

Separation of Grubbs-based catalysts with nanofiltration

Percy van der Gryp (M.Eng)



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Promoter: Prof. S. Marx (School of Chemical and Minerals Engineering)
Co-Promoter: Prof. H.C.M. Vosloo (School of Physical and Chemical Sciences)

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SUMMARY OF THESIS

This thesis describes the use of organic solvent nanofiltration (OSN) in the field of metathesis for separating homogeneous Grubbs-type catalysts from their post-reaction mixtures for the model metathesis reaction of 1-octene to 7-tetradecene and ethene. The main contributions and objectives of this study were in demonstrating:

- (i) the successful separation and re-use of different Grubbs-type catalysts from their post-reaction mixtures, and
- (ii) the successful synthesis of a newly developed catalyst, **Gr2Ph**, that demonstrated a longer catalytic lifetime for re-usability.

The study was twofold in firstly describing the catalytic performances of different Grubbs-type catalysts for the model reaction and secondly in characterizing and describing the separation performances of the 1-octene metathesis system with OSN.

In terms of catalyst performances:

The catalytic performance of different Grubbs-type precatalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and the newly developed **Gr2Ph**) was studied for the model reaction by varying operating parameters, such as reaction temperature (30 to 100 °C), catalyst load (1-octene/Ru molar ratio between 1:5000 and 1:14000) and reaction environment (reaction in the presence of various organic solvents). Quantities such as product distribution, selectivity, yield, catalyst lifetime and activity were used in comparing and evaluating the efficiency of these precatalysts with each other.

It was found that all three precatalysts **HGr1**, **HGr2** and **Gr2Ph** showed both metathesis and isomerization activity for the model reaction that was strongly temperature-dependent. Precatalysts **HGr2** and **Gr2Ph** showed significant secondary metathesis activity while precatalyst **HGr1** did not. It was found that the optimal reaction temperature for precatalyst **HGr1** was 30 °C, for precatalyst **HGr2** 50 °C and for precatalyst **Gr2Ph** 80 °C. The addition of different solvents to the reaction environment had an overall negative effect towards the formation of the primary metathesis products (PMPs) of 7-tetradecene and ethylene.

In this study it was postulated and demonstrated with molecular modelling, that the metathesis reaction of 1-octene with the different Grubbs-type precatalysts (**HGr1**, **HGr2** and **Gr2Ph**) could accurately be described by a type of release-return dissociative mechanism. It was further found

that the reaction kinetics of the model reaction with the three precatalysts (**HGr1**, **HGr2** and **Gr2Ph**) could fairly accurately be described by a set of three inter-dependent elementary reaction rate-equations.

In terms of separation performances:

Five different Grubbs-type precatalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**) and the commercially available STARMEM™ series of OSN membranes were used in this study. Parameters such as feed concentration, feed pressure, membrane pretreat-solvent and catalyst load were varied in a dead-end setup. Quantities such as the permeation rate (flux), catalyst rejection, solvent separation (selectivity), degree of swelling and contact angles were measured.

It was found that the STARMEM™ 228 membrane successfully separated the different Grubbs-type catalysts from their post-reaction mixtures to below 9 ppm with catalysts rejections greater than 99%. Relative moderate fluxes were obtained that ranged from 0.2 to 15 kg.m⁻².h⁻¹. It was shown that 7-tetradecene preferentially absorbed in the STARMEM™ 228 membrane. A solvent non-separating system was observed for binary mixtures of 1-octene, 1-tetradecene and 7-tetradecene. It was found that the predominant parameters that influenced the transport of the 1-octene metathesis system through the ST-228 membrane were solvent properties (such as viscosity) >> membrane-solvent interaction properties (such as sorption) > solvent-solvent structural properties (such as molar volume or effective molecular volume).

The experimental permeation results for the binary mixtures of 1-octene and 7-tetradecene through the STARMEM™ 228 membrane were described by using pore-flow models, solution-diffusion models and a newly developed model that incorporates structural solvent-solvent interaction. It was found that the newly developed model best described the experimental results.

A coupled reaction-separation process was applied that demonstrated the successful re-usability of the in-house synthesized catalyst, **Gr2Ph**. The turnover number was increased from 1400 for a single pass reaction to 5500 for the overall consecutively coupled reaction-separation steps of four cycles. Catalysts **Gr1**, **Gr2**, **HGr1** and **HGr2** did not show any catalytic activity after the first separation cycle due to extremely short catalytic lifetimes of less than ten hours compared to catalyst **Gr2Ph**'s three days.

The short catalytic lifetimes of the classical precatalysts such as **Gr1**, **Gr2**, **HGr1** and **HGr2** in the field of alkene metathesis were solved with the synthesizing concept of modifying and binding the dissociating ligand and anionic ligand with bidentate O,N-chelated Schiff base ligand on the second generation Grubbs-precatalyst.

Keywords: Organic solvent nanofiltration; STARMEMTM; Grubbs-type catalyst; alkene metathesis

AFRIKAANSE OPSOMMING VAN DIE PROEFSKRIF

Skeiding van Grubbs-gebaseerde katalisators met nanofiltrasie

Hierdie tesis beskryf die gebruik van organiese solvent-nanofiltrasie (OSN) in die veld van metatiese om homogene Grubbs-tipe katalisators te skei van hulle post-reaksie-mengsels vir die model-metatesereaksie van 1-okteen na 7-tetradeken en eteen. Die hoofbydraes en doelwitte van hierdie studie was om te demonstree:

- (i) die suksesvolle skeiding en hergebruik van verskillende Grubbs-tipe katalisators van hulle post-reaksie-mengsels, en
- (ii) die suksesvolle sintetisering van 'n nuut-ontwikkelde katalisator, **Gr2Ph**, wat 'n langer katalitiese leeftyd vir hergebruik gedemonstree het.

Die studie was tweedelig, deur eerstens die katalitiese vermoë van verskillende Grubbs-tipe katalisators vir die modelreaksie te beskryf en tweedens, deur die skeidingsvermoë van die 1-okteen-metatese-sisteem met OSN te karakteriseer en te beskryf.

In terme van katalisatorvermoë:

Die katalitiese vermoë van verskillende Grubbs-tipe prekatalisators (**Gr1**, **Gr2**, **HGr1**, **HGr2** en die nuut-ontwikkelde **Gr2Ph**) is vir die modelreaksie bestudeer deur bedryfsparameters te varieer soos byvoorbeeld reaksietemperatuur (30 tot 100 °C), katalisatorlading (1-okteen/Ru molêre verhouding tussen 1:5000 en 1:14000) en reaksie-omgewing (reaksie in die teenwoordigheid van verskeie organiese solvente). Eienskappe soos produkverspreiding, selektiwiteit, opbrengs, katalisator-leeftyd en -aktiwiteit is gebruik om die effektiwiteit van hierdie katalisators met mekaar te vergelyk en te evalueer.

Dit is bevind dat al drie prekatalisators **HGr1**, **HGr2** en **Gr2Ph** beide metatese en isomerisasie aktiwiteit toon vir die modelreaksie wat sterk temperatuurafhanklik is. Prekatalisator **HGr2** en **Gr2Ph** het merkbare sekondêre metatese-aktiwiteit getoon, maar prekatalisator **HGr1** nie. Daar is gevind dat die optimale reaksietemperatuur vir prekatalisator **HGr1** 30 °C was, vir prekatalisator **HGr2** 50 °C en vir prekatalisator **Gr2Ph** 80 °C. Die byvoeging van verskillende solvente tot die reaksie-omgewing het oor die algemeen 'n negatiewe effek op die vorming van PMP's.

Met behulp van molekulêre modulering word in hierdie studie gepostuleer en gedemonstreer, dat die metatiese-reaksie van 1-okteen met verskillende Grubbs-tipe prekatalisators (**HGr1**, **HGr2** en **Gr2Ph**) akkuraat beskryf kan word deur 'n tipe vrylaat-terugkeer dissosiasie-meganisme. Daar is verder gevind dat die reaksiekinetika van die modelreaksie met die drie prekatalisators (**HGr1**, **HGr2** en **Gr2Ph**) redelik akkuraat beskryf kon word deur 'n stel van drie interafhanklike elementêre reaksietempo-vergelykings.

In terme van skeidingsvermoë:

Vyf verskillende Grubbs-tipe prekatalisators (**Gr1**, **Gr2**, **HGr1**, **HGr2** en **Gr2Ph**) en die kommersieel-beskikbare STARMEM™ reeks van OSN-membrane is gebruik in hierdie studie. Parameters soos voerkonsentrasie, voerdruk, membraan-voerversorgingsoplosmiddel en voor-katalisator-lading is gevarieer in 'n standaard doodloop-opstelling. Eienskappe soos permeasie tempo (vloed), katalisatorverwerping, solventskeiding (selektiwiteit), graad van swelling en kontakhoeke is gemeet.

Daar is gevind dat die STARMEM™ 228-membraan die verskillende Grubbs-tipe katalisators suksesvol geskei het van hulle post-reaksie-mengsels tot onder 9 dpm met katalisator-verwerping meer as 99%. Relatief gemiddelde vloede wat strek van 0.2 tot 15 kg.m⁻².h⁻¹ is gevind. Daar is bewys dat 7-tetradkeen by voorkeur geabsorbeer het in die STARMEM™ 228-membraan. 'n Solvent-nie-skeidingsstelsel vir binêre mengsels van 1-okteen, 1-tetradkeen en 7-tetradkeen is gevind. Daar is gevind dat die oorheersende parameters wat die vervoer van die 1-okteen metatiese-sistelsel deur die ST-228 membraan beïnvloed solvent eienskappe (soos viskositeit), membraan-solvent interaksie-eienskappe (soos sorpsie) en solvent-solvent struktuur-eienskappe (soos molêre volume of effektiewe molekulêre volume) is.

Die eksperimentele permeasie-resultate vir die binêre mengsels van 1-okteen en 7-tetradkeen deur die STARMEM™ 228-membraan is beskryf deur porie-vloei-modelle, oplossing-diffusie-modelle en 'n nuut-ontwikkelde model wat struktuur-solvent-solvent-interaksie inkorporeer, te gebruik. Dit is bevind dat die nuut-ontwikkelde model die eksperimentele resultate die beste beskryf.

'n Gekoppelde reaksie-skeidingsproses wat die suksesvolle hergebruik van die plaaslik-gesintetiseerde katalisator, **Gr2Ph**, demonstreer, is aangewend. Die opbrengs is verhoog van 1400 vir 'n enkelladingsreaksie tot 5500 vir die algehele opeenvolgende gekoppelde reaksie-skeidingstappe van vier siklusse. Die katalisators **Gr1**, **Gr2**, **HGr1** en **HGr2** het geen katalitiese aktiwiteit getoon na die eerste skeidingsiklus nie as gevolg van uiters kort katalitiese leeftye van minder as tien uur in vergelyking met katalisator **Gr2Ph** se drie dae.

Die kort katalitiese leeftye van die klassieke prekatalisators soos **Gr1**, **Gr2**, **HGr1** en **HGr2** in die veld van alkeen-metatese is opgelos met die sintetiseringskonsep om die dissosiatiewe ligand en die anioniese ligand aan te pas en te bind aan 'n bidentaats O,N-chelaatbasis-ligand op die tweede generasie Grubbs prekatalisator.

Sleutelwoorde: Organiese-solvente-nanofiltrasie; STARMEMTM; Grubbs-tipe katalisator; alkeen-metatese

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This research started in 2005 with an informal talk that inspired me to undertake a broad investigation into two different fields with diverse paradigms. This adventure of exploring these two worlds that I started to call *Organic Solvent Nanofiltration* and *Metathesis*, led me to meet a large number of fellow explorers who helped me to complete this thesis. It is, therefore, a privilege to express my sincere gratitude towards these explorers and organisations for their continuous support and help during this adventure.

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NOMENCLATURE

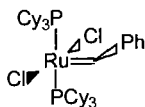
Abbreviation	Description
ADMET	Acyclic diene metathesis
#-C8	Octene where # indicates the isomer of octene, e.g. 2-C8 is 2-octene, 3-C8 is 3-octene, etc.
C# or C_#	Alkene where # indicates the carbon chain length, e.g. C7 is heptene, C9 is nonene, C14 tetradecene, etc.
CM	Cross-metathesis
DFT	Density Functional Theory
DMSO	Dimethyl sulphoxide
EYM	Enyne metathesis
H₂IMes	1,3-bis-(2,4,6-trimethylphenyl)-2-imadazolidinylidene
IP	Isomerization product
Me	Methyl
Mes	1,3-bis-(2,4,6-trimethylphenyl)
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NHC	N-heterocyclic carbene
O[^]N	Bidentate ligand coordinated to a metal at O and N
OSN	Organic solvent nanofiltration
PCy₃	Tricyclohexylphosphine
PES	Potential energy surfaces
Ph	Phenyl
PMP	Primary metathesis product
R=C	Ruthenium carbene moiety
RCM	Ring-closing metathesis
RO	Reverse osmosis
ROCM	Ring-open cross metathesis
ROM	Ring-opening metathesis
ROMP	Ring-opening metathesis polymerization
S	Selectivity
SM	Self metathesis
SMP	Secondary metathesis product
SRNF	Solvent-resistant nanofiltration
ST-120	STARMEM TM 120
ST-122	STARMEM TM 122
ST-228	STARMEM TM 228
ST-240	STARMEM TM 240
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TON	Turnover number
Ts	Tosyl
TS	Transition state
UF	Ultrafiltration

Symbol	Description	Unit
A	GC response area	-
A	Active membrane area	m^2
C_{C_8}	Concentration of 1-octene in the reactor	mol.L^{-1}
C_{IP}	Concentration of IP in the reactor	mol.L^{-1}
C_P or C_R	Final concentration of catalyst	mg.mL^{-1}
C_{PMP}	Concentration of PMP in the reactor	mol.L^{-1}
D	Diffusion coefficient	$\text{m}^2.\text{s}^{-1}$
d	Diameter	m
f	structural sizing fraction of component i	-
i	Component i	-
J	Flux (molar, or mass, or volume)	$\text{kg.m}^{-2}.\text{h}^{-1}$
K	Meter constant	$\text{m}^2.\text{s}^{-2}$
k_1	Forward rate constant for consumption of 1-octene	min^{-1}
k_2	Reverse rate constant for consumption of 1-octene	min^{-1}
k_3	Rate constant for the formation of IP+SMP	min^{-1}
l	Length of membrane thickness	m
m	Mass	mg
M	Molecular weight of solute	g.mol^{-1}
M_{dry}	Initial dried membrane mass	mg
MW	Molecular mass	g.mol^{-1}
M_{wet}	"Wetted" membrane mass	mg
M_{∞}	Swelling ratio	mg.mg^{-1}
N	Moles	mol
p	Pressure	Pa
P_i^{mass}	Mass permeability for component i	$\text{kg.m}^{-2}.\text{s}^{-1}$
R	Rejection	-
RF	GC-response factor	-
T	Time	h
T	Temperature	K
V	Volume	mL
V_i	Molar volume of component i	$\text{m}^3.\text{mol}^{-1}$
v_i	Molar volume of component i	$\text{m}^3.\text{mol}^{-1}$
x	Molar fraction	-
X	Frictional force between solute and membrane	-
z	Length of membrane	m

Greek Symbol	Description	Unit
ε	Porosity of the membrane	-
ϕ	Sorption coefficient or swelling ratio	mg.mg ⁻¹
ρ	Density	kg.m ⁻³
γ	Surface tension or energy	-
γ_i	Activity coefficient of component i	-
μ	Chemical potential	J.mol ⁻¹
χ	Dimensionless interaction parameter	-
ξ	Structural size quantity (example molar volume)	-
η	Viscosity	Pa.s
τ	Tortuosity factor	-

LIST OF CATALYSTS

Gr1



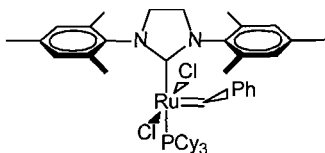
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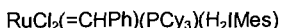
1st generation Grubbs precatalyst

[Benzylidene-bis(tricyclohexyl phosphine)dichloro ruthenium]

Gr2



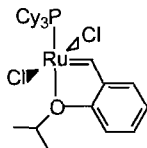
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2nd generation Grubbs precatalyst

[(1,3-Bis-(2,4,6 trimethyl-phenyl)-2-imidazolidinylidene)di-chloro(phenyl-methylene)-(tri-cyclo-hexyl-phosphine)ruthenium]

HGr1



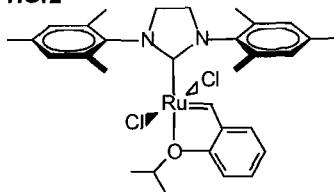
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1st generation Hoveyda-Grubbs precatalyst

[Dichloro(*o*-isopropoxyphenyl)methylene (tricyclohexylphosphine)ruthenium]

HGr2



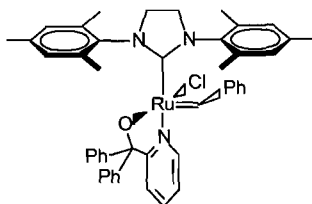
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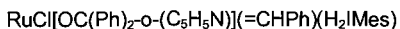
2nd generation Hoveyda-Grubbs precatalyst

[(1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenyl methylene)ruthenium]

Gr2Ph



Self-synthesized catalyst from Gr2.



2nd generation PUK-Grubbs precatalyst

[Benzylidene-chloro(1,3-bis-(2,4,6-tri-methyl-phenyl)-2-imidazolidinylidene)-{1-(2'-pyridinyl)-1,1-di-phenyl-methanolato}ruthenium]

1 INTRODUCTION

Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment... This represents a great step forward for 'green chemistry,' reducing potentially hazardous waste through smarter production.
(award committee of Nobel Prize for Chemistry, 2005)

Overview

In this chapter, a broad overview of the contents of this investigation will be presented. The chapter is subdivided into three sections, starting with the background and motivation for this investigation in Section 1.1 (Background and motivation). The aims and objectives of the investigation are formulated in Section 1.2 (Objectives) and the outline of the thesis with the scope of investigation is provided in Section 1.3 (Scope of investigation).

1.1 Background and motivation

In 2005 the research field of alkene metathesis was acknowledged for its breakthrough contributions to science when Yves Chauvin, Robert H. Grubbs and Richard R. Schrock jointly received the Nobel Prize for Chemistry.¹ The alkene metathesis reaction, as shown in Figure 1.1, can be described as a catalyst-driven organic reaction which involves the exchange of two starting alkenes to form two new alkenes (transalkylidenation).

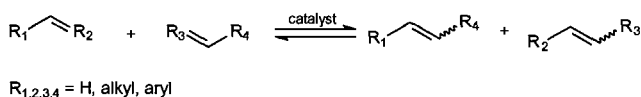


Figure 1.1 Generalized alkene metathesis reaction.

The metathesis reaction has become synthetically useful since the discovery of various well-defined transition metal carbene systems. The metal carbene systems can be either homogeneous or heterogeneous based on tungsten, molybdenum or rhodium. Especially the ruthenium based is known to be the most effective catalyst system.² Homogeneous catalysts, dispersed in a solution of reactants, have many potential advantages over the solid phase, heterogeneous catalysts as summarized in Table 1.1.

Table 1.1 Comparison of homogeneous and heterogeneous catalysts.^[a]

	Homogeneous		Heterogeneous	
	Description	Rating	Description	Rating
Activity (relative to metal content)	High	+++	Variable	-
Selectivity	High	+++	Variable	+
Sensitivity towards catalyst poisons	Low	+++	High	--
Diffusion problems	None	+++	May be important	+
Mechanistic understanding	Plausible	++	Almost impossible	--
Reaction conditions	Mild	++	Harsh	++
Catalyst recycling	Expensive	---	Not necessary	+++
Service life of catalysts (lifetime)	Extremely low	---	Long	+++

[a] adapted from reference 3

It is evident from Table 1.1 that homogeneous catalysts under mild reaction conditions are superior in terms of activity and selectivity and possess high atomic efficiency. Furthermore, catalytic properties such as chemo-, regio- and stereo-selectivity can be tuned easily because of the well-defined nature of homogeneous catalysts. These advantages were utilized in the 1990s by the research group of Grubbs⁴ when they developed the well-defined commercially

available metathesis ruthenium carbene complexes, $\text{RuCl}_2\text{LL}'(=\text{CHPh})$ [L , $\text{L}' = \text{PCy}_3$ (**Gr1**) and $\text{L}' = \text{NHC}$ (**Gr2**)]. Thanks to these Grubbs-type precatalysts and their successors such as the Hoveyda-Grubbs-type (**HGr1** and **HGr2**), as depicted in Figure 1.2, application in the metathesis field has increased exponentially.^{1,2,4-8,10} Examples of applications are the synthesis of polymers with special properties, additives to polymers and fuels, and the synthesis of biologically active compounds such as insect pheromones, herbicides and medicines.^{1,2,4-8,10}

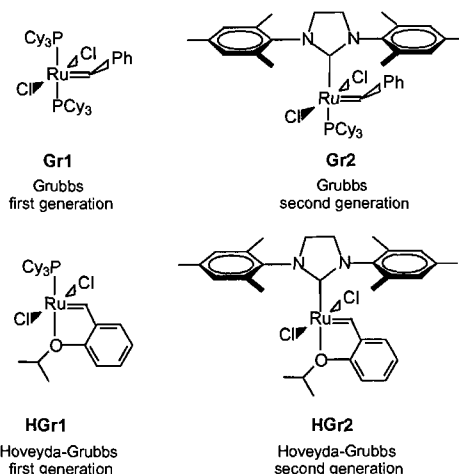


Figure 1.2 The main ruthenium carbene metathesis catalysts that are commercially available.

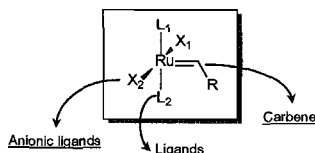
Despite all the advantages such as high activity and selectivity¹¹⁻¹³ offered by these homogeneous Grubbs-type precatalysts, there are still some drawbacks that hinder them from being successfully implemented industrially, especially in bulk chemicals such as the petrochemical sector. The two main disadvantages excluding the cost, are:^{4,14-18}

- extremely short reaction lifetime (on average less than five hours) and
- inability to be separated and recycled for re-use in an active form.

It is, therefore, the aim of this investigation to address these two disadvantages. The two disadvantages will now be discussed in turn, followed by a short presentation of solutions to these challenges that will be presented in this thesis.

Starting with the first disadvantage of catalyst stability addressed in this study and especially focusing on catalyst lifetime, some plausible solutions have been presented over the past decade to increase the catalyst lifetime. Attention has been given to increasing the catalyst initiation rate through mainly *steric and electronic modification* of the:

- alkylidene moiety (carbene unit, =CHR) and/or,¹⁸⁻²³
- ancillary-ligands (L_1 and L_2 ligands) and/or,²⁴⁻²⁷
- anionic-ligands (X 's bound to the Ru metal).²⁸⁻³¹



The lifetime of the Grubbs-type precatalysts, such as **Gr1** and **Gr2**, was also shown to increase by introducing different additives to the reaction environment.^{32,33}

Grubbs³⁴ and Verpoort³⁵⁻³⁷ used a catalyst synthesis concept of modifying and binding of the dissociating ligand, L_2 , and the anionic ligand, X_2 , with bidentate O,N-chelated Schiff base ligands that were introduced on **Gr1** and **Gr2** in an attempt to increase the catalyst stability. Other researchers from the groups of Herrmann³⁸ and Hafner³⁹ used the same design method with hemilabile pyridinyl-alcoholato, alkylphosphine and pyridinyl alcoholate ligands. Recently, Jordaan and Vosloo⁴⁰ also applied this design concept with a hemilabile pyridinyl-alcoholato ligand for the metathesis of 1-octene and showed potentially enhanced catalyst lifetimes.

In this investigation it will be shown that a newly synthesized precatalyst PUJ-Grubbs 2 (**Gr2Ph**) developed at the North-West University⁴¹ and in collaboration with the petrochemical industry (Sasol Ltd.), following the same design concept, resulted in a Grubbs-type catalyst with an improved catalyst stability that has an active lifetime of greater than three days. The newly developed **Gr2Ph** catalyst is shown in Figure 1.3.

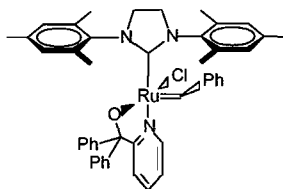


Figure 1.3 Precatalyst **Gr2Ph** used in this investigation.

The second disadvantage addressed in this study is the recovery of homogeneous catalysts in an active form from their product mixtures. Recovery of homogeneous catalysts in an active form requires energy intensive and waste-generating downstream processing which makes the industrial implementation of homogeneous catalysts less favourable from energy-saving and economical viewpoints.⁴²⁻⁴⁴ A number of important industrial processes, such as the production of adiponitrile by DuPont, acetic acid by Monsanto, and butanal by Ruhr Chemie are presently catalyzed by homogeneous catalysts.⁴⁵ This demonstrates the importance of homogeneous catalysis. Commercial application for homogeneous catalysts is generally limited to reactions requiring very low concentrations, since the quantity in the product stream is then at the parts per million level, and thus, separation of the catalyst is not necessary. Furthermore, few, if any of these industrially employed separations are aimed at recovering the catalyst in an active form; they focus on obtaining a pure (metal-free) product/solvent phase by removing any residual catalyst and catalyst decomposition fragments.⁴²⁻⁴⁴

From Table 1.1 it can be concluded that from a commercial and an environmental point of view, it would be highly desirable to develop a general method that incorporates the advantages of both homogeneous and heterogeneous catalysis into a single chemical process. The ultimate goal will be to design a catalytic system with high activity, high selectivity, efficient catalyst recycling and a high stability (lifetime). This will ultimately lead to cleaner, faster and cheaper catalytic processes and eventually to green commercial processes.

