Miller, S.A., Bonitatebus, P.J., Jr. and Hoveyda, A.H., *Organometallics*, 2002, **21**, 409
44. Rülke, R.E., Kaasjager, V.E., Wehman, P., Elsevier, C.J. and van Leeuwen, P.W.N.M., *Organometallics*, 1996, **15**, 3022
45. Pavlik, S., Gemel, C., Slugovc, C., Mereiter, K., Schmid, R. and Kirchner, K., *J. Organomet. Chem.*, 2001, **617**, 301
46. Pechmann, T., Brandt, C.D. and Werner, H., *Organometallics*, 2003, **22**, 3004
47. Herrisson, J.L., and Chauvin, Y., *Makromol. Chem.*, 1971, **141**, 161
48. Calderon, N., Ofstead, E.A., Ward, J.P., Judy, W.A. and Scott, K.W., *J. Am. Chem. Soc.*, 1968, **90**, 4133
49. Grubbs, R.H. and Brunck, T.K., *J. Am. Chem. Soc.*, 1972, **94**, 2538
50. Huijsmans, C.A.A., **Modelling and synthesis of Grubbs-type complexes with hemilabile ligands**, M.Sc dissertation, (North-West University), 2009
51. Schrock, R., Rocklage, S., Wengrovius, J., Rupprecht, G. and Fellmann, J., *J. Mol. Catal.*, 1980, **8**, 73
52. Wengrovius, J.H., Schrock, R.R., Churchill, M.R., Missert, J.R. and Youngs, W.J., *J. Am. Chem. Soc.*, 1980, **102**, 4515
53. Kress, J., Osborn, J.A., Greene, R.M.E., Ivin, K.J. and Rooney, J.J., *J. Chem. Soc., Chem. Commun.*, 1985, **13**, 874
54. Kress, J., Osborn, J.A., Amir-Ebrahimi, V., Ivin, K.J. and Rooney, J.J., *J. Chem. Soc., Chem. Commun.*, 1988, **17**, 1164
55. Kress, J., Wesolek, M. and Osborn, J.A., *J. Chem. Soc., Chem. Commun.*, 1982, **9**, 514
56. Kress, J., Osborn, J.A., Greene, R.M.E., Ivin, K.J. and Rooney, J.J., *J. Am. Chem. Soc.*, 1987, **109**, 899
57. Rouhi, A.M., *Chem. Eng. News*, 2002, **80**, 29
58. Adlhart, C. and Chen, P., *J. Am. Chem. Soc.*, 2004, **126**, 3496
59. Sanford, M.S., Love, J.A. and Grubbs, R.H., *J. Am. Chem. Soc.*, 2001, **123**, 6543

-
60. Grubbs, R.H., *Handbook of Metathesis*, Wiley-VCH, Germany, 2003
61. Ulman, M. and Grubbs, R.H., *Organometallics*, 1998, **17**, 2484
62. van Leeuwen, P.W.N.M., *Homogeneous Catalysis*, Kluwer Academic Publishers, The Netherlands, 2004
63. Booyen, K.M.A., *Metathesis and Transalkylation in Tandem Catalysis*, Ph.D thesis, (North-West University), 2007
64. van der Gryp, P., *Separation of Grubbs-based catalysts with nanofiltration*, Ph.D thesis, (North-West University), 2008
65. Nguyen, S.T. and Grubbs, R.H., *J. Am. Chem. Soc.*, 1993, **115**, 9858
66. van Schalkwyk, C., *Die Katalitiese Sintese van Lineêre Alkene via 'n Metatesereaksie*, Ph.D thesis, (Potchefstroomse Universiteit vir Christelike Hoër Onderwys), 2001
67. Jordaan, M., van Helden, P., van Sittert, C.G.C.E. and Vosloo, H.C.M., *J. Mol. Catal A: Chem.*, 2006, **254**, 145

...and the fact that the

[illegible]

... .. 2329

[illegible]

2. The following information is required to be submitted to the Commission:

[illegible]

Civilian Control of the Military

...and the fact that the *Journal of Management Studies* is a leading journal in the field of management studies.

1. The first step in the process is to identify the problem or issue that needs to be addressed. This involves gathering information and understanding the context of the problem.

...the

1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 26

• *Journal of the American Medical Association*, 2000; 283: 2639-2644

Journal of Management Education 30(6)

10

Experimental:

3

3.1 Introduction

In this chapter, the experimental procedures followed during the course of the study are discussed in detail. The following sections are discussed: § 3.2 elaborates on the solvents and analytical techniques, whilst the synthesis of the PUK-Grubbs 2-precatalyst (3) is discussed in § 3.3. In § 3.4 the procedures for metathesis reactions are discussed; this includes the experimental setup, experimental method and the GC methods used for the different 1-alkenes. Finally the discussion of the NMR-methods are provided in § 3.5.

3.2 Reagents and analytical instruments

3.2.1 Solvents and reagents

Table 3.1 summarizes the chemicals used for the synthesis of the PUK-Grubbs 2-precatalyst (3) and the metathesis reactions.

Table 3.1: Reagents and solvents used during the synthesis and metathesis reactions.

Chemical	Supplier	Purity
Benzophenone	Fluka	99%
n-Butyllithium	Sigma Aldrich	2.5M in hexanes
2-Bromopyridine	Sigma Aldrich	99%
Diethyl ether	Labchem	99%
Pentane	Labchem	99%
Toluene	Merck	99%
Tetrahydrofuran (THF)	Saarchem	99.5%
<i>tert</i> -Butyl hydroperoxide	Fluka	5.5M in decane over 4Å mol sieves.
1-Hexene	Fluka	96%
1-Heptene	Fluka	97%
1-Nonene	Fluka	95%
1-Decene	Fluka	95%
Nonane	Fluka	99%
Grubbs catalyst first and second generation	Sigma Aldrich	

3. Experimental

THF (Saarchem), toluene (Merck) and diethyl ether (Labchem) were refluxed over Na/benzophenone whereas CaH_2 was used to dry pentane (Labchem). The THF and toluene was then stored over dry molecular sieves (4Å) under an Ar atmosphere.

Dried solvents were used during the synthesis reactions whilst diethyl ether and pentane were used directly from the solvent stills. The 1-alkenes were used without any purification during the metathesis reactions.

All the gasses used were supplied by Afrox.

3.2.2 Analytical instruments

➤ Infrared spectroscopy (IR)

IR-spectra were obtained with a Bruker Tensor 27 spectrophotometer. Sample discs were prepared by mixing 0.005 g sample and 0.30 g dry KBr together and compressing the mixture into a sample disc.

➤ Nuclear Magnetic Resonance (NMR)

NMR-spectra (^1H -, ^{13}C -, and ^{31}P -NMR data) was obtained by using a Bruker Avance III ultra shield, 600MHz. The NMR samples were prepared by dissolving the crystals (15 - 20 mg) in a deuterated solvent (CDCl_3) and filtered into the NMR-tube under an inert atmosphere.

➤ Mass Spectrometry (MS)

The molecular mass of the ligand was determined by using the Micromass Autospec TOF mass spectrometer to obtain EI-spectra.

The molecular mass of the precatalyst was determined by using a Bruker Ultraflex III TOF/TOF Mass Spectrometer.

➤ Gas Chromatography (GC)

GC analysis was conducted on an Agilent 6890 and 6850 gas chromatograph. The GCs are equipped with a HP-5 (95% methyl siloxane and 5% phenyl methyl siloxane), capillary column

(30 m x 320 μm x 0.25 μm) and a HP-1 methyl siloxane (100%), capillary column (30 m x 320 μm x 0.25 μm) respectively. The detector of the GC was a flame ionisation detector (FID).

Gas Chromatography/Mass Spectrometry (GC/MS)

A GC/MS was mainly used for product verification during the metathesis reactions. An Agilent 6890N GC with a ZB-1 100% methyl siloxane capillary column (30 m x 320 μm x 1.00 μm) and Agilent 5973 mass selective detector (MSD) was used.

Parameters of the MSD were: EI-type, 230°C source, 69.9 eV, 150°C Quadrupole Analyser.

> Melting point

A Buchi B-540 was used to determine the uncorrected melting points.

> Electronic Scanning Electron Microscope (ESEM-EDS)

A FEI Quanta 200 ESEM instrument with integrated Oxford Inca 400 Insight EDS (Energy Dispersive Spectroscopy) system was used to obtain a semi-quantitative elemental analysis. Electron backscatter images were taken of the different catalysts.

The samples were loaded onto the sample holders containing Cu- and C-strips respectively. The C-strip samples were coated with Pd/Au prior to analysis, where after the samples were inserted into the electron microscope.

> Thermogravimetric Analyser (TGA)

A TA 2050 thermogravimetric analyser (TGA) was used to determine the mass changes with a variation of temperatures.

The TGA Pt-sample pan must be cleaned from residue before use whereafter the basket was placed into the apparatus and tarred. Thereafter the sample was loaded into Pt-sample pan and the analysis was commenced.

Temperature program: 40 to 900°C at 10°C min⁻¹

➤ **Differential Scanning Calorimetry (DSC)**

A TA 2010 Differential Scanning Calorimetry (DSC) instrument was used for the measuring of heat flow into a substance as a function of temperature.

Two Al-pans were used for the analysis, where the one served as a reference. The samples were weighed into the pan whereafter the pan was compressed to seal it. The pan was closed this way to ensure that the heat was spread evenly.

Temperature program: 40 to 500°C at 10°C min⁻¹

3.3 Synthesis of the existing PUK-Grubbs 2-precatalyst¹

3.3.1 Standard techniques

3.3.1.1 Apparatus for the synthesis of the PUK-Grubbs 2-precatalyst

The synthesis reactions were done under an argon (Ar) or a nitrogen (N₂) atmosphere due to the instability of the reactions towards the atmosphere. Vacuum and Schlenk techniques were used during the synthesis of the PUK-Grubbs 2-precatalyst (3). The experimental setup used for the synthesis of the precatalyst is shown in **Figure 3.1**. The double manifold was used to remove air from the glassware by flushing it with Ar, followed by the removal of small amounts of liquid via condensation into the solvent traps. Two bubblers which contained silicone oil were used to indicate the flow of the inert gas.² The anti suck back valve prevents pressure building up but also air flowing into the inert atmosphere. The solvent traps were cooled with ice and acetone to prevent the solvents to enter the vacuum pump.

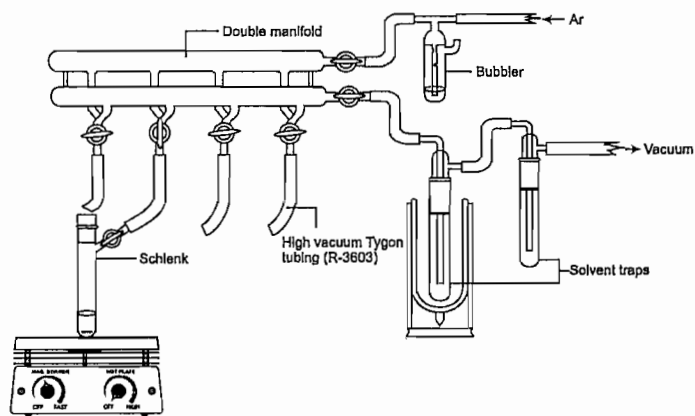


Figure 3.1: Experimental setup for Schlenk reactions.

3.3.1.2 Method for the removal of solvents under vacuum

The solvents were condensed into the solvent traps from the Schlenk tube during vacuum solvent removal. The valve of the Schlenk tube was closed and the vacuum was opened. The Schlenk tube valve was slightly opened under vacuum while the reaction mixture was stirred magnetically. It should be noted that the valve was not opened fully in order to prevent the solution from being sucked into the manifold. While the liquid was cooling down, condensation of the solvent occurred. The valve of the Schlenk tube was opened fully when condensation was completed and left open until the tube reached ambient room temperature. The Schlenk was then flushed with Ar and removed from the manifold.

3.3.1.3. Method for the filtration of a suspension under an inert atmosphere

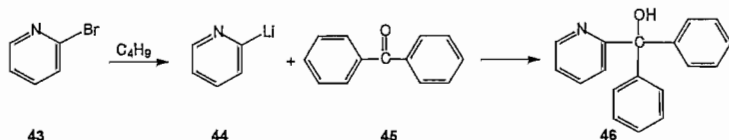
The suspension was drawn from the Schlenk into a gas-tight glass syringe under an inert atmosphere. The stainless steel needle was removed and replaced with a clean needle and a filter (Acrodisc, membrane GHPP, 0.45 μm , diam. 25 mm). The contents were then filtered slowly into a clean Schlenk under an inert atmosphere.

3. Experimental

3.3.1.4. NMR solvent preparation

The CDCl_3 used for the NMR study was pump freeze dried before use. A Schlenk was filled one eighth with 4Å molecular sieves that was already activated. The CDCl_3 was then added until the tube was filled half. The tube was then placed in liquid nitrogen under an inert atmosphere until the solvent was frozen. The tube was then removed from the liquid nitrogen and carefully placed under vacuum. The vacuum was removed at the sight of the first drops of liquid formed. The tube was then placed under an inert atmosphere until the solvent was again in liquid form. The procedure was repeated three times.

3.3.2 Synthesis of 1-(2'-pyridinyl)-2,4-dimethylpentan-3-ol (**46**)



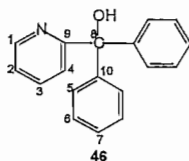
Scheme 3.1: Synthesis of the alcohol (**46**).

The synthesis of the tertiary alcohol **46** was done according to an adopted method proposed by Herrmann *et al.*³ Diethyl ether (100 mL) was cooled down to -78°C in a three neck flask. *n*-Butyllithium (40 mL (2.5M)) was added dropwise to the diethyl ether solution. Bromopyridine (9 mL (**43**)) was dissolved in 25 mL diethyl ether was added dropwise to form a lithium pyridine salt (**44**) under inert conditions. The solution turned a dark red colour followed by the addition of benzophenone (**45**). The mixture was stirred for 3 hours while the temperature was increased to room temperature. Water was added and the ether layer washed with 50 mL hydrochloric acid (HCl, 2M) four times. The acid layer was then neutralized with a sodium hydroxide (NaOH, 2M) solution. The water layer was then washed with 10 mL diethyl ether four times. Activated charcoal was added to the ether and extracted without stirring. The ether that was extracted produced a colourless solution. Sodium sulphate (NaSO_4) was added to dry the solution and filtered. Removal of the diethyl ether under reduced pressure gave white flakes of the alcohol (**46**).

Melting point: 108°C

Yield: 55%

IR-spectra: (KBr, cm^{-1}) ν_{max} 3346 (O-H stretch), 3074–3018 (C-H stretch, aromatic), 1591–1572 (C=C and C=N stretch).

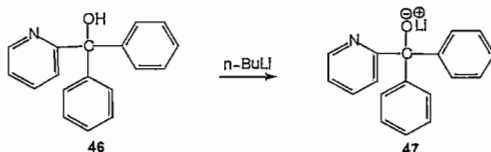


¹H-NMR data: [CDCl₃, 600 MHz, ppm] δ_{H} 8.574 (H₁, d), 7.568 (H₃, 2d), 7.222-7.192 (H₄, d), 7.042 (H₂, 2d), 6.258 (OH, s).

¹³C-NMR data: [CDCl₃, 150 MHz] δ_{C} 80.84 (C₈), 122.36 (C₂), 122.93 (C₄), 127.32 (C₇), 127.93 (C₆), 128.15 (C₅), 136.40 (C₃), 146.13 (C₁), 147.75 (C₁₀), 163.24 (C₉).

MS-spectrum: 261 m/z was obtained by using the EI-technique.

3.3.3 Synthesis of lithium diphenyl(pyridin-2-yl) methanolate (47)



Scheme 3.2: Synthesis of the salt (47).

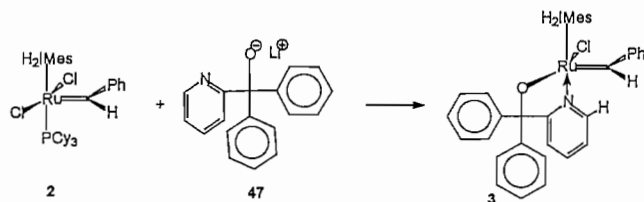
Alcohol (539 mg (46)) was weighed and dissolved in 20 mL THF. 0.9 mL *n*-Butyllithium was added dropwise to the mixture at room temperature and a precipitate formed immediately. The reaction mixture was stirred at room temperature for 2 hours. The solvent was then removed under reduced pressure and a white lithium salt (47) was obtained. The salt (47) was washed with 5 mL pentane three times and dried under reduced pressure.

Yield: 85%

Due to the salts instability no further analyses were done to confirm the product.

3. Experimental

3.3.4 Synthesis of benzyldiene-chloro(1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-[1-(2'-pyridinyl)-1,1-diphenyl-methanolato]ruthenium (3)



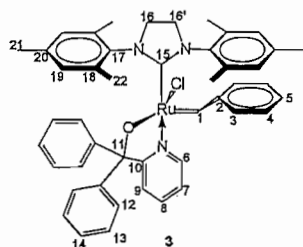
Scheme 3.3: Synthesis of the precatalyst (3).

The precatalyst (3) was synthesised according to a method proposed by Jordaan.¹ The lithium salt (104 mg (47)) and 310 mg Grubbs 2 precatalyst (2) was dissolved in 20 mL THF in a Schlenk under an inert (Ar) atmosphere. The solution was stirred for 24 hours at 40°C. The THF was removed under vacuum. The resulted product was dissolved in 5 mL toluene followed by filtration into a new Schlenk. The toluene was removed to produce a black solid. 1 mL THF and 30 mL toluene was added to the solid before the Schlenk was placed in an ultrasonic bath for 20 min. The catalyst then precipitated as a green powder in a dark solution. The green precipitate was then washed with 15 mL of pentane five times. The Schlenk was then placed under vacuum to remove the pentane and a green solid was obtained (3).

Melting point: The precatalyst decomposes at 211°C

Yield: 43%

IR-spectra: (KBr, cm^{-1}) ν_{max} 3428 (O-H stretch), 3056-2853 (C-H stretch, aromatic), 1605-1571 (C=C and C=N stretch).



¹H-NMR data: [CDCl_3 , 600 MHz, ppm] δ_{H} 6.318 (H_3 , d), 6.617 (H_4 , dd), 7.103 (H_5 , dd), 9.557 (H_6 , d), 6.924 (H_7 , dd), 7.191 (H_8 , dd), 6.531 (H_9 , dd), 6.702-7.091 (H_{12-14} , 10H's), 3.957 ($\text{H}_{16,18}$, 4H's), 6.587 ($\text{H}_{19,19'}$, 4H's), 2.149, 2.212, 2.559 ($\text{H}_{21,22,22'}$, 18H's) Carbene signal at 17.055 ppm (H_1 , s)

³¹P-NMR data: No visible peaks.

MALDI TOF: 793.261 m/z

3.4 Metathesis reactions

3.4.1. General procedures

Small scale experiments were done to determine the different products and to investigate 1-alkene reactivity under different conditions such as; different temperatures and catalyst loads. The 1-alkenes were not purified before using it during the metathesis reactions. The possible products formed during the metathesis reactions of the different 1-alkenes are given in **Appendix A**.

3.4.2. Small scale metathesis reactions

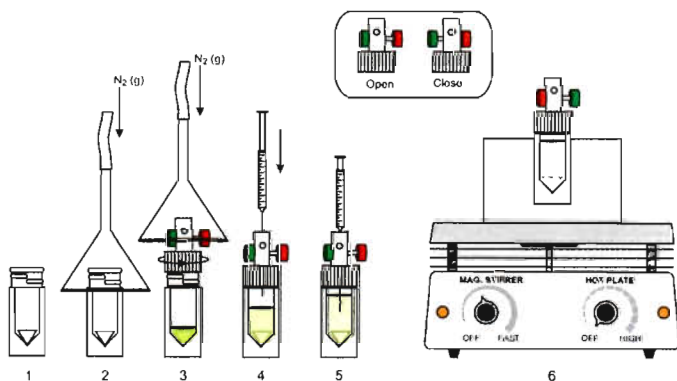


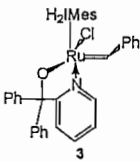
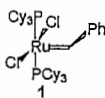
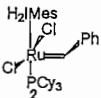
Figure 3.2: Experimental setup for small scale metathesis reactions.

The temperature for the reaction was preset and regulated with a temperature controller fitted with a thermocouple. The catalyst was weighed in the mini reactor which already contained a stirring bar and placed under Ar. The reactor was then closed and sealed (**Figure 3.2** steps 1 to 3). The reactor was placed on the magnetic stirrer at the preset temperature for 1 min (**6**). For illustration steps 4 and 5 are shown next to the heating block. The reactor was opened so that the syringe needle could be inserted (the green lid is pushed in). Nonane (0.25 mL) was added through the septum directly followed by the addition of the 5 mL 1-alkene. A sample (0.2 μ L) was taken and injected onto the GC/FID and the reactor was then closed by pushing the red lid in. The samples were taken at various intervals of 1 to 24 hours until the curve reached equilibrium.

3. Experimental

During the lifetime determining reactions, the samples were extracted and added into GC vials. The GC vials already contained 0.3 mL of toluene and 2 drops of *tert*-butyl hydrogen peroxide to quench the reaction. The stability determining reactions were done at 60°C for two different 1-alkenes. After the reactions had reached equilibrium, a pre-specified volume of the 1-alkene was added again.

Table 3.2: Amount of precatalyst used for the small scale metathesis reactions.

Precatalysts		PUK-Grubbs 2 precatalyst (mg)	Grubbs 1 (mg)	Grubbs 2 (mg)
1-Alkenes	Catalyst load Precatalyst: 1-Alkene	 3	 1	 2
1-Hexene	1:7000	4.5	4.7	4.8
	1:9000	3.5	3.7	3.8
1-Heptene	1:7000	4.0	4.2	4.3
	1:9000	3.1	3.2	3.3
1-Nonene	1:7000	3.3	3.4	3.5
1-Decene	1:7000	3.0	3.0	3.2

3.4.3. GC method for metathesis reactions

The small scale experimental samples were analysed on an Agilent 6890 and 6850 gas chromatograph and injected manually.

The GC settings varied for the different 1-alkenes:

1-Hexene:

Inlet temperature : 200°C
 N2 carrier gas flow : 2 mL.min⁻¹ at 20°C
 Injection volume : 0.2 µL
 Split ratio : 50:1
 Oven programme : 60 to 110°C at 25°C min⁻¹
 110°C for 8 min
 Detector : FID at 250°C
 H₂ flow rate : 40 mL.min⁻¹ at 20°C
 Air flow rate : 450 mL.min⁻¹ at 20°C

An example of a typical GC chromatogram for product formation during a metathesis reaction with 1-hexene is shown in Figure 3.3.

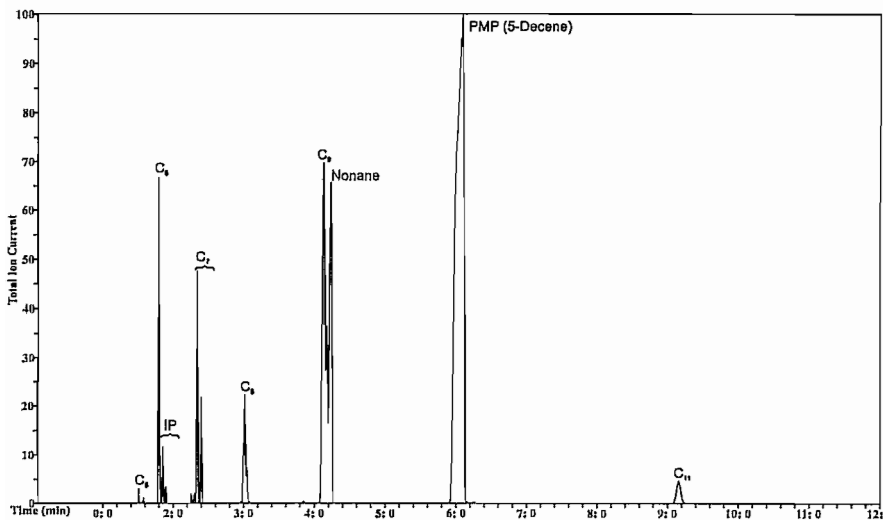


Figure 3.3: GC chromatogram during the metathesis reaction of 1-hexene with Gr2Ph (**3**). The conditions being a 1:7000 molar ratio (Ru:Alkene) at 60°C.

The only difference between the GC settings of the different 1-alkenes was the oven programmes.

3. Experimental

1-Heptene:

Oven programme : 60 to 110°C at 25°C min⁻¹
110°C for 10 min
110 to 290°C at 25°C min⁻¹
290°C for 5 min

An example of a typical GC chromatogram for product formation during a metathesis reaction with 1-heptene is shown in **Figure 3.4**.

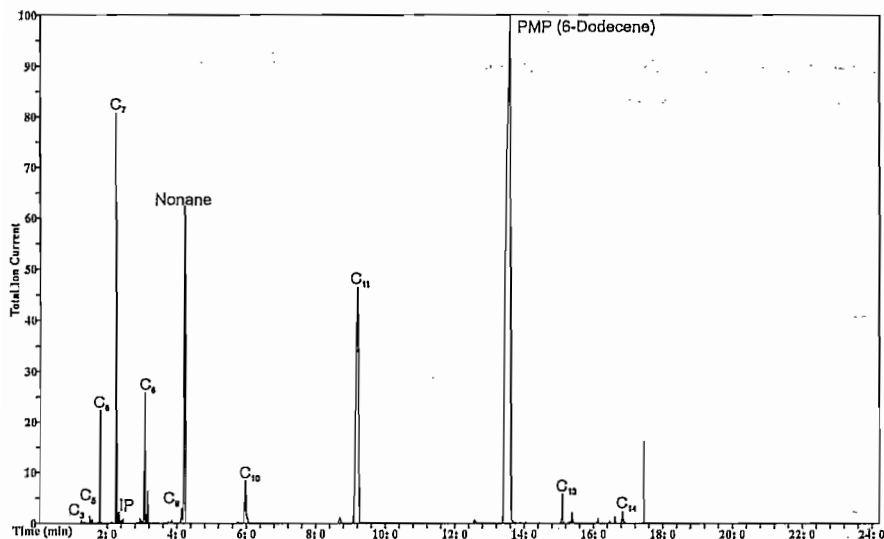


Figure 3.4: GC chromatogram during the metathesis reaction of 1-heptene with Gr₂Ph (3). The conditions being a 1:7000 molar ratio (Ru:Alkene) at 60°C.

1-Octene:¹

Oven programme : 60 to 110°C at 25°C min⁻¹
110°C for 10 min
110 to 290°C at 25°C min⁻¹

1-Nonene:

Oven programme : 60 to 110°C at 25°C min⁻¹
 110°C for 10 min
 110 to 290°C at 25°C min⁻¹

An example of a typical GC chromatogram for product formation during a metathesis reaction with 1-nonene is shown in Figure 3.5.