Elegant catalyst synthesis strategies have been presented in recent years to address this goal. These can be subdivided into two major synthesis processes, namely immobilization of the catalyst on a support⁴⁶⁻⁴⁹ and biphasic systems.⁵⁰⁻⁵³ In the first, the catalyst is anchored to some kind of soluble or insoluble support that can easily be separated by a filtration technique. This type of process is often referred to as heterogenizing homogeneous catalysts. Griffels *et al.*,⁵⁴ for example, used this method to synthesize a soluble polymer-enlarged oxazaborolidines homogeneous catalyst for the enantioselective reduction of several ketones. They used the membrane technique of organic solvent nanofiltration (OSN) to separate and recover the catalyst in an active form for re-use. Biphasic systems involve designing the catalyst so that it is solubilized in a solvent that, under some conditions, is immiscible with the reaction product. The recovery of these catalysts can also be accomplished via filtration, such as OSN, precipitation, or a liquid-liquid partition technique. Excellent review articles on these two types of system were published by Cole-Hamilton⁹ and Deshmukh *et al.*⁵⁵ Other researchers^{42-45,56-74} also found the separation technique of OSN to be a viable solution for separating and re-using different kinds of homogeneous catalysts with or without immobilization of the catalyst on a support or using biphasic systems.

In this investigation it will be shown that OSN can be used to separate different Grubbs-type catalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**) from their post-metathesis reaction mixtures. It will further be demonstrated that OSN can be used to recover and re-use a homogeneous catalyst without any immobilization or biphasization of the catalyst.

Even though other researchers have separately studied these two fields of

- a) alkene metathesis (focusing on catalyst development and reaction evaluation) and
- b) recovery of homogeneous catalysts via nanofiltration,

available data in literature for the combination of these two fields are still lacking and a detailed experimental investigation of this subject is, therefore, necessary.

The largest application of the alkene metathesis reaction is in the field of petrochemicals, for example, the Shell higher olefins process (SHOP) produces more than 10^5 tons of C_{10} and C_{20} alkenes annually.⁷⁶ In South Africa, Sasol Ltd. is using the Fischer-Tropsch process to make alkenes from synthesis gas, which can be obtained from coal or natural gas. With the use of existing process technologies such as the alkene metathesis reaction, the low value alkenes (1-heptene and 1-octene) can be converted to high value alkenes (6-dodecene and 7-tetradecene) which can then be used as detergent alcohol feedstock.¹⁰ In the South African context, the model metathesis reaction of 1-octene to 7-tetradecene and ethene will be used in this investigation.

1.2 Objectives

The main contribution of this investigation is to the research fields of OSN and alkene metathesis by demonstrating the successful separation and re-use of different Grubbs-type catalysts from their post-reaction mixtures. The broad objectives of this investigation are twofold in studying the catalytic and separation performance as follows:

(i) *Catalytic performance*

- Understand the catalytic performances of the different Grubbs-type precatalysts for the metathesis reaction of 1-octene to 7-tetradecene and ethene.
 - Evaluate the effect of reaction temperature, catalyst load and the addition of different additives on the catalytic performance.
 - Describe the mechanism and kinetic behaviour of the metathesis reaction of 1-octene for the different precatalysts.
-

(ii) Separation performance

- Understand the separation characteristic of the different Grubbs-type precatalysts through the membrane by using OSN.
- Evaluate the effect of membrane pretreatment, feed pressure, solvent concentration and catalyst load on the separation performance for the 1-octene metathesis system.
- Explore the extension of literature transport models for OSN and develop a simple model to describe the separation process of the 1-octene metathesis system.

1.3 Scope of investigation

The basic scope of this investigation is summarized in Figure 1.4. The thesis is subdivided into six chapters (including this one) that consist of the following contents, in order to achieve the above-mentioned objectives:

In **Chapter 2** a complete theoretical background and literature survey on the two research fields of metathesis and nanofiltration are presented. The focus here is to acquire knowledge, analyse, synthesize and critically appraise the different terminologies and concepts pertaining to the two fields that are relevant to this study. A brief overview of homogeneous alkene metathesis catalyst development and application, state of the art review of 1-octene metathesis, mechanisms of alkene metathesis and theoretical studies of alkene metathesis with molecular modelling are discussed. A brief overview of nanofiltration and a state of the art review on the recovery of homogeneous catalysts with OSN are presented. The transport of solvents through OSN membranes and the models used to describe the transport mechanism are elucidated.

In **Chapter 3** all the experimental apparatus and methodologies that were used in this investigation are described in detail.

Chapter 4 focuses on the metathesis reaction, reaction kinetics and mechanism for the 1-octene metathesis system with the different precatalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**). The focus here is to:

- (i) synthesize the chelated precatalyst **Gr2Ph**,
 - (ii) evaluate the metathesis reaction performances of the different precatalysts (**HGr1**, **HGr2** and **Gr2Ph**) by varying the reaction temperature, catalyst load and addition of different additives,
 - (iii) describe the reaction kinetics and,
 - (iv) propose a reaction mechanism and evaluate the alkene metathesis mechanism theoretically with molecular modelling.
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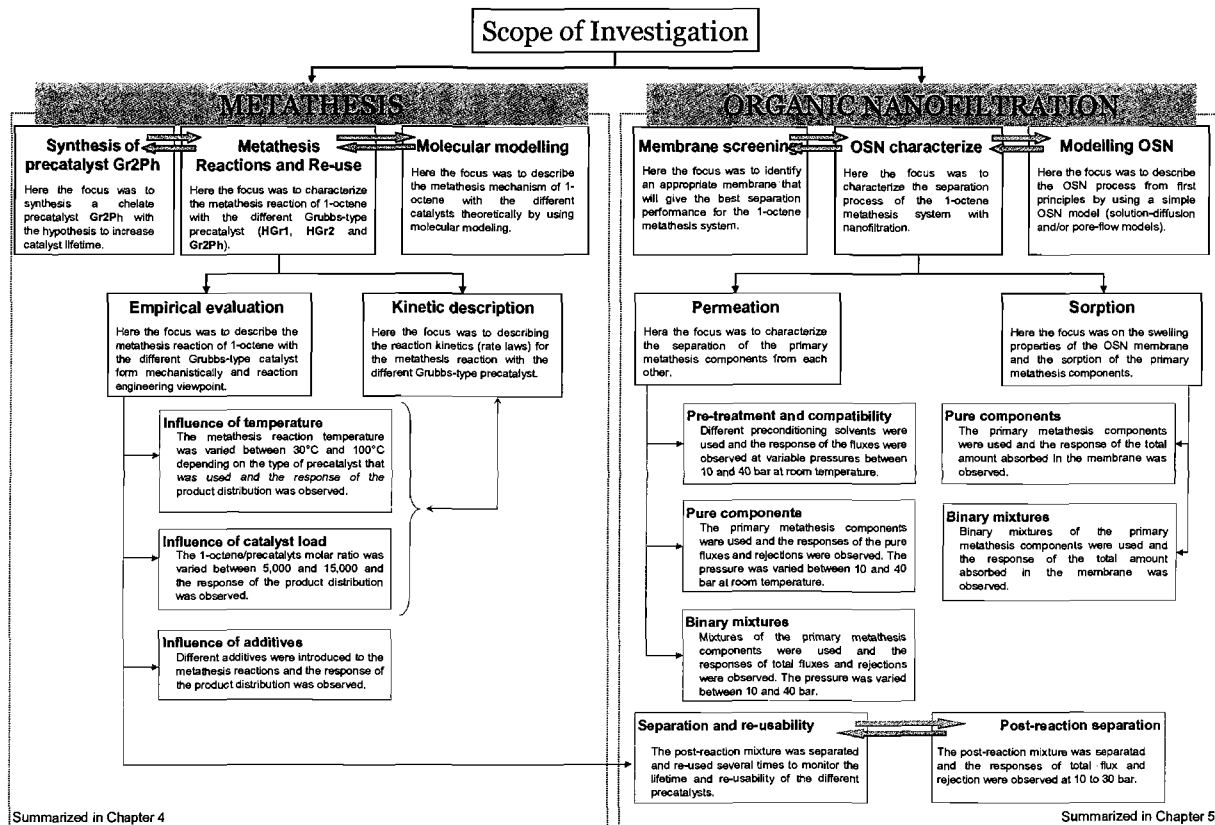


Figure 1.4 Schematically representation of the scope of this investigation.

Chapter 5 focuses on the separation process of the 1-octene metathesis system with OSN.

The focus here is to:

- (i) identify a suitable membrane that would give the best separating performance for the 1-octene metathesis system with respect to flux and rejection,
- (ii) characterize the separating process with respect to permeation (flux), catalyst retention (rejection) and sorption (amount absorbed),
- (iii) evaluate the separation and re-usability of the different precatalysts, and
- (iv) describe the separating process by using simple OSN models (pore-flow or solution-diffusion based).

Finally, **Chapter 6** summarizes the main conclusions of the work described in this thesis and gives an outlook and suggestions for future work.

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2 LITERATURE SURVEY

The next best thing to knowing something is knowing where to find it.
(Samuel Johnson, 1709-1784)

Overview

In this chapter the different terminologies, principles, literature and data that are necessary to understand the thesis, will be presented. The different concepts pertaining to the two research fields of metathesis (Section 2.1 and 2.2) and organic solvent nanofiltration (Section 2.3 and 2.4) are discussed. An investigation has been done into previous research which investigated the recovery of homogeneous catalysts, especially metathesis catalysts, via organic solvent nanofiltration.

The chapter is subdivided into four sections in order to achieve the above-mentioned aims, starting in Section 2.1 with the metathesis reaction in which a general overview, historical review, catalyst development and applications, review of related studies and the mechanism of the metathesis reaction are presented. Section 2.2 discusses the modelling of the metathesis mechanism with *theoretical molecular modelling, together with a review of molecular modelling* for alkene metathesis.

Section 2.3 presents a general overview, historical review and an up to date literature review of previous work done on the recovery of different homogeneous catalysts via organic solvent nanofiltration. Section 2.4 elucidates the modelling of solvent transport in organic solvent nanofiltration and presents previous work done on the modelling.

2.1 Metathesis Reaction

2.1.1 Introduction

Alkene metathesis is a fundamental catalytic reaction that stands amongst a handful of the most versatile ways to make carbon-carbon bonds and build molecules.^{1,2,3} As the reaction takes its course, carbon-carbon double bonds are broken apart and rearranged in a statistical fashion as depicted in Figure 2.1. The name metathesis, which was derived from the Greek word μεταθεσις (metathesis, meaning transposition), was given to this reaction for the first time by Calderon in 1967.⁴

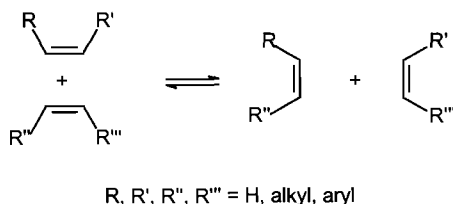


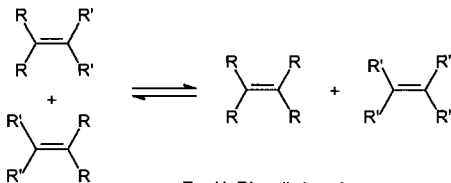
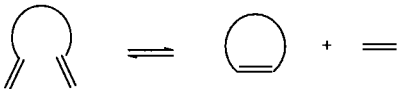
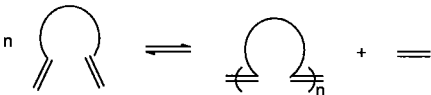
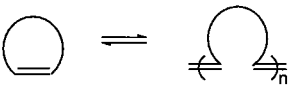
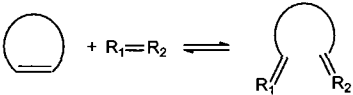
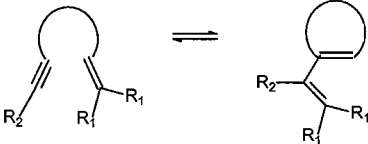
Figure 2.1 Generalized acyclic metathesis reaction.

Depending on the types of substrate and transformation, several other categories of metathesis reactions, apart from the acyclic cross-metathesis (CM) shown in Figure 2.1, have been defined, as presented in Table 2.1. These pathways involve self-metathesis (SM), ring-closing metathesis (RCM), acyclic diene metathesis (ADMET), ring-opening metathesis polymerization (ROMP), ring-opening cross metathesis (ROCM), ring-opening metathesis (ROM) and enyne metathesis (EYM).

This investigation will focus on the metathesis of 1-octene with different Grubbs-type complexes, which can lead to the formation of two isomers, i.e. cis- and trans-7-tetradecene and ethylene. A number of side reactions can also occur during this metathesis reaction. The principal side reactions that can occur, are isomerization and the subsequent self-metathesis (same alkene substrates) and cross-metathesis (different alkene substrates) of these isomerization products. Self-metathesis can be either productive or degenerative. Figure 2.2 presents some of the possible reactions that 1-octene can undergo in the presence of Grubbs-type complexes. Three major groups of products can be identified from Figure 2.2, e.g. primary metathesis products (PMP), isomerization products (IP) and secondary metathesis products (SMP). PMP refers to the products from the self-metathesis reaction of 1-octene to form 7-tetradecene (both cis- and trans-7-tetradecene) and ethene. IP refers to the products from the

double bond isomerization reactions of the terminal to internal alkenes (2-C8, 3-C8 and 4-C8). SMP refers to the cascade of products (C9 to C13) as a result of cross-metathesis and/or self-metathesis of the isomerization products of 1-octene.

Table 2.1 Different categories of alkene metathesis reactions.^{1,2,3}

Self-metathesis (SM)	 $R = H; R' = \text{alkyl, aryl}$
Ring-closing metathesis (RCM)	
Acyclic diene metathesis (ADMET)	
Ring-opening metathesis polymerization (ROMP)	
Ring-opening cross metathesis (ROCM)	
Enyne metathesis (EYM)	

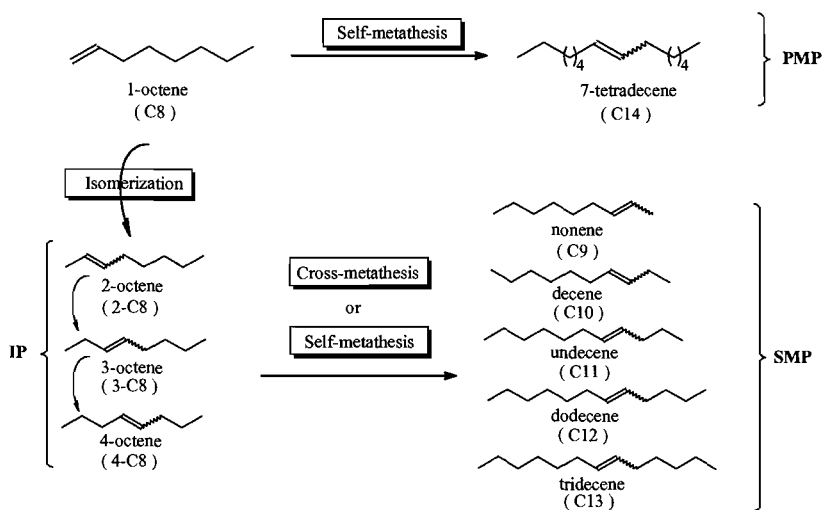


Figure 2.2 Possible reactions of 1-octene in the presence of metathesis catalysts.
[Only the longer chain alkenes are shown]

An important question can now be asked:

Why focus specifically on the metathesis of 1-octene?

From a South African perspective, the metathesis of linear α -alkenes is of special interest, as one of the major petrochemical companies in South Africa produces an abundance of alkene streams (particularly in the range of C₅ to C₉) by means of the Fischer-Tropsch conversion of synthesis gas from either coal or natural gas. Of the wide range of alkene streams produced by the Fischer-Tropsch process, only a few, such as 1-hexene, have high market values. Also, there are many higher value alkenes which are either in short supply or not available at all. There is, therefore, a significant drive to add value to these almost unique Fischer-Tropsch synthesis alkenes. Alkene metathesis can thus be used to convert the less desirable lower value alkenes present in the Fischer-Tropsch product streams to alkenes of higher value which can in turn then be used in further downstream processes. Some examples of these high value alkenes include the following:

- C₁₀ to C₁₄ linear α - or internal alkenes for the production of detergent alcohols, linear alkyl benzenes and secondary alkylethoxylates,
- C₁₅ α - or linear internal alkenes for use on long chain alcohols after hydroformylation, and
- C₁₀ to C₁₃ branched alkenes.

An example of such value adding processes for alkene metathesis is the conversion of the relative inexpensive C_8 α -alkene to the more valuable internal C_{14} alkene, which can then be utilized as detergent alcohol feedstocks, linear alkyl benzene sulfonates, secondary alkylethoxylates, modified linear alkyl benzenes or methyl branched detergent alcohols.

2.1.2 Historical Overview

As with most catalytic processes, alkene metathesis was discovered by accident.^{1,2,3} Despite the first observation of the non-catalytic metathesis reaction of propene by Schneider and Fröhlich⁵ in 1931, the discovery of the catalysed metathesis reaction is attributed to Banks and Bailey.⁶ It is traditionally believed that Banks and Bailey⁶ in 1964 serendipitously discovered the metathesis reaction, even though Eleuterio^{7,8} observed the formation of a propene-ethene co-polymer from propene in the presence of a $MoO_3/Al_2O_3/LiAlH_4$ catalytic system in 1957. Banks and Bailey made the discovery at Phillips Petroleum Company while seeking for an effective heterogeneous catalyst to replace the hydrofluoric acid catalyst used for converting olefins into high-octane gasoline. It was found that the catalytic conversion of propene over a molybdenum catalyst yielded ethene and butene, instead of the expected alkylation of the paraffin.^{2,9}

The name metathesis for this type of reaction was, however, first used by Calderon^{4,9} in 1967. Until then, the chemistry of exchange reactions and polymerization reactions had developed independently, because the use of different catalysts and conditions made the connections between these reactions less apparent. Calderon discovered that the use of $WCl_6/EtAlCl_2/EtOH$ caused both the rapid polymerization of cyclo-octene and 1,5-cyclo-octadiene, as well as the disproportionation of 2-pentene. This discovery provided the bridge that linked the polymerization and exchange reactions as being the same set of chemical reactions.^{4,9}

Some of the main historical events in developing the alkene metathesis reaction are summarized in Table 2.2.

Table 2.2 Important milestones in alkene metathesis.

Late 1950s	Eleuterio, Truett, Peters, Evering, Banks and Bailey accidentally discover alkene disproportionation during the systematic study of Ziegler-Natta polymerizations with heterogeneous catalysts: $M(CO)_6$ ($M=Mo$ or W) on Alumina, silica, Re_2O_7 .
1971	Discovery of the Chauvin Mechanism. H��riss��n and Chauvin postulate the intermediacy of metal-alkylidene and metallacyclobutane species.
1971	Katz demonstrates that Fischer-type carbene complexes of tungsten initiate alkene metathesis.
1974	Schrock develops first isolated metal-alkylidene complex, $[Ta=CHBu^t(CH_2Bu^t)_3]$
1980	Schrock verifies Chauvin's mechanism with an isolated metal-alkylidene complex and develops first isolated unimolecular metathesis catalyst, $[LnTa=CHBut]$.
1992	Grubbs introduces a series of well-defined ruthenium-alkylidene olefin metathesis catalysts.
1993	Schrock develops first chiral metathesis catalyst (Mo-alkylidene) .
1995	Grubbs and fellow researchers develop the commercial catalyst $[Ru=CHPh(PCy_3)_2Cl_2]$ which is active with functional alkenes.
1998	Schrock and Hoveyda discover the first very efficient asymmetric metathesis reaction, Schrock-Hoveyda.
1999	Work by Hermann, Grubbs, and Nolan leads to the development of the air-stable, more reactive, commercial second generation Grubbs catalyst $[Ru=CHPh(PCy_3)(L)(Cl)_2]$.
2000	Research from the groups of Hoveyda and Blechert leads to the 'Hoveyda-Grubbs' catalyst that showed improved activity towards electron deficient alkenes, such as acrylonitriles, fluorinated alkenes and others, as well as activity for tri-substituted alkene synthesis.
2005	Grubbs, Schrock and Chauvin receive the Nobel prize for chemistry for their contributions to the field of metathesis.

2.1.3 Catalyst development and applications

The historical development of the different homogeneous metathesis catalysts went roughly through three main distinct generational types of metathesis catalyst development, namely: the so called black-box generation catalysts, Schrock-type catalysts and finally today's well-known *Grubbs-type catalysts*.

The black-box generation metathesis catalysts from the mid 1950s up to the late 1970s were either multicomponent homogeneous or heterogeneous ill-defined catalytic systems based upon elements from the early transition metal series. These poorly-defined catalytic systems were either grafted onto silica or combined with a main group alkylating agent. The tungsten catalysts $\text{WCl}_6/\text{EtAlCl}_2$, for example, were useful for the polymerization of cyclopentadiene in reaction injection moulding. Other classic systems included $\text{WCl}_6/\text{Bu}_4\text{Sn}$, $\text{WOCl}_4/\text{EtAlCl}_2$, $\text{MoO}_3/\text{SiO}_2$ and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, of which the heterogeneous molybdenum-based catalysts found use in several industrial processes.^{2,3} These catalysts were, however, limited in their use owing to long initiation periods and harsh reaction conditions. Organic reactions in general were plagued by the catalysts' sensitivity to air, moisture and functional groups, in particular those bearing acidic protons.^{2,3}

Extensive basic research in organometallic chemistry was conducted to address the problems associated with the defined black-box generation multicomponent catalytic systems. This quest led to the discovery of the metal carbene complex which ushered in the Schrock-type catalysts. The term metal carbene complex refers to a compound of the general type $\text{L}_n\text{M}=\text{CRR}'$, as depicted in Figure 2.3, where the carbene moiety, $=\text{CRR}'$, is coordinated to a transition metal atom, M, and various other coordinated ligands, L_n .

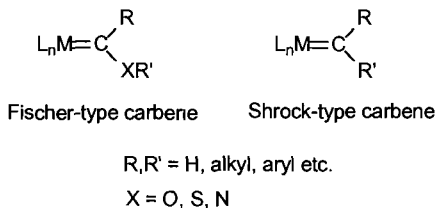


Figure 2.3 Fischer-type and Schrock-type carbene complexes.

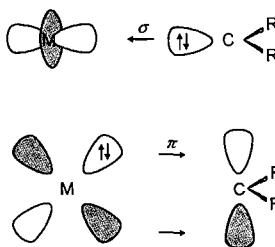
In the mid 1970s, when the development of these metal carbene complexes started, two main classes of carbene complexes were distinct from each other, namely the Fischer-type and Schrock-type carbene.¹⁰ Each of these complexes was named in honour of their discoverers, for

example the Fischer-type carbene after Ernst Otto Fischer who first reported this type of carbene and later received the Nobel Prize for his pioneering work on ferrocene with Wilkinson.¹¹ A summary of the main characteristic properties of these two classes is presented in Table 2.3.

Table 2.3 Characteristic properties of the two main classes of carbene complexes.^{12,13}

Fischer-type

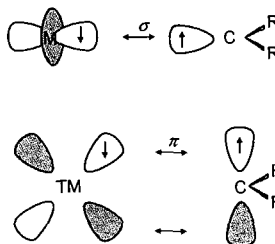
- low oxidation state metals
- middle and late transition metals Fe(0), Mo(0), Cr(0)
- pi-electron acceptor metal ligands
- pi-donor substituents on methylene group such as alkoxy and alkylated amino groups



The chemical bonding is based on electron δ -type donation of the filled metal d-orbital to the empty p-orbital of the methylene group and π electron back bonding of the filled methylene ion pair orbital to an empty metal d-orbital.

Schrock-type

- high oxidation state metals
- early transition metals Ti(IV), Ta(V)
- non pi-acceptor ligands
- non pi-donor substituents



The chemical bonding takes place when two methylene p-orbitals each containing a radical, form two covalent bonds. These bonds are polarized towards carbon and, therefore, the methylene group is a nucleophile.

The Fischer-type complexes usually have metals in a low oxidation state whose bonding with the ligand CRR' and CR is best described in terms of donor-acceptor interactions.¹² Various forms of the Fischer-type carbenes were shown to have metathesis activity, but they were rarely energetically favourable and the reaction with alkenes usually resulted in cyclopropanation. Nevertheless, the research into these complexes was significant, because it identified many of the basic organometallic processes that were intertwined with early mechanistic thinking.

The Schrock-type complexes have metals in a high oxidation state where the metal–ligand bonding should be interpreted as shared-electron multiple bond.^{12,13} In general, metal carbene complexes such as the Schrock-type complexes, where the R groups are exclusively composed of carbon and hydrogen or alkyl substituents, are better referred to as either alkylidenes or (substituted) methylidenes.¹⁴ The term alkylidene(s) will be used in this investigation to describe systems where the carbene moiety =CRR' contains no hetero-atom substituents.