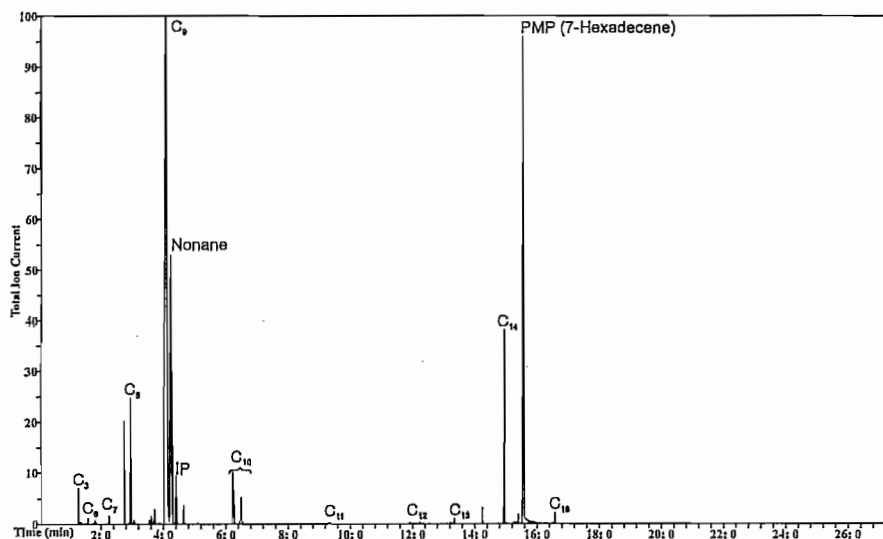


Figure 3.5 GC chromatogram during the metathesis reaction of 1-nonene with Gr2Ph (3). The conditions being a 1:7000 molar ratio (Ru:Alkene) at 60°C.

1-Decene:

Oven programme : 60 to 110°C at 15°C min⁻¹
 110°C for 10 min
 110 to 290°C at 15°C min⁻¹
 300°C for 20 min

3. Experimental

An example of a typical GC chromatogram for product formation during a metathesis reaction with 1-decene is shown in Figure 3.6.

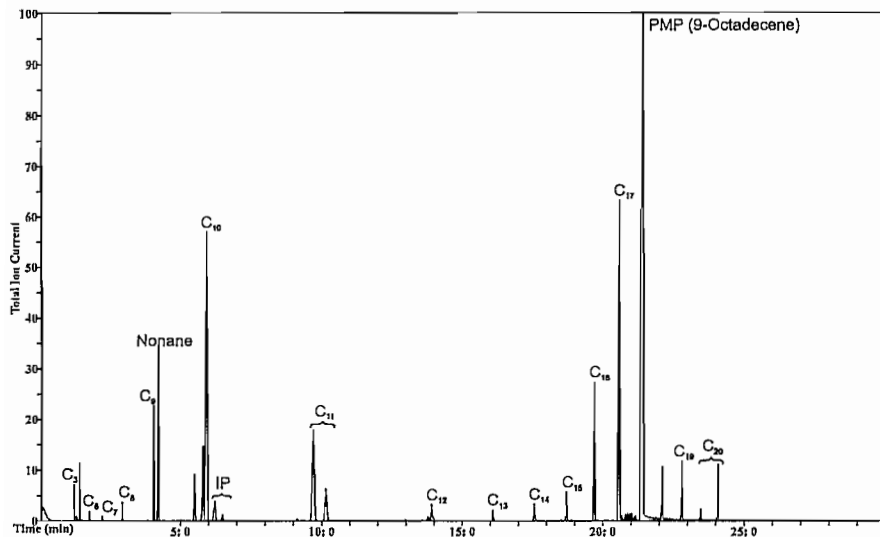


Figure 3.6: GC chromatogram during the metathesis reaction of 1-decene with Gr2Ph (3). The conditions being a 1:7000 molar ratio (Ru:Alkene) at 60°C.

An internal standard method, with nonane as internal standard (IS), was used for the determination of the mole percentage of 1-alkene converted to the primary and secondary metathesis products (PMP and SMP). A calibration curve of the area against volume was plotted to determine the GC response factor (RF). The volume of the internal standard was kept constant while the volumes of the 1-alkenes were varied (Table 3.1). The response factors obtained from the slope of the calibration curve for all the alkenes were close to 1.00 (Table 3.2).

$$RF = \frac{V_{IS}}{V_{1-Alkene}} \times \frac{A_{1-Alkene}}{A_{IS}} \quad 3.1$$

RF	=	GC response factor
$V_{1-Alkene}$	=	volume of the alkene at $t = 0$
V_{IS}	=	volume of the internal standard at $t = 0$
$A_{1-Alkene}$	=	area of the alkene
A_{IS}	=	area of the internal standard

Table 3.2: Calibration data to determine the RF.

Volume Ratio Nonane : 1-Alkene	$V_{\text{Nonane}}/V_{1\text{-Alkene}}$	$A_{\text{Nonane}}/A_{1\text{-Alkene}}$
0.25 : 1.00	0.25	0.26
0.25 : 0.75	0.33	0.35
0.25 : 0.50	0.50	0.50
0.25 : 0.25	1.00	0.93

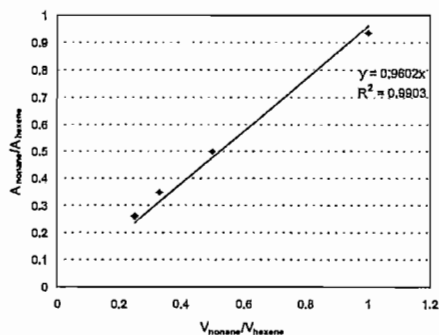


Figure 3.7: Calibration curve to determine the RF.

Table 3.3: RF of the different 1-alkenes.

1-Alkene	RF
1-Hexene	0.96
1-Heptene	1.00
1-Octene	0.98
1-Nonene	0.98
1-Decene	0.98

3. Experimental

Determining the mol percentage (mol%) conversion of the 1-alkene to the PMP, IP and SMP.

$$V_{1-Alkene} = V_{IS} \cdot \left(\frac{A_{1-Alkene}}{A_{IS}} \right) \cdot \left(\frac{1}{RF} \right) \quad 3.2$$

$$N_{1-Alkene} = \frac{(V_{1-Alkene} \times \rho_{1-Alkene})}{MW_{1-Alkene}} \quad 3.3$$

$$Mol\%_{1-Alkene} = \frac{N_{1-Alkene}}{T_{1-Alkene}} \quad 3.4$$

$N_{1-Alkene}$	=	Mol alkene
ρ	=	density of the alkene
$MW_{1-Alkene}$	=	Molecular mass of the alkene
Mol % $_{1-Alkene}$	=	Mol percentage alkene formed
$T_{1-Alkene}$	=	Total mol alkene formed

The selectivity of product formation was determined by:

$$\%selectivity = \left(\frac{\%PMP}{\%(PMP + SMP + IP)} \right) * 100 \quad 3.5$$

The TON was determined by:

$$TON = \frac{(\%PMP * (Alkene : Ru))}{100} \quad 3.6$$

A number of terminal alkenes and by-products were formed during the cross metathesis reactions of the 1-alkenes.

The samples taken from the metathesis reactions that were quenched with *tert*-butyl-hydrogen peroxide contained elevated levels of decane. The reason being that the peroxide is in a decane solution.

3.5 NMR investigation of metathesis reactions

The precatalysts were weighed into a filter (cotton wool in a pipette). The precatalyst was then filtered through with deuterated CDCl_3 solvent (0.7 mL), which was freeze dried (§3.1.5.1), under N_2 into a NMR tube. The alkene (0.1 mL) was added shortly before reaction was monitored to keep the initial reaction time of the precatalyst with the alkene as short as possible. The reactions were conducted at 30°C and monitored for 5 hrs at regular intervals. The peak integration values of the formed carbenes were normalized against the deuterated CDCl_3 signal.

3.6 References

1. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007
2. Casey, M., Leonard, J., Lygo, B. and Procter, G., *Advanced Practical Organic Chemistry*, 1990
3. Herrmann, W.A., Lobmaier, G.M., Priemeier, T., Mattner, M.R. and Scharbert, B., *J. Mol. Catal. A: Chem.*, 1997, 117, 455

Results and Discussion:

4

4.1. Introduction

In this chapter, the results obtained during the study are presented. The synthesis of the PUK-Grubbs 2-precatalyst (**3**) and the results from the Electronic Scanning Electron Microscope (ESEM) of the different precatalysts (Gr1 (**1**), Gr2 (**2**) and Gr2Ph (**3**)) used, are discussed in § 4.2. In § 4.3, the metathesis reactions of the different 1-alkenes are discussed; this includes the results obtained for the use of different precatalysts, the effects of temperature and precatalyst load (Ru:1-alkene ratio). The lifetime determining reactions of the precatalysts, using two different 1-alkenes, are given and discussed in § 4.4. In addition, the comparison and summary of the 1-alkene reactions at 60°C are provided in § 4.5. Finally the NMR-results are presented in § 4.6.

4.2 Synthesis of existing PUK-Grubbs 2-precatalyst

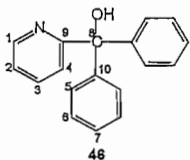
All of the synthesis procedures e.g. alcohol (**46**), salt (**47**) synthesis and the Gr2Ph (**3**) synthesis were done under an inert atmosphere by using typical schlenk techniques and dried solvents.

4.2.1 Ligand synthesis

The method for the synthesis of **46** is discussed in detail in § 3.3.2. The synthesis of the alcohol (**46**) was done by reacting bromopyridine (**43**) with *n*-butyllithium in diethyl ether, which then forms the lithium pyridine (**44**). Benzophenone (**45**) was then added to **43** to form **46**. The yield obtained for **46** was a moderate 55%. Verification of **46** was done by MS, IR, ¹H-NMR and ¹³C-NMR analyses. The results are presented in Table 4.1, while the spectra are shown in Appendix B.

4. Results and discussion

Table 4.1: The synthesized alcohol (46).

		• White flakes a product yield of 55% • Melting point of 108°C • Only one part of the phenyl ring is numbered due to the symmetry present
IR-spectra: ^a	ν_{max} 3346 (O-H stretch), 3074-3018 (C-H stretch, aromatic), 1591-1572 (C=C and C=N stretch) cm^{-1}	
¹ H-NMR data: ^b	* δ_{H} 8.574 (H ₁ , d, 1H), 7.568 (H ₃ , 2d, 1H), 7.222-7.192 (H ₄ , d, 11H), 7.042 (H ₂ , 2d, 1H), 6.258 (OH, s, 1H) ppm	
¹³ C-NMR data: ^c	* δ_{C} 80.84 (C ₈), 122.36 (C ₂), 122.93 (C ₄), 127.32 (C ₇), 127.93 (C ₆), 128.15 (C ₅), 136.40 (C ₃), 146.13 (C ₁), 147.75 (C ₁₀), 163.24 (C ₉).	
MS-spectrum:	261 m/z (EI-technique)	

^a IR with KBr.
^b The ¹H-NMR, 600 MHz.
^c ¹³C-NMR, 150 MHz.
* Solvent CDCl₃, s = singlet, d = doublet

The values obtained from the NMR correlate well with the values reported by Hermann *et al.*¹ and Jordaan.² The MS spectrum showed the molecular ion (M⁺) of 261 m/z, which indicated that the product had the same molecular mass as reported by Hermann *et al.*¹ This demonstrates that the ligand was synthesized successfully.

4.2.2 Lithium salt preparation

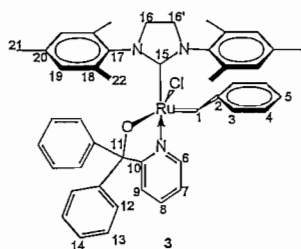
The synthesized alcohol (46) and *n*-butyllithium was dissolved in THF and stirred to form the lithium salt (47). The method for the synthesis of 47 is discussed in § 3.3.3. The synthesis of 47 resulted in a good yield of 85%, which correlates well with the literature value of 95%.² It is assumed that during the washing procedure, as discussed in § 3.3.3, the impurities are removed to obtain a white powder. Due to the instability of 47 to air, no further analyses were done to characterize the product. The product was used directly for the synthesis of Gr2Ph (3).

4.2.3 Precatalyst (3) preparation

To obtain the precatalyst (3), lithium salt (47) and Gr2 (2) react in a THF solution under inert conditions as discussed in § 3.3.4. During the synthesis of precatalyst 3 (Gr2Ph) a relatively low yield of 43% was obtained. The yield obtained is slightly less than found in literature (62.5%), but the product synthesized is pure.² The lower yield can be attributed to the washing process (§ 3.3.4) where some of the precatalyst was removed during the removal of the pentane.

Characterization of the synthesized precatalyst 3 was done by IR, ¹H-NMR, ³¹P-NMR, DSC and MALDI-TOF analyses. The results obtained are given in Table 4.2, while the spectra are shown in Appendix B.

Table 4.2: The synthesized precatalyst (3).



- Light green powder with an product yield of 43%
- Decomposition point 211°C
- Only one part of the phenyl rings are numbered due to the symmetry present

IR-spectra: ^a	$\nu_{\max}$ 3428 (O-H stretch), 3056-2853 (C-H stretch, aromatic), 1605-1571 (C=C and C=N stretch) cm^{-1}
¹ H-NMR data: ^b	* δ_{H} 6.318 (H ₃ , d), 6.617 (H ₄ , dd), 7.103 (H ₅ , dd), 9.557 (H ₆ , d), 6.924 (H ₇ , dd), 7.191 (H ₈ , dd), 6.531 (H ₉ , dd), 6.702-7.091 (H ₁₂₋₁₄ , 10H's), 3.957 (H _{16,16'} , 4H's), 6.587 (H _{19,19'} , 4H's), 2.149, 2.212, 2.559 (H _{21,22,22'} , 18H's) ppm Carbene signal at 17.055 ppm (H1, s)
³¹ P-NMR data:	No visible peaks.
MALDI TOF:	793.261 m/z

^a IR with KBr.

^b The ¹H-NMR, 600 MHz.

* Solvent CDCl₃. s = singlet, d = doublet

4. Results and discussion

The IR-spectrum, obtained by using a KBr-pellet, showed a small alcohol peak at 3428 cm^{-1} that was attributed to atmospheric moisture or to the KBr not being dry enough. The ^{31}P NMR spectrum of precatalyst **3** showed no peaks. Gr2 (**2**) contains a PCy_3 -group, therefore the ^{31}P NMR showed a phosphorus peak. When the synthesized Gr2Ph (**3**) is pure, no ^{31}P NMR peak will be visible. The reaction mixture was monitored by means of thin layer chromatography (TLC) to determine whether the reaction was completed. The TLC analysis was repeated until the green spot, which indicates Gr2Ph (**3**), did not change. Most of the Gr2 (**2**) had reacted and the non-reacted reagent was removed by the washing process. The IR and NMR-data obtained correlate with the data that was reported by Jordaan.²

The MALDI-TOF MS analysis showed that Gr2Ph (**3**) had a molecular weight of 793.261 m/z , which correlated with the theoretical calculated molecular weight.

The decomposition temperature of 211°C (as determined by a Buchi B-540) was confirmed with the DSC-data (213°C). From the DSC-data it was observed that the peak formed during the heating of the sample was an exothermic process taking place (**Appendix B**).

4.2.4 ESEM and EDS of precatalysts

During a previous study it was mentioned that different Gr1 (**1**) batches did not result in repeatable results.² Electronic Scanning Electron Microscope (ESEM) and Energy Dispersive Spectroscopy (EDS) was done to determine whether there was a difference between the batches and to compare Gr1 (**1**) with the crystal morphology of Gr2 (**2**) and Gr2Ph (**3**) used during the study. In **Figure 4.1**, photos of the different precatalysts are shown to indicate the colour differences that were observed.

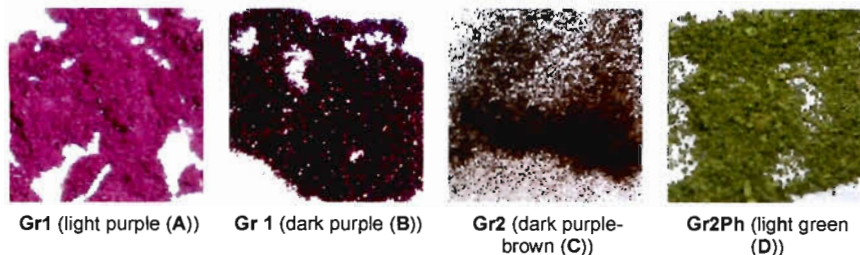


Figure 4.1: Indication of the colours of the precatalysts for further reference in the ESEM results.

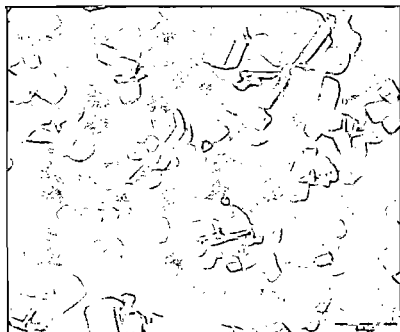
In **Figure 4.2** the different ESEM photos are shown to indicate the differences in the crystal morphology of the different precatalysts.



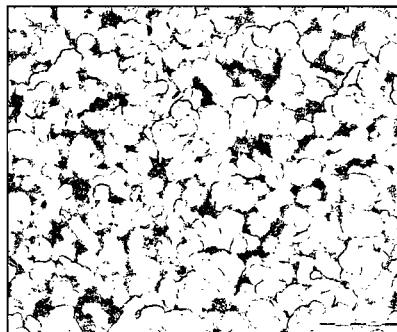
Gr1 (A)



Gr1 (B)



Gr2 (C)



Gr2Ph (D)

Figure 4.2: ESEM of the different precatalysts are: (A) the Gr1 (1) fine light purple powder, (B) Gr1 (1) dark purple-brown crystalline, (C) Gr2 (2) dark purple clustered crystalline and (D) Gr2Ph (3) light green crystalline.

It can be seen from **Figure 4.2** that there is a difference between the crystallinity of precatalysts Gr1 (1), Gr2 (2) and Gr2Ph (3). There is, however, no significant difference between the different Gr1 (1) batches **A** and **B**, except for the colour and crystal size that could be observed.

The semi-quantitative elemental analysis indicates a relative percentage of atoms present in the molecular structure of the precatalysts, shown in **Table 4.3**. These values were compared to the theoretical values, shown in **Table 4.4**. For the calculation of the theoretical values no hydrogen atoms were taken into account.

4. Results and discussion

The reason for this is that it is difficult to observe the excited state of hydrogen due to the fact that hydrogen has only one orbital with an electron. The values displayed in Table 4.3 and 4.4 are based on atomic percentage.

Table 4.3: The semi-quantitative elemental analysis of the different catalysts.

Catalyst	C (%)	N (%)	O (%)	P (%)	Cl (%)	Ru (%)
Gr 1 (1)	90.11	0	0	3.61	4.40	1.88
Gr2 (2)	86.36	7.51	0	1.31	3.41	1.40
Gr2Ph (3)	81.24	10.39	5.36	0	1.67	1.35

Table 4.4: The theoretically determined values for the atomic percentages of the precatalysts.

Catalyst	C (%)	N (%)	O (%)	P (%)	Cl (%)	Ru (%)
Gr 1 (1)	89.58	0	0	4.17	4.17	2.08
Gr2 (2)	88.46	3.85	0	1.92	3.85	1.92
Gr2Ph (3)	88.46	5.77	1.92	0	1.92	1.92

An instrumental deviation of 1% was obtained during the analysis of the precatalysts with EDS. From both tables it is clear that there is no substantial difference between the values determined from EDS analysis as compared to the theoretical calculated values. It should be taken into account that the composition of the precatalysts in terms of N- and O-atoms differ from each other. For instance, Gr2Ph (3) has one O-atom and three N-atoms, but Gr2 (2) has no O-atoms and two N-atoms. The difference between the experimental and theoretical values, especially in the N- and O values, can however be explained by the fact that EDS analysis is only an approximate analysis technique and is not as accurate as other chemical analyses techniques such as elemental analysis. The difference in reactivity between the two Gr1 (1) batches could possibly be attributed to a difference in the crystal size. This should however be investigated in detail in future studies.

4.3 Metathesis

4.3.1 Introduction

The metathesis of 1-alkenes in the presence of the Gr1 (1), Gr2 (2) and Gr2Ph (3) precatalysts were investigated and compared. The influence of the precatalyst load (Ru:1-alkene ratio) and temperature was evaluated for the different 1-alkenes and precatalysts. These different conditions were used to determine the optimum conditions for the highest reactivity with the least amount of secondary metathesis- (SMP) and isomerization product (IP) formation.

The formation of primary metathesis products (PMP), SMPs and IPs were monitored during the metathesis reactions of the 1-alkenes. Possible products that can be formed during the metathesis of 1-octene are summarized in **Table 4.5**. Details of the possible products for the metathesis of 1-hexene, 1-heptene, 1-nonene and 1-decene are illustrated in **Appendix A (Schemes 2 to 5)**.

Table 4.5: Possible reactions for 1-octene during metathesis.³

Reaction	Substrate ^a	Products ^a
Primary metathesis		
<i>Self metathesis</i>	$C=C_7$	$C=C + C_7=C_7$ (PMP) ^b
Isomerization	$C=C_7$	$C_2=C_6 + C_3=C_5 + C_4=C_4$ (IP) ^c
Secondary metathesis		
<i>Cross metathesis</i>	$C=C_7 + C_2=C_6$	$C_2=C_7 + C=C_6 + C=C_2 + C_6=C_7$ (SMP) ^d
<i>Self metathesis</i>	$C_2=C_6$	$C_2=C_2 + C_6=C_6$
Oligomerisation	$C=C_7$	C_{16}, C_{20} etc (OP) ^e

^a The hydrogens are excluded for simplicity.

^b Primary metathesis products (PMP) refer to the self metathesis products of 1-octene i.e. $C=C_7$ and $C=C$

^c Isomerization products (IP) refer to the double bond isomerization reaction of terminal to internal alkenes.

^d Secondary metathesis products (SMP) refer to the metathesis of the isomerization products of 1-octene

^e Oligomerization refers to repeated reactions of the substrate with itself.

4.3.2 Reproducibility of metathesis reactions

The experimental error for the metathesis reactions was obtained by repeating the reaction four times under the same conditions of 60°C and a precatalyst load of 1:7000 (Ru:1-hexene) with Gr1 (1) throughout the study. In **Figure 4.3** the repeatable results are illustrated as the PMP formation during the metathesis reaction against time. A standard deviation of 0.77% and an experimental error of 6.77% were obtained, thus indicating the reproducibility of the results. This is in the order of what was obtained (0.68% standard deviation and 2.00% experimental error) by van der Gryp⁴ for 1-octene reactions with Gr1 (1).

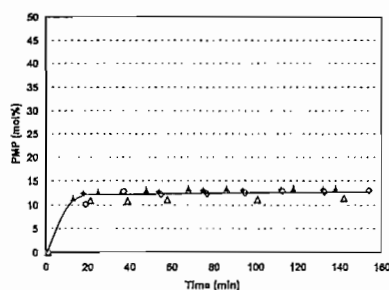


Figure 4.3: The metathesis reaction of 1-hexene with Gr1 (1) at 60°C with a 1:7000 Ru:1-hexene ratio. Reaction 1 (♦), reaction 2 (▲), reaction 3 (◇) and reaction 4 (△).

The metathesis reactions were conducted at precatalyst loads of 1:7000 and 1:9000 (Ru:alkene), as were used in previous studies.^{2,4,5} Metathesis reactions were compared at a constant temperature of 60°C. This is the temperature that accommodates the boiling points of the different 1-alkenes. Metathesis reactions with Gr2Ph (3), using a precatalyst load of 1:7000 at temperatures lower than 50°C resulted in no product formation.⁴

4.3.3 1-Hexene metathesis reactions

4.3.3.1 Introduction

During the metathesis reactions of 1-hexene the concentration of the 1-alkene decreased while the PMPs, SMPs and IPs increased. The product formation was monitored by GC-FID analysis. The PMPs formed during the metathesis reactions were found to be ethylene (C₂) and 5-decene (C₁₀), while the possible SMPs formed during the reactions are given in **Appendix A (Scheme A.2)**.

The precatalysts were evaluated at two different temperatures (55°C and 60°C) and precatalyst loads (1:7000 and 1:9000) during the metathesis reactions. The comparison between different precatalysts at constant experimental conditions is discussed in §4.3.3.2 to §4.3.3.3. Only two temperatures were used, mainly due to the low boiling point of the 1-hexene (63°C).

4.3.3.2 Effect of temperature on the metathesis reactions

The influence of reaction temperature on the 1-hexene metathesis reactions with the different precatalysts at a precatalyst load of 1:7000 (Ru:alkene) is shown in **Figure 4.4** to **Figure 4.6**. The results obtained during the metathesis reactions of 1-hexene with Gr1 (1) at 55°C and 60°C are shown in **Figure 4.4**.

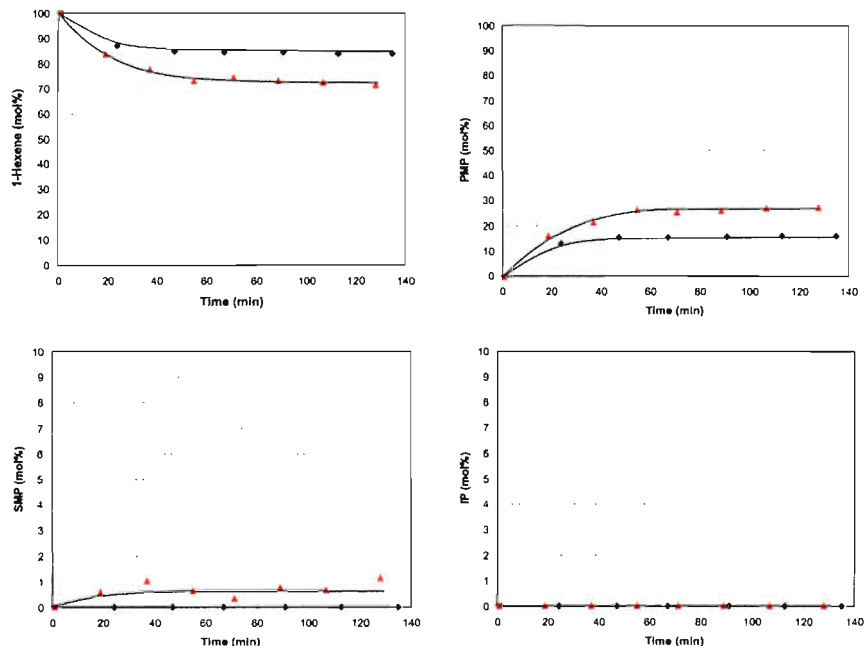


Figure 4.4: The PMP, SMP and IP formation from 1-hexene at temperatures of 55°C (♦) and 60°C (▲) for Gr1 (1) reactions.

An increase in reaction temperature resulted in an increase in the rate at which the 1-hexene is converted to the metathesis products. The metathesis reactions resulted in a 16 mol% PMP formation at 55°C within one hour, whereas 27.5 mol% PMPs were formed at 60°C. The selectivity for the PMP formation decreased from 100% to 98.39% with a temperature increase from 55°C to 60°C, due to a small amount of SMP formation of 0.5 mol%. This might have been the result of isomerization of the 1-hexene to form IPs, which is directly converted to SMPs due to self- and cross metathesis reactions. No change occurred in the IP formation between the two temperatures due to the rapid conversion into SMPs. The efficiency of the catalyst can be described by the turnover number (TON) of the metathesis reaction.⁵

4. Results and discussion

TON is defined as the amount of 1-alkene molecules that are converted to metathesis products by one molecule of catalyst. An increase in TON from 1123 to 1924 is obtained with an increase in temperature from 55°C to 60°C.