An important milestone during the Schrock-type generation period that led to modern metathesis initiators, was reached in the Schrock laboratory at the Massachusetts Institute of Technology (MIT), with the synthesis of well-defined, high oxidation state imido alkylidene complexes of tantalum, followed by tungsten and molybdenum.¹⁵ It was during the attempted synthesis of pentaneopentyltantalum that the first tantalum-alkylidene complex, $[\text{Ta}(\text{=CH-}t\text{-Bu})\text{Cl}(\text{PMe}_3)(\text{O-}t\text{-Bu})_2]$, was isolated, which catalyzed the metathesis of *cis*-2-pentene. The isolation of such electron-deficient, but stable species, allowed reactions with alkenes to be explored in more detail.^{15,16}

The molybdenum and tungsten alkylidenes of the general formula $\text{M}(\text{NAr})(\text{OR}')_2(\text{=CHR})$ were the first Schrock-type alkylidenes to become widely used, particularly the alkoxy imido molybdenum complex as shown in Figure 2.4.¹⁷⁻²¹ The extremely high activity of this Schrock-type alkylidene allowed it to react with both terminal and internal alkenes and to ROMP low-strain monomers, as well as to ring-close sterically demanding and electron-poor substrates.¹⁷⁻²² However, this catalyst and others, based on the early transition metals, were limited by the high oxophilicity of the metal centres, which rendered them extremely sensitive to oxygen and moisture.²³

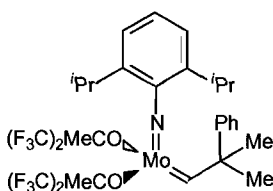


Figure 2.4 A typical Schrock-type alkylidene complex.

The third generation leap occurred in the late 1980s, with the discovery that ruthenium chlorides and tosylates such as $\text{RuCl}_3(\text{H}_2\text{O})_n$ and $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ (tos = *p*-toluenesulfonate) catalysed ROMP, with varying initiation times.^{24,25} During this period, no known ruthenium carbene species could catalyse alkene metathesis reactions, although the work on tungsten and

molybdenum alkylidenes from the Schrock-type generation, which did show considerable metathesis activity, paved the way for similar catalysts to be developed with ruthenium.

The real breakthrough came in 1992, with the synthesis of the first metathesis-active ruthenium carbene **Gr0** as shown in Figure 2.5.^{26,27} **Gr0** constituted the very first active, well-defined ruthenium metathesis pre-catalyst, whose activity was studied in the ROMP of norbornadiene. A further advance occurred when the research group of Grubbs used diazoalkanes as carbene sources for the synthesis of other ruthenium carbene pre-catalysts. An example of this was the treatment of dichlorotris(triphenylphosphine)ruthenium(II) with phenyldiazomethane, followed by one-pot ligand exchange with PCy_3 that gave the Grubbs first generation catalyst (**Gr1**) as depicted in Figure 2.5.^{28,29} **Gr1** had a faster initiating benzylidene moiety and the basic phosphine ligands gave rise to an active and highly functional group-tolerance. These properties, in addition to its resistance to decomposition in the presence of air or moisture, led to a surge in interest in alkene metathesis, particularly RCM and EYM. Commercially available **Gr1** today finds widespread application in the synthesis of organic compounds.

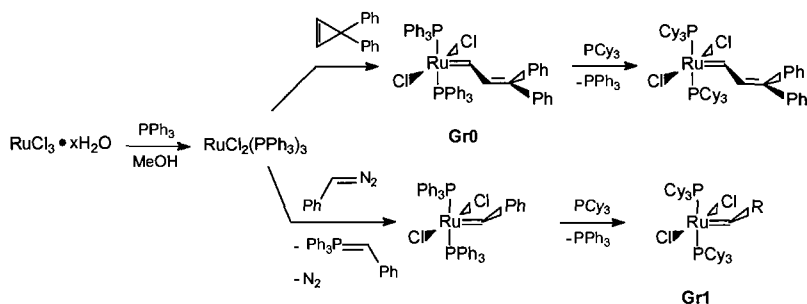


Figure 2.5 Synthesis of the zeroth and first generation Grubbs catalysts.

In contrast with Schrock-type carbenes, Grubbs-type carbenes such as **Gr0** and **Gr1** are considered neutral L-type ligands that render the metal center in a second oxidation state, although it is sometimes shown as Ru(IV) . These Grubbs-types of carbene moiety are believed to be intermediates between a Schrock-type and a Fischer-type carbene. Grubbs and coworkers³⁰ noted that functional group tolerance and activity followed opposing periodic trends as the catalyst systems were varied from left to right and bottom to top on the periodic table. Therefore, these catalysts react more selectively with alkenes as the metal centers are varied in the above-mentioned way.³⁰ This trend is illustrated for titanium, tungsten, molybdenum, and ruthenium in Table 2.4. The late transition metals showed higher reactivity towards alkenes

than the early transition metals, which reacted readily with polar functional groups such as carbonyls.³¹ This trend makes it possible to increase the functional group tolerance of an alkene metathesis catalyst by focusing on a later transition metal, such as ruthenium.

Table 2.4 Functional group tolerance of early and late transition metal alkene metathesis catalysts.³⁰

				Increasing reactivity ↑
Titanium	Tungsten	Molybdenum	Ruthenium	
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	

Increasing reactivity of metal-carbene complexes with alkenes in preference over other functional groups

The remarkable stability and tolerance that **Gr1** showed, allowed researchers to apply a variety of modifications to the ligand sphere for specific conditions. For example, the PCy_3 ligands were substituted with water-soluble phosphines, such as $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{NMe}_3^+\text{Cl}^-$.^{32,33,34} Different supported models were introduced to heterogenize the catalyst.^{35,36,37,38,39} Other variations as depicted in Figure 2.6, have been reported in an attempt to tune activity and/or stability, that include heterobimetallic complexes⁴⁰ and multidentate ligands, such as Schiff bases,^{41,42} arenes,^{43,44,45,46} and bidentate phosphines.^{47,48} Pyridine coordinated complex **3** exhibits a remarkably high activity but a short lifetime, while the alkoxy-chelated complex **6**, better known as Hoveyda-Grubbs first generation catalyst (**HGr1**), shows exceptional stability, which allows its use in reagent-grade solvents and/or in air.⁴⁹

After Herrmann and co-workers^{50,51} reported complex **7**, as given in Figure 2.7, researchers turned to N-heterocyclic carbene (NHC) ligands, sometimes referred to as “phosphine mimics” for their strong σ -donor and weak π -acceptor characteristics. Complex **7**, in which both phosphine ligands were replaced by *N,N'*-disubstituted 2,3-dihydro-1*H*-imidazol-2-ylidene units, was very stable, however, it did not show any improvement in metathesis activity, owing to a very slow initiation rate. This complex, however, served as an indicator to the stabilizing effect of

NHC ligands, and independently, the groups of Nolan,⁵² Grubbs⁵³ and Herrmann⁵⁴ pursued the idea of combining a labile phosphine group for rapid metathesis initiation with a non-labile stabilizing NHC ligand, resulting in heteroleptic complexes, as presented in Figure 2.7. These complexes were termed "second generation" catalysts due to the incorporation of a NHC-type ligand into **Gr1**. It was found that the replacement of the phosphine ligand in **Gr1** by a NHC improved the lifetime and reactivity of **Gr1**.

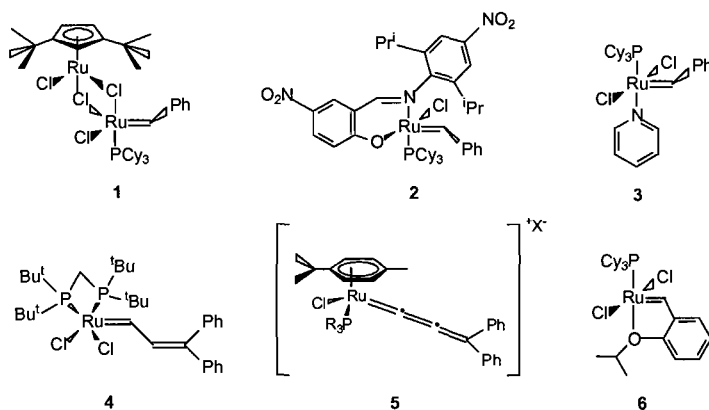


Figure 2.6 Some examples of well-defined Grubbs-type catalysts.

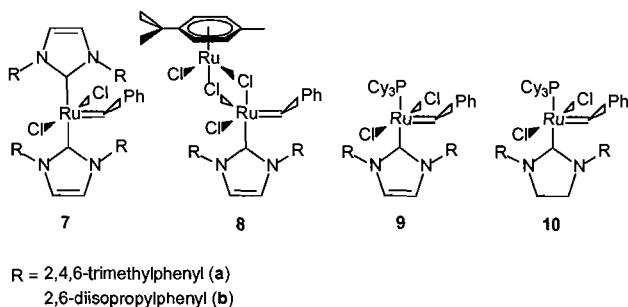


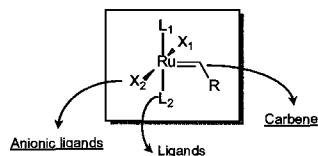
Figure 2.7 Some examples of N-Heterocyclic carbene-type catalysts.

Various authors have referred to both **9a** and **10a** as the second generation Grubbs catalyst (**Gr2**), which can be rather confusing, since these systems are structurally similar, differing only in the backbone of the NHC-ring (4,5-position). In **10a**, the 4,5-position is saturated, making the NHC ligand more electron-rich⁵⁵ and only this complex is commercially available as **Gr2**.

Catalyst **10a** has also been reported to be more active than **9**,^{56,57,58} particularly in the polymerization of highly strained alkenes such as dicyclopentadiene. In this thesis, **10a** will hereafter be referred to as **Gr2**.

Despite the high activity and selectivity that these second-generation type catalysts can offer, there are still some disadvantages (such as catalyst lifetime and separation) that hinder their industrial application. From a synthesis point of view, some innovative solutions have been presented over the past decade by researches who used a multitude of different Grubbs-type catalysts. The main focus was on increasing the catalyst initiation rate, mainly through *steric and electronic modification* of the:

- alkylidene moiety (carbene unit, =CHR)⁵⁹⁻⁶³ and/or,
- ancillary-ligands (L_1 and L_2 ligands)⁶⁴⁻⁶⁷ and/or,
- anionic-ligands (X 's bound to the Ru metal).⁶⁸⁻⁷¹



The lifetime of the Grubbs-type precatalysts, such as **Gr1** and **Gr2** were also shown to increase by introducing different additives to the reaction environment.^{72,73} An excellent review article by Deshmuk and Blechert⁷⁴ summarizes the main findings on these topics.

One innovative modification of the alkylidene moiety and ancillary-ligand worth mentioning was presented by Hoveyda and co-workers⁴⁹ when they synthesized catalyst **HGr1**, which contained an internal metal-oxygen chelate. Catalyst **HGr1** was obtained by the sequential treatment of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ with (2-isopropoxyphenyl)-diazomethane and PCy_3 . They studied the RCM reaction of five-, six-, seven- and eight-membered carbo- and heterocycles and found recovery of catalyst **HGr1** easy with chromatography, with high yield after the reaction had been completed. This was mainly due to catalyst **HGr1**'s excellent stability towards air and moisture. In 2000, the groups of Hoveyda⁷⁵ and Blechert⁷⁶ simultaneously reported the modification of complex **HGr1**, by introducing a NHC-ligand, to show that O-chelating benzyldiene moieties could be used for the synthesis of ruthenium complexes with a non-phosphine leaving ligand (**HGr2**). These 'Hoveyda-Grubbs' catalysts (**HGr1** and **HGr2**) showed improved activity towards electron deficient alkenes, such as acrylonitriles, fluorinated alkenes and others, as well as activity for tri-substituted alkene syntheses.⁷⁴ Ease of handling, stability to air and moisture, and the possibility for immobilization and catalyst reuse also conferred additional advantages on catalysts **HGr1** and **HGr2**. It was further shown that **HGr2** obtained different selectivities and reactivities towards alkene metathesis reactions as compared to **Gr2**, for e.g., the RCM of dienes as presented in Figure 2.8 was completed in less than fifteen minutes at room temperature with **HGr2**, whereas **Gr2** required higher temperatures.⁷⁶ In contrast to **Gr2**, which

proved to be an excellent catalyst for yne-ene CM, analogous reactions with catalyst **HGr2** yielded only traces of the desired products.⁷⁷

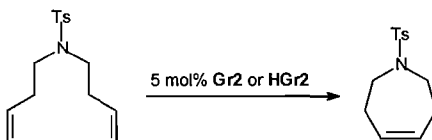


Figure 2.8 RCM reaction of a diene with **Gr2** and **HGr2**.

The catalysts framework of **HGr1** and **HGr2** subsequently served as templates for numerous steric and electronic modifications, which led to catalysts with increased initiation rates compared to **Gr2**, as depicted in Figure 2.9. Complexes **11** and **12** were developed by the group of Grela⁷⁶ while complexes **13** and **14** were developed by Blechert.⁷⁹⁻⁸²

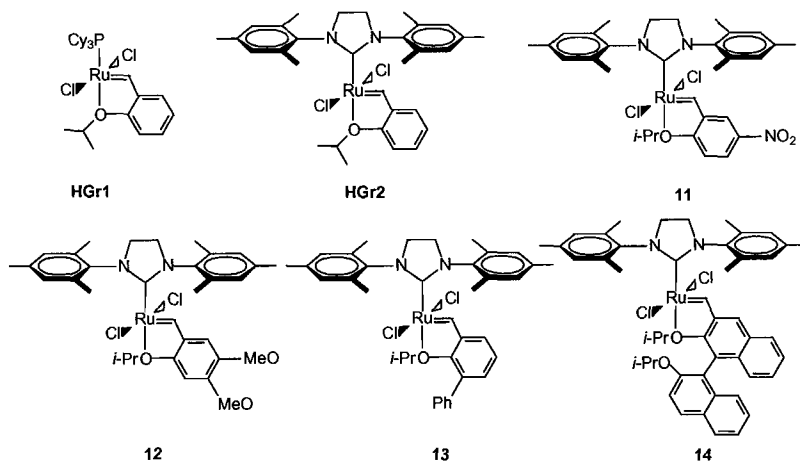


Figure 2.9 Different Hoveyda-Grubbs-type catalysts.

Another interesting modification is the ancillary and anionic ligands with the incorporation of hemilabile bidentate ligands (chelating ligands) as presented in Figure 2.10. A number of ruthenium carbene systems with hemilabile ligands for application in ROMP, RCM and CM have been published.⁶³⁻⁹⁰ Grubbs *et al.*⁸⁴ and later Verpoort *et al.*^{85,86} introduced bidentate O,N-chelated Schiff-base ligands on **Gr1** and **Gr2** to give complexes **15a** and **15b**. Several groups incorporated a 2-pyridinylcarbinol type of O,N-chelated ligand to give complexes **16** to **19**.^{83,87,88} These complexes were active for ROMP, RCM and CM with increased stability. Jordaan *et al.*⁹⁰

used complexes **16a** and **18**, to demonstrate that the incorporation of hemilabile bidentate ligands into **Gr1** and **Gr2** increased the stability and activity of these complexes for the metathesis reaction of 1-octene.

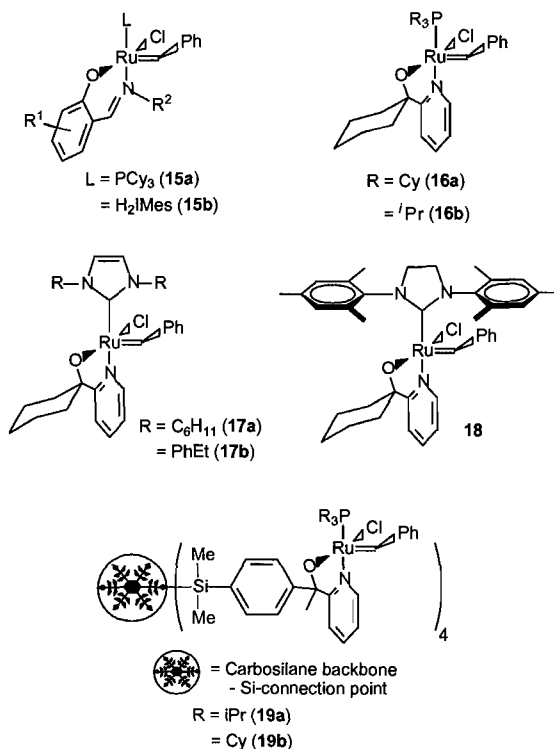


Figure 2.10 Different hemilabile bidentate Grubbs-type precatalysts.

Other interesting modifications are presented in Figure 2.11.

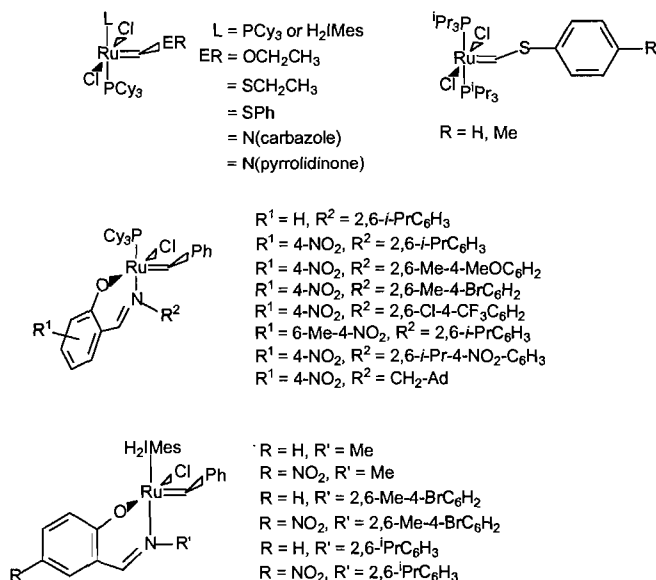


Figure 2.11 Some examples of alkylidene moiety and/or ancillary-ligands and/or anionic-ligands modifications.

2.1.4 Mechanism of alkene metathesis

At the end of the 1960's the metathesis reaction was very mysterious and the mechanism was unknown. Catalytic systems were either oxides such as WO_3/SiO_2 or Ziegler-Natta-derived systems such as WCl_6 (or MoCl_5) and $\text{AlX}_n\text{R}_{3-n}$ or (SnR_4) .⁹ At first it was debated whether an alkyl or alkylidene group was exchanged during alkene metathesis. Experiments conducted by Calderon and Mol using isotopically labelled alkenes demonstrated that the groups interchanged in alkene metathesis were alkylidenes.⁹ The exact mechanism of the reaction and the role played by the metal species, however, remained unclear.

Several theories about the mechanism of alkylidene exchange were developed at that time, but these could not explain the results of some metathesis reactions. Examples of such theories were the metallo-cyclobutane complex of Calderon,⁹¹ metallo-tetramethylene complex of Pettit,⁹² and later the metallo-cyclopentane models of Grubbs.⁹³ Figure 2.12 illustrates some of these proposed intermediates that were later disproved.

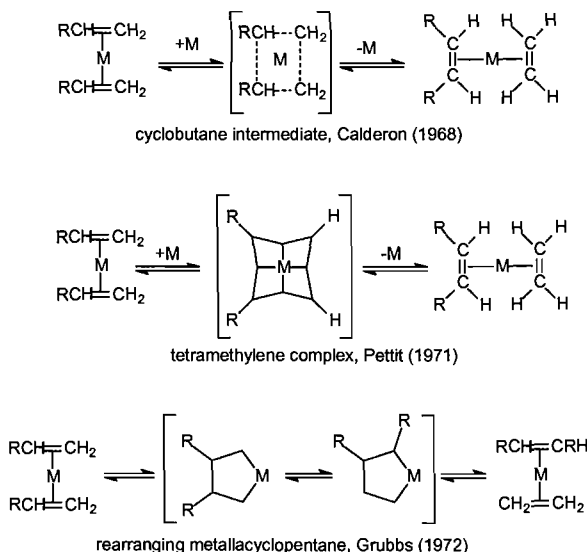


Figure 2.12 Representations of proposed intermediates for alkene metathesis that were later disproved.

It was not until 1971 that Yves Chauvin and his student Jean-Louis Hérisson published their viable metathesis mechanism.⁶⁴ Chauvin and Hérisson combined reports by Fischer⁶⁵ on the synthesis of a tungsten-carbene complex, that of Natta⁶⁶ on the polymerization of cyclopentene through ring-opening catalyzed with a mixture of WCl_6 and AlEt_3 , and that of Banks and Bailey⁶ on the formation of ethylene and 2-butene from propene catalyzed with $\text{W}(\text{CO})_6$ on alumina, to better understand the metathesis reaction mechanism.

Chauvin suggests that the alkene metathesis reaction is initiated by a metal carbene or more precisely a metal-alkylidene, as demonstrated in Figure 2.13. During the first step an alkene coordinates onto the metal atom of the metal carbene, followed by the shift of the coordinated alkene to form the metallacyclobutane intermediate. Then the topologically identical shift of a new coordinated alkene in the metallacyclobutane occurs in a direction perpendicular to the initial alkene shift. This forms a metalalkylidene to which the new alkene is coordinated and then liberated. This new alkene contains a carbene from the catalyst and the other carbene from the starting alkene. The new metalalkylidene contains one of the two carbenes of the starting alkene and it can re-enter into a catalytic cycle of the same type as the first one. In fact, depending on the orientation of the coordinated alkene, the new catalytic cycle can give two different metallacyclobutenes, one leading to the symmetrical alkene and the other one leading to the starting alkene.

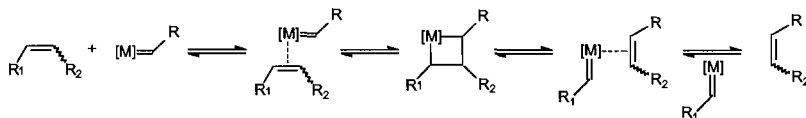


Figure 2.13 Metallacyclobutane mechanism of Chauvin.

Chauvin and Herrison⁹⁴ also presented experimental support for their proposed mechanism that could not be explained by other theories. Furthermore, the Chauvin mechanism had experimental support by the groups of Grubbs,^{98,99} Katz,¹⁰⁰ Schrock and others. For this reason it is today the accepted mechanism for alkene metathesis, summarized by the following four basic steps:

- (1) coordination of the alkene to the metal center of a carbene (or alkylidene) complex,
- (2) a [2+2] cycloaddition forming a metallacyclobutane intermediate,
- (3) a cycloreversion step, and
- (4) decooordination of the alkene.

All these steps are reversible as shown in Figure 2.13.

The first research of the alkene metathesis mechanism with ruthenium carbenes (Grubbs-type precatalyst) was focused on the RCM of diethyl diallylmalonate.¹⁰¹ It was found that the mechanistic pathway involves substitution of an alkene for the phosphine ligand. However, it was unknown at that time whether the alkene binding preceded the loss of the phosphine ligand (known as the associative pathway illustrated in Figure 2.14) or if the phosphine ligand dissociation precedes the alkene binding (known as the dissociative pathway illustrated in Figure 2.14). Later the group of Grubbs^{102,103} proved by kinetic and mechanistic studies, that the dissociative pathway was the operative mechanism. The group of Chen^{104,105,108} provided mass spectrometric evidence for the dissociative substitution of a phosphine ligand with an alkenic substrate during the ruthenium catalyzed alkene metathesis reaction in the gas phase, which supported Grubbs's findings.

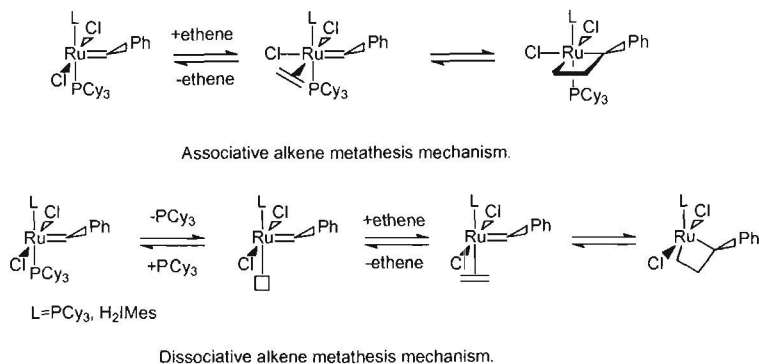


Figure 2.14 Associative and dissociative pathway mechanisms.

The mechanistic pathway for the productive metathesis reaction of 1-octene with a Grubbs-type precatalyst (**Gr1** or **Gr2**) is illustrated in Figure 2.15 and Figure 2.16.^{101,102} The mechanistic pathway, as suggested by Sanford *et al.*¹⁰³ and adapted for the 1-octene system by Jordaan *et al.*¹⁰⁷, consists of three steps, namely: the dissociation step (**A** to **B**), the activation cycle (**B** to **F**) and the catalytic cycle.

The mechanism initializes with the dissociation of the phosphine ligand from the 16-electron Ru species **A** to the active 14-electron species **B**. The activation takes place as the 1-octene coordinates onto the 14-electron intermediate **B** to form the π complex **C**. Complex **C** then undergoes a formal [2+2] cyclo-addition to form a metallo-cyclobutane ring **D**, which in turn returns to a new π complex **E**. The methyldiene species **F1** forms with the release of the alkene and then enters the catalytic cycle as illustrated in Figure 2.16. When the 1-octene coordinates, as shown in **C3** and **C4**, heptyldiene (**F3**, **F4**) is produced instead of the methyldiene complex **F1**. The heptyldiene also enters the catalytic cycle.

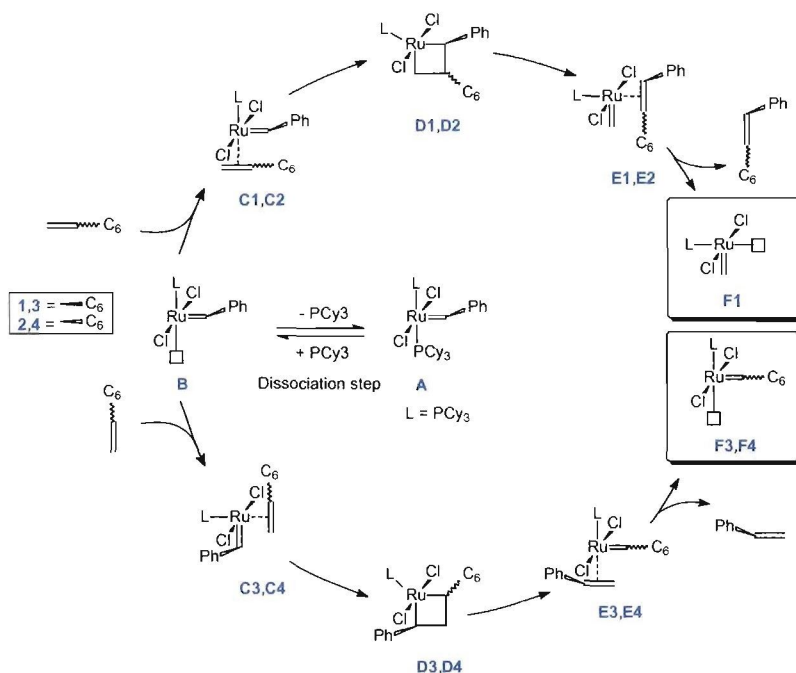


Figure 2.15 Dissociation step (A to B) and the activation cycle (B to F) for the productive metathesis of 1-octene with Gr1 or Gr2.

To summarize the dissociation step and activation cycle: the precatalyst complex **A** is converted to either a methyldiene complex **F1** or a heptylidyne complex **F3** or **F4** before it can proceed to the catalytic cycle. During the productive catalytic cycle the methyldiene complex, **F1**, enters from the left and is coordinated with 1-octene to convert to heptylidyne (**F3** and **F4**) to produce ethene. The heptylidyne complex then coordinates with 1-octene and converts to methyldiene **F1** to produce either *cis*-7-tetradecene or *trans*-7-tetradecene, depending on how the 1-octene coordinates with the heptylidyne complex (either into **a** or out **b** of the plane). The cycle will continue to convert methyldiene to heptylidyne and then the heptylidyne back to methyldiene to produce ethene and 7-tetradecene until all the 1-octene is converted or, more likely, the catalyst has dissociated.

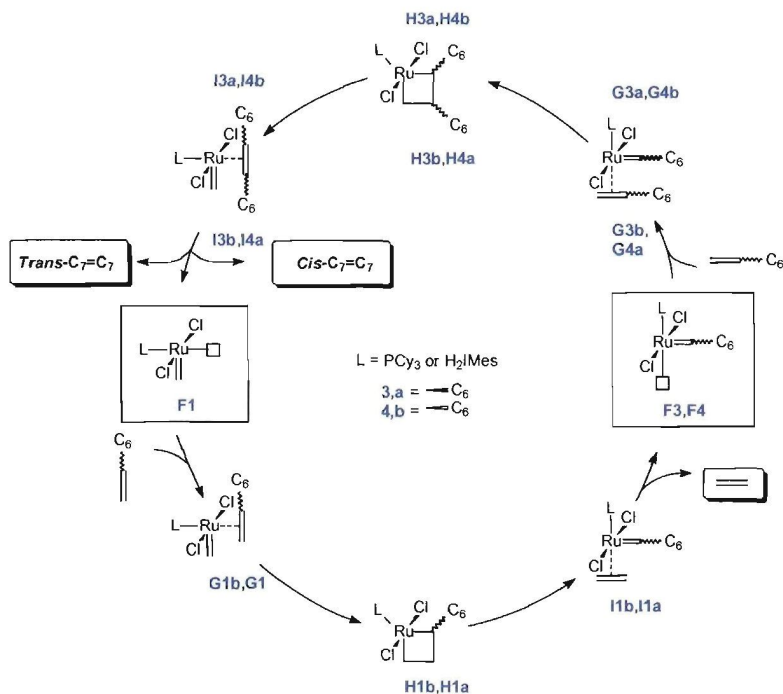


Figure 2.16 Catalytic cycle for the productive metathesis of 1-octene with Gr1 or Gr2.

The mechanistic pathway for the productive metathesis reaction of 1-octene with the Hoveyda-type precatalyst (**HGr1** or **HGr2**) is not reported in literature. However, it is essentially the same as with Gr1 or Gr2. The only main difference in the two mechanisms is related to the dissociation step, or more accurately, the initiation step. Hoveyda and co-workers proposed a type of release-return mechanism for RCM, as illustrated in Figure 2.17.

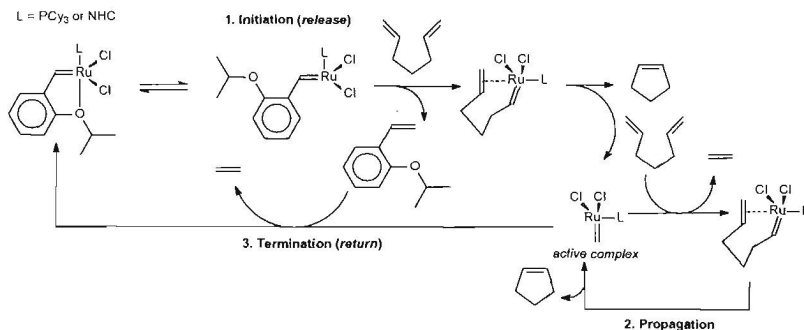


Figure 2.17 Hoveyda-Grubbs-type mechanism with HGr1 or HGr2.

As can be seen from Figure 2.17, during the initiation step the internal oxygen chelate is recoordinated to create an open position on the ruthenium atom. The Ru-O (ether) bond is dissociated by the rotation of the phenyl group around the aromatic carbon-carbene carbon bond to create an open position, as illustrated in Figure 2.18. After the initiation step the same activation cycle as with Gr1 or Gr2 is followed, with the exception that isopropoxystyrene (or related derivatives) are formation dependent on the type of substrate molecule that is used.

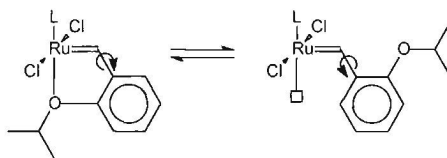


Figure 2.18 Proposed initiation step for a Hoveyda-Grubbs-type catalyst.

The absence of the dissociation phosphine which can intercept and de-activate certain Ru carbenes is one of the key reasons for the unique reactivity profiles observed for the Hoveyda-Grubbs-type complexes. It is possible, as demonstrated in Figure 2.17, that the initial Ru complex can co-exist in equilibrium with the active release complex. After initiating several catalytic alkene metathesis cycles and upon complete consumption of the starting alkene substrate, the methyldiene active complex can encounter the initially released isopropoxystyrene (or related derivatives) to regenerate the starting catalysts through the termination cycle and return to its initial state.

2.2 Modelling of the alkene metathesis reaction

2.2.1 Introduction

Moore *et al.*¹⁰⁸ pointed out that computer modelling methods, computational chemistry and molecular modelling play important roles in chemistry, both as aids in interpreting experimental results and as means of explaining these results. The term *theoretical chemistry* may be defined as a mathematical description of chemistry, whereas *computational chemistry* is generally used when a mathematical method is developed well enough that it can be automated for implementation on a computer. In theoretical chemistry, algorithms and computer programs are usually developed by chemists, together with physicists, to predict atomic and molecular properties and reaction paths for chemical reactions. Computational chemists, on the other hand, simply apply existing computer programs and methodologies to answer specific chemical questions. *Molecular modelling* is the combination of theoretical methods and computational techniques to model or mimic the behaviour of molecules and molecular systems.

There are areas in chemistry where it is difficult or even impossible to obtain experimental results. A good example in the field of metathesis is the determination of the nature of the reaction intermediates or transition states. As Adlhart and Chen¹⁰⁹ stated: "... while there is currently a general agreement on the dissociative mechanism, there is an ongoing discussion on the individual steps. They involve the nature of the metallacyclobutane which is considered as either an intermediate or a transition state ...". Molecular modelling can be applied as a tool to investigate the reaction mechanisms that allow a researcher to calculate the energies along the entire reaction path from reactant(s) to product(s), especially the relative stabilities of proposed intermediates and transition states. Furthermore, molecular modelling can be used to investigate reactions in which the active species either have very short lifetimes or are present in very low concentrations, so that they can easily be isolated.

It is, therefore, the focus of this section to present some fundamental concepts and theories relevant to understanding and describing the mechanistic reaction pathways for the metathesis reaction. A state of the art literature review on molecular modelling for alkene metathesis will also be presented.

2.2.2 Theoretical background

It is not the aim of this section to reproduce fundamental concepts and theories related to molecular modelling, as there are abundant publications and reviews available on these topics, for e.g. Leach,¹¹⁰ Young¹¹¹ and Moore¹⁰⁸. The concepts and theories related to the potential energy surfaces (PES) will, however, be summarized, as PES will be used in this study to explore and describe the reaction mechanisms via molecular modelling. Through the construction of a PES, namely a plot of energy vs. reaction coordinate, a number of quantities can be found and analysed in connection with the chemical system, for example the equilibrium and transition state (TS) geometries and energies. The PES is the most complete description of all the conformers, isomers and energetically accessible motions of the system, and one of the most common computational methods to study reaction mechanisms.¹¹¹ Figure 2.19 illustrates a typical one-dimensional PES with the different topological features that can be found from a PES-graph.

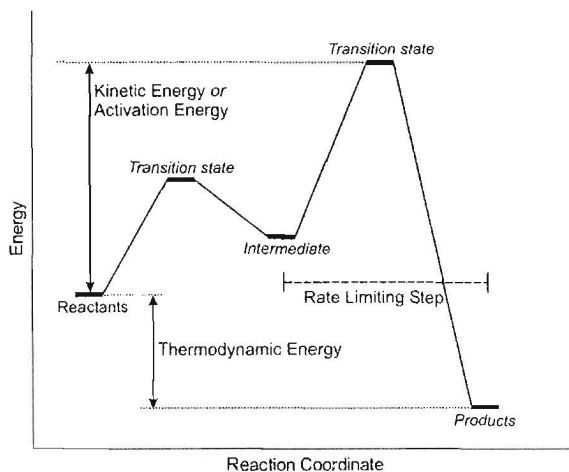


Figure 2.19 Typical illustration of points on a one dimensional potential energy surface.

The energy minimum and maximum points on the PES are usually referred to as stationary points, where the first derivative of the energy is zero with respect to the internal or Cartesian coordinates. The energy minima, also referred to as local minima, correspond to stable molecules (reactants and products). There may be a very large number of minima on the energy surface and the minimum with the very lowest energy is known as the global energy minimum (not depicted in Figure 2.19). The highest point on the pathway between two minima is known

as the saddle point with the arrangement of the atoms being the transition structure, corresponding to the transition states (TS). An intermediate on the PES refers to species that may be too reactive during a reaction to allow easy isolation and characterization. The energy minima along the PES given in Figure 2.19 correspond to equilibrium geometries with the relative energies relating to thermochemical stabilities. Therefore, the overall process in Figure 2.19 is thermodynamically favoured (exothermic). The position of the TSs along the reaction pathway usually corresponds to TS geometries and their energies to kinetic or activation energies, relative to the local minima. The reaction step that involves the highest TS energy is referred to as the rate-limiting step of the reaction.

2.2.3 Review of molecular modelling with Grubbs-based systems for alkene metathesis

The principal steps of the alkene metathesis mechanism are presented in Section 2.1.4. Although there is general agreement on these principal steps, the detailed mechanism has been the subject of intense experimental^{40,104,105,106,112-117} and computational^{48,106,109,113-129} studies. Until recently, molecular modelling studies on alkene metathesis remained scarce and mainly focused on titanium, molybdenum and tungsten catalyst complexes.¹³⁰⁻¹³³ After the discovery of the **Gr1** precatalyst, interest in molecular modelling has increased. Most of the molecular modelling studies consider only a few species of the catalytic cycle, focusing either on the ruthenium carbene formation process^{113,118-121} or on selected intermediates of the catalytic cycle.^{48,106,122,123,124} There are also studies which deal with the complete mechanism and/or alternative reaction pathways up to the cleavage of the metallacyclobutane.^{109,114,115,117,126-129} In the majority of these studies a truncated model system for **Gr1** and **Gr2** (*inter alia* PH_3 , PMe_3 and H_2IH instead of PCy_3 and H_2IMes) and ethylene as substrate was used. Furthermore, there is currently an ongoing discussion on the individual steps and the role substrates, ligands and solvents play in the reaction mechanism. These discussions lead to the following questions:

- What is the real nature of the metallacyclobutane? Is it an intermediate or a transition state?
 - What is the configuration of the halides in the metallacyclobutane? Is it *cis* or *trans*?
 - What is the real rate-limiting step? Is it metallacyclobutane formation or a ligand dissociative step?
 - What are the effects of substrates, ligands and solvents on the metathesis reaction? Is it strongly depended or does it have no effect?
 - What are the pathways of the termination or deactivation step in the alkene metathesis catalyst decomposition?
-

Adlhart and Chen¹⁰⁹ postulate different reaction pathways, as presented in Figure 2.20, for the cleavage of the metallacyclobutane for Gr1 and Gr2. They claim that the given set of pathways is complete in the sense that it covers every plausible reaction mechanism. These pathways can be divided into two main classes, namely (i) the associative pathway and (ii) the dissociative pathway.

The associative pathway assumes that the alkene simply coordinates to the catalyst, forming an 18-electron alkene π complex, followed by the actual [2+2] cycloaddition and cycloreversion steps to form the product, as presented in path 1/4. The pathways 5 – 8 given in Figure 2.20 are dissociative in the sense that there is at least one intermediate where a phosphine ligand is dissociated. Dissociation of the phosphine may occur either before (as given in path 2) or after (as given in paths 1 and 3) coordination of the alkene. The alkene in the five-coordinate Ru alkene complex may be either in *cis* (as given in paths 5 and 6) or in *trans* (as given in path 7) position with respect to the phosphine.

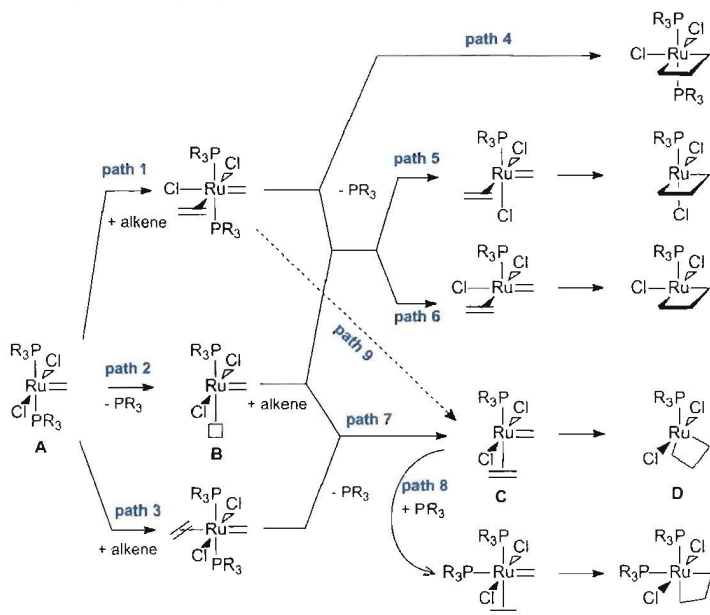


Figure 2.20 Postulated reaction mechanism pathways for alkene metathesis with Grubbs-type precatalysts.

Adlhart and Chen¹⁰⁹ found that the trans dissociative pathway 2/7 was the most favourable pathway. This is in agreement with previous studies completed by Aagaard,¹²⁶ Weskamp *et al.*¹³⁴ and Vyboishchikov *et al.*¹¹⁴ Furthermore, they calculated that the rate-limiting step for the overall reactions of **Gr1** with different substrates (ethylene, ethyl vinyl ether and norbornene) was metallocyclobutane formation and for **Gr2** phosphine ligand dissociation.

Aagaard *et al.*¹²⁶ modelled pathways 1/4 and 2/6 in the first *ab initio* molecular dynamic study at the DFT level with a simple PH₃ **Gr1** model system. They found a higher reactivity for the 14-electron complex **B** relative to the 16-electron complex **A**. They also found that the dissociation of one of the phosphines was necessary, and would lead to an active species which was in agreement with experimental observations.

Hansen *et al.*⁴⁸ performed studies of model compounds with cis- and trans-phosphine ligands, as a preliminary analysis to the syntheses of diphosphanymethane complexes. They found that a small bite angle was needed to achieve relative cis geometry of the coordinating P-atoms.

In 1999 the first comparison between different catalysts was studied by Weskamp *et al.*,¹³⁴ when they calculated the binding energy of the different ligands in bisphosphines and heteroleptic (pre)catalysts with NHC ligands. They found that the NHC ligands had higher binding energies than phosphine ligands and the binding energies they calculated were in valuable quantitative agreement with the experimental data.

In 2000, Adlhart *et al.*¹⁰⁶ studied pathway 2/7 with the simple PH₃ **Gr1**-model system. They first presented an estimation of the energy required to dissociate one of the phosphines, the alkene uptake energy, and the energy barrier for the metathesis reaction.

Vyboishchikov *et al.*¹¹⁴ investigated the associative pathway 1/4, the cis dissociative pathway 2/5 and the trans dissociative pathway 2/7 for truncated systems of **Gr1** and **Gr2**. They found a preference for the dissociative path 2/7 in the ΔG_{298}^0 surface with trans orientation of the incoming alkene, since a high barrier for initial alkene coordination impeded the other possibilities.

Cavallo¹²³ focused on the effect of substrate, ligand and solvent and found that the role of solvent was mainly to facilitate phosphine dissociation while not affecting alkene coordination. Forman *et al.*,⁷² for example, found that phenol as solvent had an enhancing role in the metathesis cycle with **Gr1**. They proposed, via molecular modelling, that the phenol coordinated through a hemilabile interaction of the OH group with the metal centre to stabilize the 14-

electron intermediate species. Adlhart and Chen¹⁰⁹ found that the metathesis reaction was strongly depended on the alkene substrate and ancillary ligand. For example, the presence of electron-withdrawing phosphine ligands would destabilize the 14-electron metallacyclobutane intermediate **D** (as shown in Figure 2.20) relative to the 14-electron carbene species **B** (as shown in Figure 2.20). The reason for this was that electron deficiency in **B** was partly compensated by conjugation with the carbene, while in the metallacyclobutane the compensation for electron deficiency was interrupted. The metallacyclobutane was also found to be an intermediate which is more stable than the alkene carbene complex for NHC-containing systems, but less stable for the phosphine systems. Adlhart and Chen¹⁰⁹ found this to be true during the degenerative alkene metathesis reaction of **Gr1** with ethene, but experimentally concluded that the metallacyclobutane was a transition state rather than an intermediate. In contrast, Romero and Piers¹³⁵ provided experimental evidence that the ruthenacyclobutane was an intermediate. This illustrates the ongoing debate on the transition or intermediate properties of the metallacyclobutane.

It has recently been communicated by Janse van Rensburg *et al.*¹²⁵ that substrate-induced decomposition of the Ru-alkylidene complex is possible. They studied this observation by means of molecular modelling and experimental investigations and proposed that the decomposition involved a β -hydride transfer from a ruthenacyclobutane intermediate to form a coordinative unsaturated Ru-complex, which should be inactive for metathesis. Jordaan¹³⁶ stated that molecular modelling can, therefore, be of immense use in understanding catalytic reactions and in postulating the source of side reactions, e.g. isomerization, which is sometimes difficult to determine experimentally. Janse van Rensburg *et al.*¹²⁵ proposed that the isomerization of alkenes during the Ru-catalysed metathesis reaction arises from the substrate-induced decomposition of the catalyst, as indicated in Figure 2.21.

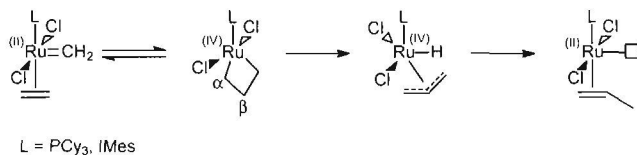


Figure 2.21 Substrate-induced catalyst decomposition during ruthenium-catalysed alkene metathesis.

The Sasol group further studied the elimination of the competitive isomerization process and developed an improved, more active, first generation ruthenium alkylidene system, Phobcat. They studied fundamental aspects of the reactivity and stability of Phobcat as compared to **Gr1** and **Gr2** via molecular modelling. They proposed that the higher conversions obtained for the Phobcat can be attributed to its similarity to **Gr2** instead of **Gr1**. This is possibly due to the phoban-Cy ligand of Phobcat, displaying twofold symmetry similar to the NHC ligands, despite not having a formal twofold symmetry, as opposed to the threefold symmetry of PCy₃.

Jordaan *et al.*¹⁰⁷ has recently reported the complete mechanistic pathway 2/7 and catalyst cycle for the 1-octene metathesis reaction in the presence of **Gr1**. They found that the formed heptylidene species was kinetically and thermodynamically favoured as the active species, with *trans*-tetradecene the more thermodynamically favoured product to form. Their molecular modelling results were in agreement with the experimental results obtained with NMR and GC/MSD experiments. Jordaan¹³⁸ also performed computational studies with different chelating ligands on **Gr1** and **Gr2**.

To the author's knowledge, no computational and/or molecular modelling investigation has been reported for the Hoveyda-Grubbs-type systems of **HGr1** or **HGr2** and the newly synthesized catalyst **Gr2Ph**. This study will, therefore, address this shortcoming in the field.

2.3 Organic Solvent Nanofiltration

2.3.1 Introduction

The membrane is at the heart of every membrane process and can be defined as a permselective barrier or interphase between two phases.¹³⁷ A schematic representation of a typical membrane separation process is presented in Figure 2.22.

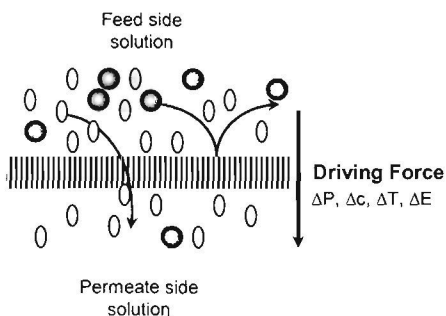


Figure 2.22 Representation of a two-phase system separated by a membrane.

Phase 1 is usually considered as the feed or upstream side while phase 2 is considered the permeate or downstream side. Separation is achieved because the membrane, under a certain driving force, has the ability to transport one component from the feed mixture more readily than any other component.

The membrane separation performance is usually determined by two separation quantities or parameters, namely (i) the flux of the different solvents through the membrane and (ii) the rejection of the different solutes by the membrane. The solvent flux, J , as given in Equation 2.1 is defined as the amount (volume, mass or mol) of a given solvent that permeated through the membrane per unit time and area.

$$J = \frac{V}{A \times t} \quad (2.1)$$

where

V volume solvent permeated through membrane

A effective membrane area

t time required to permeate V amount of solvent

The rejection (R) of a given solute is determined by Equation 2.2:

$$R = \left(1 - \frac{C_p}{C_R} \right) \cdot 100\% \quad (2.2)$$

where

C_p final concentration of the catalyst in the permeate

C_R final concentration of the catalyst in the retentate

The different types of membrane processes can be categorized according to the driving force that is applied to facilitate the separation. The driving force can be one or a combination of any of the following: (i) pressure difference, (ii) concentration difference or (iii) electric potential difference across the permselective membrane.

The focus of this investigation falls within the category of pressure driven membrane processes. In this category, solutes such as homogeneous catalysts can easily be removed from a liquid feed stream. Four types of pressure driven membrane processes are generally distinguished from each other, namely: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).¹³⁷ The differences between these classifications are summarized in Table 2.5.

Table 2.5 Overview of the different pressure driven membrane processes.¹³⁷

	Applied Pressure (bar)	Permeability Range (L·h ⁻¹ ·m ⁻² ·bar ⁻¹)	Transport mechanism	Application range
MF	0.1 - 2	> 50	Bulk Flow	Removal of particles
UF	1 - 5	10 - 50	Bulk Flow	Removal of macromolecules
NF	5 - 15	1.4 - 12	Bulk Flow, Solution Diffusion and Charge Effects	Removal of multivalent ions and relatively small organic molecules
RO	10 - 100	0.05 - 1.4	Solution Diffusion	Removal of ions and organic molecules

NF is the most recent of the different pressure driven membrane processes and has been used increasingly, with success, as an alternative to RO. NF has separation capabilities of molecular weights (MW) between 200 and 1000 (Zhao & Yang., 2006)¹³⁹ and has been extensively applied in water treatment for removal of organic matter,^{140,141} salts,¹⁴²⁻¹⁴⁴ dyes¹⁴⁵ and organic molecules.¹⁴⁶⁻¹⁴⁹

Presently, as Florian *et al.*¹⁵⁰ stated: "Great interest in NF is being devoted to the filtration of organic solutions, which can be applied in very interesting strategic fields, such as the pharmaceutical industry, fine chemistry, and even petrochemistry. However, instead of using the established NF membranes for aqueous application, solvent-resistant nanofiltration (SRNF) membranes are required." The first generation of nanofiltration membranes, which were polymeric RO membranes, did not allow application in organic solvents. This was due to the lack of chemical resistance of the polymer membranes against organic solvents, leading to losses in performance. During the last 10 to 15 years there has been considerable academic activities in developing SRNF membranes, recently referred to as Organic Solvent Nanofiltration (OSN) membranes. In the last 5 years an increasing number of commercial OSN membranes have been brought to the market.