The results obtained from the metathesis reactions using Gr2 (2) under the same reaction conditions as for Gr1 (1), resulted in similar trends, but with higher PMP formations (Figure 4.5).

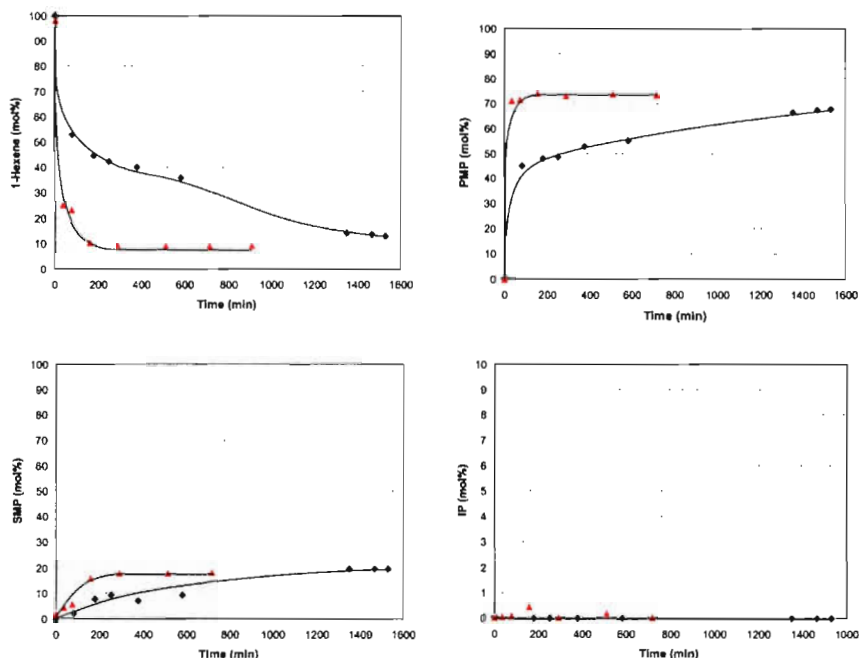


Figure 4.5: The PMP, SMP and IP formation from 1-hexene at temperatures of 55°C (♦) and 60°C (▲) for Gr2 (2) reactions.

The product formation for the 55°C reaction was found to be 55 mol% at 583 min as the equilibrium of the reaction was reached. The metathesis reaction conducted at 60°C had a PMP formation of 70.8 mol% at 34 min at which time the reaction was at equilibrium. This indicated that the increase in temperature increases the reaction rate and therefore shortens the time needed to reach equilibrium. With an increase in temperature, the PMP formation increased by 5.5 mol%, the selectivity and TON increased by 2.8 mol% and 386 respectively. The selectivity changed from 77.5 mol% to 80.3 mol%, whilst the TON increased from 4726 to 5113.

No IP formation was observed during either of these reactions, indicating that the small amount of IPs that might have formed had rapidly been converted into SMPs. This clarifies the distinct increase in the SMP formations.

The results obtained during the metathesis reactions of 1-hexene with Gr2Ph (**3**), with a precatalyst load of 1:7000 (Ru:1-hexene), is shown in **Figure 4.6**.

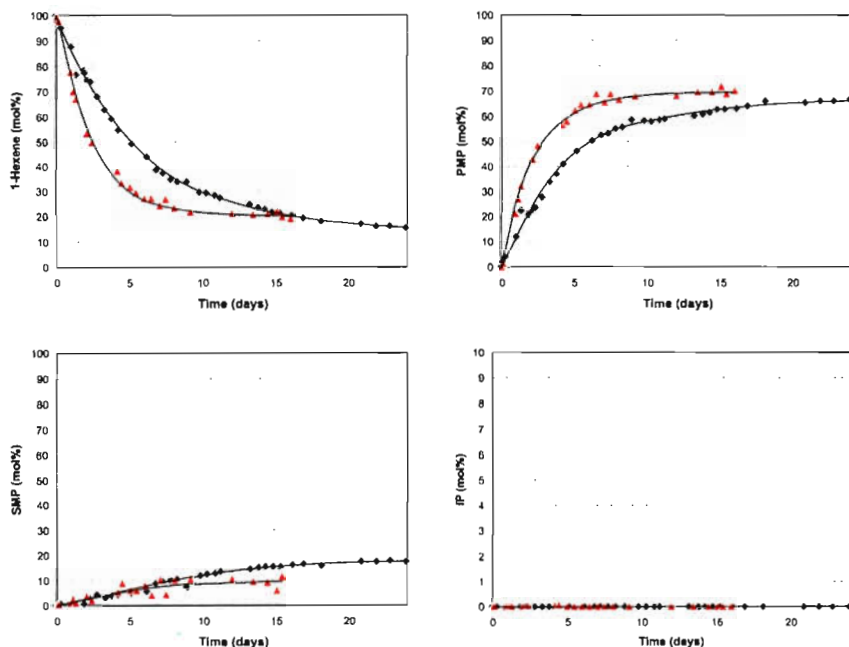


Figure 4.6: The PMP, SMP and IP formation from 1-hexene at temperatures of 55°C (♦) and 60°C (▲) for Gr2Ph (**3**) reactions.

Although the Gr2Ph (**3**) reaction rate was very slow, a noticeable difference between the rates at the two temperatures were observed during these metathesis reactions. For the metathesis reaction at 60°C, an increase in the reaction rate, TON, selectivity and PMP formation was observed. The increase in selectivity from 79.2 mol% to 87.1 mol% indicated that the metathesis reaction at a higher temperature with precatalyst **3** (Gr2Ph) favours the self metathesis of 1-hexene, thus increasing the PMP formation from 66.9 mol% at 55°C to 70.4 mol% at 60°C. As the activity increased as a result of increasing temperatures, the lifetime of the catalyst was shortened.

4. Results and discussion

The isomerization reaction of the 1-hexene was preferred at 55°C, where the isomers are then converted to SMPs by means of cross- and self metathesis reactions. The cross metathesis occurs between the IPs and 1-hexene and the self metathesis of different IPs form the SMPs as shown in **Scheme 2.3**.

4.3.3.3 Effect of precatalyst load on the metathesis reactions

The difference between the precatalyst loads of 1:7000 and 1:9000 (Ru:1-hexene) on the metathesis reactions investigated at 60°C for 1-hexene with the precatalysts (Gr1 (**1**), Gr2 (**2**) and Gr2Ph (**3**)) are presented in **Figure 4.7** to **Figure 4.9**. In **Figure 4.7** the results obtained during the Gr1 (**1**) metathesis reactions are shown.

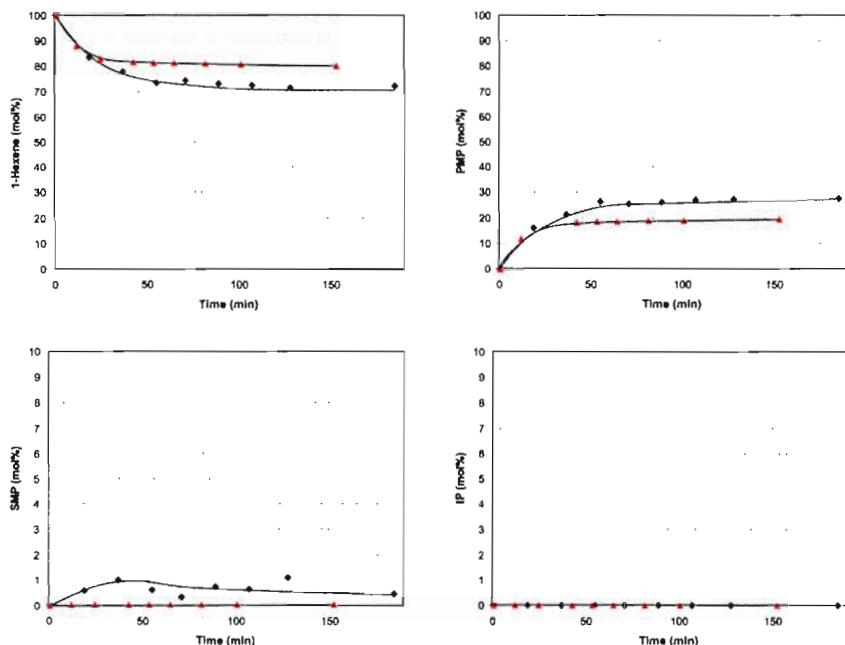


Figure 4.7: The PMP, SMP and IP formation from 1-hexene with precatalyst loads of 1:7000 (♦) and 1:9000 (▲) for Gr1 (**1**).

An increase of the precatalyst load from 1:7000 to 1:9000 resulted in only slight differences for the Gr1 (**1**) metathesis reactions. The reaction rate, TON (1924 to 1380), PMP (7.8 mol%) and SMP formation (0.4 mol%) decreased with the increase in precatalyst load.

This is the result of less catalyst available in the reaction mixture to initiate the 1-hexene conversion to PMPs. For the decrease in the SMP formation the selectivity of the 1:9000 precatalyst load reactions were slightly increased.

The difference between the precatalyst loads obtained for the metathesis reactions of 1-hexene with Gr2 (2) at 60°C is shown in **Figure 4.8**.

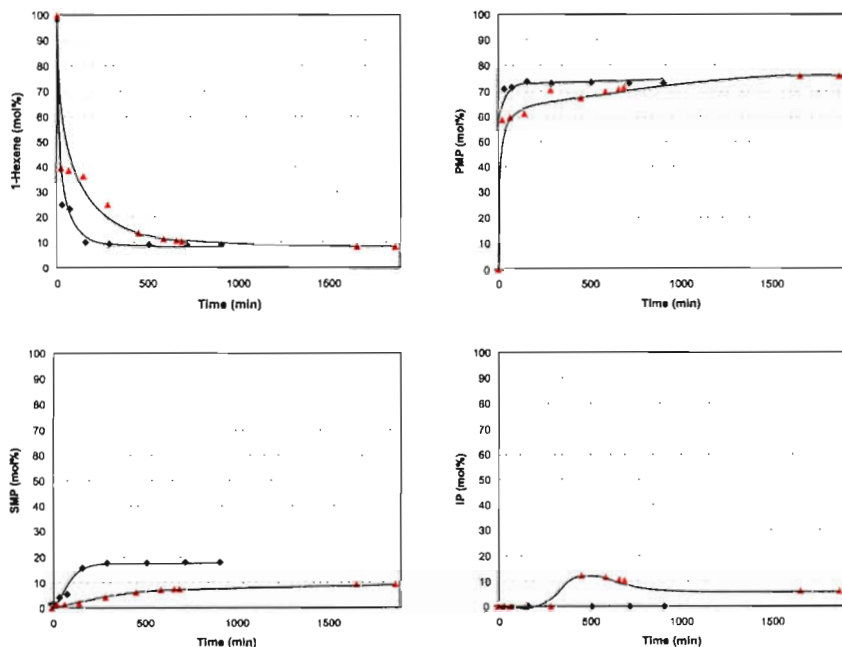


Figure 4.8: The PMP, SMP and IP formation from 1-hexene with precatalyst loads of 1:7000 (♦) and 1:9000 (▲) for Gr2 (2).

As the precatalyst load was increased, a slight increase was observed in the TON (5113 to 5351), selectivity (80.3% to 83.3%), PMP formation (73 mol% to 76.4 mol%) and IP formation (0 mol% to 5.9 mol%). The increase in the selectivity of the precatalyst towards the PMP formation resulted in the decrease of SMP formation (8.5 mol%) during the 1:9000 reactions. The PMP formation for the 1:7000 reactions occurred at a faster rate than for the 1:9000 reactions due to the larger amount of precatalyst available in the 1:7000 reaction mixtures.

4. Results and discussion

The increase observed in the IP formation for the 1:9000 reactions can be attributed to the fact that there is less catalyst present in the reaction mixture to convert into the SMPs when compared to the 1:7000 reactions. This is the reason for the 0 mol% IPs during the 1:7000 reactions with the elevated SMP formation.

The metathesis reactions of 1-hexene with Gr2Ph (**3**) at 60°C with a variation in Ru:1-hexene ratios are shown in Figure 4.9.

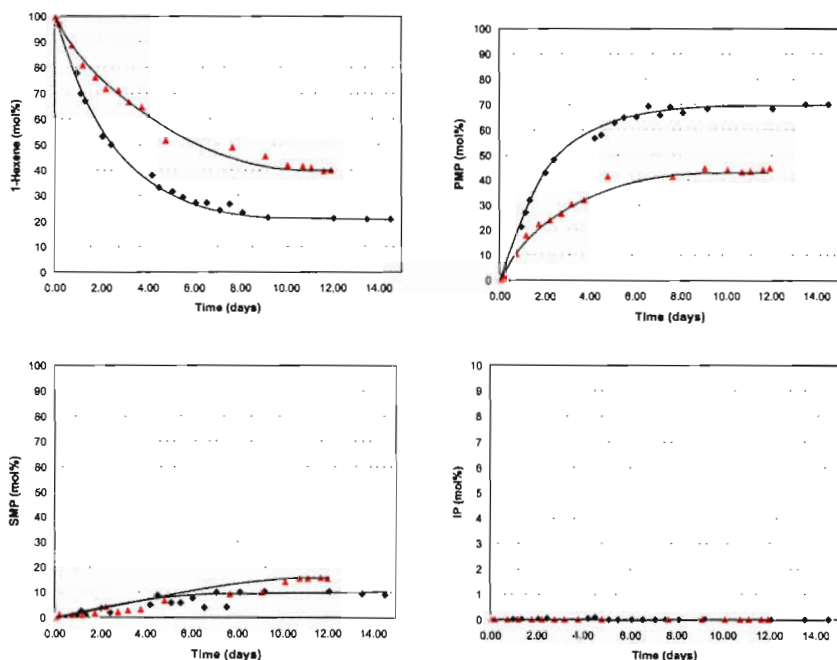


Figure 4.9: The PMP, SMP and IP formation from 1-hexene with precatalyst loads of 1:7000 (♦) and 1:9000 (▲) for Gr2Ph (**3**).

As the precatalyst load increased, less of the Gr2Ph (**3**) was present in the reaction mixture for the 1:9000 ratio reaction. The reaction rate for the 1:7000 precatalyst load reactions was higher and the equilibrium for the reaction started to take place after nine days. For the 1:9000 precatalyst load reaction, the start of equilibrium for the reaction was observed after eleven days and increasing amounts of competing isomerization reactions occurred, thus forming more SMPs. The decrease in reaction rate resulted in a decrease of TON, whilst the increase in SMP formation resulted in the decrease of selectivity towards the PMP formation.

4.3.3.4 Pre-treatment of Gr1 metathesis reactions

In the improved metathesis reactions of Gr1 (1) with 1-hexene, the precatalyst was heated at 60°C for 10 min as a pre-treatment step, where after the 1-hexene and nonane was added. 1-Hexene reactions with Gr1 (1) at 60°C with a precatalyst load of 1:7000 (Ru:alkene) showed an increase in PMP formation (**Figure 4.10**) after the pre-treatment of the precatalyst. This result was also observed by Roscher⁶ when using 1-octene with a precatalyst load of 1:9000 (Ru:alkene) and a 10 min pre-treatment period at 60°C. Reactions 1 to 3 were pre-treated, while reaction 4 was a neat metathesis reaction of 1-hexene with Gr1 (1).

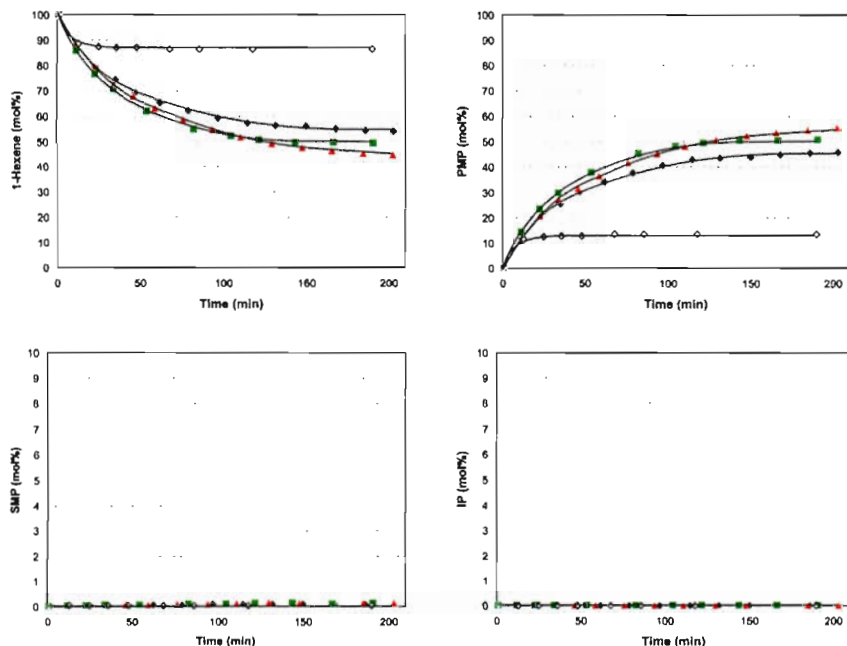


Figure 4.10: The PMP, SMP and IP formation for different Gr1 (1) metathesis reactions: 1 (♦), 2 (▲), 3 (■) and 4 (◇).

After the pre-treatment of the precatalyst (reactions 1 to 3) the PMP formation, lifetime, TON and reaction rate increased significantly when compared to reaction 4. A slight increase of selectivity resulted in an insignificant decrease of SMP formation. The heating process of the precatalyst, before the metathesis reaction commences, can be described as an activation of the precatalyst, therefore a preliminary investigation was done on the pre-treated Gr1 (1).

4. Results and discussion

This effect can also be seen when the results of **Figure 4.3** and **Figure 4.4** are compared. The result of the 60°C metathesis reaction in **Figure 4.4** has a higher PMP formation and this was the result of pre-treatment with heat. This pre-treatment time is shorter than 10 minutes and this is the reason for a lower PMP formation when compared to the results from **Figure 4.10**.

The pre-treatment of Gr1 (1) with heat resulted in an improvement of product formation and was also studied under ESEM-EDS to determine differences in the crystal structures. Other analytical techniques (IR, TGA and DSC) were used to verify any possible differences that might have occurred during the pre-treatment (**Appendix B**).

The ESEM and EDS of Gr1 (1) was done after it was pre-treated with heat and then compared to a non-treated sample in **Figure 4.11** and **Table 4.4**.



Figure 4.11: ESEM of Gr1 (1) after different pre-treatment conditions.

E was not submitted to any pre-treatment, but F was heated for 40 min at 60°C. The reason for the pre-treatment was due to the differences in the activity and lifetime of the metathesis reactions of Gr1 (1). From **Figure 4.11** it is evident that there is no significant difference in the crystalline morphology after the precatalyst had been pre-treated.

In **Table 4.6** the EDS results for the pre-heated precatalyst are given for different heat treatment periods. No hydrogen atoms were taken into account.

Table 4.6: The semi-quantitative elemental analysis of Gr1 (1) under different conditions.

Time (minutes)	C (%)	P (%)	Cl (%)	Ru (%)
0	90.11	3.61	4.40	1.88
5	92.55	3.00	3.03	1.43
10	92.57	3.02	3.05	1.36
20	91.56	3.38	3.43	1.64
40	91.96	3.12	3.43	1.50

From **Table 4.6** it is clear that the period of heat treatment had no significant influence on the atomic composition of the precatalyst. From the DSC no exothermic or endothermic processes were observed before the decomposition point that was observed at 206°C for the precatalyst (**Appendix B**). The TGA results showed no indication of any mass loss at around 60°C but the first mass decrease was observed at 208°C (**Appendix B**). From the IR-spectra no differences were observed, thus indicating that no noticeable change took place during the pre-treatment of Gr1 (1) (**Appendix B**).

These observations led to the conclusion that no activation of the precatalyst took place due to the fact that the PCy₃-group was still coordinated onto the Ru-metal. In § 2.5, Scheme 2.15 the activation of the precatalyst (1 to 11) is demonstrated.

4.3.3.5 Summary of 1-hexene metathesis reactions

In **Table 4.7** the effect of the three precatalysts under different reaction conditions are compared in terms of the selectivity (S), activity, k_{initial} and TON. The k_{initial} values were determined from the initial slope of the PMP formation reaction curves. The same procedure was used for the determination of the k_{initial} values for all the other metathesis reactions. The PMP, SMP, IP, S and TON values given in **Table 4.7** are based on the last values obtained during the reactions.

4. Results and discussion

Table 4.7: Comparison between the different precatalysts for 1-hexene metathesis reactions.

Precatalyst	T (°C)	Ru: Alkene ratio	PMP (mol %)	SMP (mol %)	IP (mol %)	%S ^a	TON	k _{initial} (mol.s ⁻¹)
Gr1 (1)	55	1:7000	16	0	0	100	1123	3.58 (±0.22) x 10 ⁻⁴
Gr2 (2)		1:7000	67.5	19.6	0	77.5	4727	3.82 (±0.24) x 10 ⁻⁴
Gr2Ph (3)		1:7000	66.9	17.5	0	79.2	4683	5.23 (±0.52) x 10 ⁻⁶
Gr1 (1)	60	1:7000	27.5	0.5	0	98.4	1924	6.17 (±0.41) x 10 ⁻⁴
		1:7000*	45.8	0.1	0	99.8	3206	6.15 (±0.76) x 10 ⁻⁴
		1:7000*	55.3	0.1	0	99.8	3873	6.22 (±0.44) x 10 ⁻⁴
		1:7000*	51.4	0.1	0	99.8	3600	8.55 (±0.83) x 10 ⁻⁴
Gr2 (2)		1:7000	73.0	17.9	0	80.3	5113	1.50 (±0.17) x 10 ⁻³
Gr2Ph (3)		1:7000	70.4	10.4	0	87.1	4926	1.22 (±0.45) x 10 ⁻⁵
Gr1 (1)		1:9000	19.7	0.1	0	99.8	1380	5.24 (±0.59) x 10 ⁻⁴
Gr2 (2)		1:9000	76.4	9.4	5.94	83.3	5351	1.09 (±0.18) x 10 ⁻³
Gr2Ph (3)		1:9000	44.5	15.5	0	74.1	3117	5.63 (±0.48) x 10 ⁻⁶

^a Selectivity calculated towards the PMPs.

* Gr1 (1) reactions with improved results.

When comparing the results of the three different precatalysts at 55°C, Gr2 (2) indicated the best PMP formation, the highest reaction rate and TON. The selectivity for the Gr1 (1) reactions were, however, the best, although in the rest of the categories its performance reflected to be poorly when compared to the other two precatalysts used. This supports the fact that the incorporation of a NHC-ligand improved the activity and stability of the precatalyst.⁷

The selectivity and PMP formation of Gr2Ph (3) and Gr2 (2) were almost the same, but the reaction rate was significantly lower for the Gr2Ph (3) than for the Gr2 (2) reaction. For these conditions (55°C, 1:7000 precatalyst load) with 1-hexene the precatalyst with the best performance, in terms of TON, k_{initial} and PMP formation, is Gr2 (2).

As discussed in §4.3.3.2, the increase in the reaction temperature resulted in an increase of reaction rates, TON and PMP formation. These trends were observed because of the increasing collisions between the molecules at higher temperatures. The SMP formation for Gr1 (1) and Gr2 (2) also increased with the temperature increase.

When the results of the other metathesis reactions at 60°C were compared with the results of the improved Gr1 (1) reactions, the selectivity of the Improved Gr1 (1) was the highest. The TON of the pre-treated Gr1 (1) showed an increase when compared to the Gr1 (1) reactions without the pre-treatment, but remains lower than the Gr2 (2) and Gr2Ph (3) reactions.

The different Ru:1-alkene ratios are discussed in §4.3.3.3 for the separate precatalysts. The same trends were observed for the different precatalysts. When the molar ratio was increased, the concentration of the catalyst decreased in the reaction mixture, resulting in lower activity. The variation of the precatalyst loading (1:7000 and 1:9000) showed no significant changes in the reaction rates, TON and selectivity of the Gr1 (1) metathesis reactions, but for the Gr2Ph (3) reactions the selectivity, TON, reaction rate and PMP formation decreased significantly. The selectivity, TON and PMP formation for the Gr1 (1) and Gr2Ph (3) reactions decreased, but for the Gr2 (2) reactions an increase was observed.

During a metathesis study of 1-hexene at 60°C with a Grubbs 2 type precatalyst, a PMP formation of 54.1 mol%, IP formation of 34.7 mol% and SMP formation of 12.1 mol% was observed. The Ru:1-hexene ratio used was 1:1000.⁸ In terms of the PMP formation, these results are not as good as the Gr2 (2) and Gr2Ph (3) used during this study. It seems that a decrease in the Ru:1-hexene ratio of the precatalyst increases the isomerization reactions and thus result in a decrease of the selectivity of the precatalyst. The same observation can be made when comparing the results of the Gr2 (2) results of different precatalyst ratios at a constant temperature.

A study regarding the variation of the Ru:1-alkene ratio with 1-octene at 25°C with Gr1 (1) revealed an increase in PMP formation with an increase of Ru present in the reaction mixture.³ The SMPs however also increased for these Gr1 (1) metathesis reactions. The observation was not made for the Gr2 (2), which led to the conclusion that 1:9000 is the optimum ratio for the Gr2 (2) metathesis reactions at 60°C.

4.3.4 1-Heptene metathesis reactions

4.3.4.1 Introduction

During the metathesis reactions of 1-heptene the concentration of the 1-alkene decreased while the PMPs, SMPs and IPs increase. The product formation was monitored by GC analysis. The PMPs formed during the metathesis reactions were found to be ethylene (C_2) and 6-dodecene (C_{12}) while the SMPs formed during these reactions are given in **Appendix A (Scheme A.3)**.

The precatalysts were tested at three different temperatures (60°C, 70°C and 80°C) and two precatalyst loads (1:7000 and 1:9000). The comparison between different precatalysts at constant experimental conditions are discussed in §4.3.4.2 to §4.3.4.3.

4.3.4.2 Effect of temperature on the metathesis reactions

The difference between the metathesis reactions of 1-heptene with the precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)) are shown in **Figure 4.12** to **Figure 4.14**. The results obtained for the reactions with Gr1 (1) at 60°C, 70°C and 80°C are illustrated in **Figure 4.12**.