These commercial OSN membranes have found application across a broad range of separation problems, as summarized by the article of Boam and Nozari¹⁵¹:

- Solvent exchange (e.g. exchanging a high boiling point solvent, such as toluene, for a low boiling point solvent, like methanol),
- Solvent recovery,
- Solvent separation and separation of catalysts for reuse or recycling,
- Product purification (e.g. separation of antibiotics from organic solvents),
- Natural product fractionation, and
- Removal of heavy metals (e.g. palladium) and enantiomer separation.

The development of OSN membranes such as the STARMEMTM series, MPF series and Desal membranes has made the non-destructive, energy-efficient separation and concentration of catalysts from products feasible.¹⁵² OSN membranes can thus be used to exploit the molecular weight difference between typical Grubbs-type catalysts ($> 600 \text{ g.mol}^{-1}$) and reaction products ($< 400 \text{ g.mol}^{-1}$) to achieve the desired separation.

2.3.2 Historical background of OSN

Excellent reading for a short introduction to the historical development of non-aqueous NF systems is presented in the paper of Bhanushali *et al.*¹⁵³ Interest in this field dates back to the mid 1960's when Sourirajan and his co-workers¹⁵⁴⁻¹⁵⁷ first published data on the use of RO for non-aqueous systems. They used mainly cellulose acetate membranes with different types of organic solvents (aliphatic, aromatic, polar and non-polar) and found, for example, that ethanol could preferentially be separated from xylene-ethanol and n-heptane-ethanol systems. When the membrane was coated with a hydrophobic layer, the direction of separation could be reversed.

Later in the 1970's Paul and co-workers¹⁵⁸⁻¹⁶¹ studied the transport properties for different organic solvents (aliphatic, aromatic, polar and non-polar) through lightly cross-linked natural rubber membranes. The membranes had the tendency to swell and compacted at high applied feed pressures, hindering the separation of the solvent mixtures by some of the membranes.

In 1983, the group of Sourirajan¹⁵⁶ continued with their pioneering work and demonstrated the separation of organic and inorganic solutes from methanol with different cellulose acetate membranes. Niwa *et al.*¹⁶² also used cellulose acetate membranes, as well as five different composite membranes (PEC-1000, FT-30 BW, FT-30 SW, NS-100 P1700 and NS-100 P3500) to concentrate aqueous methyl ethyl ketone, tetrahydrofuran, and ethyl acetate solutions. At organic feed concentrations above 8%, the membranes started to swell and lose their separation properties.

It was only from the mid 1980's onwards that the real breakthrough in the field of OSN was ushered in when Exxon-Mobil filed several patents¹⁶³⁻¹⁶⁵ on the development of asymmetric polyimide membranes for the separation of oil from dewaxing solvents. This led to an increased publications of OSN-data pertaining to the oil processing industry in the 1990s, for example by Raman *et al.*,^{166,167} Schmidt *et al.*¹⁶⁸ and White and Nitsch.¹⁶⁹ This finally culminated in the first large-scale OSN membrane unit that has operated since 1998 at the Exxon-Mobil's Beaumont, TX refinery. The OSN unit recovers approximately 300×10^6 litres per year of clean solvent for internal recycling.¹⁷⁰

Raman *et al.*^{166,167} developed a novel OSN membrane process for separating free fatty acids from a model crude vegetable oil with methanol. Schmidt *et al.*¹⁶⁸ studied the separation of mineral oil from a range of organic solvents, using a wide range of commercially available membranes. White and Nitsch¹⁶⁹ reported the successful transition between bench scale study

and commercial scale operation of a polyimide OSN membrane for the separation of light hydrocarbon solvents from lube oil filtrates.

The early 1990's patents, such as those by Linder *et al.*¹⁷¹ and White *et al.*,¹⁷² helped in developing commercially available solvent resistant membranes. Examples of these commercially available OSN membranes are the STARMEM™ and MPF series, respectively from W.R. Grace and Co. and Koch; additional OSN membranes are supplied by SolSep BV. These stable OSN membranes led to an exponential increase of interest in the field of OSN, ranging from the recovery of solvents in lube oil dewaxing processes, the re-use of extraction solvents in the food industry, the recovery of homogeneous catalysts in chemical synthesis, decolouration of waste streams, purification of pharmaceutically active ingredients and many more.

It is however, worthy to mention other researchers from the late 1990's, such as Machado and coworkers^{173,174} and Bhanushali and coworkers,¹⁵³ who contributed significantly to the fundamental research with a view to elucidating the transport mechanism of OSN. The OSN transport mechanism is still under discussion, as it is far more complex than aqueous NF transport.

It was after the successful demonstration and application of OSN to homogeneous catalysts by the group of Jacobs,¹⁷⁵⁻¹⁷⁸ Livingston¹⁷⁹⁻¹⁸⁴ and other researchers¹⁸⁵⁻¹⁸⁹ in the late 1990s, that interest in the field of OSN as an alternative method for separation and re-use of homogeneous catalysts has increased. A state of the art review of this topic is presented in the following section.

2.3.3 Review of Homogeneous Catalyst Separation using OSN

Homogeneous catalyst recovery is a relatively new niche in membrane technology that appeared in the late 1990's when more stable commercially available nanofiltration membranes for different organic environments were introduced. A summary of some of the recent publications in the field of OSN, focusing on the separation of different kinds of homogeneous catalysts, are given in Table 2.6.

Table 2.6 Summary of previous work done on the separation of different homogeneous catalysts via OSN.

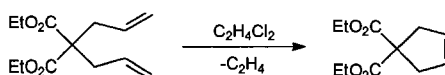
Year	Homogeneous Catalyst	Catalyzed Reaction Type	Catalyst Molecular Weight (g/mol)	Membrane	Rejection	Reference
1996	Chiral polymer-enlarged	Diethylzinc addition	9600	PAH-20	0.998	190
1998	Oxazaborolidines	Reduction of ketones	13800	MPF-50	>0.98	191
1999	Dendritic Palladium based	Allylic Substitution	10200	MPF-50	0.999	189
2000	Rhodium based	Hydroformylation	n.a.	MPF-60	n.d.	193
2001	Sharpless dihydroxylation catalyst	Dihydroxylation	>20000	unknown	n.d.	194
	Ru-BINAP	Asymmetric hydrogenation	929	MPF-60	>0.97	175
	Rh-EtDUPHOS	Asymmetric hydrogenation	723	MPF-60	>0.98	175
	BPPM catalyst	Asymmetric hydrogenation	>7460	YC05	0.991	195
	Heck-catalyst	Heck reaction	749	STARMEM 122	0.9	179
				MPF-50	n.a	
				MPF-60	n.a	
2002	TOABr	Substitution reaction	546	STARMEM 122	>0.99	180
	TOABr	Substitution reaction	546	MPF-50	0.48	181
				MPF-60	0.86	
				Desal-5	0.62	
				STARMEM 122	>0.99	
				STARMEM 120	>0.99	
				STARMEM 240	>0.99	
				Silicone	>0.99	
				Rubber		
				EPDM Rubber	>0.99	
	TBABr	Substitution reaction	322	MPF-50	0.61	181
				MPF-60	0.89	
				Desal-5	0.55	
				STARMEM 122	>0.99	
				STARMEM 120	>0.99	
				STARMEM 240	0.8	
				Silicone	>0.99	
				Rubber		
				EPDM Rubber	>0.99	
	Jacobsen	Chiral Epoxidation	622	MPF-50	>0.814	182
				STARMEM 122	>0.958	
				STARMEM 120	0.996	
				STARMEM 240	0.954	
				Desal-5	>0.779	

Table 2.6 (cont.) Summary of previous work done on the separation of different homogeneous catalysts via OSN.

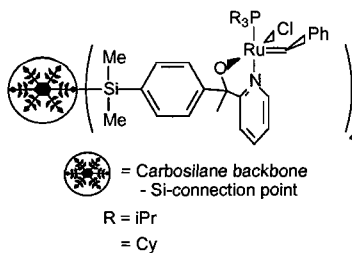
Year	Homogeneous Catalyst	Catalyzed Reaction Type	Catalyst Molecular Weight (g/mol)	Membrane	Rejection	Reference
2002	Pd-BINAP	Asymmetric carbon-carbon bond	849	MPF-50	>0.934	182
				STARMEM 122	1	
				STARMEM 120	1	
	Wilkinson	Hydrogenation and Reduction	925	STARMEM 240	>0.949	182
				Desal-5	>0.886	
				MPF-50	>0.578	
				STARMEM 122	0.98	
				STARMEM 120	0.994	
	Grubbs-type	Alkene Metathesis	3230	STARMEM 240	0.787	188
				Desal-5	0.93	
				MPF-60	n.d.	
2003	Wilkinson	Hydrogenation and Reduction	925	SiO-membrane	>0.999	197
2004	Pd(II)-complex	Diels-Alder reaction	unknown	Silicalite membranes	>0.97	187
2005	Wilkinson	Hydrogenation and Reduction	925	Zeolite PDMS	0.78	196
				ZSM-5	0.98	
2006	Co-Jacobsen	Hydrolytic kinetic resolution of epoxides	626	USY	0.98	176 * tested in a dead end cell .
				MPF-50	0.81	
				COK M2	0.98*	
				COK M2	0.83	
				PDMS	0.86*	
				PDMS	0.78	
				TFC-SR2	0.82	
				Desal GE	≈0.2	
	Ru-BINAP	Asymmetric hydrogenation with ionic liquid	794	MPF	≈0.15	184
				P005F	≈0.1	
				NF-PES-10	≈0.1	
				Desal DL	≈0.05	
	Palladium based	Suzuki reaction	n.d	STARMEM 122	>0.94	183

To the author's knowledge, the only investigation previously conducted with OSN and any metathesis reaction was done in 2000 by Wijkens *et al.*¹⁸⁸ They studied the separation and re-use of different Grubbs-type complexes that were immobilised on a carbosilane dendrimers support, as illustrated in Figure 2.23. The classical RCM reaction of diethyl diallyl malonate to diethyl-3-cyclopentene dicarboxylate was used in their investigation. The activity per metal centre of the dendritic catalysts was found to be comparable to that of the corresponding mononuclear catalyst. However, Wijkens *et al.*¹⁸⁸ did not have any success in separating the catalyst in an active form for re-use. They proposed that the MPF-60 OSN membrane surface that had been used, probably deactivated the catalyst and that the separation and re-use via membrane technology would only be successful if more stable OSN membranes had been

available.



Reaction



Catalyst used

Figure 2.23 Grubbs-type dendritic catalyst in the metathesis of diethyl diallyl malonate.

Even though Wijkins and his co-workers¹⁸⁸ did not have any success in separating their metathesis catalytic system in an active form using the OSN technique, in 1998 Giffels *et al.*,¹⁹¹ and other researchers recently, demonstrated that the method of OSN could be used successfully.

Giffels *et al.*¹⁹¹ first demonstrated the successful use of a commercially available OSN membrane (MPF-50 from Koch Int.) for the recovery of a homogeneous catalyst. Both Giffels *et al.*¹⁹¹ and Wijkins *et al.*¹⁸⁸ used the MPF-series of membranes. Giffels *et al.*¹⁹¹ did not use a metathesis Grubbs-type catalyst but a soluble polymer-enlarged oxazaborolidines homogeneous catalyst for the enantioselective reductions of several ketones, as demonstrated in Figure 2.24. Their membrane reactor operating process showed higher enantioselectivity compared to the normal batch operating process where the ketone was added in one portion. The total turnover number of the system was enhanced from 10 to 500.

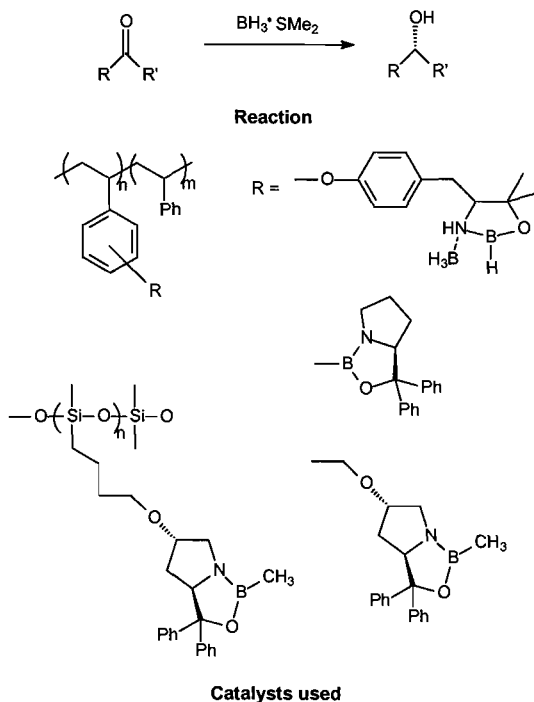


Figure 2.24 Enantioselective reductions of several ketones with different soluble polymer-enlarged oxazaborolidines catalysts.

Rissom *et al.*¹⁰² also tested two immobilized oxazaborolidine catalysts which were based on the Corey-diphenylprolinol, under similar catalytic reaction conditions as Giffels *et al.*,¹⁰¹ see Figure 2.24. They found that the polysiloxane-bound catalyst could be used for 200 residence times at almost quantitative conversion and 96.8% enantiomer excess (ee). A rejection of 98.50% was obtained by using the MPF-50 membrane. The polystyrene-bound catalyst showed a constant conversion (>99%) and enantioselectivity (96.8%) for greater than 400 residence times. A rejection of 99.94% was obtained for this catalyst system. The average ee for both catalysts was somewhat lower, as compared to the original Corey catalyst (>99% ee); however, the total turnover number was increased from 100 for a single batch to 1374 for the membrane reactor system.

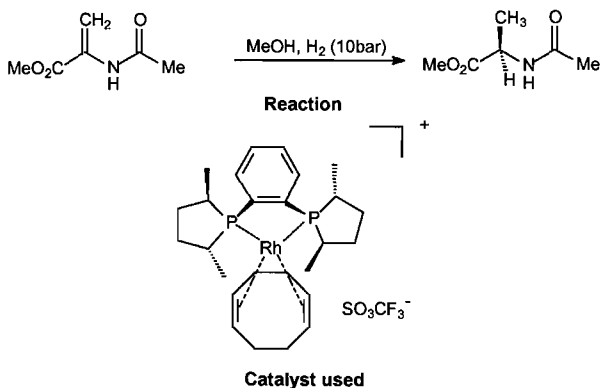
It was only after the successful demonstration and application of OSN by the group of Jacobs, with the commercially available MPF-series of membranes, and later by the group of Livingston with the STARMEMTM series of membranes, that the interest in the field of OSN has increased.

The work done by De Smet *et al.*¹⁷⁵ illustrated the potential use of OSN for the separation and re-use of homogeneous catalysts. De Smet *et al.*¹⁷⁵ investigated the chemo- and enantioselective hydrogenation of methyl-2-acetamidoacrylate with a Rh-EtDUPHOS catalyst, as can be seen in Figure 2.25(a). During 10 cycles, a significant decrease in enantiomer excess and conversion was observed, that could not solely be ascribed to incomplete rejection of the catalysts by the membrane (MPF-60), because the rejection was greater than 97%. It was, therefore, proposed by De Smet *et al.*¹⁷⁵ that the phenomenon could be ascribed to a slow deactivation of the catalyst, probably as a result of oxidation of the phosphines.

In a second reaction, De Smet *et al.*¹⁷⁵ used a Ru-BINAP catalyst as shown in Figure 2.25 (b) for the chemo- and enantioselective hydrogenation of dimethyl itaconate. A small decrease in enantiomer excess and conversion was observed; but this could be completely attributed to minor washout of the catalyst, since the rejection was greater than 98%. No deactivation or decomposition of the catalyst was observed.

Recently Wong *et al.*¹⁸⁴ also studied this reaction with the addition of ionic liquid (IL). The addition of the IL to the reaction solution was to enhance the enantioselectivity of the Ru-BINAP catalyst. Different ILs were added to the reaction, such as trihexyl(tetradecyl)phosphonium chloride (CyPhos101), Tetraphenylphosphonium chloride (TPPCI) and tetrabutylammonium chloride (TBACl). Wong *et al.*¹⁸⁴ used the STARMEMTM-type of membrane, STARMEMTM 122, to retain the catalyst and IL, whilst allowing the permeation of the product. They found, for example, that the optimized methanol/CyPhos101 system where the catalyst and IL over eight cycles were recycled with catalyst re-addition, gave a turnover number of 28 000 with no loss of activity or enantioselectivity. De Smet *et al.*¹⁷⁵ however, obtained only a total turnover number of 1950 for ten cycles. The catalyst and IL's rejection for the methanol/CyPhos101 system of Wong *et al.*¹⁸⁴ varied from 93.1% to 99.9% with the different IL concentrations that were used.

a)



b)

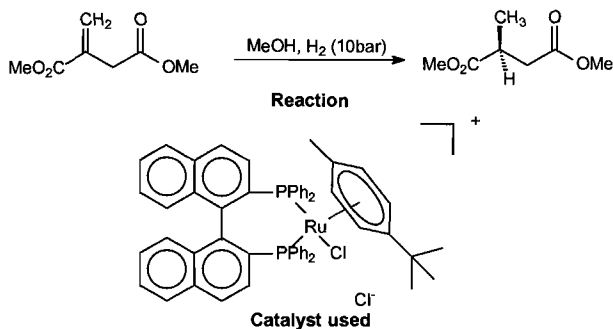


Figure 2.25 Enantioselective hydrogenation of (a) methyl-2-acetamidoacrylate with Rh-EtDUPHOS catalyst and (b) dimethyl itaconate with a Ru-BINAP catalyst.

Nair *et al.*^{179,180} and Luthra *et al.*¹⁸¹ studied the phase transfer catalytic reaction of bromoheptane into iodoheptane with toluene as solvent, using an aqueous solution of potassium iodide, as can be seen in Figure 2.26. Tetraoctylammonium bromide was used as the phase transfer catalyst (PTC) and different commercially available NF-membranes (MPF-50, MPF-60, Desal-5, STARMEM™ 122, 120 and 240) were used for the OSN process. The STARMEM™ series of membranes had the best performance for both catalyst rejection and permeate flux. The best performance resulted in a PTC rejection of greater than 99% and a solvent flux of greater than $10 \text{ L.m}^{-2}.\text{h}^{-1}$, with negligible product rejection. The PTC was 100% recycled and re-used in subsequent reactions. No loss in catalyst activity was observed over a cycle of three consecutive reactions.

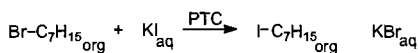
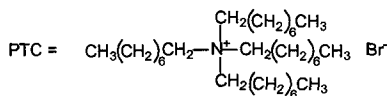
**Reaction****Catalyst used**

Figure 2.26 The phase transfer catalytic reaction of bromoheptane into iodoheptane with tetraoctylammonium bromide as catalyst.

Nair *et al.*^{179,180} also studied the reaction of styrene and iodobenzene to form *trans*-stilbene with a palladium-based Heck catalyst in different organic solvents, as can be seen in Figure 2.27. They used the MPF-series of membranes and the STARMEM™ 122 membrane. It was found that the STARMEM™ 122 had better separation and permeation characteristics than the MPF-series.

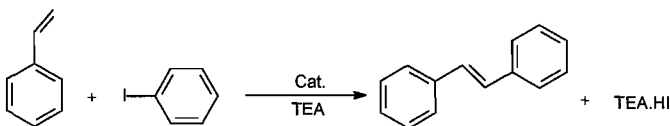
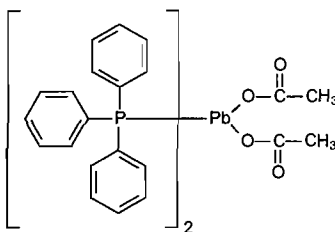
**Reaction****Catalyst used**

Figure 2.27 Heck-coupling reaction of styrene and iodobenzene to *trans*-stilbene.

Scarpello *et al.*¹⁸² demonstrated the non-destructive separation of three organometallic catalysts commonly used in commercial organic synthesis, namely the Jacobsen catalyst, the Wilkinson catalyst and a Pd-BINAP catalyst as depicted in Figure 2.28. Different OSN membranes were used ranging from the STARMEM™-series, MPF-50 and Desal-5 membranes in a selection of organic solvents (ethyl acetate, tetrahydrofuran and dichloromethane). They found good catalyst rejection (>95%) coupled with good solvent fluxes (>50 L.m⁻².h⁻¹).

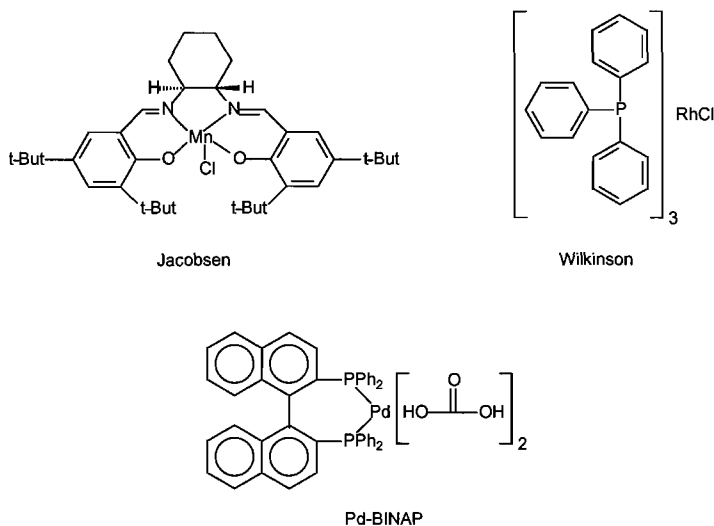


Figure 2.28 Different organometallic catalysts used in the work by Scarpello *et al.*¹⁸²

Aerts *et al.*^{176,178} recently studied the hydrolytic kinetic resolution (HKR) of 1,2-epoxyhexane and styrene oxide with a Co-Jacobsen catalyst, as can be seen from Figure 2.29. They used a range of commercially available NF-membranes (Desal DL and Desal GE from Osmonics; P005F, N30F and NF-PES-10 from NADIR; TFC-SR2, MPF-44 and MPF-50 from Koch; PERVAP 2201, 2510, 2256, 1060 and 1070 from Sulzer) and three laboratory prepared membranes (COK M2, PDMS and a ceramic membrane developed by VITO). These membranes were subjected to retention tests of the Co-Jacobsen in diethylether, isopropanol and under solvent-free conditions. The NF tests performed in diethylether showed that the COK M2 membrane afforded the best results and it was applied in the development of a membrane reactor for the hydrolytic kinetic resolution (HKR) of the epoxides. A slight decrease in conversion was observed over the different cycles and this was strongly attributed to the partial deactivation of the catalyst (rejection was 98%).

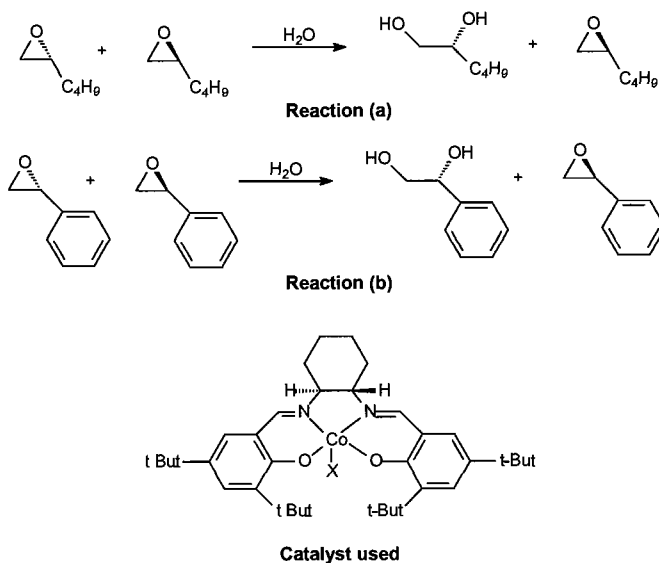


Figure 2.29 Hydrolytic kinetic resolution of epoxides, (a) 1,2-epoxyhexane and (b) styrene oxide, with a Co-Jacobsen catalyst.

Van den Broecke *et al.*¹⁸⁸ studied the hydrogenation of 1-butene in supercritical CO_2 (scCO_2), as can be seen in Figure 2.30. They used a fluorous derivative of the Wilkinson's catalyst in combination with a microporous silica membrane that had an average pore size of 0.6 nm. The catalyst was completely rejected in the continuous membrane reactor and the process was operated under continuous conditions for 75 hours, which is equivalent to 32 reactor volumes. A decrease in activity (conversion drop from 40% to 33%) was observed that was probably due to the oxidation of the catalyst by oxygen and not due to catalyst leaching.

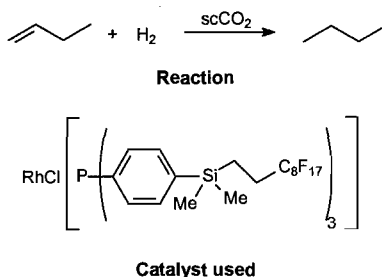


Figure 2.30 Hydrogenation of 1-butene in supercritical CO_2 (scCO_2) with a fluorous derivative of Wilkinson's catalyst.