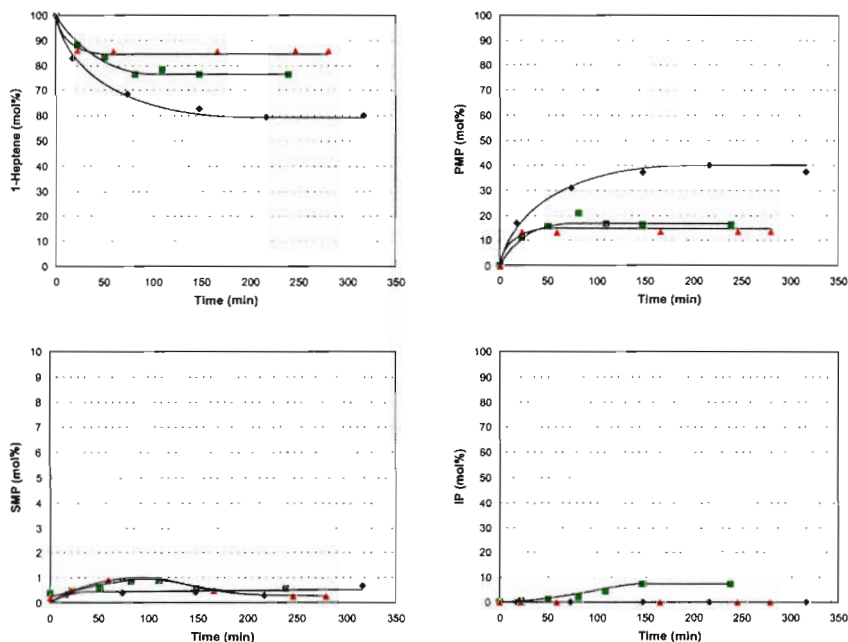


Figure 4.12: The PMP, SMP and IP formation from 1-heptene at temperatures of 60°C (♦), 70°C (▲) and 80°C (■) with Gr1 (1).

For an increase in the reaction temperature a lower activity and lifetime of the precatalyst was observed in **Figure 4.12**. The equilibrium was reached in 23 min for the 80°C metathesis reactions, but it took the 60°C reaction 217 min to reach equilibrium. At 70°C the reaction reached a maximum PMP formation of 13.3 mol% after 23 min. A decrease in the reaction rate was observed after 23 min for the PMP formation, which resulted in an additional 0.5 mol% PMP formation after 258 min. At higher temperatures the lifetime of the precatalyst was shorter due to the fact that Gr1 (1) decomposed faster at higher temperatures (>50°C).⁹ Competing metathesis reactions, such as isomerization, were also observed with an increase in reaction temperatures.

The increasing isomerization reactions resulted in a 7 mol% increase in IP formation, which then resulted in an increase of SMP formation at 80°C. Furthermore an increase in the by-products resulted in the decrease of the selectivity of the reaction towards PMP formation.

4. Results and discussion

The results obtained for the metathesis reactions of 1-heptene with Gr2 (**2**) at different temperatures are shown in Figure 4.13.

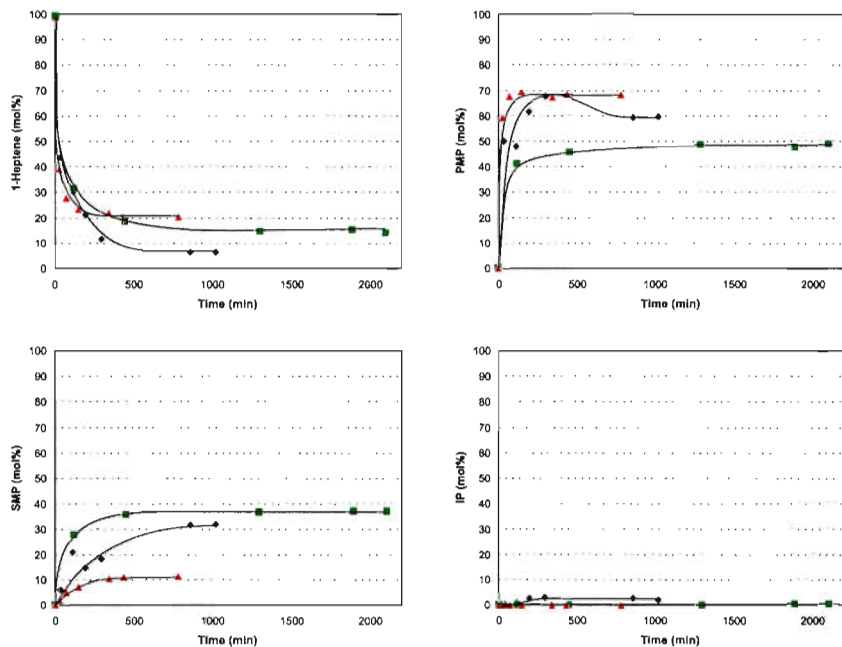
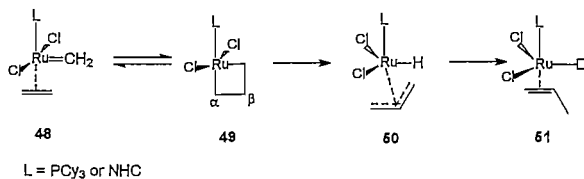


Figure 4.13: The PMP, SMP and IP formation at temperatures of 60°C (♦), 70°C (▲) and 80°C (■) with Gr2 (**2**).

In general a temperature increase resulted in an increase of the reaction rate, PMP formation, TON and selectivity. A significant increase of PMP formation towards 70°C of 21.5 mol% was observed, but only a slight increase was observed at 80°C (2.1 mol%). The highest PMP value for the 60°C reaction was obtained at 294 min (67.3 mol%), where after the PMPs decreased significantly with 20.5 mol% to 46.8 mol%. The sudden decrease in PMPs resulted in an increase in SMP and IP formation of 18.2 mol% and 2.6 mol% respectively. This observation can be attributed to the high initial reaction rate, which results in high levels of ethylene being formed. The reactors used are closed systems and ethylene build-up was possible. According to Janse van Rensburg *et al.*,¹⁰ the ethylene coordinates to the Ru-metal carbene, which results in the formation of hydride species (Scheme 4.1 (50)).



Scheme 4.1: The evaluated decomposition mechanism for the methyldiene specie.¹⁰

The active species (**48** and **49**) are lost and the formation of the inactive metathesis species (**51**) takes place. This 14 electron species (**51**) has two coordination sites on the Ru and could follow different decomposition pathways.¹⁰

These hydride species (**50**) causes isomerization products to form through a hydride decomposition mechanism (**Scheme 4.1**). The decrease in IPs at 70°C resulted in the significant decrease in SMP formation and an increase in the selectivity towards the formation of PMPs.

An increase in PMP formation showed that more products were formed for every molecule of precatalyst present in the reaction mixture, resulting in an increase of TON. The SMP formation at 80°C was the highest and is attributed to the decomposition of the precatalyst at high temperatures.² This leads to an increase in isomerization reactions and prevents high PMP formation. The metathesis reaction conducted at 70°C showed the highest PMP formation and selectivity, thus being the optimum temperature for the Gr2 (**2**) reactions with a precatalyst load of 1:7000.

The results obtained for the metathesis reactions of 1-heptene with Gr2Ph (**3**) at different temperatures are shown in **Figure 4.14**.

4. Results and discussion

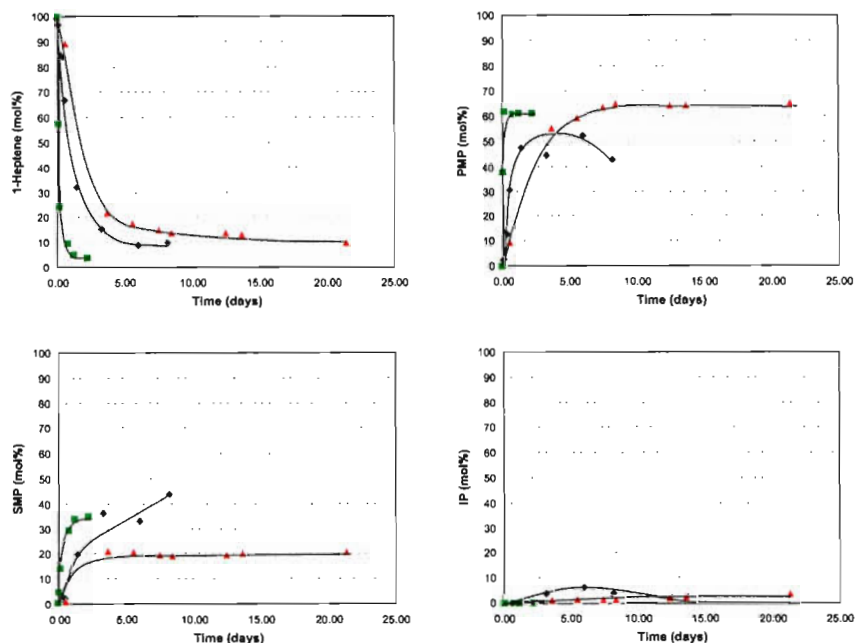


Figure 4.14: The PMP, SMP and IP formation from 1-heptene at temperatures of 60°C (♦), 70°C (▲) and 80°C (■) with Gr2Ph (3).

The temperature increase of the metathesis reactions resulted in a significant increase in PMP formation at 70°C and a slight increase at 80°C of 24.2 mol% and 4.4 mol%, respectively, when compared to the PMPs formed at 60°C. A selectivity increase of 25.7% and 11%, respectively, was observed for the metathesis reactions at 70°C and 80°C. The TON of the different reactions showed an increase of 1424 and 308, whereas the formation of SMPs decreased. The initial reaction rate of the metathesis reaction at 80°C was the highest ($4.56 \times 10^{-4} \text{ mol.s}^{-1}$), where the maximum PMP formation was obtained within 3 days (61.5 mol%). Although the reaction reached equilibrium earlier than the other two reactions, more SMPs (34.9 mol%) were formed which in turn reduced the selectivity of the reaction.

No isomerization products were observed for the metathesis reactions conducted at 80°C. Only an increase of SMP formation occurred, which was the result of the IPs being converted by cross- and self metathesis. The reason for this observation is attributed to the rapid conversion of the IPs to SMPs. The metathesis reaction at 70°C obtained high amounts of PMPs with a high selectivity, lifetime and small amounts of SMPs.

The reactions conducted at 70°C were observed to be the optimum conditions for the reaction. For the metathesis reaction at 60°C, it was observed that PMP formation increased up to 52.2 mol% and then decreased to 42.8 mol%. This observation was the result of the ethylene formation in the reactor. The ethylene coordinates to the catalyst, forming hydride species that increased isomerization reactions (Figure 4.14).¹⁰ The effect of the occurring isomerization reactions can be observed through the increase in IP and SMP formations.

4.3.4.3 Effect of precatalyst load on the metathesis reactions

The effect of the Ru:1-heptene ratio variation on the metathesis reactions was investigated at 60°C for Gr1 (1), Gr2 (2) and Gr2Ph (3). The precatalyst ratios used for the study were 1:7000 and 1:9000 (Ru:1-heptene), which are presented in Figure 4.15 to Figure 4.17. The metathesis reactions of Gr1 (1) with 1-heptene at these precatalyst loads are shown in Figure 4.15.

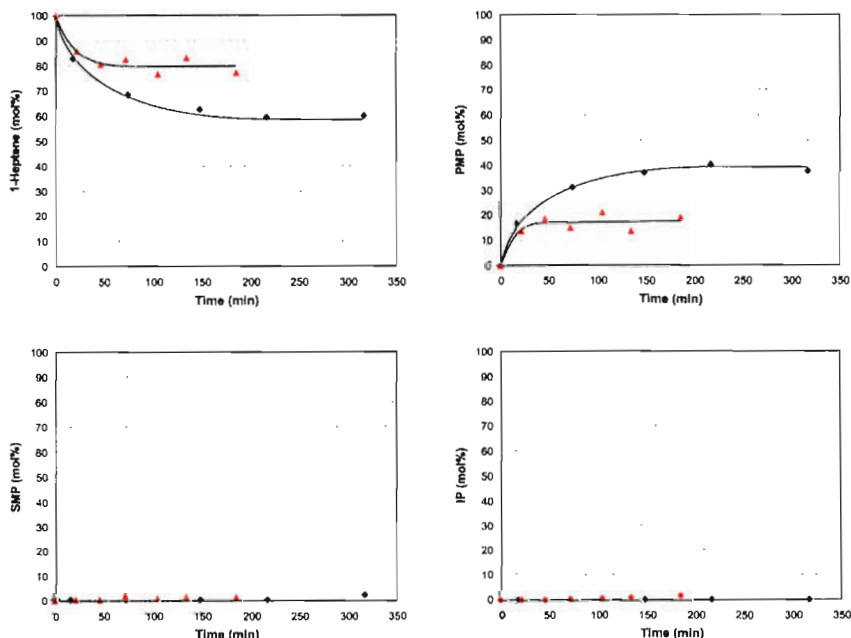


Figure 4.15: The PMP, SMP and IP formation from 1-heptene at precatalyst loads of 1:7000 (♦) and 1:9000 (▲) with Gr1 (1).

4. Results and discussion

Differences in the PMP formations were observed during the variation of the precatalyst loads for the metathesis reactions of Gr1 (1). The PMP formation decreased due to the fact that less precatalyst was available in the reaction mixture to be able to react with the 1-heptene. The decrease in precatalyst concentration also resulted in a decrease of the initial reaction rate (6.37×10^{-4} to 2.98×10^{-4} mol.s⁻¹) and TON (2631 to 1370) of the metathesis reactions. The IP formation increased but did not have any effect on the SMP formation. The reason for this observation can be that most of the precatalyst decomposed before the cross- and self metathesis reaction could convert the IPs to form SMPs or that the precatalyst was only selective towards PMP formation at these reaction conditions.

The metathesis reactions of Gr2 (2) with 1-heptene for different precatalyst loads at 60°C are shown in **Figure 4.16**.

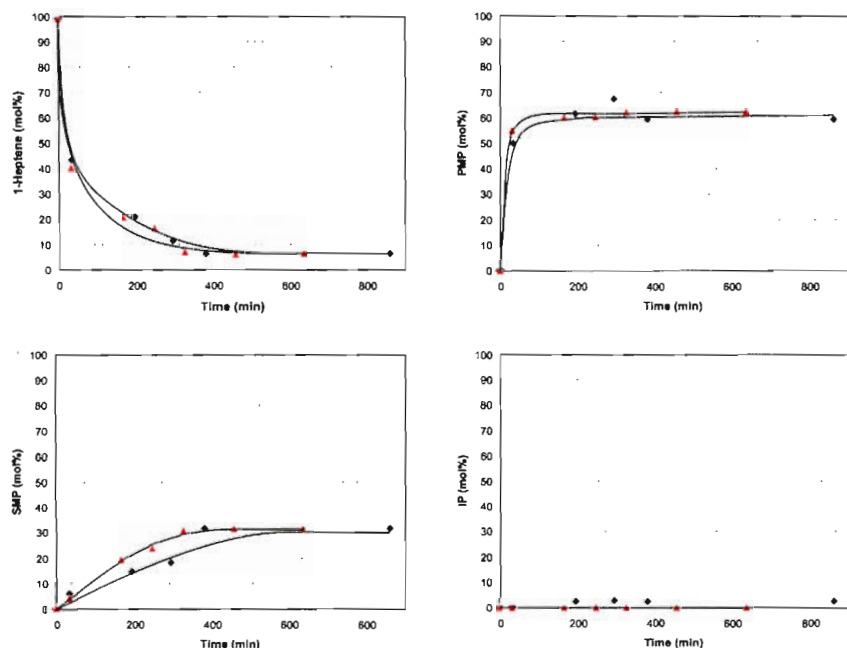


Figure 4.16: The PMP, SMP and IP formation from 1-heptene at precatalyst loads of 1:7000 (♦) and 1:9000 (▲) for Gr2 (2).

A slight decrease in the reaction rate (1.09×10^{-3} to 8.73×10^{-4} mol.s⁻¹) and IP formation (5.46% decrease) was observed when the amount of precatalyst, for the metathesis reactions with 1-heptene were decreased from 1:7000 to 1:9000. The decrease in IP formation resulted in the decrease of SMP formation due to the lower concentration of IPs that could be converted to the SMPs during cross- and self metathesis reactions. The selectivity of Gr2 (2) at a precatalyst load of 1:9000 showed an increase when less SMPs are formed and the competing reactions decrease to form higher amounts of PMPs.

The metathesis reactions of Gr2Ph (3) with 1-heptene for different precatalyst loads at 60°C are shown in **Figure 4.17**.

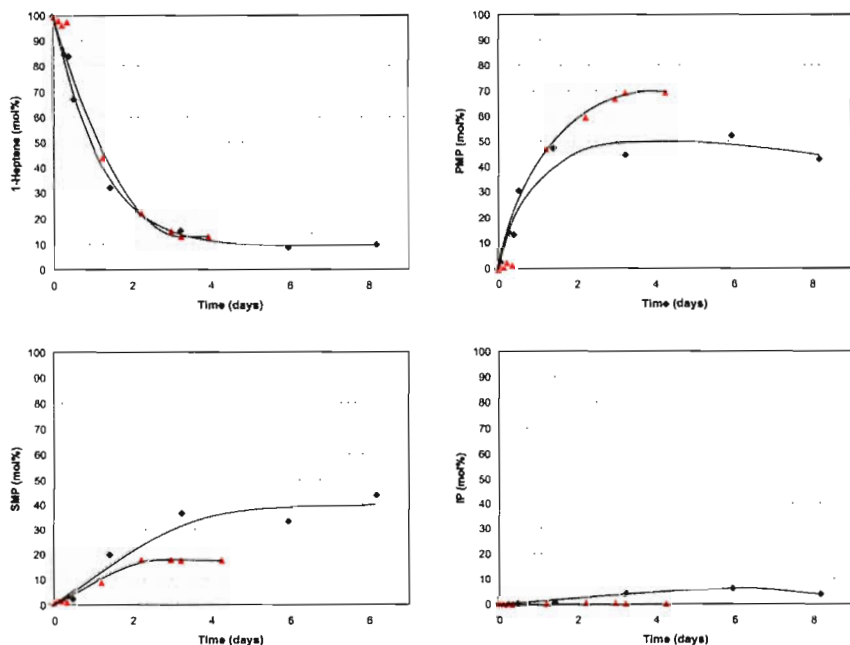


Figure 4.17: The PMP, SMP and IP formation from 1-heptene at precatalyst loads of 1:7000 (♦) and 1:9000 (▲) for Gr2Ph (3).

An increase of 25.3 mol% for PMP formation, 33.6% for selectivity and 1769 for TON was observed at a precatalyst load of 1:9000. The reaction rate, SMP and IP formation decreased for these metathesis reactions with 0.8×10^{-5} mol.s⁻¹, 30.4 mol% and 3.7 mol% respectively.

4. Results and discussion

The TON of the reaction increased while there was less catalyst present in the reaction mixture to convert the 1-heptene to PMPs. This means that more 1-heptene molecules were converted to products per precatalyst and that this conversion to products took longer because of the lower concentration of precatalyst, resulting in the lower reaction rate of the metathesis reactions.

The decrease in IP formation resulted in a decrease in SMP formation, which in turn led to an increase in selectivity towards the PMP formation of the metathesis reaction with a precatalyst load of 1:9000. During the metathesis reaction with a 1:7000 precatalyst ratio, a similar trend was observed for the reaction at 60°C as shown in **Figure 4.13**, indicating that the decomposition effect, due to the ethylene accumulation, was prominent for the Gr2-type precatalysts used in this study for 1-heptene metathesis.

4.3.4.4 Summary of 1-heptene metathesis reactions

In **Table 4.8** the three precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)) are compared in terms of the selectivity (S), TON, $K_{initial}$ and product formations under different reaction conditions.

Table 4.8: Comparisons between the different precatalysts for 1-heptene metathesis reactions.

Precatalyst	T (°C)	Ru: Alkene ratio	PMP (mol %)	SMP (mol %)	IP (mol %)	%S ^a	TON	k _{initial} (mol.s ⁻¹)
Gr1 (1)	60	1:7000	37.6	2.2	0	94.5	2631	6.37 (±1.63) × 10 ⁻⁴
Gr2 (2)		1:7000	46.8	36.5	5.46	52.7	3278	1.09 (±0.14) × 10 ⁻³
Gr2Ph (3)		1:7000	44.1	47.7	4.2	46.0	3089	2.23 (±0.34) × 10 ⁻⁵
Gr1 (1)		1:9000	19.6	1.3	1.8	86.3	1370	2.98 (±0.63) × 10 ⁻⁴
Gr2 (2)		1:9000	57.8	35.6	0	61.9	4044	8.73 (±1.13) × 10 ⁻⁴
Gr2Ph (3)		1:9000	69.4	17.3	0.5	79.6	4858	1.43 (±0.82) × 10 ⁻⁵
Gr1 (1)	70	1:7000	13.8	0.3	0	98.2	966	3.74 (±0.73) × 10 ⁻⁴
Gr2 (2)		1:7000	68.3	11.3	0	85.8	4783	1.40 (±0.21) × 10 ⁻³
Gr2Ph (3)		1:7000	64.5	20.5	4.9	71.7	4513	2.38 (±0.12) × 10 ⁻⁵
Gr1 (1)	80	1:7000	16.1	0.5	7.0	68.1	1129	3.23 (±0.52) × 10 ⁻⁴
Gr2 (2)		1:7000	48.9	37.1	0	56.8	3420	3.69 (±0.12) × 10 ⁻⁴
Gr2Ph (3)		1:7000	48.5	36.5	0	57.0	3397	4.56 (±0.36) × 10 ⁻⁴

^a Selectivity calculated towards the PMPs.

The increase in temperatures from 60°C to 70°C for the metathesis reactions, resulted in an increase of PMP formation for Gr2 (2) and Gr2Ph (3), but the opposite was observed for the Gr1 (1) reactions. This observation can be explained by the fact that Gr1 (1) decomposes at the higher temperatures and that the other two precatalysts are more tolerant towards the higher temperature.⁹ In general the reaction rates for the Gr2 (2) reactions were higher than those of the other two precatalysts under the stated reaction conditions. The observation between the reaction rates of Gr1 (1) and Gr2 (2) metathesis reactions were made by Jordaan.² The exception was the metathesis reaction with Gr2Ph (3) at 80°C, where the reaction rate was the highest of the three precatalysts.

4. Results and discussion

This observation can be due to the higher available energy because of the higher temperature, resulting in an easier dissociation of the hemilabile ligand to create an open coordination site for 1-heptene to coordinate to the Ru-metal centre. These reaction conditions (a precatalyst load of 1:7000 at 80°C) were found to be the optimum conditions for the metathesis reactions of 1-heptene with Gr2Ph (3).

For the metathesis reactions at 60°C with Gr2 (2) and Gr2Ph (3), the lower temperatures showed an increase in the IP formation which led to an increase in SMP formation and a decrease in selectivity towards the PMP formation. At higher temperatures (80°C to 150°C) Gr2 (2) decomposes to a hydride specie (50) and the efficiency of the catalyst decreases.¹¹ The decomposition resulted in an increase in IP and SMP formation due to the isomerization reactions for the metathesis reactions of 1-alkenes with Ru-based precatalysts.

With an increase of the Ru:alkene ratio, the precatalyst concentration in the reaction mixture decreased, leading to a decrease in catalyst and substrate contact, which in turn led to a decrease in activity of the reaction. The opposite was observed for the Gr2 (2) and Gr2Ph (3) precatalysts. The explanation for this observation could be that the precatalyst load of 1:9000 is the optimum ratio for these metathesis reactions. The optimum conditions resulted in an increase in selectivity, TON and PMP formation, whilst the SMP and IP formation decreased.

The decomposition reactions, due to the occurrence of ethylene accumulation in the reactor, had the largest impact on the metathesis reactions of 1-heptene with precatalysts Gr2 (2) and Gr2Ph (3) at 60°C. As previously stated the ethylene reacts with the metal carbenes, which then results in the formation of hydride species and the decomposition of the precatalysts.¹⁰ This observation was not made for the Gr1 (1) reactions due to the slower reaction rates. The reason for this observation was that the reactions conducted with precatalysts (Gr2 (2) and Gr2Ph (3)) resulted in higher PMP formations than for the Gr1 (1) metathesis reactions, which resulted in higher levels of ethylene formation within a closed system.

4.3.5 1-Nonene metathesis reactions

4.3.5.1 Introduction

During the metathesis reactions of 1-nonene the concentration of the 1-alkene decreased while the PMPs, SMPs and IPs increased. The product formation was monitored by GC analysis. The PMPs formed during the metathesis reactions were found to be ethylene (C₂) and 8-hexadecene (C₁₆), while the SMPs formed during the reactions were hydrocarbons of C₃ to C₁₈ as shown in Appendix A (Scheme A.4).

The metathesis reactions were only conducted at one temperature, namely 60°C, due to substrate availability. The comparison between different precatalysts at constant experimental conditions is discussed in §4.3.5.2. 1-Nonene was used as received until the results of the first reactions with Gr1 (1) were obtained, thereafter the 1-nonene was purified. The 1-nonene was purified by filtering it through an alumina column under N₂ to remove the 1-hexanol before using it for the metathesis reactions. The alumina was dried at 600°C overnight prior to use.

4.3.5.2 Reactions at 60°C and 1:7000 precatalyst load

The metathesis reactions were initially performed without the purification of the 1-nonene, which led to the observation that no significant products were obtained for reactions with Gr1 (1). In the MSD chromatogram (Figure 4.18) it was indicated that 1-hexanol was the only oxygenated impurity present in the 1-nonene mixture. For the sample injected into the MSD, nonane was used as a solvent. A neat sample of the nonane was tested to determine whether any impurities were present that could influence the product formations, but none were observed.

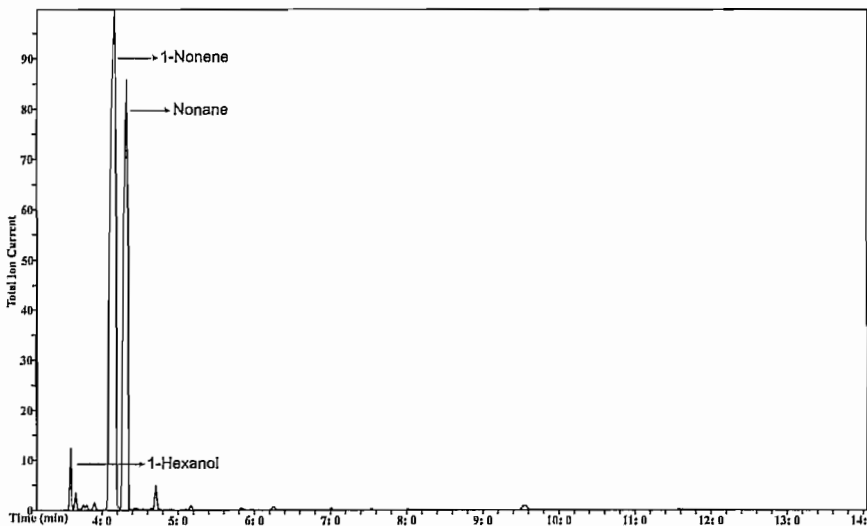


Figure 4.18: An example of a MSD chromatogram of the unpurified 1-nonene prior to use in the metathesis reaction.

The ratio of the peak areas between the 1-hexanol peak and that of the 1-nonene was 0.58% before purification. After purification the ratio decreased to 0.29% of 1-hexanol present in the mixture.

4. Results and discussion

After purification of the 1-nonene, metathesis reactions with Gr1 (1) were performed and a significant amount of product formation was observed (Figure 4.19).

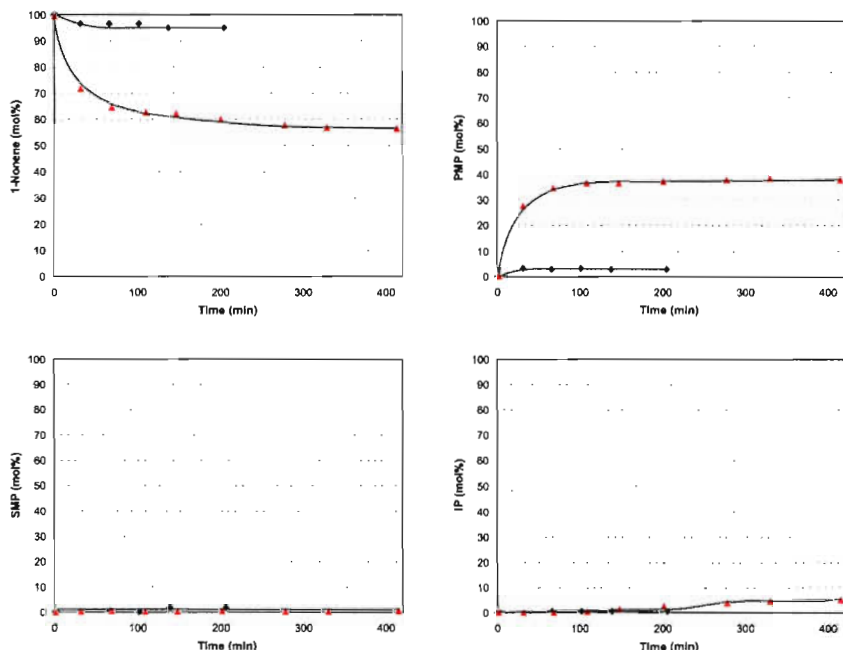


Figure 4.19: The PMP, SMP and IP formation from unpurified (♦) and purified 1-nonene (♦) with Gr1 (1).

A significant difference could be observed between the reactions with the purified and unpurified 1-nonene. After a large amount of 1-hexanol (0.29%) was removed the reaction rate, TON, selectivity, PMP and IP formation increased. Studies conducted on the metathesis reactions of 1-octene with Gr1 (1), Hoveyda-Grubbs first (6) and second (7) generation precatalysts, in the presence of water, ethanol and butanol revealed the effect of solvents on product formation.^{3,4} From these studies it was evident that the presence of solvents such as alcohols impedes product formation. It is believed that these solvents donate a H-ion which can partake in the reaction and deactivate the catalyst by means of hydrolysis.³

The results obtained for the metathesis reactions of purified 1-nonene with Gr2 (2) at 60°C, are shown in **Figure 4.20**.

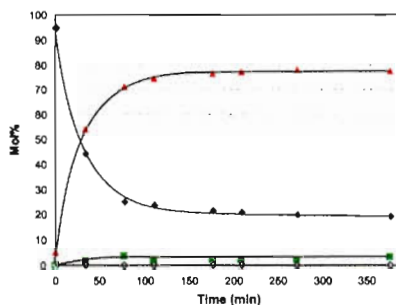


Figure 4.20: The PMP, SMP and IP formation during the metathesis reaction of purified 1-nonene for Gr2 (2). 1-Nonene (♦), PMP (▲), SMP (■) and IP (◇).

During the metathesis reaction of 1-nonene with Gr2 (2), a significant amount of PMPs (78.3 mol%) were formed within 273 min before the reaction equilibrium was reached. This indicated a high reaction rate due to the high product formation within a short time. The self metathesis reaction of 1-nonene was found to be the preferred reaction, due to the low IP and SMP (<5 mol%) formations and the high PMP formation. The efficiency of the catalyst at the stated reaction conditions was high, as a high TON (5438) was obtained for the reaction. A decrease of 0.6 mol% in the PMPs was observed while an increase in the SMP formation of 1.24 mol% was observed.

The results obtained for the metathesis reactions of purified 1-nonene with Gr2Ph (3) at 60°C, are shown in **Figure 4.21**.

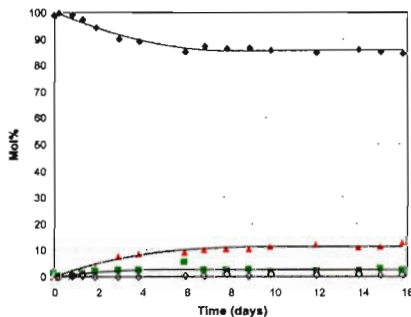


Figure 4.21: The PMP, SMP and IP formation from the purified 1-nonene for Gr2Ph (3). 1-Nonene (♦), PMP (▲), SMP (■) and IP (◇).

4. Results and discussion

During the metathesis reaction of 1-nonene with Gr2Ph (3), only a small amount of PMPs (12.8 mol%) were formed within a 6 day period before the equilibrium of the reaction was reached. This indicated that the reaction rate was extremely slow ($1.28 \times 10^{-6} \text{ mol.s}^{-1}$). The selectivity (81.6 mol%) for the reaction was moderate, with a small amount of SMP and IP formation (2.4 mol% and 0.5 mol%). The efficiency of the precatalyst under the stated reaction conditions was low as indicated by a low TON of 898. The low concentration of 1-hexanol present in the 1-nonene reaction mixture led to the low PMP formation.

4.3.5.3 Summary of 1-nonene metathesis reactions

In Table 4.9 the three precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)) are compared in terms of the selectivity (S), TON, k_{initial} and product formations at 60°C with a precatalyst load of 1:7000 (Ru:1-nonene).

Table 4.9: Comparisons between the different precatalysts for 1-nonene metathesis reactions at 60°C with a 1:7000 Ru:1-nonene ratio.

Precatalyst	PMP (mol %)	SMP (mol %)	IP (mol %)	%S ^a	TON	k_{initial} (mol.s ⁻¹)
Gr1 (1) (unpurified)	3.0	1.5	0.3	62.4	212	$5.50 (\pm 0.63) \times 10^{-5}$
(purified)	37.7	0.7	5.1	86.9	2642	$4.35 (\pm 0.55) \times 10^{-4}$
Gr2 (2)	77.7	3.1	0	96.1	5438	$8.15 (\pm 2.05) \times 10^{-4}$
Gr2Ph (3)	12.8	2.4	0.5	81.6	898	$1.28 (\pm 0.52) \times 10^{-6}$

^a Selectivity calculated towards the PMPs.

After the purification of the 1-alkene, the PMP formations, reaction rates, selectivity and TON of the Gr1 (1) and Gr2 (2) metathesis reactions were significantly higher than for the Gr2Ph (3) precatalyst. When the alcohol concentration within the 1-alkene mixture was decreased, the negative effect was not noticeable when using the Grubbs precatalysts 1 and 2. This can be attributed to the fact that the low concentrations of H⁺-ions formed have no impact on the dissociation of the PCy₃-group; thus having no influence on the decomposition of the catalysts. Dinger and Mol¹² suggested that the Grubbs precatalysts form a hydride when primary alcohols are present during the reaction. These reactions are increased at elevated reaction temperatures. The hemilabile ligand creates the open coordination site more easily towards the lower concentration of 1-hexanol in ratio to the 1-nonene, which increases the decomposition process of the catalyst. No further purifications were attempted due to the limited amount of 1-nonene available.

4.3.6 1-Decene metathesis reactions

4.3.6.1 Introduction

During the metathesis reactions of 1-decene the concentration of the 1-decene decreased while the PMPs, SMPs and IPs increased. The product formation was monitored by GC analysis. The PMPs formed during the metathesis reactions were found to be ethylene (C_2) and 9-octadecene (C_{18}), while the SMPs formed during the reactions were of varying hydrocarbon lengths as given in **Appendix A (Scheme A.5)**. The precatalysts were tested at three different temperatures. The comparison between the different precatalysts at constant experimental conditions is discussed in **§4.3.6.2**. The 1-decene was used as received.

4.3.6.2 Effect of temperature on the metathesis reactions

The influence of reaction temperature (60°C, 80°C and 100°C) on the 1-decene metathesis reactions with the different precatalysts and a precatalyst ratio of 1:7000 (Ru:1-decene) are shown in **Figure 4.22** to **Figure 4.24**. The results obtained for the metathesis reactions of 1-decene with Gr1 (**1**) for a precatalyst load of 1:7000 at different temperatures are shown in **Figure 4.22**.

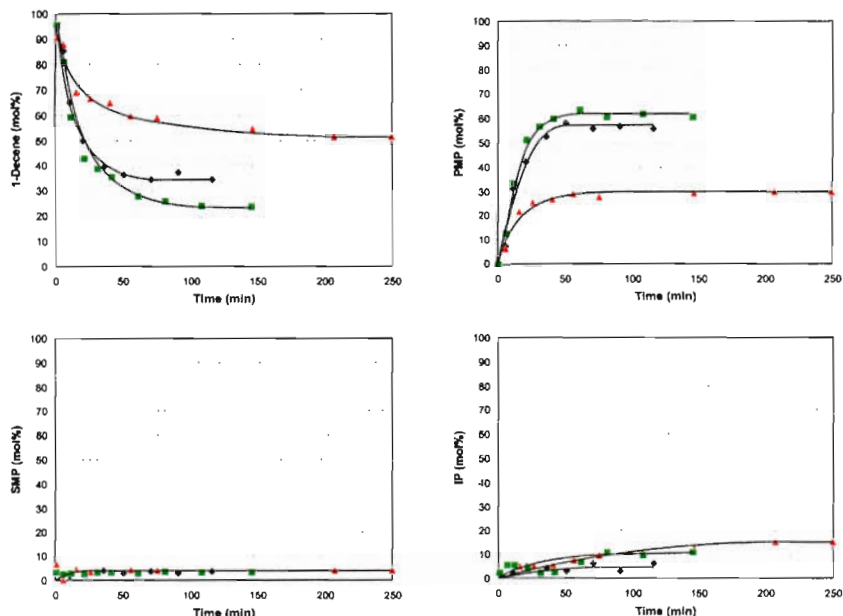


Figure 4.22: The PMP, SMP and IP formation from 1-decene at temperatures of 60°C (♦) 80°C (▲) and 100°C (■) with Gr1 (**1**).

4. Results and discussion

The initial reaction rate was high for the first 20 to 30 min, where after the rate decreased and the maximum PMP product formation was obtained at 120 to 150 min. The trend for the metathesis reaction of Gr1 (1) with 1-decene is comparable to the reaction trend observed at 30°C for the PMP formation of 1-decene reactions as studied by Booysen.¹³ Booysen¹³ observed that the reaction rate decreased after an hour and the maximum PMP formation obtained was 52 mol%. The 30°C reaction was monitored for 5 hours and the reaction only reached equilibrium after 4 hours. The equilibrium for the metathesis reactions conducted at the higher temperatures (60°C, 80°C and 100°C) was reached earlier due to the increase in the activity of the catalyst.

The PMP formation increased for reaction temperatures 60°C and 100°C, but a significant decrease in the SMP (0.7 mol%) formation was observed for the 100°C reaction. This increase in SMP formation resulted in the decrease of the reaction selectivity. The reaction at 80°C was not as successful as the reactions at 60°C and 100°C, but PMP formation of 29.8 mol% was still observed. The competing reaction at 80°C was the isomerization reaction, which led to elevated IP formation of 15.1 mol%.

SMP formation was observed at the 80°C reaction, but it was at the same level as the other temperature reactions (60°C and 100°C). The low SMPs indicate that the cross- and self metathesis reactions at 80°C are slower and thus not the competing factors for the low PMP formation. During the self- and cross metathesis reactions of the IPs, SMPs were formed and this resulted in a low selectivity of the catalyst towards PMPs.

The difference between the PMP formations and reaction rates of the metathesis reactions conducted at 60°C, 80°C and 100°C can be due to pre-treatment as discussed in § 4.3.3.4. The reaction at 60°C had the same improved results as the reactions with 1-hexene in terms of the conversion of alkenes. The IP and SMP formation for the reactions with 1-decene was higher than for the 1-hexene reactions, but this can be attributed to alkene chain lengths. The result obtained at 100°C was also due to the pre-treatment with heat, because it was assumed that the catalyst would decompose and the equilibrium was reached earlier in the reaction. The assumption was made because *Forman et al.*⁹ stated that the catalyst decomposes at temperatures higher than 50°C. The Gr1 (1) metathesis reaction at 80°C was repeated where similar results were obtained.

The optimum conditions for the metathesis reactions with 1-decene and Gr1 (1) were found to be at 100°C. This reaction had the highest PMP formation (60.3 mol%), TON (4218), reaction rate ($1.40 \times 10^{-3} \text{ mol.s}^{-1}$) and a high selectivity (81.4%) with the lowest SMP formation of 3 mol%.

The results obtained for the metathesis reactions of 1-decene with Gr2 (2) for a precatalyst load of 1:7000 at different temperatures are shown in Figure 4.23.

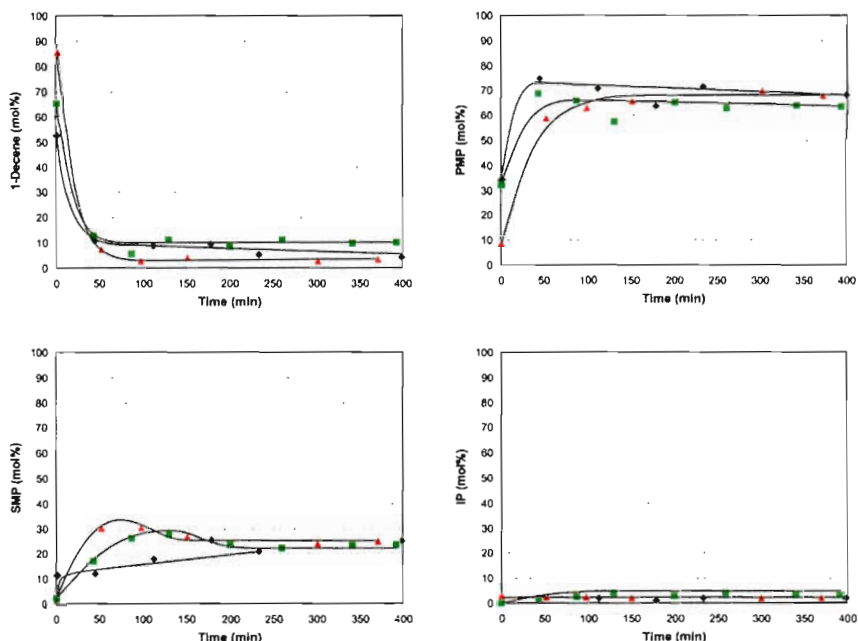


Figure 4.23: The PMP, SMP and IP formation from 1-decene at temperatures of 60°C (♦) 80°C (▲) and 100°C (■) with Gr2 (2).

The increase in reaction temperature resulted in an increase in TON from the 60°C to the 80°C reactions (4648 to 4779), but a decrease in the TON at 100°C (TON of 4421) was observed. The optimum temperature for the PMP formation during metathesis reactions with Gr2 (2) and 1-decene was observed to be 80°C. For the reaction conducted at 80°C the amount of IPs decreased from 3.36 mol% to 2.36 mol% due to cross- and self metathesis reactions, converting the IPs to SMPs. A 23.2 mol% increase was observed for the SMPs. For the metathesis reaction of 1-decene with Gr2 (2) at 80°C, a significant amount of PMPs were formed within 100 min before the reaction equilibrium was reached or decomposition of the precatalyst took place. This indicated a high reaction rate ($6.61 \times 10^{-4} \text{ mol.s}^{-1}$) as indicated by the high product formation within a short period of time. The PMP, SMP and IP formed during each of the metathesis reactions resulted in selectivities of 71.9% (60°C), 71.4% (80°C) and 70.4% (100°C). Therefore 80°C was the optimum temperature for the metathesis reaction. This can be attributed to the fact that the reaction had the highest PMP formation (68.3 mol%), TON (4779) and reaction rate with the lowest IP formation of 2.4 mol%. The selectivity was only a moderate 71.4%.

4. Results and discussion

The results obtained for the metathesis reactions of 1-decene with Gr2Ph (3) for a precatalyst load of 1:7000 at different temperatures are shown in **Figure 4.24**.

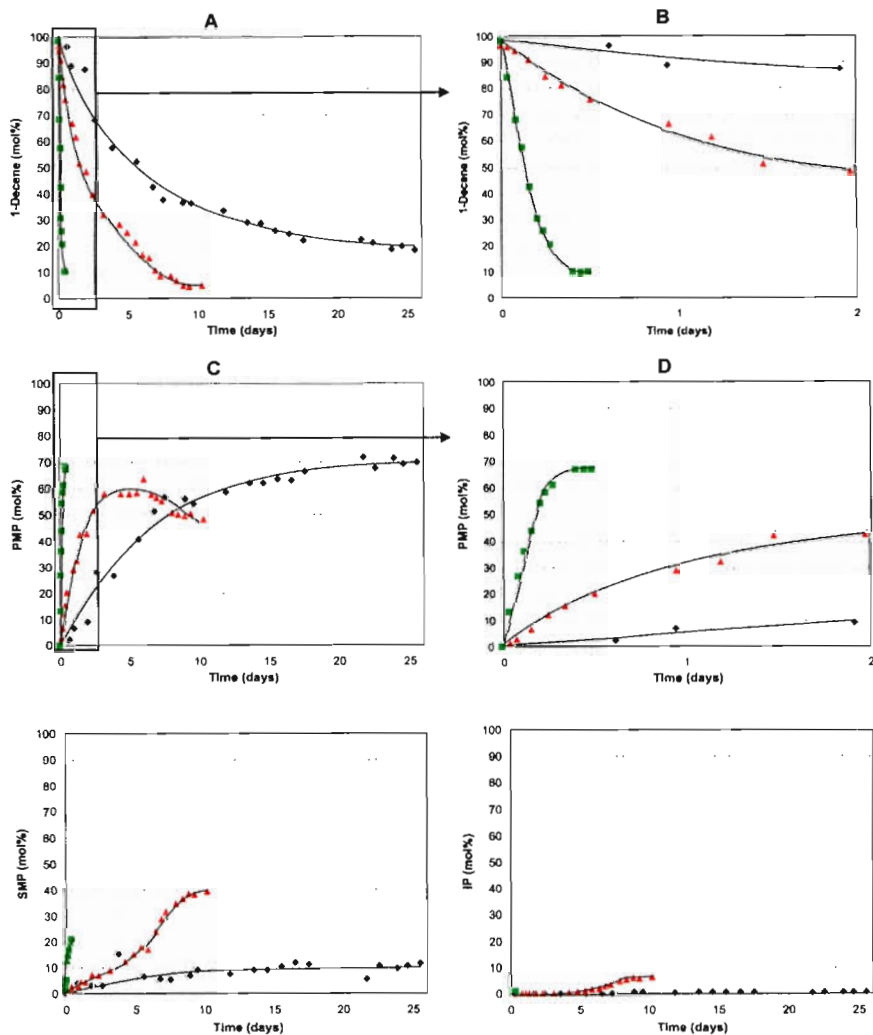


Figure 4.24: The PMP, SMP and IP formation from 1-decene at temperatures of 60°C (♦) 80°C (▲) and 100°C (■) with Gr2Ph (3).

Graph A shows where the 1-alkene conversion was completed for the metathesis reactions at 60°C and 80°C. From Figure 4.24 it appears that the 100°C reaction did not reach completion. In graph B only the first two days of the metathesis reactions are shown to illustrate that the reaction at 100°C did indeed reach equilibrium. The same enlarged illustration for C was given to demonstrate the PMP formation of the 100°C metathesis reaction in D.

The PMP formation for the metathesis reaction of 1-decene with Gr2Ph (3) decreased from 60°C to 80°C with 21.9 mol% and for the 100°C reaction it decreased with 3.2 mol%. The IP formation for the reaction at 80°C increased from the beginning of the reaction from 0.62 mol% to 6.84 mol% and this resulted in the increase of the SMPs during the reaction from 2.54 mol% to 39.6 mol%. The optimum temperature for metathesis reactions with Gr2Ph (3) was 60°C where the highest PMP formation (70.4 mol%), selectivity (85.2%) and TON (4931) occurred. Furthermore at these conditions the lowest SMP (11.7 mol%) and IP (0.6 mol%) formations were observed. Within the first day the metathesis reaction at 100°C produced the maximum PMPs (67.2 mol%) and had the highest reaction rate. The PMP formations of the other temperatures after a day were 6.7 mol% (60°C) and 29.3 mol% (80°C).

The effect of the ethylene, as discussed for the metathesis reactions of 1-heptene, on the PMP formation was observed for the 80°C metathesis reaction of 1-decene with Gr2Ph (3). This was however not observed for the 60°C and 100°C reactions. For the 100°C reactions the samples were taken at shorter time intervals, thus preventing the accumulation of ethylene in the reactor due to pressure release during sampling. The reason for sampling at shorter time intervals was due to the fast reaction rate at 100°C. The reaction rate for the 60°C reactions were much slower, therefore resulting in the slower formation of ethylene. Although the reaction rate of the 80°C reactions was faster than for the 60°C reactions, sampling was not done as regularly as for the 100°C reaction. This resulted in an ethylene accumulation in the reactor.

4.3.6.3 Summary of 1-decene metathesis reactions

In Table 4.10 the effects of different precatalysts with 1-decene under different conditions are compared in terms of the selectivity, activity, product formation and TON.

4. Results and discussion

Table 4.10 Comparisons between the different precatalysts for 1-decene metathesis reactions.

Precatalyst	T (°C)	PMP (mol %)	SMP (mol %)	IP (mol %)	%S ^a	TON	k _{Initial} (mol.s ⁻¹)
Gr1 (1)	60	55.8	3.7	6.1	85.1	3903	1.25 (±0.30) × 10 ⁻³
Gr2 (2)		66.4	25.9	2.5	71.9	4648	4.15 (±1.09) × 10 ⁻⁴
Gr2Ph (3)		70.4	11.7	0.6	85.2	4931	3.69 (±0.66) × 10 ⁻⁶
Gr1 (1)	80	29.8	3.7	15.1	61.3	2086	7.22 (±1.90) × 10 ⁻⁴
Gr2 (2)		68.3	25.0	2.4	71.4	4779	6.61 (±0.26) × 10 ⁻⁴
Gr2Ph (3)		48.5	39.6	6.8	51.1	3395	1.29 (±0.82) × 10 ⁻⁵
Gr1 (1)	100	60.3	3.0	10.7	81.4	4218	1.40 (±0.23) × 10 ⁻³
Gr2 (2)		63.2	23.1	3.5	70.4	4421	5.39 (±0.26) × 10 ⁻⁴
Gr2Ph (3)		67.2	21.2	1.3	74.9	4705	9.69 (±0.66) × 10 ⁻⁵

^a Selectivity calculated towards the PMPs.

From **Table 4.10** it is clear that the metathesis reactions for precatalysts Gr1 (1) and Gr2Ph (3) were least efficient at 80°C in terms of PMP formation, but it was the optimum temperature for the PMP formation of Gr2 (2) metathesis reactions with 1-decene. The optimum temperature for PMP formation for Gr1 (1) and Gr2Ph (3) were at 60°C and 100°C respectively. At optimum conditions for PMP formation, the performances of the catalysts were efficient, (with TON of 3979 (1), 4779 (2) and 4931 (3)). Gr2Ph (3) had the longest lifetime when compared to Gr1 (1) and Gr2 (2) indicating that the replacement of the PCy₃-group with the N^oO-ligand improves the lifetime and stability at higher temperatures. The increase in lifetime indicated that the complex was more stable, which resulted in a slower decomposition of the catalyst. The initial rate at which products were formed was slow and competing reactions started to increase with the extended lifetime of Gr2Ph (3). The selectivity of the three precatalysts was the highest at 60°C, but Gr1 (1) had the highest selectivity, followed by Gr2Ph (3) and Gr2 (2).

4.4 Comparison of 1-alkene metathesis reactions

To compare the synthesized complex Gr2Ph (3) to Gr1 (1) and Gr2 (2), during metathesis reactions, the same reaction conditions were used: 60°C with a precatalyst load of 1:7000 (Ru:alkene). The temperature was chosen to compare the precatalysts at the highest temperature possible due to the low boiling point of 1-hexene.

No metathesis products were observed with Gr2Ph (3) for metathesis reactions conducted at temperatures lower than 50°C. This observation was made after a reaction time of 420 min and with a precatalyst load of 1:7000 (Ru:alkene).⁴

The data obtained at the comparative conditions are used to compare the 1-alkenes as shown in Table 4.11.

Table 4.11: Comparisons between the different precatalysts for 1-alkene metathesis reactions at 60°C with a 1:7000 Ru:1-alkene ratio.

Precatalyst	Alkene	PMP (mol %)	SMP (mol %)	IP (mol %)	%S ^a	TON	k _{initial} (mol.s ⁻¹)
Gr1 (1)	Hexene	27.5	0.5	0	98.4	1924	6.17 (±0.41) x 10 ⁻⁴
Gr2 (2)		73.0	17.9	0	80.3	5113	1.50 (±0.17) x 10 ⁻³
Gr2Ph (3)		70.4	10.4	0	87.0	4926	1.22 (±0.45) x 10 ⁻⁵
Gr1 (1)	Heptene	37.6	2.2	0	94.5	2631	6.37 (±1.63) x 10 ⁻⁴
Gr2 (2)		46.8	36.8	5.5	52.7	3278	1.09 (±0.14) x 10 ⁻³
Gr2Ph (3)		44.1	47.7	4.2	46.0	3098	2.23 (±0.34) x 10 ⁻⁵
Gr1 (1)	Nonene	37.7	0.7	5.1	86.9	2642	4.35 (±0.55) x 10 ⁻⁴
Gr2 (2)		77.7	3.1	0	96.1	5438	8.15 (±2.05) x 10 ⁻⁴
Gr2Ph (3)		12.8	2.4	0.5	81.6	898	1.28 (±0.52) x 10 ⁻⁶
Gr1 (1)	Decene	56.8	2.9	3.0	90.5	3979	1.25 (±0.30) x 10 ⁻³
Gr2 (2)		66.4	25.9	2.5	71.9	4648	4.15 (±1.09) x 10 ⁻⁴
Gr2Ph (3)		70.4	11.7	0.6	85.2	4931	3.69 (±0.66) x 10 ⁻⁶

^a Selectivity calculated towards the PMPs.

During the metathesis reactions of 1-hexene with precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)), no IP formation was observed but the formation of SMPs was however, still observed. This indicated that there were IPs formed during the metathesis reactions. The IPs could have been converted to SMPs through cross- and self metathesis reactions, but it was only formed in low concentration. The metathesis reactions with the four 1-alkenes resulted in the selectivity of the Gr1 (1) reaction to be the highest, and the PMP formation and TON of almost all the Gr2 (2) reactions to be the highest. Literature supports this observation as it was stated that the replacement of the PCy₃-group with a NHC-ligand improves the activity and stability of Gr1 (1).¹⁴

After the replacement of the PCy₃-group of the Gr2 (2) precatalyst with a N^o hemilabile ligand, the lifetime increased and PMP formation was almost the same as for the Gr2 (2) reactions. This shows that the hemilabile ligand is an improvement on the lifetime of the reactions conducted with Gr1 (1) and Gr2 (2). An increase of TON was also observed when compared to the Gr1 (1) reactions but similar to those of the Gr2 (2) reactions.