2.4 Modelling of solvent transport in OSN

2.4.1 Introduction

One of the main focus points and challenges in the current field of OSN is the elucidation of the transport mechanism, which is far more difficult than the traditional aqueous NF. Currently, there is no universally accepted model to describe the OSN transport. Various approaches to solving this challenge are reported in literature.^{153,174,177,199-206} Different reasons can be contributed to the non-universal models, for example, the wide range of hydrophobic/hydrophilic balances, viscosities and surface tensions among the different solvents and solvent mixtures.¹⁷⁷ Moreover, since OSN-membranes can be synthesized following a variety of techniques,²⁰⁶ their physico-chemical variety is enormous, ranging from dense to porous, from polymeric to ceramic. A whole set of models, therefore, exists, ranging between the two extreme types of models, namely: (1) the solution-diffusion²⁰¹⁻²⁰⁴ and (2) the pore-flow.^{174,199,205} As Peeva *et al.*²⁰⁰ stated:

“ the solution diffusion model has been shown to work well ... and was chosen as the main approach for this study ... however, for nanofiltration membranes of other types and structures the solution diffusion model may not be appropriate, and the pore flow models might provide a better description. “

L.G. Peeva *et al.* / *J. Membr. Sci.* 236 (2004) 121–136

The basic derivations of these two models and a resistance-in-series based model are discussed in this section. Furthermore, a state of the art review of solvent transport in OSN is given.

2.4.2 Theory of mass transport through a membrane

The theory of mass transport through a membrane, focusing on the NF process, involves the transport of a solvent and/or solute (permeant) in a solution across the membrane from the feed-side to the permeate-side, due to an acting force. The driving force that causes the transport of the permeant across the membrane is the gradient in its chemical potential. The flux, J_i , of component i , is thus related to the driving force of the gradient in chemical potential by a proportionality factor, L_i (which is usually not constant), given in Equation 2.3:

$$J_i = -L_i \nabla \mu_i \quad (2.3)$$

In most NF cases the membrane is viewed as an infinite plane sheet and, therefore, the flux can be described as one-dimensional and Equation 2.3 is simplified to:

$$J_i = -L_i \frac{d\mu_i}{dz} \quad (2.4)$$

where the z-direction is perpendicular to the membrane surface orientation. All the common driving forces, such as gradients in concentration, pressure and electromotive force (though not considered in this study), can be reduced to the chemical potential gradients and their effect on flux expressed by Equation 2.4.

By only considering the driving forces generated by concentration and pressure gradients, the chemical potential can be expressed as:

$$d\mu_i = RT \times d \ln(\gamma_i c_i) + v_i dp \quad (2.5)$$

where c_i is the molar concentration (mol/mol) of component i , γ_i is the activity coefficient linking concentration with activity, p is the pressure and v_i is the molar volume of component i .

For an incompressible phase, such as a liquid or a solid membrane, volume does not change with pressure and thus, integrating Equation 2.5 with respect to concentration and pressure, gives:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + v_i (p - p_i^0) \quad (2.6)$$

where μ_i^0 is the chemical potential of pure i at a reference pressure p_i^0 .

For compressible gases, the molar volume changes with pressure and thus, using the ideal gas laws and integrating Equation 2.5, gives:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + RT \ln \frac{p}{p_i^0} \quad (2.7)$$

To ensure that the reference chemical potential μ_i^0 is identical in Equation 2.6 and 2.7, the reference pressure p_i^0 is defined as the saturation vapour pressure of i , p_i^{sat} .

Equation 2.6 and 2.7 can then be rewritten as:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + v_i (p - p_i^{sat}) \quad (2.8)$$

for incompressible liquids and the membrane phase, and as:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + RT \ln \frac{p}{p_i^{sat}} \quad (2.9)$$

for compressible gases.

A number of assumptions must be made to define any model of permeation²⁰⁷, the general assumptions governing NF transport are:

- The fluids on either side of the membrane are in equilibrium with the membrane material at the interface. This assumption means that there is a continuous gradient in chemical potential from one side of the membrane to the other.

$$\mu_{i,FM} = \mu_{i,MF} \quad (2.10a)$$

$$\mu_{i,P} = \mu_{i,MP} \quad (2.10b)$$

- The rates of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane. This appears to be the case in almost all membrane processes, but may fail, for example, in transport processes involving chemical reactions such as facilitated transport, or in diffusion of gases through metals, where interfacial absorption can be slow.

2.4.2.1 Solution-diffusion model

The solution-diffusion model was developed by Lonsdale and co-workers in 1965 and was later revisited by Wijmans and Baker²⁰⁷ and Paul,²⁰⁸ and describes the transport of a permeant (solvent or solute) through a membrane in three steps, i.e:

1. initial sorption of the permeant from the feed liquid (corresponding to a thermodynamic equilibrium according to the basic assumption of irreversible process thermodynamics) onto the feed side of the membrane,
2. diffusion of the permeant through the thickness of the membrane (polymer film) consecutive to a chemical potential gradient, and
3. desorption of the permeant into the liquid phase on the permeate side of the membrane.

Step 1 is referred to as sorption, Step 2 as diffusion and Step 3 as desorption. The process is illustrated in Figure 2.31.

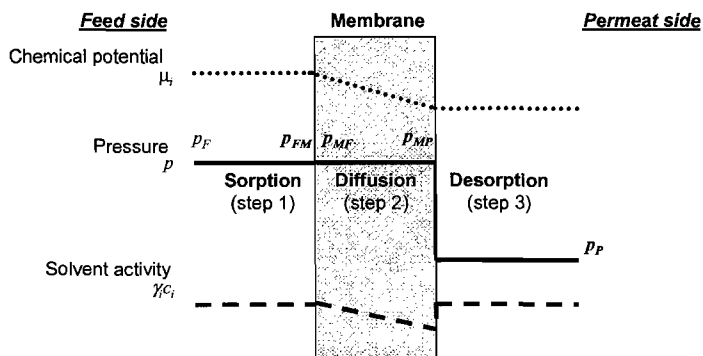


Figure 2.31 Schematic representation of solution-diffusion model.

The appropriate equations for the solution-diffusion model for transport in OSN will now be derived. The approach is to use the first assumption of the solution-diffusion model, namely that the chemical potential of the feed and permeate fluids is in equilibrium with the adjacent membrane surfaces. From this assumption, the chemical potential in the fluid and membrane phases can be equated using the expressions for chemical potential given in Equation 2.6. By rearranging these equations, the concentration of the differing species in the membrane at the fluid interface ($c_{i,MF}$ and $c_{i,MP}$) can then be obtained in terms of the pressure and composition of the feed and permeate fluids. These values for $c_{i,MF}$ and $c_{i,MP}$ can then be substituted into Fick's law as expressed in Equation 2.11, to give the desired OSN solution-diffusion model.

$$J'_i = -D_{i,M} \frac{dc_i}{dz} \quad (2.11)$$

Using equation 2.10a for the *Feed side* and substituting it in Equation 2.8:

$$\mu_{i,F}^0 + RT \ln(\gamma_{i,FM} c_{i,FM}) + v_i (p_{FM} - p_i^{sat}) = \mu_{i,F}^0 + RT \ln(\gamma_{i,MF} c_{i,MF}) + v_i (p_{MF} - p_i^{sat}) \quad (2.12)$$

$$\therefore c_{i,MF} = \frac{\gamma_{i,FM}}{\gamma_{i,MF}} c_{i,FM} = K_i c_{i,FM} \quad (2.13)$$

where $K_i = \frac{\gamma_{i,FM}}{\gamma_{i,MF}}$ is the sorption coefficient.

Using Equation 2.10b for the *Permeate side* and substituting Equation 2.8:

$$\mu_{i,P}^0 + RT \ln(\gamma_{i,MP} c_{i,P}) + v_i (p_P - p_i^{sat}) = \mu_{i,P}^0 + RT \ln(\gamma_{i,MP} c_{i,MP}) + v_i (p_{MP} - p_i^{sat}) \quad (2.14)$$

$$\therefore \ln \left(\frac{\gamma_{i,P} c_{i,P}}{\gamma_{i,MP} c_{i,MP}} \right) = \frac{v_i (p_{MP} - p_P)}{RT} \quad (2.15)$$

$$\therefore c_{i,MP} = \frac{\gamma_{i,P}}{\gamma_{i,MP}} c_{i,P} \exp \left(-\frac{v_i (p_{MP} - p_P)}{RT} \right) \quad (2.16)$$

$$\therefore c_{i,MP} = \frac{\gamma_{i,FM}}{\gamma_{i,FM}} \frac{\gamma_{i,MF}}{\gamma_{i,MF}} \frac{\gamma_{i,P}}{\gamma_{i,MP}} c_{i,P} \exp \left(-\frac{v_i (p_{MP} - p_P)}{RT} \right) \quad (2.17)$$

If the assumption is made that there is no change in activity across the membrane, that is

$\frac{\gamma_{i,MF}}{\gamma_{i,MP}} = 1$, and using $K_i = \frac{\gamma_{i,FM}}{\gamma_{i,MF}}$, equation 2.17 simplifies to:

$$c_{i,MP} = \frac{\gamma_{i,P}}{\gamma_{i,FM}} K_i c_{i,P} \exp \left(-\frac{v_i (p_{MP} - p_P)}{RT} \right) \quad (2.18)$$

Peeva *et al.*²⁰⁰ also used this assumption to derive their model as given in Equation 2.21. The expressions for the concentrations within the membrane at the interface in Equation 2.13 and 2.16 can now be substituted into Fick's law expression, Equation 2.9, to yield:

$$J'_i = \frac{D_{i,M} K_i}{l} \left[c_{i,FM} - c_{i,P} \frac{\gamma_{i,P}}{\gamma_{i,FM}} \exp \left(-\frac{v_i (p_{MP} - p_P)}{RT} \right) \right] \quad (2.19)$$

Wijmans and Baker²⁰⁷ derived the case where the activation coefficients are equal:

$$J_i = \frac{D_{i,M} K_i}{l} \left[c_{i,FM} - c_{i,P} \exp\left(-\frac{v_i(p_{MP} - p_P)}{RT}\right) \right] \quad (2.20)$$

Peeva *et al.*²⁰⁰ stated that the $c_{i,P}$ could be eliminated by calculating the mole fraction in terms of fluxes rather than concentration, and divide both sides of Equation 2.19 by the molar volume v_i to obtain the molar flux of component i for a binary mixture as:

$$J_i = \frac{D_{i,M} K_i}{lv_i} \left[c_{i,FM} - \frac{J_i}{J_i + J_j} \frac{\gamma_{i,P}}{\gamma_{i,FM}} \exp\left(-\frac{v_i p}{RT}\right) \right] \quad (2.21)$$

with p the applied pressure across the membrane.

Allowing $\frac{D_{i,M} K_i}{lv_i} = P_{i,M}$, the membrane permeability, then Equation 2.21 yields:

$$J_i = P_{i,M} \left[c_{i,FM} - \frac{J_i}{J_i + J_j} \frac{\gamma_{i,P}}{\gamma_{i,FM}} \exp\left(-\frac{v_i p}{RT}\right) \right] \quad (2.22)$$

Silva *et al.*²⁰³ used a Stefan-Maxwell-type of equation to derive the same correlation as Equation 2.22.

2.4.2.2 Pore-flow model

The pore-flow models date back to the early 1970's when, for example, Sourirajan and co-workers²⁰⁹ proposed the sorption-capillary flow (PSCF) model in the field of RO. The PSCF model assumes that the mechanism of separation is determined by both surface phenomena and fluid transport through pores in the membrane. In contrast to the solution-diffusion models, the pore-flow models assume stable pores to be inside the membrane and that the driving force for the transport is the pressure gradient across the membrane.

Starting by combining Equation 2.4 and 2.5 and neglecting the concentration gradient in the membrane, gives Equation 2.23:

$$J_i = -Lv_i \frac{dp_i}{dz} \quad (2.23)$$

Equation 2.23 can then be integrated across the membrane to give the classical Darcy's law that describes flow of a fluid through a porous medium:

$$J_i = \frac{kp}{l} \quad (2.24)$$

where k is Darcy's law coefficient equal to L_v of Equation 2.4.

Silva *et al.*²⁰³ used a Stefan-Maxwell-type of equation to derive the correlation for their pore-flow model:

$$J_i = -\alpha'_i \frac{c_{i,ME} \beta_o}{\eta_i} \frac{\varepsilon}{\tau} \nabla p \quad (2.25)$$

where α' is the viscous flow characterization parameter, β_o the membrane viscous flow parameter, η the solvent viscosity, ε the porosity of the membrane and τ the tortuosity factor.

They stated that for small permeating species such as solvents in relation to the pore size, the viscous selectivity is one. Furthermore, the membrane viscous flow parameter is the specific permeability and depends on membrane structure. If the membrane is composed of approximately cylindrical pores, the classical Hagen-Poiseuille equation (Equation 2.26) is obtained from Equation 2.25:

$$J' = \left(\frac{\mathcal{E} d_{pore}^2}{32l\tau} \right) \left(\frac{\Delta p}{\eta} \right) \quad (2.26)$$

2.4.2.3 Transition between solution-diffusion and pore-flow mechanism

It is clear from the previous sections that the solution-diffusion model as illustrated in Figure 2.31 and the pore-flow model in Figure 2.33 differ in the way the chemical potential gradient in the membrane phase is expressed. The solution-diffusion model assumes that the pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed only as a concentration gradient. The pore-flow model assumes that the concentrations of solvent and solute within a membrane are uniform and that the chemical potential gradient across the membrane is expressed only as a pressure gradient.

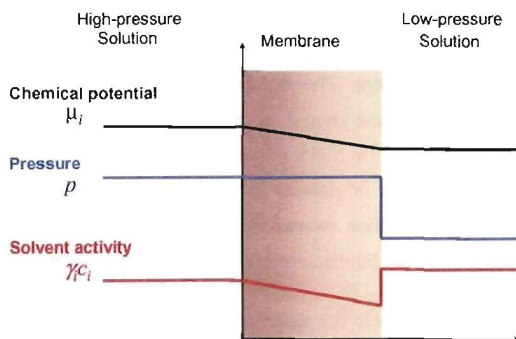


Figure 2.32 Illustration of the pressure driven permeation of a one-component solution through a membrane according to the solution-diffusion model.

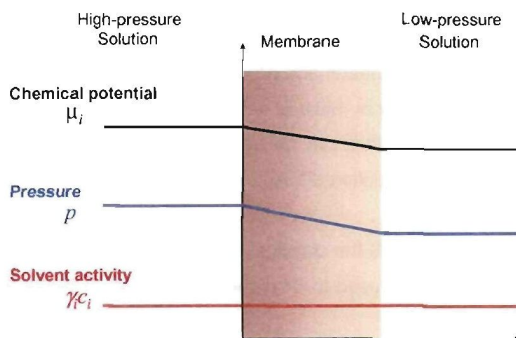


Figure 2.33 Illustration of the pressure driven permeation of a one-component solution through a membrane according to the pore-flow model.

According to Wijmans and Baker²⁰⁷ the transition between these two mechanisms seems to occur with membranes that have very small pores in the nanofiltration range. They believe that the difference lies in the relative permanence of the pores. In a solution-diffusion membrane the pores are present as statistical fluctuations that appear and disappear on about the same timescale as the motions of the permeants moving across the membrane, while in a pore-flow membrane the pores are relatively fixed and do not fluctuate in position or volume during the time that the permeants move through the membrane. The larger the pores are, the more likely they are to be present for a long enough time to produce pore-flow characteristics in the membrane. Wijmans and Baker,²⁰⁷ therefore, give a rough rule of thumb for the transition between pore-flow (permanent) and solution-diffusion (transient) flow, which appears to be in the range of 5 to 10 Å diameter. This explains why some researchers observe that pore-flow models describe their system better than solution-diffusion models, and visa versa.

In addressing this transition phenomenon that may be present in some systems, a possible combination of the two types of model may present a plausible solution. One such model is the solution-diffusion-imperfection model. The solution-diffusion-imperfection model is an early modification of the solution-diffusion model to include pore flow in addition to diffusion of solvents through a membrane as the mechanisms of transport.²¹⁰ This model recognizes that there may be small imperfections or defects (pores) on the surface of membranes through which transport can occur. Another interesting type of transition model is the so-called resistance-in-series model that will be discussed broadly in the review section.

2.4.3 Review of OSN models for solvent transport

Many mechanistic and mathematical models that describe solvent transport through OSN-membranes have been proposed. Some of these descriptions rely on relatively simple concepts, while others are far more complex and require sophisticated solution techniques. Many of these models and theories have their roots in RO. Excellent reviews include Jonsson,²¹¹ Soltanieh and Gill,²¹² Mazid,²¹³ Dickson,²¹⁴ Rautenbach and Albrecht,²¹⁵ Wijmans and Baker,²⁰⁷ Bhanushali *et al.*,¹⁹⁹ Paul,²⁰⁸ and a brief summary by Silva *et al.*²⁰³ The different types of OSN models can be divided into two main categories that can be used alone or in combination with each other, namely the pore-flow based and solution-diffusion based models.

From the pore-flow based models the classical Hagen-Poiseuille equation for viscous flow, as given in Equation 2.26, is usually used to describe the physical or hydraulic transport through porous membranes.

$$J' = \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right) \left(\frac{\Delta p}{\eta} \right) \quad (2.26)$$

where J' is the solvent volumetric flux, ε the porosity, d the average pore diameter, Δp the differential pressure across the membrane, η the liquid viscosity, l the membrane thickness, and τ the tortuosity factor. Pore tortuosity, τ , is normally defined as the ratio of the true length of the flow path and the straight-line distance between the beginning and end points. In many cases, the pore geometry and geometry distribution are unknown, so the tortuosity factor reduces to an adjustable parameter. This model was established, nearly at the same time but independently from each other, by Hagen in 1839 and by Poiseuille in 1841. The model, commonly named after both researchers, was developed on the basis of the flow of blood, and is used to determine the viscosity of fluids in a capillary viscosimeter.²¹⁶

Robinson *et al.*²⁰⁸ found that the pore-flow model of Hagen-Poiseuille successfully explained their experimental data. They studied the permeation of *n*-alkanes (*n*-hexane and *n*-heptane), *i*-alkanes (*i*-hexane, *i*-heptane and *i*-octane) and cyclic (cyclohexane and xylene) compounds in a polydimethylsiloxane-polyacrylonitrile (PDMS-PAN) composite OSN membrane. In addition, they found that similar solvents affected their own membrane properties, that is, their own specific value of $\left(\frac{\varepsilon d_{pore}^2}{32l\tau}\right)$. They stated that this indicated that the non-porous PDMS type of membrane behaved as if the membrane had pores. Even though they found the Hagen-Poiseuille model adequate in describing their experimental results, it is, however, from a physical viewpoint not an appropriate model. Furthermore, Silva *et al.*²⁰³ also argued that a pressure gradient across a thin PDMS layer is not possible, based on mechanics and arguments presented by Paul and Ebra-Lima¹⁶⁸ and, therefore, the pore-flow interpretation of the experimental data is not clear. Whu *et al.*²¹⁷ also used the Hagen-Poiseuille model to describe fluxes through the commercial OSN membrane MPF60.

Silva *et al.*²⁰³ used the Hagen-Poiseuille model to describe the permeation of methanol-toluene and ethyl acetate-toluene mixtures through a STARMEMTM 122 membrane. Two types of Hagen-Poiseuille models were used, a one-parameter model and a two-parameter model. The one-parameter model was the classic model as given in Equation 2.26 where the permeability term $\left(\frac{\varepsilon d_{pore}^2}{32l\tau}\right)$ was determined with the arithmetic averages of the different pure solvents. For the two-parameter Hagen-Poiseuille model, the idea that the physical properties of the membrane changed with the solvent due to different solvent-polymer interactions, was incorporated through the use of an approximate approach to describe the term $\left(\frac{\varepsilon d_{pore}^2}{32l\tau}\right)_{mix}$ for the solvent mixtures. A concentration average of the pure solvent values was considered, assuming no viscous selectivity and a linear pressure profile inside the membrane in Equation 2.26, yielding:

$$J' = \left(\frac{\Delta p}{\eta_{mix}}\right) \left[v_1 c_{1(m)} \left(\frac{\varepsilon d_{pore}^2}{32l\tau}\right)_1 + v_2 c_{2(m)} \left(\frac{\varepsilon d_{pore}^2}{32l\tau}\right)_2 \right] \quad (2.27)$$

where v_1 and v_2 are the partial molar volumes of solvent 1 or 2 and c_1 and c_2 are the molar concentrations. The one-parameter model described the experimental results poorly, while the two-parameter model provided much better predictions. The two-parameter model did not

describe the methanol-toluene system (relative non-ideal system) well, while for the ethyl acetate-toluene system (relatively non-polar system) the model described it moderately better.

Jonsson and Boesen²¹⁸ modified the Hagen-Poiseuille model, as given by Equation 2.28, to obtain a combined viscous flow and frictional model for the description of transport of solutes through reverse osmosis membranes. This model, also named the finely-porous model, is based on the description of mass balances, and the molecular weight, M , of the solute is introduced as a second solvent parameter.

$$J' = \frac{\epsilon d_{pore}^2}{32l\tau} \left[\frac{1}{1 + \frac{d_{pore}^2}{32\eta} \frac{X_{sm}c}{M}} \right] \frac{\Delta p}{\eta} \quad (2.28)$$

where c is the molar concentration, M molecular weight of the solute and X_{sm} represents the frictional force between the solute and the membrane. Geens *et al.*²¹⁹ stated that this model can be adapted to describe pure solvent flux by replacing the mass balance of the solute with the pure solvent. The same equation is obtained, in which M represents the molecular weight of the solvent and X_{sm} a friction factor between the solvent molecules and the pore wall.

Geens *et al.*²¹⁹ used both the classical Hagen-Poiseuille and the Jonsson and Boesen finely-porous models to describe the permeation results of a series of binary mixtures (water-methanol, water-ethanol and methanol-ethanol) with seven different membranes (Desal-5-DK, Desal-5-DL, N30F, NFPES-010, MPF-44, MPF-50 and SolSep-030505). Both models showed fairly good correlation with the experimental data and relatively lower error variances for MPF-44, SolSep-030505 and N30F than for the other membranes. The average model error variance from experimental results for all the membranes was 1.08% for the Hagen-Poiseuille and 0.36% for the Jonsson and Boesen model. This indicates that the Jonsson and Boesen model is a slightly better correlation than the Hagen-Poiseuille model for the system of Geens *et al.*²¹⁹

Machado *et al.*¹⁷⁴ developed a resistance-in-series model based on viscous and surface forces for the permeation of different solvents and solvent mixtures (methanol, ethanol, propanol, butanol, pentanol, water, hexane, pentane and acetone) through a MPF-50 membrane. They propose that the solvent transport through the membrane consists of three main steps:

1. transfer of the solvent into the top active layer which is characterized by surface resistance,
2. viscous flow through the NF pores, and
3. viscous flow through the support layer pores.

All are expressed by viscous resistances, as presented in Figure 2.34 and Equation 2.29.

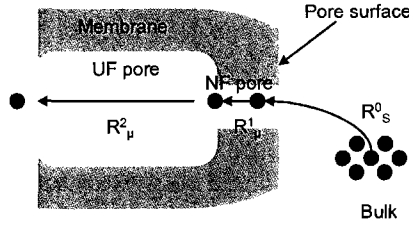


Figure 2.34 Representation of the three flow resistances encountered by a solvent.

$$J = \frac{\Delta p}{R_T} = \frac{\Delta p}{R_s^0 + R_\mu^1 + R_\mu^2} \quad (2.29)$$

where Δp is the transmembrane pressure, R_s^0 is the surface resistance at the pore entrance, R_μ^1 is viscous resistance during flow through the NF portion of the pore and R_μ^2 is viscous resistance during flow through the UF portion of the pore. Viscous resistance of the support layer is omitted in the model as it is negligible compared to total membrane resistance. Surface resistance arises from the difference in surface energy between solvent molecules and the solid membrane surface.

Surface resistance, R_s^0 , is determined by:

$$R_s^0 = \frac{k_M^0}{(d_p^1)^2} (\gamma_c - \gamma_L) \quad (2.30)$$

where k_M^0 is a constant that is determined by the pore characteristics of the membrane, d_p^1 is the mean pore diameter of the first pore layer, γ_c is the critical surface tension of the membrane, which is determined by the Zisman plot, and γ_L is the surface tension of the solvent.

The viscous resistance, R_μ^1 , in the NF layer is given by the capillary flow equation:

$$R_\mu^1 = k_M^1 \frac{\eta}{(d_p^1)^2} \quad (2.31)$$

where η is the viscosity of the solvent and k_M^1 is a geometric membrane constant which takes into account the porosity and tortuosity factors.

The viscous resistance for the UF layer, R_μ^2 , is given by:

$$R_\mu^2 = k_M^2 \frac{\eta}{(d_p^2)^2} \quad (2.32)$$

By substituting the various equations (2.30, 2.31 and 2.32), stated for the individual viscous resistances into equation 2.29, the following equation for the viscous flux is obtained:

$$J = \frac{\Delta p}{\phi[(\gamma_c - \gamma_L) + f_1\eta] + f_2\eta} \quad (2.33)$$

with $f_1 = \frac{k_M^1}{k_M^0}$,

$$f_2 = \frac{k_M^2}{(d_p^2)^2}$$

and $\phi = \frac{k_M^2}{(d_p^2)^2}$

where f_1 and f_2 are solvent-independent parameters characterizing the NF and UF sublayers, ϕ the solvent parameter, γ_c the critical surface tension of the membrane material and η is the surface tension of the solvent. This model is also based on the dependency of two parameters, namely, the solvent viscosity and the difference in surface tension between the solid membrane material and the liquid solvent. The introduction of the latter parameter is very innovative and makes this model highly valuable. The model is in good agreement with the experimental data.