4. Results and discussion

Metathesis reactions conducted by Huijismans⁵ with 1-octene and Gr2Ph (3) at 60°C with a precatalyst load of 1:9000, showed that the catalyst had a very high activity due to the formation of 83 mol% PMPs within the first hour, where after equilibrium was reached after 995 min.

The equilibrium was not reached as quickly as for the metathesis reactions of 1-hexene, 1-heptene, 1-nonene and 1-decene with Gr2Ph (3). The highest PMP formations were obtained in the metathesis reactions with 1-hexene (70.4 mol%) and 1-decene (70.4 mol%). The PMPs formed were only observed after 24 and 25 days, respectively, indicating that the activity was lower than observed for 1-octene reactions and that the equilibrium was reached later.

The difference in the PMP formation between the 1-alkenes used in this study and 1-octene is attributed to the different experimental setups. The 1-octene reactions that were conducted in a larger reactor with a bubbler system, by Jordaan² and Huijismans⁵, prevented the ethylene accumulation in the reactor. The metathesis reactions conducted on the small reactor was in a closed system, causing ethylene to accumulate which could have influenced the reaction negatively by suppressing the PMP formation, due to catalyst decomposition. The ethylene coordinates to the Ru metal and forms a hydride species (50), resulting in the decomposition of the catalyst.¹⁰ For the smaller scale reactions the initial rate of PMP formation decreased after 4 days and the SMPs started to increase for the 1-hexene and 1-decene reactions. These ethylene effects on the metathesis reactions were observed mainly for 1-heptene and 1-decene reactions with Gr2 (2) and Gr2Ph (3). This might be due to the moderate and high reaction rates for the conversion of the 1-alkenes to PMPs.

Mtshatsheni¹⁵ investigated the metathesis reactions of 1-octene with Gr1 (1) and Gr2 (2) by using the small scale reactors. The Ru:1-octene ratio used was 1:100 at a reaction temperature of 50°C in the presence of chlorobenzene (PhCl). The PMP formation for the 1-octene reactions were higher (40 mol%) than for the 1-hexene (27.5 mol%), 1-heptene (37.6 mol%) and 1-nonene (37.7 mol%) reactions, but lower than for the 1-decene (56.8 mol%) metathesis reactions, indicating that the metathesis reactions of Gr1 (1) with the longer alkene chains results in higher PMP formations than for the shorter chain lengths. Higher PMP formations for the metathesis reactions in this study were expected because the temperatures were higher than the reactions conducted by Mtshatsheni.¹⁵ The PMP formation of the Gr2 (2) reaction was 47 mol% and the IP formation 10 mol% at 50°C, whereas higher PMPs were formed for 1-hexene (73 mol%), 1-heptene (46.8 mol%) and with 1-nonene (77.7 mol%). The metathesis reactions at 50°C and 100°C were monitored for 300 min by Mtshatsheni¹⁵ and no ethylene effects were observed, although the small reactors were used.

During a previous study³ it was observed that the addition of the solvent PhCl gives rise to optimum metathesis activity when compared to other solvents (Et₂O, cyclohexane and nitrobenzene) in the metathesis reactions of Gr1 (1).³

The combination of the bubbler system and an inert atmosphere were used during the metathesis reactions of 1-octene to prevent catalyst decomposition. Ethylene accumulation in the large system was prevented by the use of a bubbler and N₂. This prevented the Gr1 (1) and Gr2 (2) catalysts from forming carbonyl species.¹² These carbonyl species can be converted into the hydride species (50) leaving the catalyst inactive for metathesis reactions.

Metathesis reactions for 1-octene with Gr2 (2) monitored for 420 min at different temperatures resulted in no ethylene decomposition of the catalysts.² The increase in temperature resulted in an increase in the PMP formation, but an increase in the SMPs was also observed.² The PMP increase was observed for the 1-heptene and 1-decene reactions, but not for the SMP formations. The reason for these observations was because of the ethylene effects on the catalysts decomposition. The Gr1 (1) reactions were also monitored for the time mentioned and the highest PMP formation was obtained for the 35°C reactions. The higher temperatures (60°C, 70°C and 80°C) resulted in a lower PMP formation due to the decomposition of the catalyst at higher temperatures.² This observation was, however, not made for 1-hexene and 1-decene metathesis reactions at higher temperatures. The results obtained for these reactions can be due to the pre-treatment of the precatalyst that increased its stability towards higher temperature reactions. Similar observations were made for the metathesis reactions of 1-hexene and 1-heptene.

Metathesis reactions with 1-octene and Gr2Ph (3) at different temperatures (50°C, 60°C, 70°C, 80°C, 90°C and 100°C) and a precatalyst load of 1:7000 were investigated by van der Gryp⁴ for 420 min. An increase in the PMP formations were observed for the temperatures up to 90°C where after a dramatic decrease was observed. The maximum PMP formation was obtained for the reaction conducted at 80°C, but this reaction also had the highest SMP formation.

Jordaan² observed that *cis* and *trans* PMP conformations formed during a metathesis reaction of 1-octene and Gr1 (1) at 25°C. The two conformers were also observed by van der Gryp⁴ for metathesis reactions of 1-octene with Gr2Ph (3) at temperatures ranging from 50°C to 100°C. The different PMP conformers were only observed for the metathesis reactions of 1-nonene in this study. The two conformers were present at the first observation of PMP formation. As the PMP concentrations increased during the reaction, only one product peak was visible (Figures 3.3 to 3.6). The same observation was made for the metathesis reactions of 1-octene with Gr2Ph (3) at 60°C by Huijsmans.⁵ The reason for this being that the volatility of the conformers is similar.

The oven programs were changed to determine if the conformers could be separated, but with no success.

The reaction rate of the Gr1 (1) reactions are different for the different alkene lengths. From the data in Table 4.9 it seems that the shorter the alkene chain length the slower the metathesis reactions. The observation made for the metathesis reactions conducted with precatalysts Gr2 (2) and Gr2Ph (3) was that the reaction rates are slower for the longer 1-alkenes. These two precatalysts have large ligands attached to the Ru metal and the sterical hindrance may have an influence on the reaction rate of the longer 1-alkenes. Grubbs and Ulman¹⁶ observed that the effect of the steric bulk of the substrate and the ligands, coordinated onto the Ru metal, has an influence on the reaction rates.

The low concentration 1-hexanol present in the 1-nonene mixture has a large impact on the metathesis reactions with Gr2Ph (3) and not on the other two precatalysts used. This is the reason for the 12.8 mol% PMP formation for the 1-nonene metathesis reactions. The equilibrium for the metathesis reaction was reached early (6 days) at a low temperature, while the equilibrium was reached after a longer period of time for the other 1-alkene metathesis reactions with Gr2Ph (3).

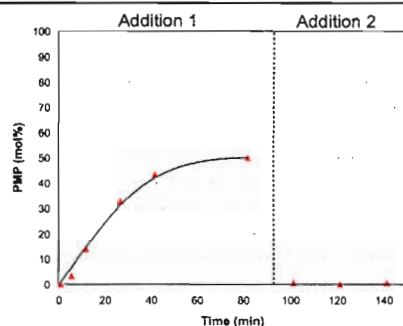
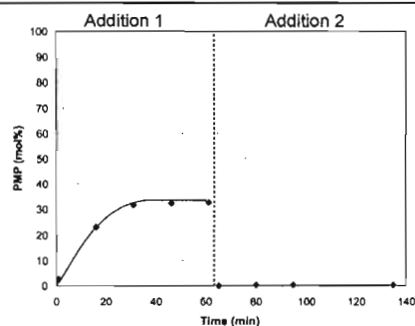
4.5 Catalyst lifetime metathesis reactions

To determine the lifetime of Gr2Ph (3), an additional 2.5 mL of the 1-alkenes were added when most of the 1-alkenes were converted, as discussed in § 3.4.2. Only one addition of the 1-alkenes was made to determine whether the precatalysts were still active after equilibrium was reached. The results obtained were compared to the performance of Gr1 (1) and Gr2 (2) to determine the lifetime improvement of the hemilabile ligand coordinated onto the Ru-metal centre, precatalyst Gr2Ph (3), shown in Figure 4.25.

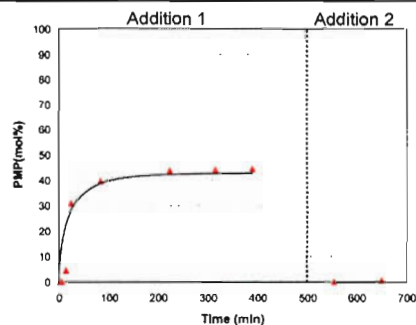
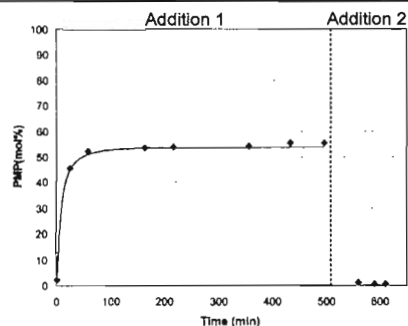
1-Hexene

1-Heptene

Gr1 (1)



Gr2 (2)



Gr2Ph (3)

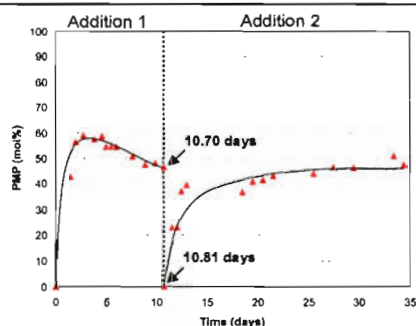
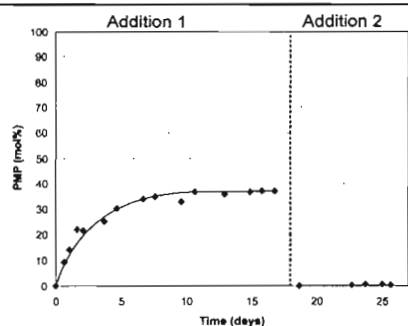


Figure 4.25: The lifetime determining metathesis reactions with Gr1 (1), Gr2 (2) and Gr2Ph (3) for the PMP formation for 1-hexene (●) and 1-heptene (▲) reactions.

4. Results and discussion

The graphs in **Figure 4.25** show the PMP formation in the metathesis reaction with the precatalysts (Gr1 (1), Gr2 (2) and Gr2Ph (3)) and the time it takes the precatalysts to convert the 1-alkenes to maximum PMP formation. From **Figure 4.25** (the PMP formation of the 1-heptene reaction with Gr2Ph (3)) and **Figure 4.26** (the 1-heptene conversion and SMP and IP formations) it appears that the time of the experimental data point for the first addition (10.7 days) coincides with the time of the first experimental data point of the second addition (10.81 days). The reason for is that the time axes of the figures are in days, although the second reaction was only commenced a few hours after the first reaction reached equilibrium.

The lifetime determining reaction of 1-hexene with Gr2Ph (3) was repeated, but the PMP formation was still low, with no activity observed after the second addition of 1-hexene. The lifetime determining reaction for 1-heptene with Gr2Ph (3) shows that the catalyst is still active when 1-heptene was added for the second time. The reaction rate decreased during the second addition from $1.45 \times 10^{-5} \text{ mol.s}^{-1}$ to $6.66 \times 10^{-6} \text{ mol.s}^{-1}$ due to the increase in the Ru:1-alkene ratio. When looking at the PMP formation for the Gr2Ph (3) reaction, the PMPs started to decrease after five days. This might be attributed to the ethylene accumulation in the mini reactor. The ethylene formation as discussed in **Scheme 4.1**, results in the formation of the catalyst hydride (50) and promotes the isomerization reaction.

The graphs in **Figure 4.26**, illustrate the SMP and IP formation as well as the decrease in the 1-heptene.

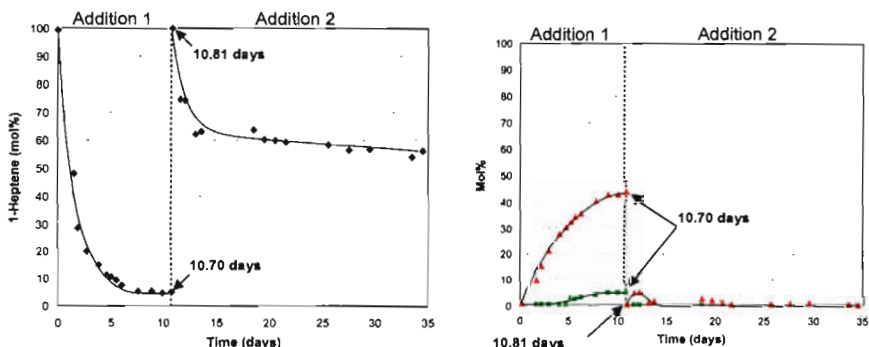


Figure 4.26: The alkene conversion ($\blacklozenge$) as well as the SMP ($\blacktriangle$) and IP ($\blacksquare$) formation from 1-heptene at 60°C with Gr2Ph (3).

From the data in **Figure 4.26** it can be seen that the metathesis reaction of 1-heptene reached equilibrium conditions, while the PMPs started to decrease as it was converted to SMPs.

During the second addition the reaction rate was slower, which resulted in a slower ethylene formation and the decomposition of some of the catalyst, thus resulting in no decrease in the PMP formation. The IP and SMP formations decreased as the ratio of Ru:1-alkene increased as discussed for Figure 4.17.

In addition the metathesis reaction of 1-heptene at 60°C in §4.3.4.2 was conducted in a 5 mL reactor. The rate of these reactions were slower with less PMPs formed (6.8 mol%) than for reactions conducted in larger reactors. The lifetime determining reactions were conducted in a 10 mL reactor where there was a larger volume available for the ethylene to accumulate in, resulting in a larger PMP conversion.

In Table 4.12 the product formations, reaction times, selectivity and TON of each addition is shown.

Table 4.12: Comparisons between the different precatalysts for the lifetime determining reactions for 1-heptene and 1-hexene at 60°C.

Precatalyst	Addition	Alkene	Time (min)	PMP (mol %)	SMP (mol %)	IP (mol %)	S (%)	TON	k_{initial} (mol.s ⁻¹)
Gr1 (1)	1	Hexene	61	32.7	1.7	0	95.2	2292	9.11 (±1.81) × 10 ⁻⁶
	2		135	0.3	0.3	0	51.7	18	-
	1	Heptene	82	50.0	3.5	0	93.4	3499	7.67 (±0.63) × 10 ⁻⁴
	2		142	0.5	2.3	0	18.2	36	-
Gr2 (2)	1	Hexene	497	55.4	4.3	0	92.8	3879	1.20 (±0.23) × 10 ⁻³
	2		590	0.5	0.2	0	70.6	35	-
	1	Heptene	391	44.5	4.4	0	91.1	3117	7.50 (±0.35) × 10 ⁻⁴
	2		650	0.7	0.5	0	57.0	48	-
Gr2Ph (3)	1	Hexene	24 097	37	4.9	0	88.4	2592	6.73 (±0.30) × 10 ⁻⁶
	2		41 261	0.3	0.7	0	31.7	21	-
	1	Heptene	15 405	46.4	43.9	4.5	51.4	3251	1.45 (±0.57) × 10 ⁻⁵
	2		49 605	47.5	0.1	0	99.8	3321	6.66 (±0.75) × 10 ⁻⁶

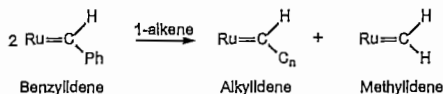
4. Results and discussion

The general observation was that the reaction rate and TON decreased after the addition of the 1-alkenes. This could be due to the fact that the Ru:alkene ratio becomes larger when a sample is extracted, leading to less catalyst to perform the metathesis reaction or that a percentage of the catalyst has decomposed. This also has an impact on the PMP formation and selectivity of the reactions. The lifetime reaction of 1-heptene with Gr2Ph (3) showed an increase in the PMP formation after the second addition of the 1-alkene.

Gr2Ph (3) showed an increase in lifetime for the 1-heptene reactions, thus meaning it was still active after the second addition, when compared to Gr1 (1) and Gr2 (2). The metathesis reactions for Gr1 (1) were active for 61 min. with 1-hexene and 82 min. with 1-heptene. Gr2 (2) was active for 497 min. with 1-hexene and 391 min. for 1-heptene, whilst Gr2Ph (3) was active for 24 097 min. (16 days) with 1-hexene and 49 605 min. (34 days) for 1-heptene. From these observations it could be said that the synthesized Gr2Ph (3) showed an improvement in catalyst lifetime. The optimum PMP formation for the 1-heptene reactions with Gr2Ph (3) was at 2.75 days with a TON of 4129 and a selectivity of 73.7%. After 2.75 days, however, the ethylene reacted with the precatalyst and isomerization reactions decreased all of these values.

4.6. NMR characterization of carbene species

In addition a ^1H -NMR investigation was conducted to identify the carbene species during the metathesis reactions of 1-hexene and 1-octene with Gr1 (1) and Gr2Ph (3) in deuterated chloroform (CDCl_3). These reactions were investigated with a precatalyst load of 1:40 (Ru:1-alkene) at 30°C . The metathesis reaction of 1-octene with Gr1 (1) was done to compare to the results obtained in a previous study of which the reaction temperature was 30°C , and a 300MHz NMR instrument was used.² Scheme 4.2 illustrates the formation of the carbene species that were formed during the metathesis reactions.



Scheme 4.2: The formation of the alkylidene and methylidene species during the metathesis reaction with a 1-alkene.

4.6.1. NMR investigation of Gr1

The carbene species formed during the metathesis reactions of the 1-octene and 1-hexene at 30°C with Gr1 (1) are illustrated in Figure 4.27 and Figure 4.28, respectively.

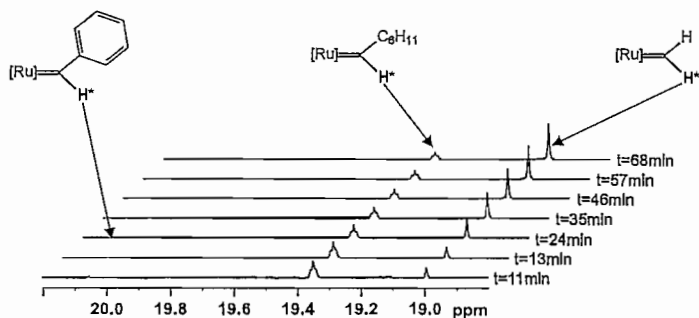


Figure 4.27: The ^1H -NMR spectra for the carbene proton resonance signals of a 1-octene metathesis reaction with Gr1 (1) at 30°C in CDCl_3 .

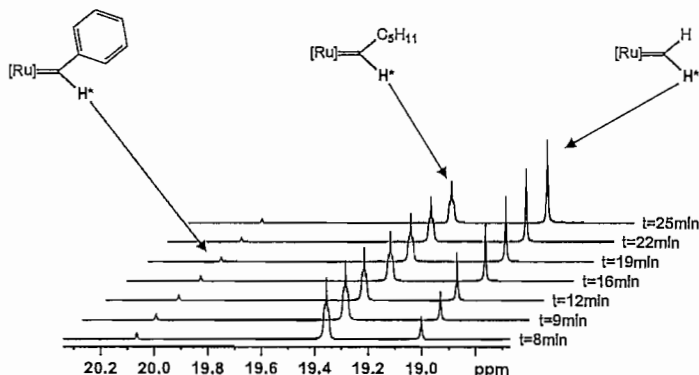


Figure 4.28: The ^1H -NMR spectra for the carbene proton resonance signals of a 1-hexene metathesis reaction with Gr1 (1) at 30°C in CDCl_3 .

Three carbene peaks were already present at the reaction times of 11 min for the 1-octene and 8 min for the 1-hexene metathesis reactions. The H_a -proton (H^*) of the carbene ligand is influenced by the group attached to the carbene C-atom. The chemical shift for the H_a -carbene proton (H^*) for benzylidene of Gr1 (1) was observed as a singlet at a high δ -value (lower magnetic field) of 20.06 ppm. The chemical shift for the H_a -carbene proton for heptylidene was observed as a triplet signal at a δ -value of δ 19.35 ppm. For the methylidene the chemical shift for the H_a -carbene proton (H^*) was observed as a singlet at a lower δ -value (higher magnetic field) of δ 19.00 ppm. The resonance values obtained for the different carbene species correlated with the results of Jordaan *et al.*¹⁷

4. Results and discussion

The heptylidene and methyldene resonance signals were observed after the first 14 min of the metathesis reaction conducted at 25°C in CDCl_3 with 1-octene and Gr1 (1). The observation of the different carbene species after a short reaction time illustrates a fast reaction rate for these metathesis reactions.¹⁷ The changes in the intensity of the resonance signals during the course of the metathesis reactions of 1-octene and 1-hexene with Gr1 (1) are illustrated in Figures 4.29 and 4.30.

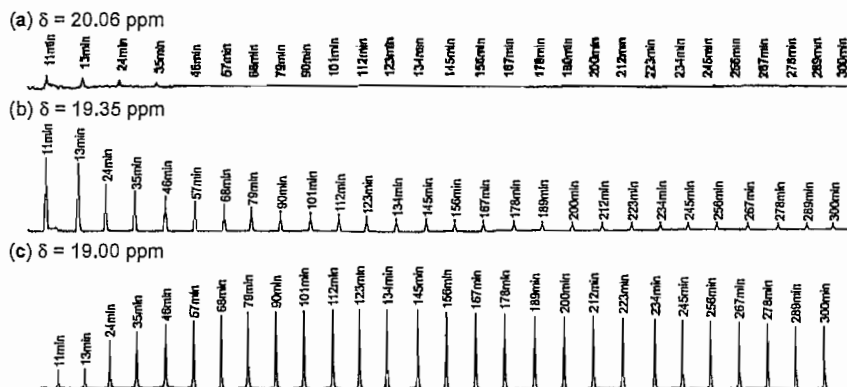


Figure 4.29: The ^1H -NMR spectra of the carbene proton (H_a) area of a 1-octene metathesis reaction with Gr1 (1) at 30°C in CDCl_3 .

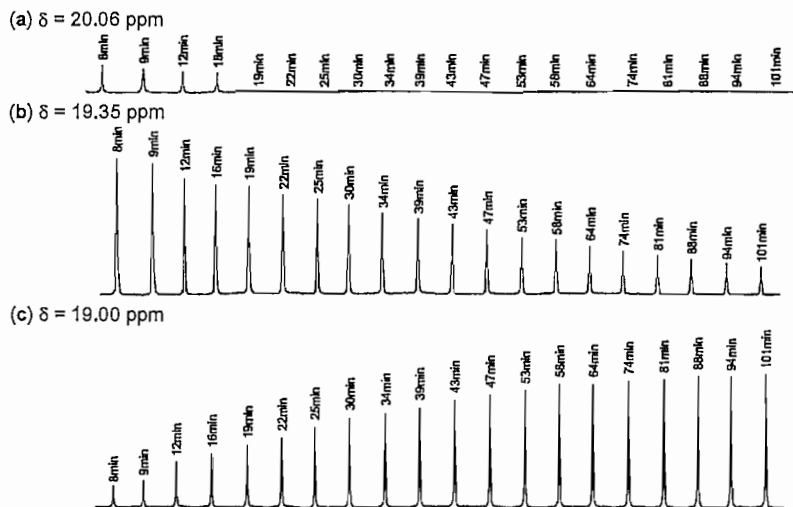


Figure 4.30: The ^1H -NMR spectra of the carbene proton (H_a) area of a 1-hexene metathesis reaction with Gr1 (1) at 30°C in CDCl_3 .

For both of these metathesis reactions with Gr1 (1), a decrease of the benzylidene was observed with a simultaneous increase in the alkylidene and methylidene formation. This suggests that the benzylidene was converted into the other two carbene species. All of the benzylidene was converted after 46 min for the 1-octene reaction and after 17 min for the 1-hexene reaction.

The heptylidene signal showed a significant increase within 11 min followed by a gradual decrease for 5 hours during the 1-octene metathesis reactions as shown in **Figure 4.29 (b)**. The pentylidene signal (**Figure 4.30 (b)**) showed a significant increase within 8 min and then a gradual decrease for 101 min during the 1-hexene metathesis reactions.

This observation can be due to the decomposition of the catalyst during the metathesis reactions. For both of the 1-alkene metathesis reactions the benzylidene was rapidly converted into the alkylidene species, but the formation of the methylidene was slower. Ulman and Grubbs¹⁶ observed that the alkylidene species was more reactive when compared to the methylidene during the metathesis reactions of alkenes with Gr1 (1). The same trend was observed by Jordaan *et al.*¹⁷

The methylidene formation for the 1-octene and 1-hexene had a gradual increase for the first 79 min (**Figure 4.29 (c)**) and 58 min (**Figure 4.30 (c)**), respectively, for the metathesis reactions. During the metathesis reactions of 1-octene and 1-hexene the benzylidene was converted to the alkylidene and methylidene species. The conversion of the benzylidene to the alkylidene was faster than the methylidene formation. The rapid formation of the alkylidene species, the kinetically favoured species, was also observed by Ulman *et al.*,¹⁶ during the investigation of the metathesis reactions of linear alkenes with Gr1 (1). The results obtained are in correlation with what was found in literature. This confirms that the correct experimental method was followed.

Figure 4.31 shows an illustration of the alkene resonance signals, with C and D depicting the terminal- and internal alkenes, respectively.

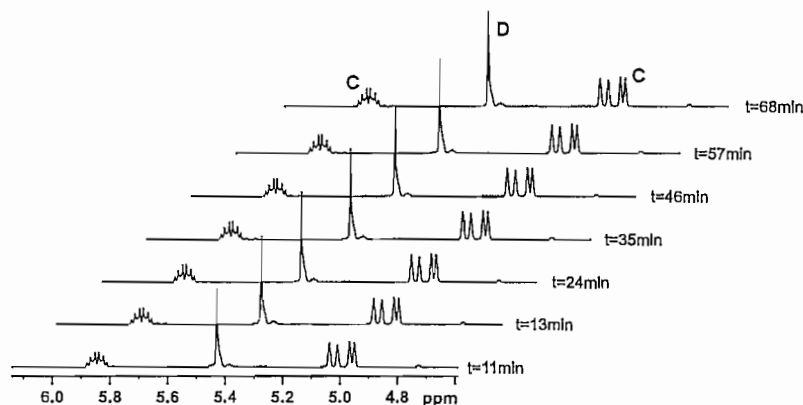
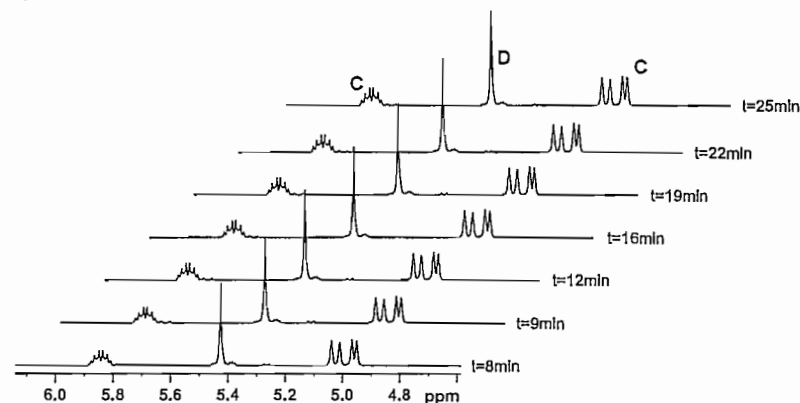
A - C₈B - C₆

Figure 4.31: The ^1H -NMR spectra of the alkene resonance signal of 1-octene (A) and 1-hexene (B) of the metathesis reaction with Gr1 (1) at 30°C in CDCl_3 .

It should be noted that the NMR-spectra does not specify the amount and type of internal- and terminal alkenes present, but a wide variety of alkenes were formed during the metathesis reactions of 1-octene and 1-hexene with Gr1 (1). This figure illustrates that metathesis products were observed within the first 11 min (1-octene) and 8 min (1-hexene) of the reactions with Gr1 (1).

4.6.2. NMR investigation of Gr2Ph

The carbene species that was formed during the metathesis reactions of 1-octene and 1-hexene at 30°C with Gr2Ph (3) in CDCl_3 are illustrated in Figure 4.32 and Figure 4.33 respectively.

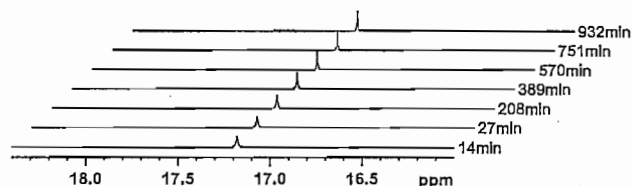


Figure 4.32: The ^1H -NMR spectra of the carbene proton signal of a 1-octene metathesis reaction with Gr2Ph (3) at 30°C in CDCl_3 .

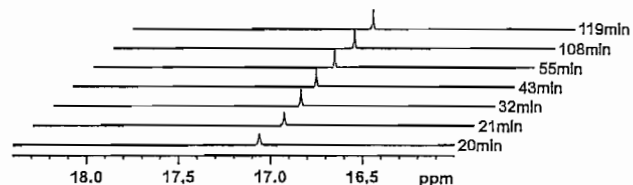


Figure 4.33: The ^1H -NMR spectra of the carbene proton signal of a 1-hexene metathesis reaction with Gr2Ph (3) at 30°C in CDCl_3 .

The H_a -proton resonance signal of the carbene proton of the benzylidene of Gr2Ph (3) appears at a δ -value of 17.06 ppm and no other resonance signals were observed in the carbene resonance signal area (δ -values of 21 to 15 ppm). The changes in the signal intensity during the course of the metathesis reactions of 1-octene and 1-hexene with Gr2Ph (3) are illustrated in Figures 4.34 and 4.35, respectively.

(1) $\delta = 17.18$ ppm

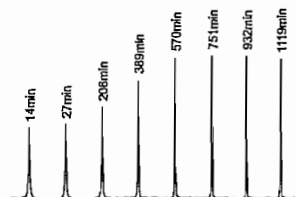


Figure 4.34: The ^1H -NMR spectra of the carbene proton (H_a) area of a 1-octene metathesis reaction with Gr2Ph (3) at 30°C in CDCl_3 .

(1) $\delta = 17.18$ ppm



Figure 4.35: The ^1H -NMR spectra of the carbene proton (H_α) area of a 1-hexene metathesis reaction with Gr2Ph (**3**) at 30°C in CDCl_3 .

The metathesis reactions with Gr2Ph (**3**) showed an increase in benzylidene for 9.5 and 4.7 hours for 1-octene and 1-hexene respectively, where after a gradual decrease was noted for the 1-hexene reaction. For the metathesis reaction of two different 1-alkenes with the same precatalyst (Gr1 (**1**)), the same trends were observed for the formation of carbene signals. These observations can then also be assumed for the Gr2Ph (**3**) metathesis reaction.

It was anticipated that the benzylidene will decrease while being converted into the alkylidene and methylidene and that a chemical shift will be observed for the different species. A NMR investigation of a hemilabile ligand (**8**) conducted by Jordaan² at 50°C in CDCl_3 , showed five different carbene resonance signals. These peaks correlate well with the group coordinated to the metal centre for benzylidene, methylidene and heptylidene (**Scheme 2.16** nr **3**, **33**, **36**) as well as the de-coordinated form of the benzylidene and methylidene carbenes (**Scheme 2.16** nr **27**, **31**, **32**).

The only carbene peak observed was at the δ value of the benzylidene signal as stated in § 4.2.3 (**Table 4.2**). The change of the resonance signal intensity of this benzylidene signal resembles the methylidene carbene profile of the Gr1 (**1**) reactions. This might be attributed to the different carbene signals coinciding at a δ -value of 17.06 ppm.

Figure 4.36 shows an illustration of the alkene resonance signals, with **C** and **D** depicting the terminal- and internal alkenes respectively.

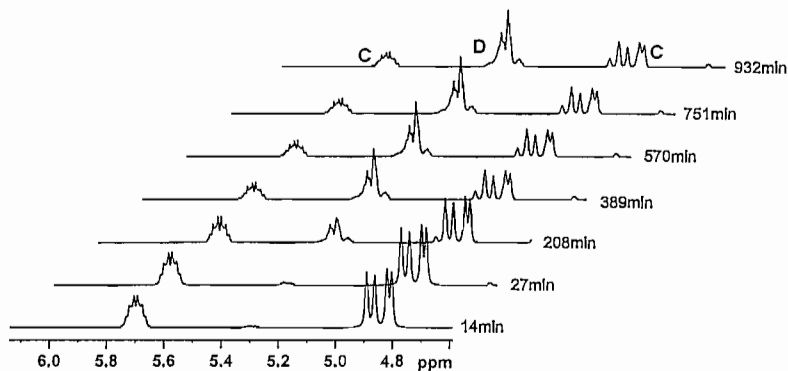
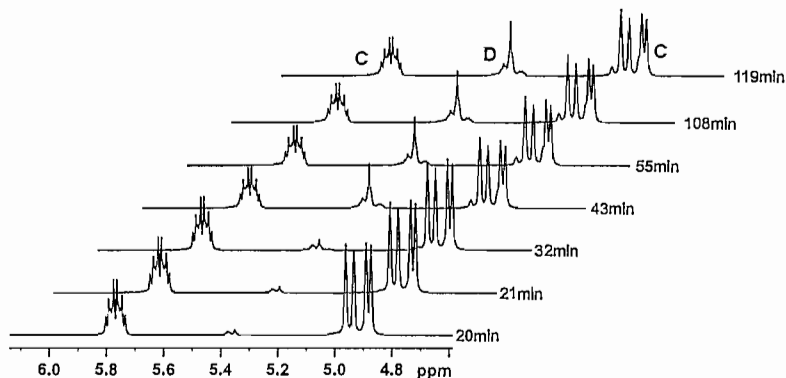
A - C₈B - C₆

Figure 4.36: The ¹H-NMR spectra of the alkene resonance signals of 1-octene (A) and 1-hexene (B) for metathesis reactions with Gr2Ph (3) at 30 °C in CDCl₃.

Although only one carbene resonance signal was observed, alkene metathesis did occur. It is well known that metathesis products are formed during metathesis reactions conducted with Gr1 (1).^{11,13,15-17} As illustrated in Figure 4.31 one can observe the terminal- and internal alkenes. In Figure 4.36 the internal alkenes (D) are present, but in small amounts at 14 and 20 min. The increase in the signal intensity demonstrates the formation of more metathesis products, thus confirming that metathesis products were formed for the Gr2Ph (3) reactions.

4. Results and discussion

From these two figures the observation can be made that the rate at which the metathesis products are formed for the Gr1 (1) reactions are faster than for the Gr2Ph (3) metathesis reactions. This observation was also made for the metathesis reaction with 1-hexene, 1-heptene, 1-nonene and 1-decene in § 4.3.

From § 4.4 it was also observed that the reaction rates are different for these two precatalysts. Van der Gryp⁴ stated that metathesis was not possible for Gr2Ph (3) reactions at temperatures below 50°C when using a precatalyst load of 1:7000. These metathesis reactions were monitored for 420 min at 30°C and no products were observed. From the NMR study conducted at 30°C, metathesis products were formed with a precatalyst load of 1:40 (Ru:1-alkene). This means that the amount of catalyst available in the reaction mixture at this low temperature is important for metathesis products to form.

In Figure 4.37 and Figure 4.38 chromatograms are shown to illustrate the metathesis products formed during the reactions of 1-hexene and 1-octene at 30°C in the presence of CDCl_3 .

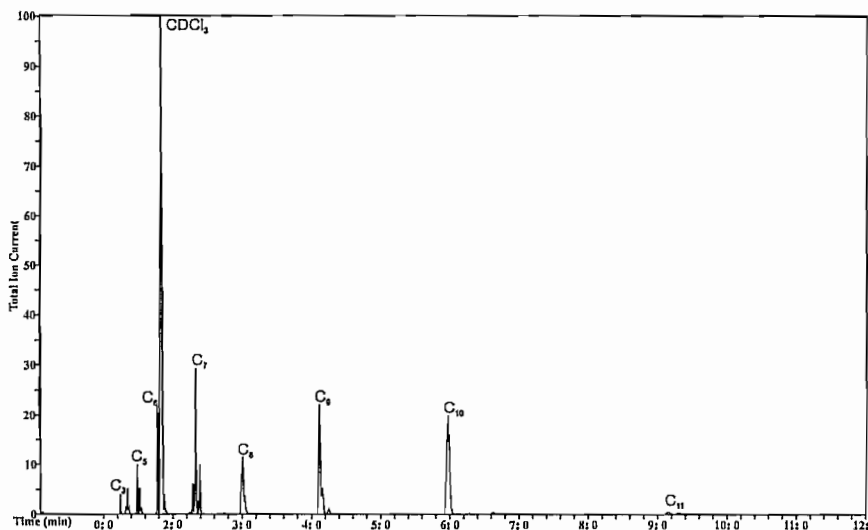


Figure 4.37: A chromatogram of the NMR investigation of 1-hexene with Gr2Ph (3) at 30°C in CDCl_3 .

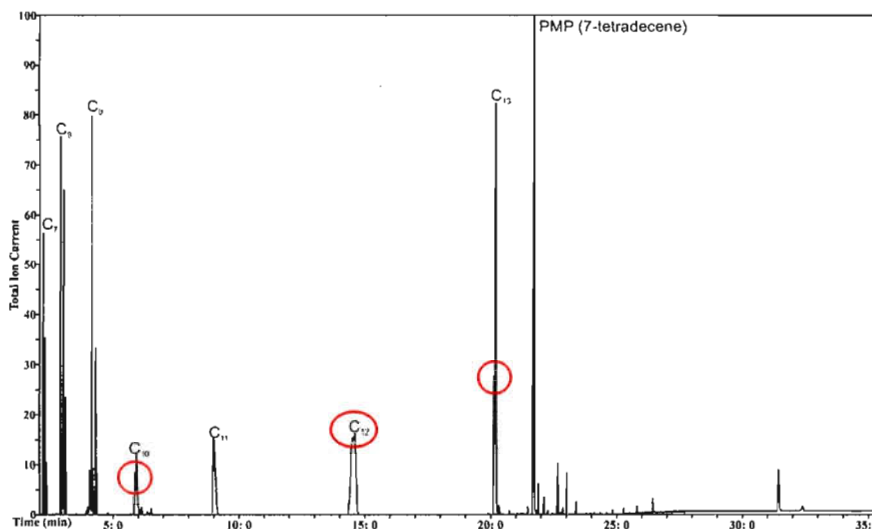


Figure 4.38: A chromatogram of the NMR investigation of 1-octene with Gr₂Ph (**3**) at 30°C in CDCl₃.

From **Figure 4.36 A** and **B** it was observed that the formation of internal alkenes was slow during the metathesis reactions for 1-octene and 1-hexene. The formation of the SMPs (nonene and tridecene) was observed to be high from **Figures 4.37** and **4.38** when compared to the PMP formations. The increase in the concentration of the catalyst might result in the formation of metathesis products but it also increases the isomerization reactions. Jordaan¹⁷ and van Sckalkwyk³ also made the observation that the increase in the concentration of catalyst available in the reaction mixture increases the isomerization reactions which then results in an increase in SMP formations. This indicates that although only one carbene was observed during the NMR-investigation and not five as stated in a previous study with a similar type of precatalyst (hemilabile precatalyst), metathesis products were still obtained. From the metathesis reactions of Gr₂Ph (**3**) with the 1-hexene a larger amount of SMPs were observed for the lower temperature reactions, thus correlating with the observation made during the NMR investigation.

As stated in § 4.4, the different conformers (*cis* and *trans*) for the 1-octene reactions were observed by Jordaan² and **Figure 4.38** is an illustration of this observation. The SMP products shown in **Figure 4.38** also show that a distinction can be made between the different conformers. It was also observed from the metathesis data obtained from 1-hexene reactions that no distinction could be made between the conformers, as illustrated in **Figure 4.37**.

4.7. Closing remarks

Three main aspects were addressed in this chapter, which include:

- 1) the synthesis of Gr2Ph (3) for the confirmation of repeatability,
- 2) the catalytic performances of Gr1 (1), Gr2 (2) and Gr2Ph (3) for the metathesis reactions of different 1-alkenes (1-hexene, 1-heptene, 1-nonene and 1-decene) and
- 3) the characterization of the active species present during the metathesis reactions with precatalyst 3 by means of NMR.

The Gr2Ph (3) precatalyst was successfully synthesized and characterized as mentioned in § 4.2.

Furthermore it was found that the metathesis reactions of the different 1-alkenes with precatalysts 1, 2 and 3 were strongly influenced by temperature effects. The metathesis reaction with Gr1 (1) were more selective towards the PMP formation than Gr2 (2) and Gr2Ph (3), thus indicating that 2 and 3 have a higher SMP and IP formation. Metathesis reactions with Gr1 (1) could be improved when the precatalyst was pre-treated with heat. This change in the preparation method resulted in an increased lifetime and a higher PMP formation. The initial reaction rate of Gr1 (1) was higher than for the other two precatalysts, but the lifetime of Gr2 (2) and Gr2Ph (3) was longer.

The NMR investigation was done to determine the different active species present during metathesis reactions of 1-octene and 1-hexene with precatalyst 3. It was found that metathesis reactions conducted at 30°C and a 1:40 Ru:alkene ratio had a product formation which was high in SMPs and IPs. It was found that the products were formed through a mechanism where only one carbene species was present.

4.8. References

1. Hermann, W.A., Lobmaier, G.M., Priemeier, T., Mattner, M.R. and Scharbert, B., *J. Mol. Catal. A: Chem.*, 1997, **117**, 455
2. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007
3. van Schalkwyk, C., *Die Katalitiese Sintese van Linieëre Alkene via 'n Metatesereaksie*, Ph.D thesis, (Potchefstroomse Universiteit vir Christelike Hoër Onderwys), 2001

4. van der Gryp, P., *Separation of Grubbs-based catalysts with nanofiltration*, Ph.D thesis, (North-West University), 2008
5. Huijismans, C.A.A., *Modelling and synthesis of Grubbs-type complexes with hemilabile ligands*, M.Sc dissertation, (North-West University), 2009
6. Roscher, P., *Modellering en sintese van Grubbs-tipe komplekse met imienligande*, M.Sc dissertation, (North-West University), 2009
7. Haung, J., Schanz, H.-J., Stevens, E.D. and Nolan, S.P., *Organometallics*, 1999, **18**, 2370
8. Bai, C.-X., Zhang, W.-Z. and He, R., *3rd International Conference of Functional Molecules*, 2005, Dalian, 269
9. Forman, G.S., McConnell, A.E., Tooze, R.P., Janse van Rensburg, W., Meyer, W.H., Kirk, M.M., Dwyer, C.L. and Serfontein, D.W., *Organometallics*, 2005, **24**, 4528
10. Janse van Rensburg, W., Steynberg, P.J., Meyer, W.H., Kirk, M.M. and Forman, G.S., *J. Am. Chem. Soc.*, 2004, **126**, 14332
11. Mahahle, M.M.D., *Isomerization of Alkenes using Metal Carbenes and Related Transition Complexes*, Ph.D thesis, (Potchefstroom University for Christian Higher Education), 2005
12. Dinger, M.B. and Mol, J.C., *Organometallics*, 2003, **22**, 1089
13. Booyesen, K.M.A., *Metathesis and Transalkylation in Tandem Catalysis*, Ph.D thesis, (North-West University), 2007
14. Ritter, T., Hejl, A., Wenzel, A.G., Funk, T.W. and Grubbs, R.H., *Organometallics*, 2006, **25**, 5740
15. Mtshatsheni, K.N.G., *Metathesis of alkenes using ruthenium carbene complexes*, M.Sc dissertation, (North-West University), 2005
16. Ulman, M. and Grubbs, R.H., *Organometallics*, 1998, **17**, 2484
17. Jordaan, M., van Helden, P., van Slittert, C.G.C.E. and Vosloo, H.C.M., *J. Mol. Catal. A: Chem.*, 2006, **254**, 145

Conclusions and recommendations: 5

5.1 Conclusions

5.1.1 Introduction

The main aim of this study was to optimize the metathesis reaction conditions for precatalyst Gr2Ph (3), first synthesized by Jordaan¹, by using different 1-alkenes for metathesis reactions and comparing the results obtained to those at Gr1 (1) and Gr2 (2). Jordaan¹ found that 3, with the N⁺O hemilabile ligand, increased the lifetime and activity during the metathesis reactions of 1-octene in comparison to Gr2 (2). This study determined if the same conclusions could be made for other 1-alkenes as was made for 1-octene by Jordaan¹ and van der Gryp.²

5.1.2 Repeatability of Gr2Ph (3)

The synthesis of ligand 46 and precatalyst 3 were successfully done with yields of 55% and 43% respectively. The moderate yield for the precatalyst was the result of the washing procedure where some of the product was extracted together with the pentane.

5.1.3 Metathesis reactions of 1-alkenes

Metathesis reactions with 1-octene and precatalyst 3 were studied by Jordaan¹ and van der Gryp.² Both reported an improvement in the precatalyst lifetime for the reactions.

The anomalies observed during the metathesis reactions, were the improvement of the Gr1 (1) product formations and lifetime, the alcohol effect on hemilabile precatalysts and the influence of ethylene on the product formations. The Gr1 (1) reactions showed an increase in the catalyst's lifetime and activity with the pre-treatment of heat (60°C). This could be due to the stabilization of the P-C degradation during the pre-treatment and this prevents a quick decomposition during metathesis reactions at the higher temperatures (55°C and 60°C). From the 1-nonene metathesis reactions it could be seen that the coordination of the alcohol onto the hemilabile precatalyst (3) results into the decomposition of the precatalyst when lower concentrations are present in the reaction mixture than for the Gr1 (1) and Gr2 (2) precatalysts, as discussed in § 4.3.4.2. The reason for this might be that, the dissociation of the hemilabile ligand to create the open coordination site is more likely to occur than the dissociation of the PCy₃-group from Gr1 (1) and Gr2 (2) when alcohols are present.

5. Conclusions and recommendations

The reactions conducted in the small scale reactors has the disadvantage of a closed system, which leads to the accumulation of ethylene which in turn resulted in the decrease of the amount of PMPs present at the end of these reactions. This was mainly observed for the metathesis reactions of 1-heptene and 1-decene with the Gr2-type precatalysts. The mechanism for this observation is shown in **Scheme 4.1**. This occurs during the reactions with the Gr2-type precatalyst because of the high TONs resulting in an increase in 1-alkene conversions.

Metathesis reactions for the four different 1-alkenes and three different precatalysts, at different temperatures with a precatalyst ratio of 1:7000 are summarized in **Table 5.1**.

Table 5.1: The metathesis reactions conducted at a Ru:alkene ratio of 1:7000.

Temperature	Hexene		Heptene			Nonene	Decene		
	55°C	60°C	60°C	70°C	80°C	60°C	60°C	80°C	100°C
Gr1 (1)									
PMP (mol%)	16	27.5	37.6	13.8	16.1	37.7	55.8	29.8	60.3
SMP (mol%)	0	0.5	2.2	0.3	0.5	0.7	3.69	3.7	3.0
IP (mol%)	0	0	0	0	7.0	5.1	6.1	15.1	10.7
S (%)	100	98.4	94.5	98.2	68.1	86.9	85.1	61.3	81.4
TON	1123	1924	2631	966	1129	2642	3903	2086	4218
k_{initial} (mol.s ⁻¹) $\times 10^4$	3.58 (± 0.22)	6.17 (± 0.41)	6.37 (± 1.63)	3.74 (± 0.73)	3.23 (± 0.52)	4.35 (± 0.55)	12.5 (± 3.00)	7.22 (± 1.90)	14.0 (± 2.30)
Gr2 (2)									
PMP (mol%)	67.5	73	46.8	68.3	48.9	77.7	66.4	68.3	63.2
SMP (mol%)	19.6	17.9	36.5	11.3	37.1	3.1	25.9	25.0	23.1
IP (mol%)	0	0	5.46	0	0	0	2.5	2.4	3.5
S (%)	77.5	80.3	52.7	85.8	56.8	96.1	71.9	71.4	70.4
TON	4727	5113	3278	4783	3420	5438	4648	4779	4421
k_{initial} (mol.s ⁻¹) $\times 10^4$	3.82 (± 0.24)	15.0 (± 1.70)	10.9 (± 0.14)	14.0 (± 2.10)	3.69 (± 0.12)	8.15 (± 2.05)	4.15 (± 1.09)	6.61 (± 0.26)	5.39 (± 0.26)
Gr2Ph (3)									
PMP (mol%)	66.9	70.4	44.1	64.5	48.5	12.8	70.4	48.5	67.2
SMP (mol%)	17.5	10.4	47.7	20.5	36.5	2.4	11.7	39.6	21.2
IP (mol%)	0	0	4.2	4.9	0	0.5	0.6	6.8	1.3
S (%)	79.2	87.1	46.0	71.7	57.0	81.6	85.2	51.1	74.9
TON	4683	4926	3089	4513	3397	898	4931	3395	4705
k_{initial} (mol.s ⁻¹) $\times 10^6$	5.23 (± 0.52)	12.2 (± 4.50)	22.3 (± 3.40)	23.8 (± 1.20)	456 (± 36.0)	1.28 (± 0.52)	3.69 (± 0.66)	12.9 (± 8.20)	96.9 (± 6.60)

From the data illustrated in **Table 5.1** it can be said that Gr2 (**2**) is an improvement on Gr1 (**1**) metathesis reactions as stated by different research groups that the NHC-ligand improves the lifetime and reactivity.³⁻⁵ The results obtained from Gr2Ph (**3**) reactions, is an improvement on Gr1 (**1**) reactions in terms of the PMPs and TON, but not the selectivity and the initial reaction rates. The initial reaction rates of the Gr1 (**1**) reactions, where a PCys-group is coordinated to the Ru, is faster than the precatalysts with a NHC-ligand. This NHC-ligand stabilizes the precatalyst, resulting in a slower dissociation reaction than for the Gr1 (**1**) reactions. In addition to the NHC-ligand coordinated to the Ru, the Gr2Ph precatalyst has an additional ligand (N⁺O-ligand) that stabilizes the precatalyst. The PMPs, SMPs, IPs, TON and selectivity of Gr2Ph (**3**) is in the same order as for the Gr2 (**2**) metathesis reactions. The Gr2-type precatalysts produced the best product formations at higher temperatures, whereas precatalyst **1** decomposes at these temperatures (80°C and 100°C), when a 1:7000 ratio was used. In terms of the optimum conditions for the Ru:alkene ratios, no significant differences were observed between 1:7000 and 1:9000 reactions.

The need in the industry and aim of research groups is to find a precatalyst with a longer lifetime, higher TON and tolerable towards impurities. It has been found that precatalyst **3** is an improvement towards the lifetime and TON.

5.1.4 NMR Investigation of carbene species

The method for the NMR investigation was confirmed by using Gr1 (**1**) and 1-octene in CDCl₃ at 30°C and then comparing the results to that of Jordaan *et al.*⁶ and Mtshatsheni.⁷ The three carbene signals were visible in the range of 20 to 16 ppm of the ¹H NMR-spectra for both of the metathesis reactions of 1-octene and 1-hexene. A single carbene signal was observed at 17.2 ppm for the benzylidene, methyldene and alkylidene, for the metathesis reactions of 1-octene and 1-hexene with precatalyst **3**. This observation can be attributed to the carbene species coinciding at this δ -value of 17.2 ppm or that the mechanism takes place via an alternative route. The NMR investigation of a hemilabile precatalyst **9** and **10** by Jordaan¹ resulted in the formation of five different carbene species. An alternative reason for the one carbene signal might also be that **3** is not hemilabile during metathesis reactions of 1-alkenes. The product formation for the Gr1 (**1**) reactions were faster than for the Gr2Ph (**3**) reactions as illustrated in **Figures 4.31** (§ 4.6.1) and **4.36** (§ 4.6.1). The metathesis products obtained for these metathesis reactions resulted in a high concentration of isomerization products present in the reaction mixture. The increase of the precatalyst concentration led to a decrease in selectivity towards the PMP formation and was also observed by Jordaan¹ and van Schalkwyk.⁸

5.2 Recommendations

Further investigations are needed to clarify some of the anomalies observed during this study:

- Since preheating of Gr1 (1) seems to increase the activity and lifetime of the precatalyst, it would be useful to understand what changes takes place during the pre-treatment of the precatalyst.
- To investigate if pre-treatment with heat can change the lifetime and activity of other Ru precatalysts.
- Determination of the decomposing mechanism for the hemilabile precatalysts in the presence of alcohols.
- Since metathesis of the Gr2Ph (3) took place at the low temperatures used during the NMR-investigation without the observation of the alkylidene and methyldiene complexes, it will be interesting to determine the mechanism followed to obtain the products.
- The synthesized precatalyst used during this study was compared to Gr1 (1) and Gr2 (2) during the metathesis reactions of 1-alkenes. Metathesis reactions for ROMP, RCM and ADMET will have to be investigated and compared to the results of Gr1 (1) and Gr2 (2) reactions.