Zhao and Yuan¹³⁶ found significantly different fluxes of methanol through the STARMEMTM 228 membranes when treated with different organic solvents. This means that f_1 and f_2 are probably solvent-dependent rather than independent and ϕ is not constant for a specific solvent-membrane system where the membrane has been treated with other solvents. Yang *et al.*²²⁰ also expressed doubts over the predictive power of the resistance-in-series model, as it was not applicable to other systems. The model was developed for hydrophobic membranes, but it seems to be inadequate for the description of fluxes through hydrophilic membranes. Moreover, for each solvent-membrane combination, an empirical parameter ϕ must be determined as a measure of the interaction between a solvent and the membrane material. Geens *et al.*²¹⁹ found that the model of Machado *et al.*¹⁷⁴ described their system extremely well

with an average deviation error of 0.17%, that was even better than the Hagen-Poiseuille and the Jonsson and Boesen models.

The solution-diffusion based models are usually considered predominant in dense membranes such as the STARMEM™-series. The solution-diffusion model used most often is the model first proposed by Lonsdale (see Equation 2.18). White and Nitsch¹⁶⁹ calculated permeation coefficients for this model for toluene, methylethyl ketone (MEK) and lube oil through a polyimide membrane made from Matrimid-5218. Later, White (2002) also investigated the transport of a series of asymmetric polyimide OSN membranes with normal and branched alkanes (*n*-Decane, *n*-Hexadecane, *n*-Docosane and Pristane) and aromatic compounds (1-Methyl-naphthalene, 1-Phenylundecane). The experimental results were again found to be consistent with the classical solution-diffusion model (Equation 2.20):

$$J'_i = \frac{D_{i,M} K_i}{l} \left[c_{i,FM} - c_{i,P} \exp\left(-\frac{v_i(p_{MP} - p_P)}{RT}\right) \right] \quad (2.20)$$

Stafie *et al.*²⁰² studied the permeations of sunflower oil/hexane and polyisobutylene/hexane through a composite polydimethylsiloxane (PDMS) membrane with a polyacrylonitrile (PAN) support, and found that the system could be well described with the classical solution-diffusion model.

Bhanushali *et al.*¹⁵³ used the classical solution-diffusion model and proposed that the pure solvent permeability coefficient $\left(A_i = \frac{D_{i,M} K_i}{l} \right)$ could be approximated by four parameters, namely:

- the solvent viscosity η ,
- the solvent molar volume V_m (as a measure for molecular size),
- the surface energy or tension of the solid membrane material γ_{sv} , and
- a sorption value ϕ (as a measure for membrane-solvent interactions).

$$J \propto A \propto \left(\frac{V_m}{\eta} \right) \left(\frac{1}{\phi^n \gamma_{sv}} \right) \quad (2.34)$$

where V_m is the solvent molar volume, η is the solvent viscosity, ϕ is the sorption value for the solvent, n is an empirical constant and γ_{sv} is the surface tension or energy. With this approach, Bhanushali *et al.*¹⁵³ were the first to suggest an influence of at least three parameters: i.e.

viscosity, molecular size and the affinity between the solvent and the membrane material, that enabled the model to incorporate differences in polarity. The model showed good correlation with pure solvent experimental data and Geens *et al.*²¹⁰ even commented that the Bhanushali *et al.*¹⁵³ approach at that stage, best described solvent transport through relatively dense NF-membranes. Geens *et al.*²¹⁰ adapted the approach of Bhanushali *et al.*¹⁵³ by replacing the interaction parameter, which is a combination of sorption value and membrane tension, by a single parameter to describe the affinity. They proposed that the effect of membrane-solvent interactions and the consequent contribution to the resistance against permeation can better be described by a single parameter of surface tension difference between the liquid solvent and the solid membrane surface ($\Delta\gamma$), as was also suggested by Machado *et al.*¹⁷⁴

$$J \propto A \propto \left(\frac{V_m}{\eta \Delta\gamma} \right) \quad (2.35)$$

The modified model by Geens *et al.*²¹⁰ described their experimental data well. Although it gave a better correlation with the experimental data than the classical Hagen-Poiseuille and Jonsson and Boesen²¹⁸ models, it could not match the model proposed by Machado *et al.*¹⁷⁴

Peeva *et al.*²⁰⁰ used the derived solution-diffusion as given in Equation 2.22 to describe their system fairly well.

$$J_i = P_{i,M} \left[c_{i,FM} - \frac{J_i}{J_i + J_j} \frac{\gamma_{i,P}}{\gamma_{i,FM}} \exp\left(-\frac{v_i p}{RT}\right) \right] \quad (2.22)$$

Silva *et al.*²⁰³ also used Equation 2.22 to predict permeation of binary mixtures (methanol-toluene and ethyl acetate-toluene) through the STARMEM™ 122 membrane. They found that the model described their system fairly well and concluded that it was possible to predict solvent fluxes for solvent mixtures using pure solvent data.

There are other models in the literature that combine the concepts of solution-diffusion and pore-flow mechanism. One such model is the solution-diffusion-imperfection model.²²¹ This model takes into account both the diffusive transport and the viscous transport that may occur through imperfections in the membrane. The model is based on the solution-diffusion model with an extra term for the viscous flow and is represented by Equation 2.36.

$$J = \frac{c_{iM} D_{iM} v_i}{RTl} \Delta p + \frac{c_{iM} B_o}{\eta l} \Delta p \quad (2.36)$$

where c_{iM} is the concentration of solvent i in the membrane, D_{iM} the diffusivity in the membrane, v_i the molar volume, l the membrane thickness, B_o a hydraulic parameter, which is a measure of the openness of the membrane and η the viscosity of the solvent. The first term on the right-hand side of Equation 2.36 describes the diffusive transport through the membrane, whereas the second term represents the viscous flow through the imperfections.

In conclusion, a summary of the main OSN models is presented in Table 2.7.

Table 2.7 Summary of the main OSN models reported in literature.

Model	Equation	Based on
Hagen-Poiseuille	$J' = \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right) \left(\frac{\Delta p}{\eta} \right)$	Pore-flow
Jonsson and Boesen	$J' = \frac{\epsilon d_{pore}^2}{32l\tau} \left[\frac{1}{1 + \frac{d_{pore}^2}{32\eta} \frac{X_{sm}c}{M}} \right] \frac{\Delta p}{\eta}$	Pore-flow
Silva <i>et al.</i> (Hagen-Poiseuille, 2-parameters)	$J' = \left(\frac{\Delta p}{\eta_{mix}} \right) \left[v_1 c_{1(m)} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)_1 + v_2 c_{2(m)} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)_2 \right]$	Pore-flow
Machado <i>et al.</i>	$J = \frac{\Delta p}{\phi[(\gamma_c - \gamma_L) + f_1\eta] + f_2\eta}$	Pore-flow (resistance-in-series)
Solution-diffusion (classical)	$J'_i = \frac{D_{i,M} K_i}{l} \left[c_{i,FM} - c_{i,P} \exp \left(- \frac{v_i (p_{MP} - p_P)}{RT} \right) \right]$	Solution-diffusion
Bhanushali <i>et al.</i>	$J \propto A \propto \left(\frac{V_m}{\eta} \right) \left(\frac{1}{\phi^n \gamma_{sv}} \right)$	Solution-diffusion
Geens <i>et al.</i>	$J \propto A \propto \left(\frac{V_m}{\eta \Delta \gamma} \right)$	Solution-diffusion
Peeva <i>et al.</i>	$J_i = P_{i,M} \left[c_{i,FM} - \frac{J_i}{J_i + J_j} \frac{\gamma_{i,P}}{\gamma_{i,FM}} \exp \left(- \frac{v_i p}{RT} \right) \right]$	Solution-diffusion
Solution-diffusion-imperfection	$J = \frac{c_{iM} D_{iM} v_i}{RTl} \Delta p + \frac{c_{iM} B_o}{\eta l} \Delta p$	Solution-diffusion and pore-flow

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3 EXPERIMENTAL

Equipped with his five senses, man explores the universe around him and calls the adventure science.
(Edwin Powell Hubble, The Nature of Science 1954)

Overview

In this chapter, all the experimental procedures that were followed during the investigation will be discussed in detail. The chapter is subdivided into seven sections, namely: the materials used (Section 3.1), synthesis of precatalyst **Gr2Ph** (Section 3.2), metathesis experiments (Section 3.3), OSN permeation experiments (Section 3.4), OSN sorption experiments (Section 3.5), supporting OSN experiments such as determining viscosity, contact angle, etc. (Section 3.6) and finally the reaction-separation and recycling experiments (Section 3.7).

3.1 Materials

3.1.1 Membranes used

Commercially available polyimide STARMEM™ series of organic solvent nanofiltration membranes (ST-120, ST-122, ST-228 and ST-240) were purchased from Membrane Extraction Technology Ltd.¹ The manufacturer's specification sheets for these membranes are summarized in Table 3.1. Polyimide membranes such as the STARMEM™ series are typically manufactured from Matrimid 5218 and Lenzing P84 polymers as depicted in Figure 3.1.²⁻⁴ Scanning electron microscope (SEM) images of these membranes are presented in Figure 3.2. The membranes have previously been used for the successful separation of different homogeneous transition metal catalysts such as the Jacobsen, Wilkinson and Pd-BINAP in several reactions, ranging from the Heck reaction and Suzuki couplings to asymmetric hydrogenations.⁵⁻⁸

Table 3.1 Summary of the manufacturer's specification sheets for the STARMEM™ series of membranes.

	STARMEM 120 (ST-120)	STARMEM 122 (ST-122)	STARMEM 228 (ST-228)	STARMEM 240 (ST-240)
Membrane-type	polyimide	polyimide	polyimide	polyimide
MWCO ^a	200	220	280	400
Permeability ^b	20 L.m ⁻² .h ⁻¹	30 L.m ⁻² .h ⁻¹	10 L.m ⁻² .h ⁻¹	20 L.m ⁻² .h ⁻¹

All STARMEM™ membranes were found to be stable in the following solvents:

Alcohols	Butanol, Ethanol, Isopropanol, Methanol
Alkanes	Hexane
Aromatics	Toluene, Xylene, Dichlorobenzene
Ethers	Methyl <i>tert</i> -butyl ether
Ketones	Acetone, Methyl ethyl ketone, Methyl isobutyl ketone
Others	Acetic acid, Acetonitrile, Butyraldehyde, Ethyl acetate

a. Based on rejection of normal alkanes dissolved in toluene, MWCO = molecular weight cut-off, defined as MW for 90% rejection.

b. Pure toluene at 55 bar.

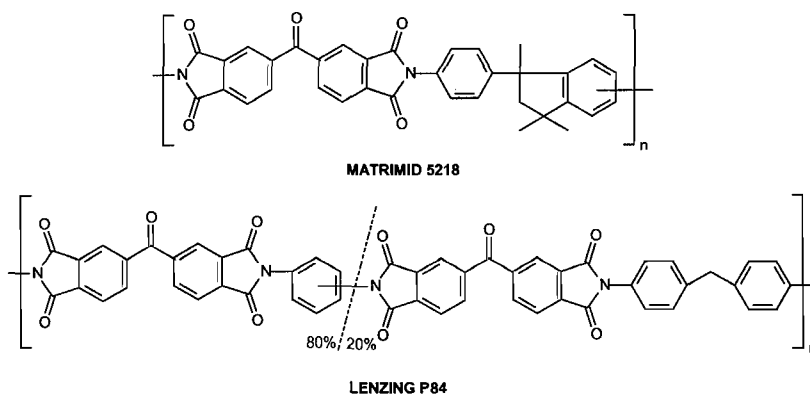


Figure 3.1 Chemical structures of Matrimid 5218 and Lenzing P84.

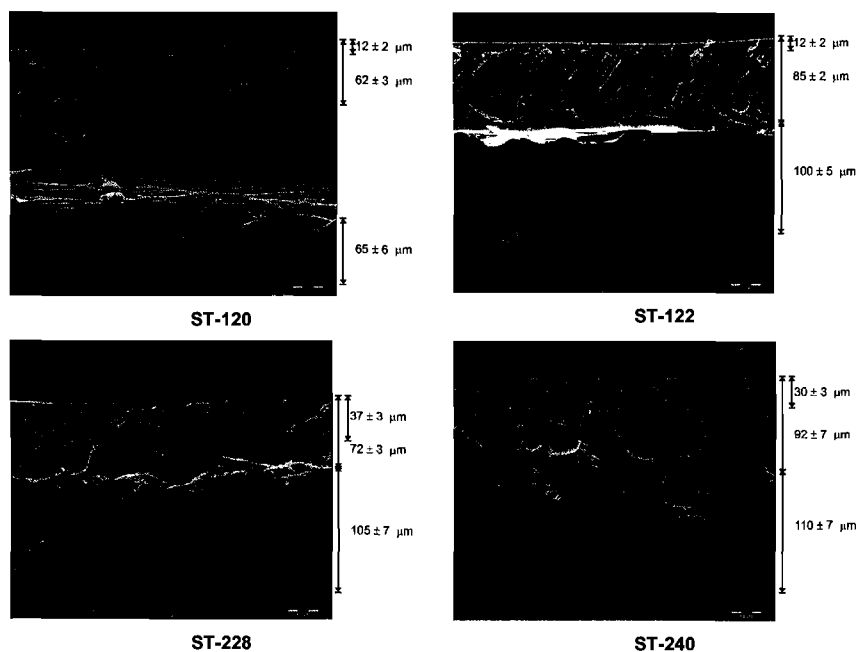


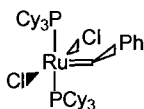
Figure 3.2 Cross-sectional SEM images of the different membranes.

3.1.2 Precatalysts used

The Grubbs-type precatalysts used in this investigation are summarized in Table 3.2.

Table 3.2 Summary of the Grubbs-type precatalysts used in this study.

Gr1



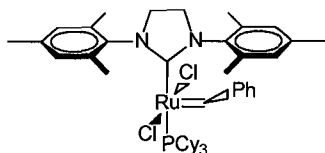
Commercially available from Sigma Aldrich.



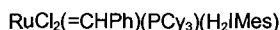
1st generation Grubbs precatalyst

[Benzylidene-bis(tricyclohexyl phosphine)dichloro ruthenium]

Gr2



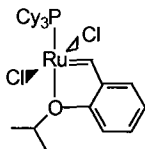
Commercially available from Sigma Aldrich.



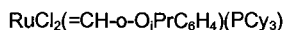
2nd generation Grubbs precatalyst

[(1,3-Bis-(2,4,6 trimethyl-phenyl)-2-imidazolidinidenene)di-chloro(phenyl-methylene)-(tri-cyclo-hexyl-phosphine)ruthenium]

HGr1



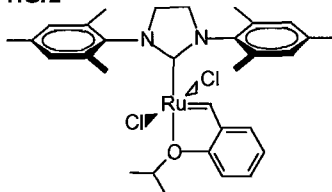
Commercially available from Sigma Aldrich.



1st generation Hoveyda-Grubbs precatalyst

[Dichloro(o-isopropoxyphenylmethylene) (tricyclohexylphosphine)ruthenium]

HGr2



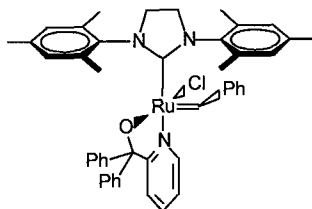
Commercially available from Sigma Aldrich.



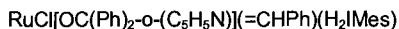
2nd generation Hoveyda-Grubbs precatalyst

[(1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenyl methylene)ruthenium]

Gr2Ph



Self-synthesized catalyst from Gr2.



2nd generation PUK-Grubbs precatalyst

[Benzylidene-chloro(1,3-bis-(2,4,6-tri-methyl-phenyl)-2-imidazolidinylidene)-{1-(2'-pyridinyl)-1,1-di-phenyl-methanolato}ruthenium]

3.1.3 Chemicals used

The chemicals used for the synthesis of precatalyst **Gr2Ph** are given in Table 3.3.

Table 3.3 Chemicals used for the synthesis of Gr2Ph.

Chemical	Supplier	Purity
2-Bromopyridine	Sigma Aldrich	99%
Butyllithium solution	Sigma Aldrich	(2.5 M in hexanes)
Diethyl ether	Labchem	-
Benzophenone	Fluka	99%
Tetrahydrofuran (THF)	Associated chemical enterprise, RSA	99%
Pentane	Saarchem	70-80% n-pentane 20-30% iso-pentane
Toluene	Rochelle	99.8%
Na ₂ SO ₄	Labchem	99%
NaOH	B&M scientific	98%
HCl	Saarchem	-
Activated charcoal	Bio-zone chemical	-

Pentane was refluxed with calcium hydride (CaH₂) and distilled over 4Å molecular sieves under a nitrogen atmosphere. Tetrahydrofuran (THF), toluene and diethyl ether were refluxed with sodium and benzophenone and distilled over 4Å molecular sieves under nitrogen atmosphere.

1-Octene (98%) purchased from Aldrich was used for the self-metathesis reactions without further purification. For gas chromatographic (GC) analyses 99.8% toluene (Rochelle), 99% nonane (Sigma Aldrich), tert-butyl hydroperoxide solution (Fluka), 99% dichloromethane (Saarchem) and 99.5% acetone (Saarchem) were used. Ultra-high purity nitrogen, air, argon and hydrogen gases were supplied by Afrox.

Membrane pretreatment was done with the same toluene that was used for GC analyses, 99.9% ethanol (Rochelle) and 99.8% acetic acid (Merck). 1-Octene (98%) from Sigma Aldrich, 95% 1-tetradecene (Sigma Aldrich) and 97% 7-tetradecene (Sigma Aldrich) were used for the different permeation experiments.

3.2 Synthesis of precatalyst Gr2Ph

The synthesis procedure of precatalyst **Gr2Ph** consisted of three consecutive syntheses steps, namely: the preparation of a pyridinyl alcoholato ligand (Section 3.2.1) for the synthesis of a lithium salt (Section 3.2.2) that was used in the synthesis of complex **Gr2Ph** from **Gr2** (Section 3.2.3).

3.2.1 Synthesis of 1,1-Diphenyl-1-(2'-pyridyl)methanol ligand

The preparation of the tertiary alcohol **L1** was done according to an adapted method proposed by Herrmann *et al.*^{9,10} and Jordaan *et al.*,¹¹ which is a simple two-step synthesis route as can be seen in Figure 3.3.

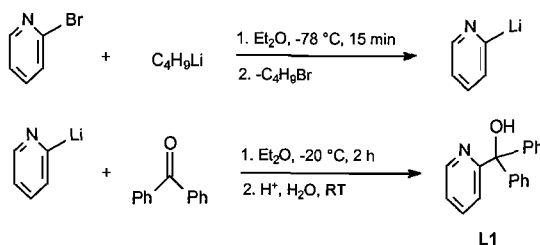


Figure 3.3 Simple two step synthesis route of **L1**.

The synthesis reaction for **L1** was carried out in a round bottomed flask under Ar atmosphere. The flask was initially flushed with a stream of Ar for five minutes before the reagents were added. Diethyl ether (100 mL) was added to the flask and cooled down to $-78\text{ }^\circ\text{C}$. Thereafter, 100 mmol butyllithium solution in hexane (40 mL of 2.5 M) was added. A yellow solution was formed. A solution of 95 mmol (9.05 mL) 2-bromopyridine in 25 mL diethyl ether was added dropwise to the yellow solution over a period of thirty minutes during which time the colour of the solution changed from yellow to dark-red. The solution was stirred for a further fifteen minutes and allowed to warm up to $-20\text{ }^\circ\text{C}$. After the solution had reached $-20\text{ }^\circ\text{C}$, 105 mmol benzophenone was added to the reaction mixture and the solution turned milky-green. The solution was then stirred for two hours at $-20\text{ }^\circ\text{C}$ and allowed to warm to room temperature. Water (50 mL) was added to the solution and stirred, after which the ether phase was extracted with 5 x 20 mL of 2 M hydrochloric acid (HCl) solution. The acid layers were combined and neutralised with 120 mL sodium hydroxide (NaOH 2 M solution). The neutralised water layer was extracted with diethyl ether. After drying the ether phase with sodium sulfate (Na_2SO_4), it was decanted and allowed to slowly evaporate. A light yellow solution resulted, which was treated with activated charcoal and filtered. Colourless crystals were formed.

3.2.2 Synthesis of lithium salt

L1 (2 mmol, 534 mg) was dissolved in 20 mL THF at room temperature (RT) under Ar atmosphere. Thereafter 2 mmol (0.9 mL of a 2.5 M solution in hexane) butyllithium (BuLi) was added dropwise to the reaction mixture and stirred for two hours. The solvent was then removed under reduced pressure to give a white lithium salt. Thereafter the salt was washed with 2 x 5 mL pentane and the solvent removed with a syringe. The salt (yield 95%) was finally dried under vacuum.

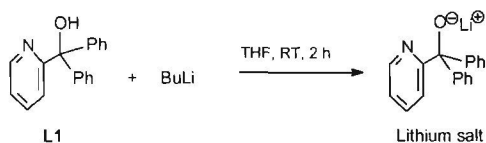
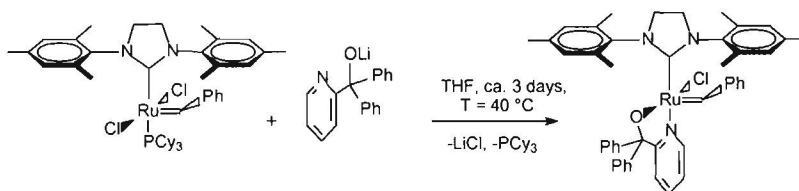


Figure 3.4 Synthesis of lithium salt.

3.2.3 Synthesis of Gr2Ph from Gr2

The synthesis reaction for **Gr2Ph** was carried out in a round bottomed flask under Ar atmosphere. The flask was initially flushed with a stream of Ar for five minutes before the reagents were added. A solution of 2 mmol lithium salt in 5 mL THF was added dropwise to a solution of 2 mmol of **Gr2** in 15 mL THF. The reaction mixture was stirred at 40 °C for three days until the presence of **Gr2** was no longer detected with thin layer chromatography (TLC). The reaction scheme is presented in Figure 3.5.



3.3 Metathesis experiments

3.3.1 Standard apparatus and methodology

The standard reaction setup with all the required equipment used to conduct metathesis reactions is well described in the literature, see e.g.: Jordaan *et al.*,¹¹ Lehman *et al.*¹² and Dinger *et al.*¹³ The experimental apparatus used in this study to generate the metathesis data and a schematic diagram are shown in Figure 3.6.

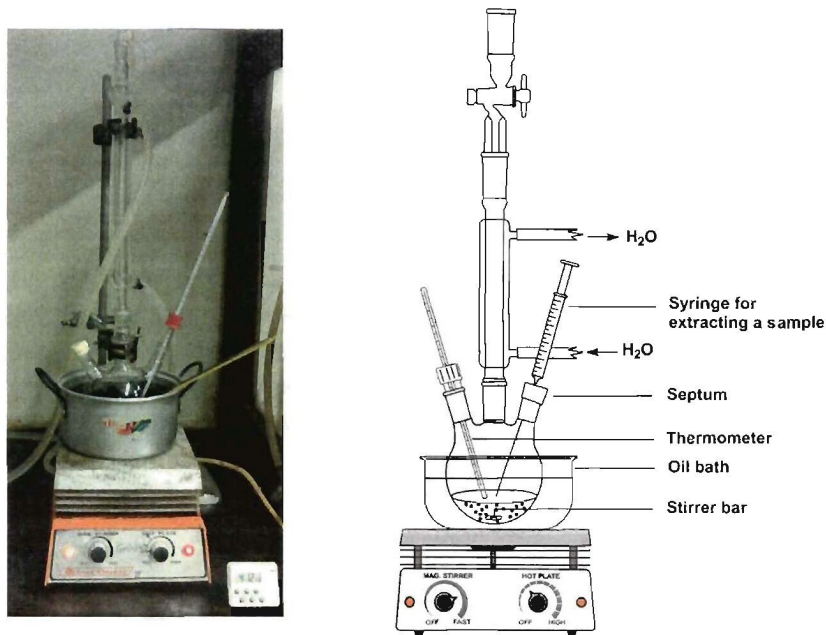


Figure 3.6 Photo and schematic diagram of metathesis apparatus.

The self-metathesis reactions of 1-octene were carried out in a 250 mL three-necked round-bottomed flask fitted with a condenser, thermometer and septum. 1-Octene (20 mL, 127.4 mmol) was transferred to the reaction flask and heated to the desired reaction temperature (ranging from 30 to 100 °C) by immersing the flask into an oil bath and allowing the flask to equilibrate to the desired temperature before introducing the precatalyst. In each case, the flask was allowed to vent to the atmosphere. No additional solvents were added. The desired amount of precatalyst, in the range of 7 to 22 mg, was added to the flask and the reaction mixture was continuously stirred with a magnetic stirrer bar until the formation of the primary metathesis products was complete.

Samples of 0.3 mL were withdrawn by syringe during the reaction at different time intervals and added to a solution of 0.1 mL nonane, 0.3 mL toluene and 2 droplets of *tert*-butyl hydrogen peroxide for analysis by GC/FID. Nonane was used as an external standard, while toluene was used to increase sample volume and *tert*-butyl hydrogen peroxide was used as a quencher.