5.3 References

1. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007
2. van der Gryp, P., *Separation of Grubbs-based catalysts with nanofiltration*, Ph.D thesis, (North-West University), 2008
3. Scholl, M., Ding, S., Lee, C.W. and Grubbs, R.H., *Org. Lett.*, 1999, **1**, 953
4. Huang, J., Schanz, H.-J., Stevens, E.D. and Nolan, S.P., *Organometallics*, 1999, **18**, 5375
5. Huang, J., Stevens, E.D., Nolan, S.P. and Petersen, J.L., *J. Am. Chem. Soc.*, 1999, **121**, 2674
6. Jordaan, M., van Helden, P., van Sittert, C.G.C.E. and Vosloo, H.C.M., *J. Mol. Catal A: Chem.*, 2006, **254**, 145
7. Mithatsheni, K.N.G., *Metathesis of alkenes using ruthenium carbene complexes*, M.Sc dissertation, (North-West University), 2005

8. van Schalkwyk, C., *Die Katalitiese Sintese van Linieêre Alkene via 'n Metatesereaksie*, Ph.D thesis, (Potchefstroomse Universiteit vir Christelike Hoër Onderwys), 2001

Acknowledgements:

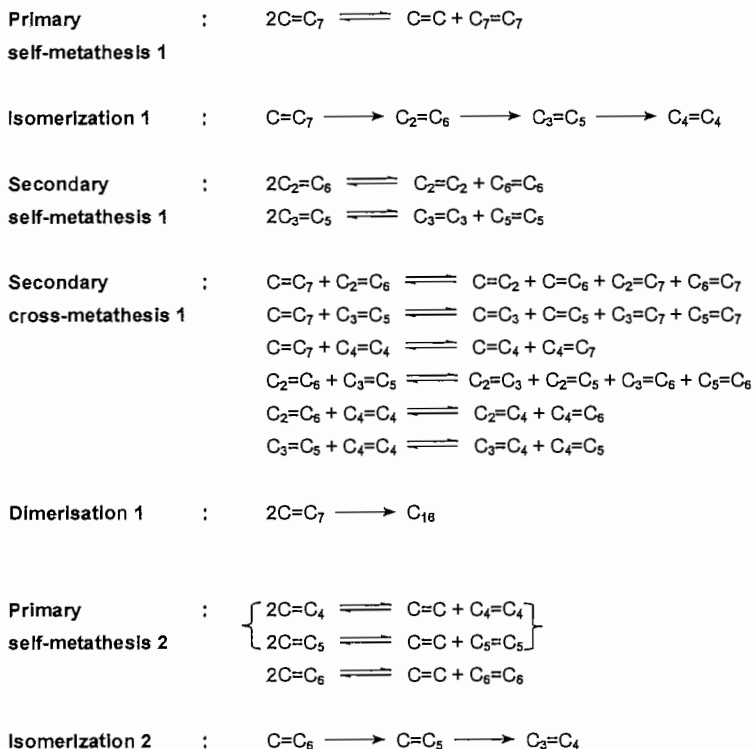
I would like to thank the people that made a difference and without whom this study would not have been completed:

Soli deo Gloria

- ❖ Dr. Johan Jordaan, my supervisor, for his limitless suggestions, guidance and motivation during this study. Especially for never being too busy to listen to any of my problems.
- ❖ Dr. Percy van der Gryp, my co-supervisor, for his suggestions and guidance during this study.
- ❖ Dr. Cornie van Sittert for listening to me and the encouragement throughout this study.
- ❖ All the students in the Catalysis and Synthesis group, especially Ronél Roscher for noticing the changing factor in my metathesis reactions.
- ❖ André Jourbert for the NMR analysis and help with the method development for the NMR-investigation. Dr. Tiedt for the ESEM-analyses. Mrs. Van der Walt, Mnr. Fouché and Dr. Williams for their help with labware.
- ❖ C*change, the North-West University and the Chemical Resource Beneficiation (CRB) for the financial support.
- ❖ My parents for their understanding, motivation, love and support. Also for believing in me. My family and friends for their love and support.
- ❖ Burgert Hattingh for his love, motivation, encouragement and help for the past two years.

Appendix A:

During the metathesis of alkenes different reactions can occur, as illustrated in **Scheme A.1**. The different reactions consist of isomerization, cross-metathesis and self-metathesis reactions. For example: 1-octene can undergo isomerization to 2-, 3- and 4-octene. These isomerization products can undergo cross-metathesis to form SMPs. The SMPs can undergo isomerization, primary and secondary metathesis. The process of metathesis can be repeated until C_2 to C_{14} alkenes are formed. Longer carbon chain alkenes can be formed by oligomerization reactions.^{1,2}



Scheme A.1: Possible products formed during the metathesis reactions of 1-octene.

Appendix A

Secondary self-metathesis 2	:	$C=C_5 + C_3=C_4 \rightleftharpoons C=C_3 + C=C_4 + C_3=C_5 + C_4=C_5$
	:	$C_2=C_5 + C_3=C_4 \rightleftharpoons C_2=C_3 + C_2=C_4 + C_3=C_5 + C_4=C_5$
	:	$C_2=C_5 + C_3=C_4 \rightleftharpoons C_2=C_3 + C_2=C_4 + C_3=C_5 + C_4=C_5$
Secondary cross-metathesis 2	:	$2C_2=C_5 \rightleftharpoons C_2=C_2 + C_5=C_5$
	:	$2C_3=C_4 \rightleftharpoons C_3=C_3 + C_4=C_4$
Dimerisation 2	:	$2C=C_6 \longrightarrow C_{14}$
Primary self-metathesis 3	:	$2C=C_4 \rightleftharpoons C=C + C_4=C_4$
	:	$[2C=C_5 \rightleftharpoons C=C + C_5=C_5]$
Isomerization 3	:	$C=C_5 \longrightarrow C_2=C_4 \longrightarrow C_3=C_3$
Secondary self-metathesis 3	:	$2C_2=C_3 \rightleftharpoons C_2=C_2 + C_3=C_3$
Secondary cross-metathesis 3	:	$C=C_5 + C_2=C_4 \rightleftharpoons C=C_2 + C=C_4 + C_2=C_5 + C_4=C_5$
	:	$C=C_5 + C_3=C_3 \rightleftharpoons C=C_3 + C_3=C_5$
	:	$C_2=C_4 + C_3=C_3 \rightleftharpoons C_2=C_3 + C_3=C_4$
Dimerisation 3	:	$2C=C_5 \longrightarrow C_{12}$
Trimerisation 3	:	$3C=C_5 \longrightarrow C_{18}$

Scheme A.1 cont: Possible products formed during the metathesis reactions of 1-octene.

Primary self-metathesis 4	:	$2\text{C}=\text{C}_4 \rightleftharpoons \text{C}=\text{C} + \text{C}_4=\text{C}_4$
Isomerization 4	:	$\text{C}=\text{C}_4 \rightleftharpoons \text{C}_2=\text{C}_3$
Secondary self-metathesis 4	:	$2\text{C}_2=\text{C}_3 \rightleftharpoons \text{C}_2=\text{C}_2 + \text{C}_3=\text{C}_3$
Secondary cross-metathesis 4	:	$\text{C}=\text{C}_4 + \text{C}_2=\text{C}_3 \rightleftharpoons \text{C}=\text{C}_2 + \text{C}_3=\text{C}_3 + \text{C}_2=\text{C}_4 + \text{C}=\text{C}_4$
Dimerisation 4	:	$2\text{C}=\text{C}_4 \longrightarrow \text{C}_{10}$
Trimerisation 4	:	$3\text{C}=\text{C}_4 \longrightarrow \text{C}_{15}$
Primary self-metathesis 5	:	$2\text{C}=\text{C}_3 \rightleftharpoons \text{C}=\text{C} + \text{C}_3=\text{C}_3$
Isomerization 5	:	$\text{C}=\text{C}_3 \longrightarrow \text{C}_2=\text{C}_2$
Secondary self-metathesis 5	:	—
Secondary cross-metathesis 5	:	$\text{C}=\text{C}_3 + \text{C}_2=\text{C}_2 \rightleftharpoons \text{C}=\text{C}_2 + \text{C}_2=\text{C}_3$
Dimerisation 5	:	$2\text{C}=\text{C}_3 \longrightarrow \text{C}_8$
Trimerisation 5	:	$3\text{C}=\text{C}_3 \longrightarrow \text{C}_{12}$
Tetramerisation 5	:	$4\text{C}=\text{C}_3 \longrightarrow \text{C}_{16}$

Scheme A.1 cont: Possible products formed during the metathesis reactions of 1-octene.

Appendix A

Primary : $2C=C_2 \rightleftharpoons C=C + C_2=C_2$
self-metathesis 6

Isomerization 6 : —

Secondary : —
self-metathesis 6

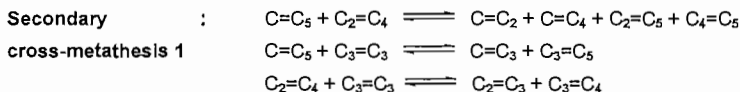
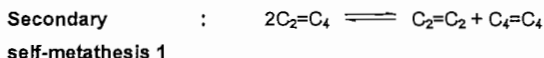
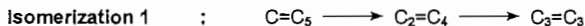
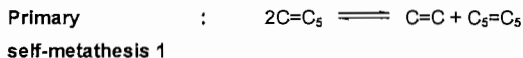
Secondary : —
cross-metathesis 6

Dimerisation 6 : $2C=C_2 \longrightarrow C_6$

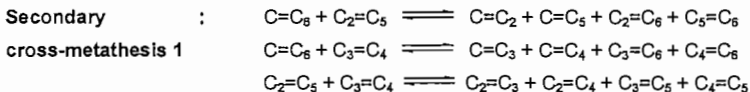
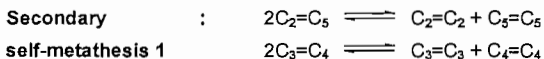
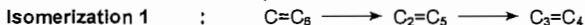
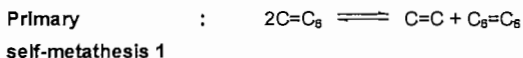
Oligomerisation 6 : $3C=C_2 \longrightarrow C_9$
 $4C=C_2 \longrightarrow C_{12}$
 $5C=C_2 \longrightarrow C_{15}$
 $6C=C_2 \longrightarrow C_{18}$

Scheme A.1 cont: Possible products formed during the metathesis reactions of 1-octene.

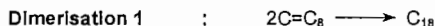
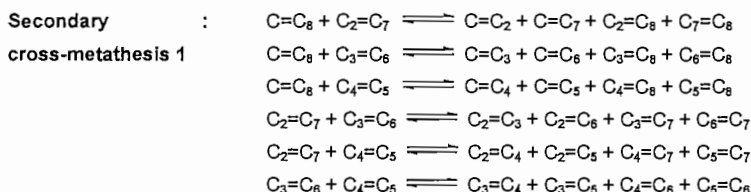
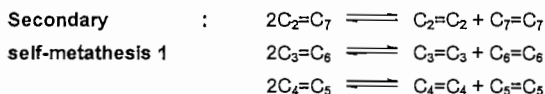
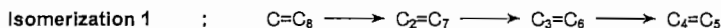
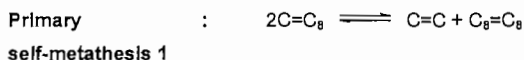
Metathesis reactions with 1-hexene, 1-heptene, 1-nonene and 1-decene also give a range of different metathesis products. The different reactions are illustrated in **Schemes A.2, A.3, A.4 and A.5.**

1-Hexene

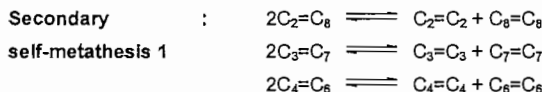
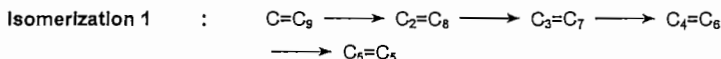
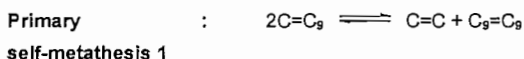
Scheme A.2: Possible products formed during the metathesis reactions of 1-hexene.

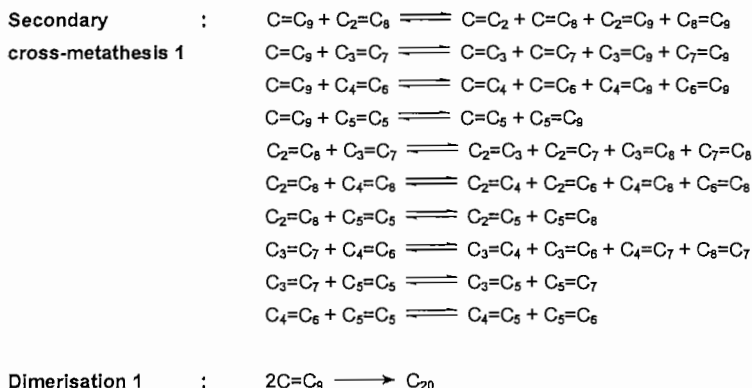
1-Heptene

Scheme A.3: Possible products formed during the metathesis reactions of 1-heptene.

1-Nonene

Scheme A.4: Possible products formed during the metathesis reactions of 1-nonene.

1-Decene



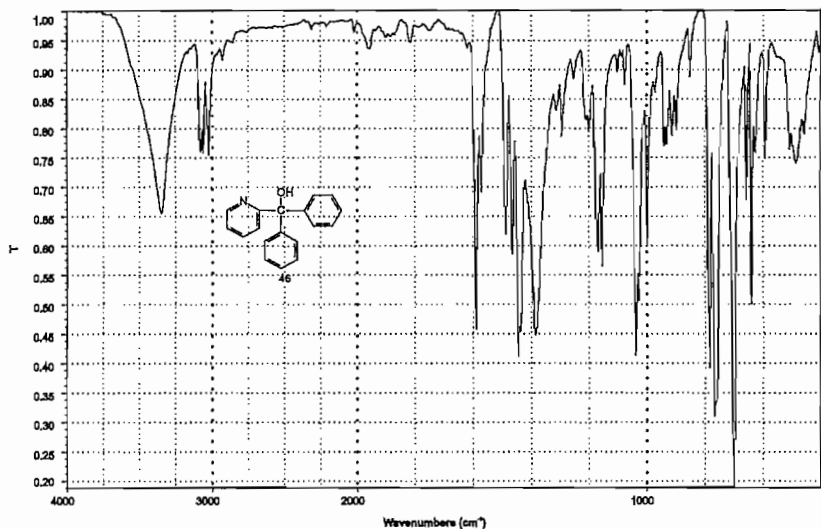
Scheme A.5: Possible products formed during the metathesis reactions of 1-decene.

1. van Schalkwyk, C., *Die Katalitiese Sintese van Lineêre Alkene via 'n Metatesereaksie*, Ph.D thesis, (Potchefstroomse Universiteit vir Christelike Hoër Onderwys), 2001
2. Jordaan, M., *Experimental and Theoretical investigation of New Grubbs-type Catalysts for the Metathesis of Alkenes*, Ph.D thesis, (North-West University), 2007

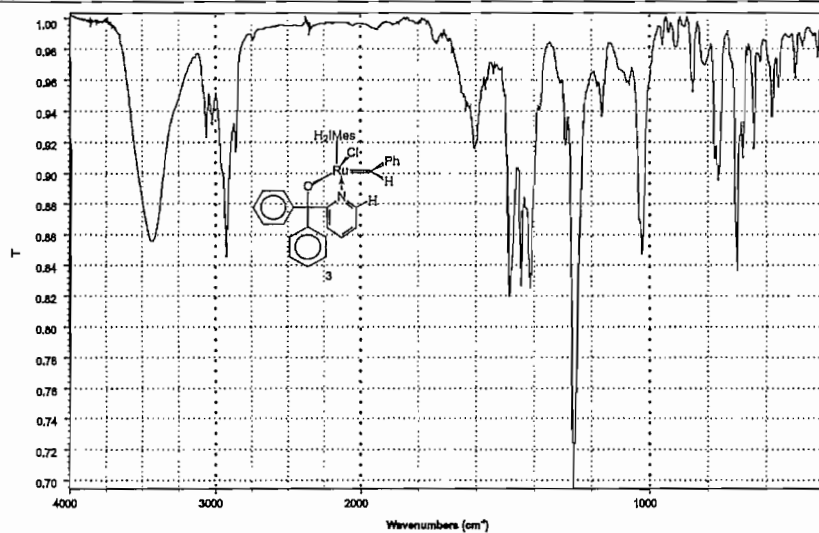
Appendix B:

Copies of the spectra used during this study:

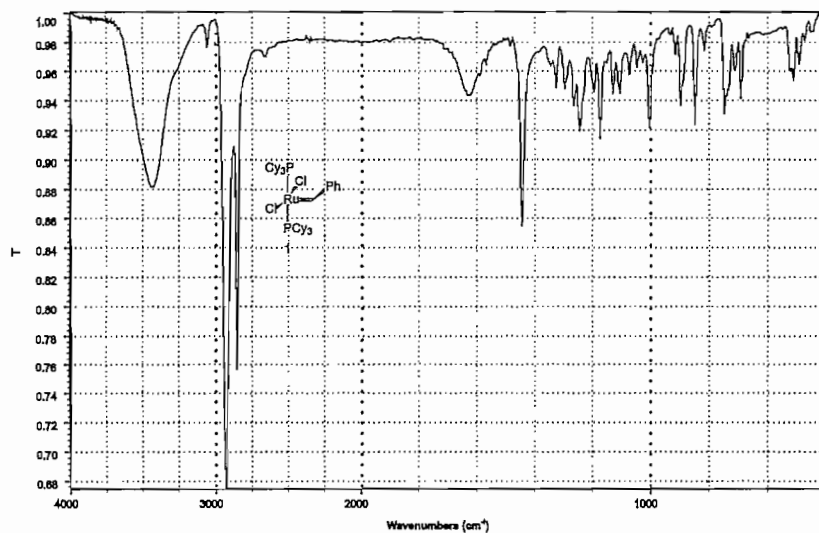
IR-spectra



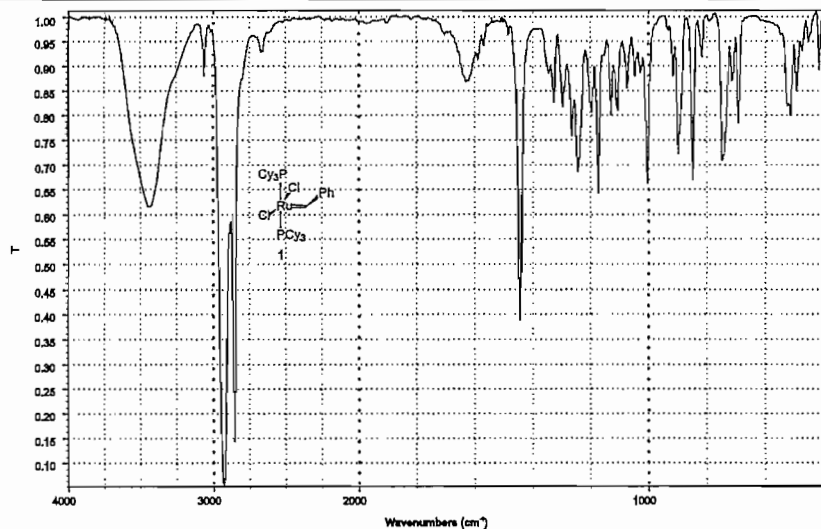
Spectrum B.1: The IR-spectrum of ligand 46.



Spectrum B.2: The IR-spectrum of precatalyst 3.

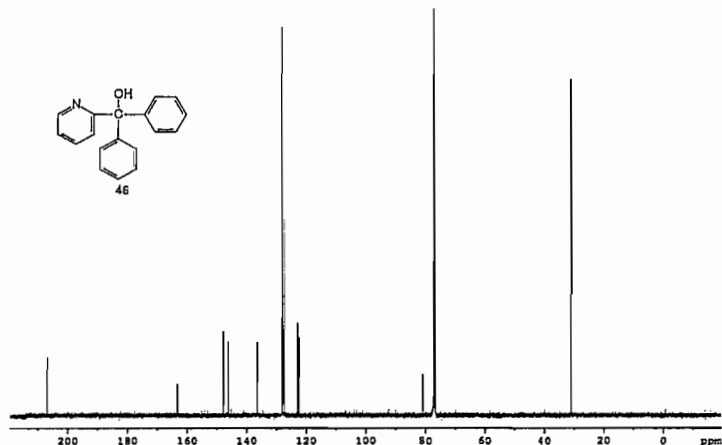


Spectrum B.3: The IR-spectrum of precatalyst 1 without pre-treatment.

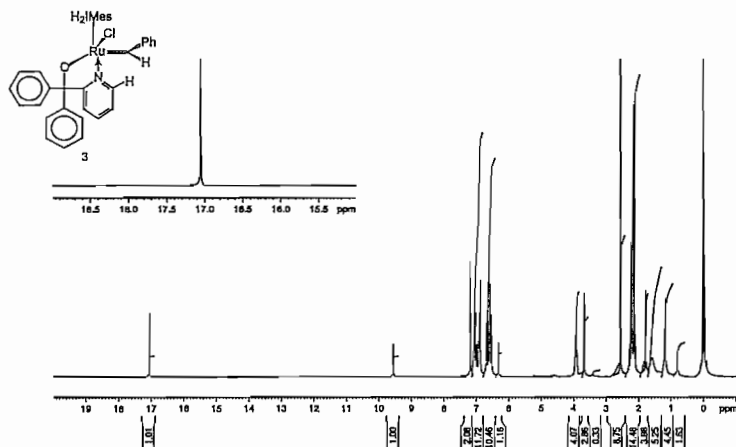
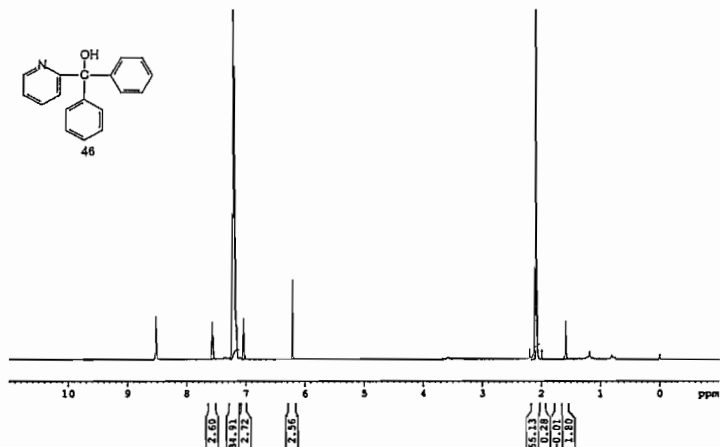


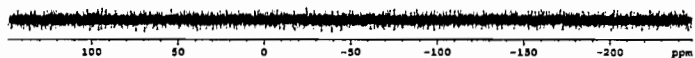
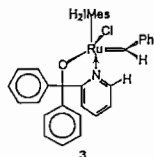
Spectrum B.4: The IR-spectrum of precatalyst 1 with heat pre-treatment of 10min.

¹H NMR-spectra



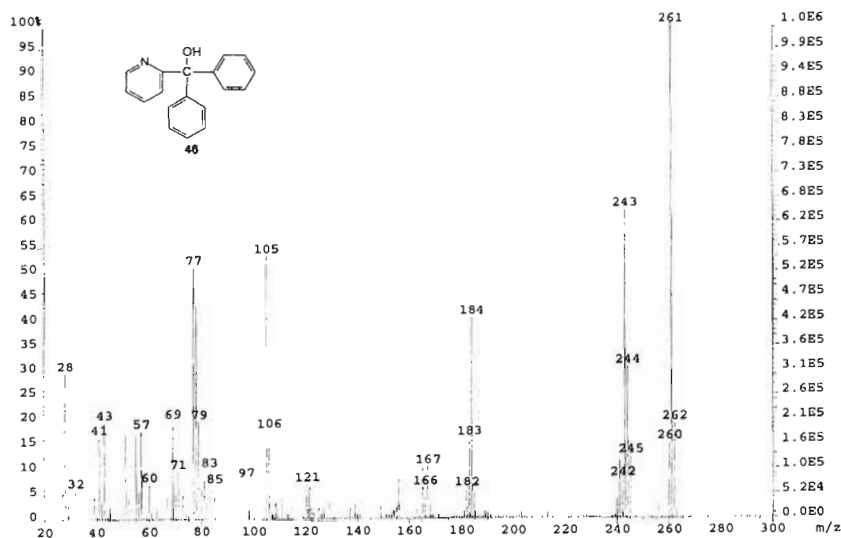
Spectrum B.5: ¹H NMR spectrum of ligand 46.

Spectrum B.6: ¹H NMR spectrum of precatalyst 3.¹³C NMR-spectraSpectrum B.7: ¹³C NMR spectrum of ligand 46.

^{31}P NMR-spectra

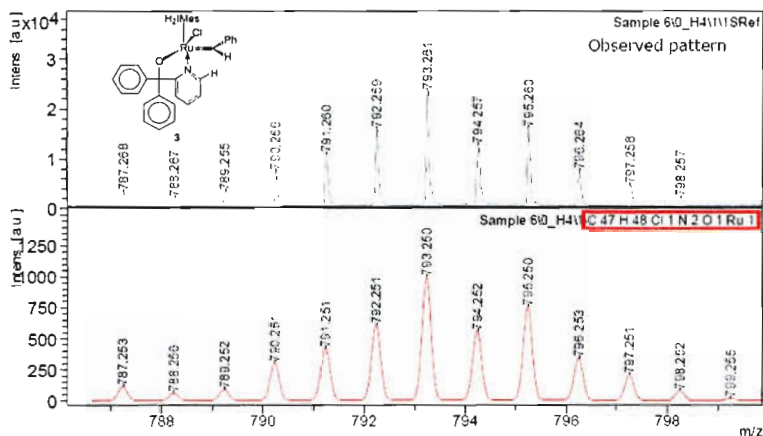
Spectrum B.8: ^{31}P NMR spectrum of precatalyst 3.

MS-spectra



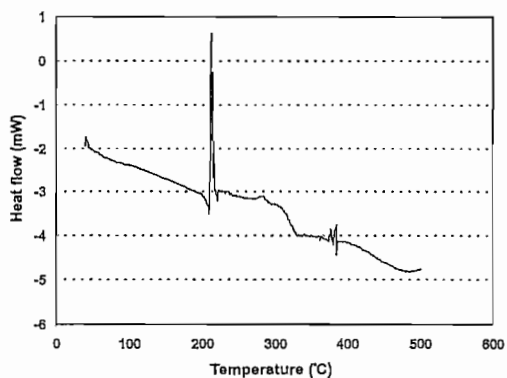
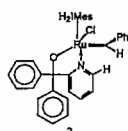
Spectrum B.9: MS chromatogram of ligand 48.

MALDI-TOF MS-spectra

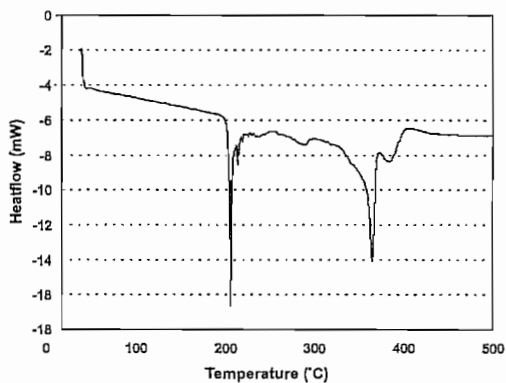
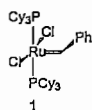


Spectrum B.10: MALDI-TOF MS chromatogram of precatalyst 3.

DSC-data

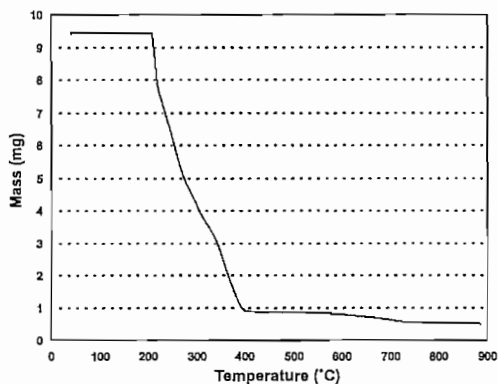
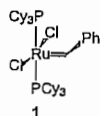


Spectrum B.11: Graph of the DSC-data of precatalyst 3.



Spectrum B.12: Graph of the DSC-data of precatalyst 1.

TGA-data



Spectrum B.13: Graph of the TGA-data of precatalyst 1.