3.3.2 Analytical equipment and methodology

3.3.2.1 Gas chromatograph (GC-analysis)

An Agilent 6890 gas chromatograph equipped with an Agilent 7683 auto-injector, HP-5 capillary column (30 m x 320 μm x 0.25 μm) and a flame ionization detector (FID) was used for analyses. The GC analysis conditions were: inlet temperature of 200 $^{\circ}\text{C}$; N_2 carrier gas flow rate of 2 $\text{mL}\cdot\text{min}^{-1}$; injection volume 0.2 mL (auto injection); split ratio of 50:1; oven programming of 60 $^{\circ}\text{C}$ for 5 min, 60 to 110 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}\cdot\text{min}^{-1}$, 110 $^{\circ}\text{C}$ for 5 min; 110 to 290 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}\cdot\text{min}^{-1}$, 290 $^{\circ}\text{C}$ for 5 min; FID detector at 300 $^{\circ}\text{C}$; H_2 flow rate of 40 $\text{mL}\cdot\text{min}^{-1}$; air flow rate of 450 $\text{mL}\cdot\text{min}^{-1}$.

An external standard method was used to determine the product distributions. A sample of 0.3 mL from the reaction mixture was added to a solution of 0.1 mL nonane, 0.3 mL toluene and 2 droplets of *tert*-butyl hydrogen peroxide. Nonane was used as an external standard, while toluene was used to increase sample volume and *tert*-butyl hydrogen peroxide was used as a quencher. The volume (V_i) of a given component i in the GC vial was calculated with Equation 3.1 and thereafter the different mol percentages (mol%) of the product distributions.

$$V_i = V_{\text{nonane}} \cdot \left(\frac{A_i}{A_{\text{nonane}}} \right) \cdot \left(\frac{1}{\text{RF}} \right) \quad (3.1)$$

where

V_i	volume to be calculated of a given component i in the GC vial
V_{nonane}	volume of the external standard nonane (0.1 mL) added to GC vial
A_i	Area of a given component i for the GC-chromatograph
A_{nonane}	Area of the external standard nonane for the GC-chromatograph
RF	GC-response factor

Thereafter the mol (N_i) of a given component i was calculated with Equation 3.2:

$$N_i = \frac{(V_i \times \rho_i)}{MW_i} \quad (3.2)$$

where

- N_i mol to be calculated of a given component i
 V_i volume of a given component i calculated by equation 3.1
 ρ_i density of a given component i
 MW_i molecular mass of a given component i

The GC response factor (RF) was determined from two calibration curves shown in Figure 3.7 and Figure 3.8. The ratio of 1-octene or 7-tetradecene and the external standard areas were plotted against different volume ratios of 1-octene or 7-tetradecene and the external standard. The external standard volume was kept constant at 0.1 mL. RF values of 1.0139 for 1-octene and 1.0100 for 7-tetradecene were calculated from the slopes of the calibration curves. A RF value of 1 was used for this study.

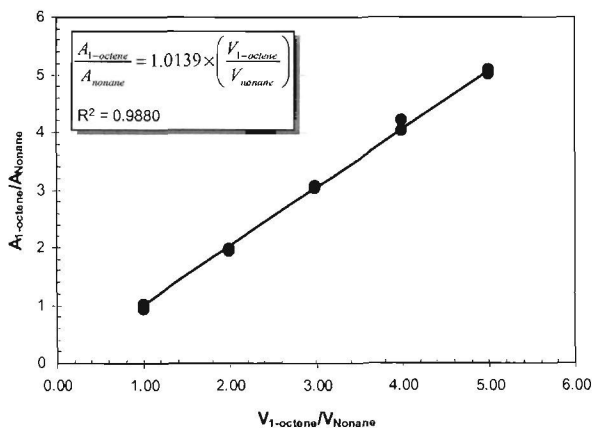


Figure 3.7 Calibration curve for determining the GC response factor for 1-octene.

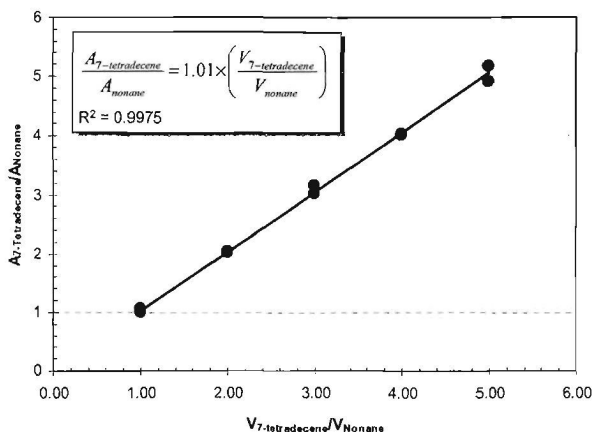


Figure 3.8 Calibration curve for determining the GC response factor for 7-tetradecene.

3.3.2.2 Nuclear magnetic resonance spectroscopy (NMR-analysis)

^1H -NMR (300 MHz) and ^{31}P -NMR (121 MHz) spectra were obtained using a Varian Gemini 300 spectrometer and the Bruker Avance 600 MHz Spectrometer with QNP Probe.

A 1 mL NMR tube was placed in a Schlenk tube and the air removed under vacuum. The Schlenk tube was then flushed with Ar and the procedure repeated twice. The precatalyst (0.031 mmol) was weighed out into the NMR tube and again placed in the Schlenk tube to put the sample under Ar. Deuterated toluene (0.75 mL) was added to the sample and the tube was closed and shaken to dissolve the solids. The NMR tube was then placed in the NMR instrument for analysis.

3.4 OSN permeation experiments

3.4.1 Apparatus and description

The standard OSN set-up with all the required equipment used to conduct OSN permeation experiments is well described in the literature, for e.g.: See Toh *et al.*¹⁴ and Scarpello *et al.*⁵ The experimental apparatus used in this study to generate the permeation data is shown in Figure 3.9 and a schematic diagram in Figure 3.10.

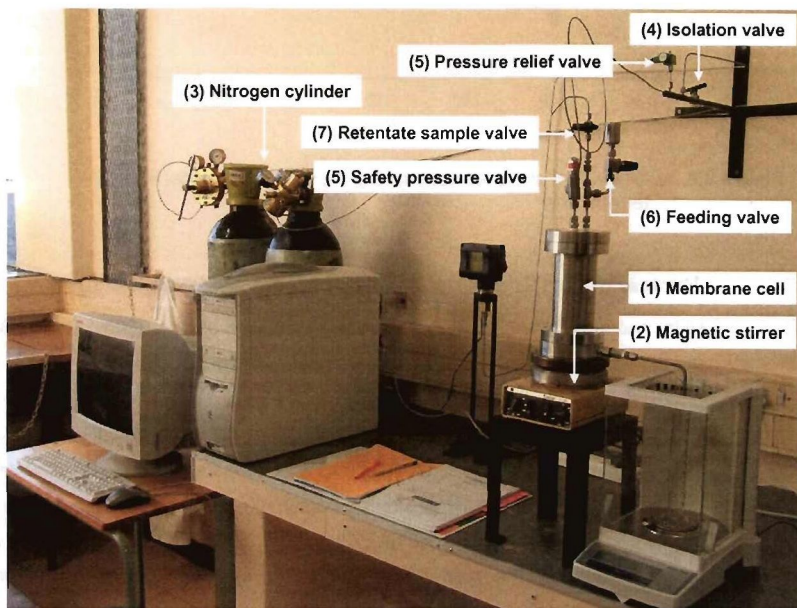


Figure 3.9 Photo of the OSN permeation apparatus used during this investigation.

All OSN experiments were investigated with a self-built stainless steel dead-end pressure cell. The membrane pressure cell consisted of a cylindrical stainless steel chamber with removable end plates, as shown in Figure 3.11, Figure 3.12 and Figure 3.13. The chamber had an inside diameter of 45 mm that gave the membrane an active surface area of 15.9 cm². Membrane discs were cut to the desired size from A4 sheets and tightly fixed in the cell between the O-rings and a porous stainless steel disk. The membrane's active layer was facing the solvent. The cell was placed on a magnetic stirrer that was used to stir a Teflon-coated stirring bar in the cell at 300 rpm. The stirring was done to minimize the possibility of concentration polarization in

the cell. All experiments were carried out at room temperature (20 to 23 °C). Ultra High Purity (UHP) nitrogen gas was used to pressurize the cell at different pressures, ranging from 10 to 40 bar. The permeating solution was collected in a measuring cylinder and weighed with a mass scale connected to a computer.

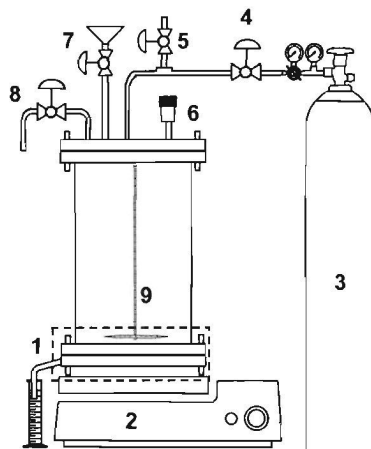


Figure 3.10 Schematic representation of pressure cell set-up. [1. Membrane cell; 2. Magnetic stirrer; 3. Nitrogen cylinder; 4. Isolation valve; 5. Pressure release valve; 6. Safety pressure valve; 7. Feeding valve; 8. Retentate sample valve; 9. Teflon magnetic stirrer bar.]

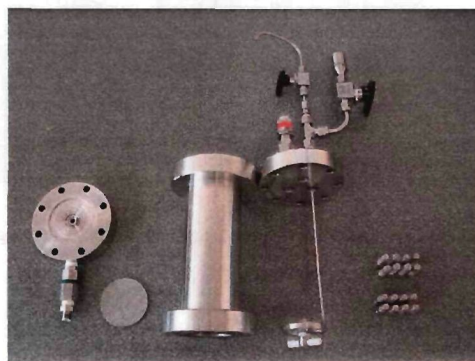


Figure 3.11 Photo of membrane cell.

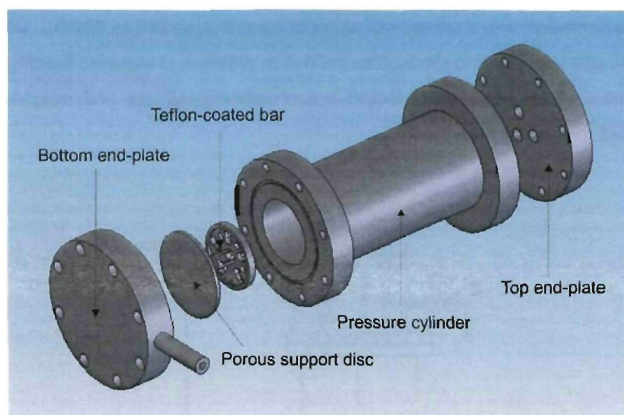


Figure 3.12 SolidWorks rendering of the different parts of the membrane cell.

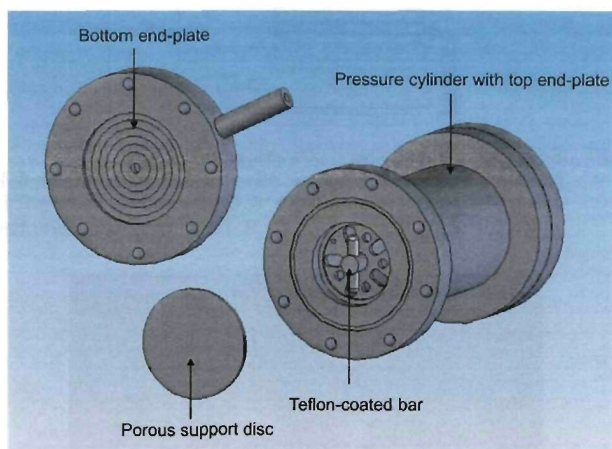


Figure 3.13 SolidWorks rendering of membrane cell from a bottom angle view.

3.4.2 Methodology of solvent permeation

The OSN process was characterized by different solvents and/or solvent mixtures with regard to compatibility (stability), pretreatment, a break-in procedure to obtain steady-state conditions and steady-state characterization.

3.4.2.1 Compatibility tests

A standard method⁵ of assessing the compatibility (stability) of a membrane with a given solvent was used in this study. Both physical stability and compatibility at moderate pressures (10 to 50 bar) were tested. The physical stability was assessed by visual inspection for any sign of dissolution of the membrane by the solvent or colouration of the membrane's active surface. A small piece of the membrane was cut out from an A4 sheet and placed in a Petri dish filled with the given solvent. The membrane was soaked in the solvent for a minimum period of two days and inspected at regular time intervals for any signs of active layer dissolution, cracking or bending.

Membrane-solvent compatibility tests were performed by loading the membrane cell with 50 mL of a given solvent and measuring the permeation rate through the membrane. The cell was pressurized at 30 bar and the system was evaluated as incompatible if no flux was obtained under these conditions and higher pressures. The cell was left for at least four days at these conditions to confirm no permeation.

3.4.2.2 Pretreatment

The hydrophobic polyimide STARMEM™ series of membranes were supplied in a dry form. Indiscernible preservation oil was present on top of the membrane to protect it from drying out. According to the manufacturers, this preservation oil could be washed out easily with a solvent like toluene by allowing the solvent to permeate for at least 15 minutes at a pressure of 20 to 40 bar. Jezowska *et al.*¹⁵ found that pretreating flat sheet membranes made the membrane more homogeneous. Zhao *et al.*¹⁶ reported that the type of solvent used for the pretreatment could result in reorganization of the membrane structure, changes in membrane pore size and hydrophobicity of the membrane. The membranes were, therefore, pretreated with different solvents (toluene, 1-octene, ethanol and acetic acid). The reasons for choosing the pretreatment solvents that were used, were:

- Toluene: It is recommended by the manufacturer of the membrane and will serve as a standard to measure the performance of the alternative pretreatments.
 - 1-Octene: Seeing that 1-octene is used as reagent in the metathesis reaction, it is reasonable to use it as a pretreatment solvent to possibly cut out additional costs associated with pretreatment.
-

- Ethanol: A well-known solvent that is easily accessible and is a strong polar component.
- Acetic acid: A relatively weak acid that can easily dissolve lubricating oil with relative polar properties.

The pretreatment to remove the preservation oil was done by loading the membrane pressure cell with 30 mL of the given solvent and allowing 20 mL of the solvent (or at least one hour) to permeate through the membrane. The cell was pressurized at 30 bar and the solvent that permeated was discarded. If more than 20 mL had permeated before one hour had elapsed then the cell was depressurized and a fresh 20 mL solvent was re-introduced into the cell. The cell was thereafter pressurized to 30 bar and the process was repeated until all the preservation oil was washed out. The cell was then thoroughly washed out with the desired solvent (1-octene, 7-tetradecene, 1-tetradecene, H₂O, etc., or combinations thereof) that was used for steady-state characterization.

3.4.2.3 Break-in procedure to acquire steady-state

It is stated in literature⁵ that the membrane must be "broken-in" before any characterization can be done at steady-state conditions. The reason for this is to minimize the effect of irreversible membrane compaction and to establish steady-state conditions. The membrane was, therefore, broken-in by permeating the solvent or solvent-mixture through the membrane at the desired pressure until steady-state conditions were observed. The cell was first thoroughly washed out with the desired solvent or solvent-mixtures and thereafter fresh solvent or solvent-mixtures of 50 mL were introduced in the cell. A maximum of 30 mL was allowed to permeate through the membrane. The permeating solution was measured by an electronic scale connected to a computer that monitored the mass increase with time. The permeating volume was also monitored at intervals of 5 mL with a millisecond stopwatch.

If steady-state permeating conditions had not been reached, then the cell was depressurized and the solvent or solvent-mixture was re-introduced into the cell. The cell was then pressurized to the desired pressure and the process was repeated until steady-state permeating conditions were established.

When steady-state permeating conditions had been established the last three permeating solvent-mixtures (3 x 5 mL) were analysed by GC to determine if composition steady-state had been established. If the composition steady-state had not been reached the cell was depressurized and the solvent-mixture was re-introduced into the cell once more. The cell was then pressurized to the desired pressure and the process was repeated until composition steady-state had also been established.

3.4.2.4 Steady-state permeation characterization

The cell was loaded with 50 mL of the given solvent or solvent-mixtures and pressurized to the desired pressure. The permeating solvent or solvent-mixtures were measured by an electronic scale connected to a computer that monitored the mass over time. The permeating volume was also monitored with a millisecond stopwatch for intervals of 5 mL. The steady-state characterization was stopped after 30 mL of the solvent or solvent-mixture had permeated through the membrane. The last three permeating solvent-mixtures (3 x 5 mL) and the remaining retentate (20 mL) were analysed by GC.

The fluxes of the different solvent and/or solvent-mixtures were determined by measuring the time difference, Δt , required to collect a certain volume of permeate V_p (or mass m_p). The flux could then be calculated from Equation 3.3:

$$J = \frac{V_p}{A \cdot \Delta t} \quad (3.3)$$

where A is the effective membrane area.

3.4.3 Methodology of catalyst rejection

The method used to characterize the OSN process for the different catalysts, especially focusing on the rejection, is similar to the procedure discussed in Section 3.4.3 for the solvents. Only membranes that had been pretreated and broken-in, using the procedure outlined in section 3.4.3, were used to obtain rejection data. The cell was loaded with 50 mL of a post-metathesis reaction mixture and pressurized to the desired pressure. The permeating volume was monitored with a millisecond stopwatch for intervals of 10 mL. The OSN process was stopped after 30 mL had permeated through the membrane. The permeating solution (3 x 10 mL) and remaining 20 mL retentate were thereafter analysed with atomic absorption spectroscopy to determine the rejection characteristics. The cell was thoroughly washed out with pure 1-octene after each catalyst rejection experiment.

The rejection (R) of a given catalyst was calculated by equation 3.4:

$$R = \left(1 - \frac{C_p}{C_R} \right) \cdot 100\% \quad (3.4)$$

where

C_p final concentration of catalyst in the permeate

C_R final concentration of the catalyst in the retentate

3.4.4 Analytical equipment and methodology

The Agilent 6890 GC, as described in Section 3.3.2, was used for analysing the concentration of the different feed and permeating solvent-mixtures.

Flame atomic absorption spectroscopy (FAAS) was used to analyse the rejection of the different catalysts. The sample solutions containing the catalyst needed to be pretreated before analyses with FAAS could be conducted. The main reason was that the alkene environment showed no response signal for the ruthenium complex and, therefore, needed to be transferred into a more suitable environment. An acidified solution of ethanol and acetone was shown to be suitable. Therefore, the sample solution was transferred into a 100 mL round neck flask and evaporated, using vacuum distillation until a small amount (less than 2 mL) of the solution was left.

Care was taken not to evaporate all the liquid solution as the catalyst complex tended to adhere to the flask which made it difficult to dissolve. The solution was then allowed to cool down to room temperature and 5 mL HCl was slowly added. The solution was stirred for one minute and 8 mL acetone was added and again stirred for one minute. After this, 30 mL ethanol was added to the flask and stirred until the precipitation had dissolved into the solution. The solution had a greenish-brown color. The greenish-brown solution was then transferred into a 50 mL Erlenmeyer flask and ethanol was added until the final solution had a volume of 50 mL. The solution was then thoroughly shaken and analysed with FAAS.

Standard solutions of the different precatalysts were also prepared according to the method described above and analysed to obtain calibration curves. Typically obtained calibration curves and calibration data are presented in Table 3.4 and Figure 3.14.

Table 3.4 Standard readings of Gr2Ph for FAAS calibration.

Sample concentration ($\mu\text{m.mL}^{-1}$)	RSD	Mean absorption (-)	Reading	Reading	Reading	Reading
0		0.000	-0.001	-0.001	-0.001	-0.001
19	3.3	0.010	0.010	0.010	0.010	0.011
53	3.9	0.029	0.030	0.031	0.030	0.028
86	5.6	0.051	0.051	0.048	0.050	0.055
122	3.8	0.081	0.078	0.085	0.082	0.079
160	2.1	0.110	0.109	0.109	0.109	0.114
200	2.3	0.144	0.141	0.146	0.148	0.141

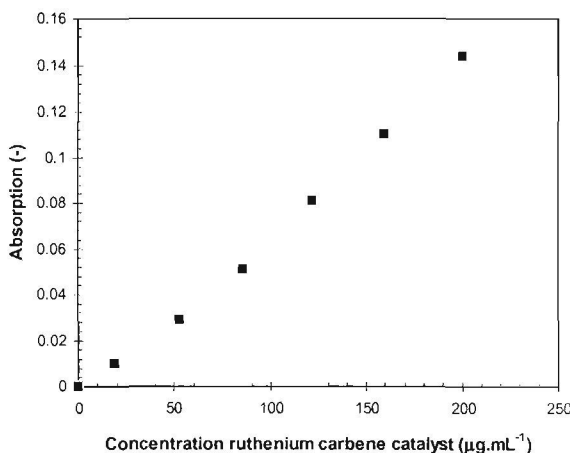


Figure 3.14 Calibration curve of Gr2Ph with FAAS.

3.5 OSN sorption experiments

The sorption or swelling experiments were determined at room temperature by using the standard method, well described in the literature (see e.g. Aminabhavi *et al.*¹⁷ and Stafie *et al.*¹⁸). Dry strips of membrane samples were weighed (M_{dry}) and then immersed in different flasks containing pure 1-octene or 7-tetradecene or binary mixtures of 1-octene and 7-tetradecene. Thereafter, at different time intervals, the mass increases of the membrane samples were monitored by weighing the membrane samples (M_{wet}). Care was taken to wipe off the excess liquid by pressing the membrane samples between layers of tissue paper. Each weighing of the membrane sample was completed within 30 seconds and the sample immediately returned back to the flask solution to minimize evaporation of the solvent. This process was repeated until no further mass increase was observed, which indicated that sorption equilibrium had been reached. The swelling degree (SD) of the membrane or sorption capabilities of the solvent-membrane interaction was calculated with Equation 3.5:

$$SD = \left(\frac{M_{wet} - M_{dry}}{M_{dry}} \right) \cdot 100\% \quad (3.5)$$

where

M_{dry} initial dried membrane mass (mg)

M_{wet} "wetted" membrane mass (mg)

3.6 OSN supporting experiments

3.6.1 Density

The densities of the different components (1-octene, 1-tetradecene and 7-tetradecene) and their binary mixtures were determined at room temperature by measuring the mass of 10 mL. The repeatability and accuracy of the density measurements were determined by conducting six consecutive experiments with water and ethanol.

3.6.2 Viscosity

The viscosities of the different components (1-octene, 1-tetradecene and 7-tetradecene) and their binary mixtures were determined by using a standard U-tube viscosity meter method as described by Aulton¹⁹ and Koekemoer *et al.*²⁰ A thoroughly cleaned, dried and calibrated Ostwald U-tube viscometer as shown in Figure 3.15 was used to measure the different viscosities. All the measurements were conducted at room temperature.

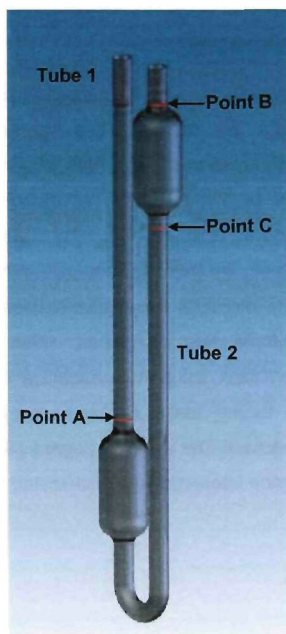


Figure 3.15 Schematic representation of a standard Ostwald U-tube viscometer.

The desired liquid was carefully poured into tube 1 up to point A, as depicted in Figure 3.15. The liquid was then slowly sucked up from tube 1 into tube 2 to point B. Thereafter, the liquid was allowed to flow freely under the influence of gravity from point B to point C. The time it took for the liquid to flow from point B to C was measured with a millisecond stopwatch. Ten consecutive experiments were repeated.

Distilled water was used to calibrate the viscometer, as the viscosity and density of water are well-known. The meter constant was calculated by using Equation 3.6 and the average measured time it took the water to fall freely from point B to point C.

$$K = \frac{\eta}{t \times \rho} \quad (3.6)$$

where

K meter constant ($\text{m}^2 \cdot \text{s}^{-2}$)

t measured time for water to flow from point B to C

ρ density of water ($\text{kg} \cdot \text{m}^{-3}$)

The calibration constant for the viscometer was calculated as $7.3 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-2}$. The viscosity of a liquid can then be determined by using the viscometer and Equation 3.7.

$$\eta = K \times t \times \rho \quad (3.7)$$

where

K meter constant ($\text{m}^2 \cdot \text{s}^{-2}$)

t measured time for the desired liquid to flow from point B to C

ρ density of desired liquid ($\text{kg} \cdot \text{m}^{-3}$)

The repeatability and accuracy of the viscosity measurements were determined by conducting six consecutive experiments with ethanol. The error of accuracy was calculated as 1.33% while the error of repeatability was calculated as 0.38%.

3.6.3 Contact angle

The different contact angles for the components, 1-octene, 7-tetradecene and H₂O, were determined at room temperature. A liquid drop was carefully applied with a syringe to the solid membrane surface, as indicated in Figure 3.16. A digital photo was taken of the specific shape of the droplet. The drop shape is characteristic of the interactions in a 3-phase system as depicted by the insertion in Figure 3.16.

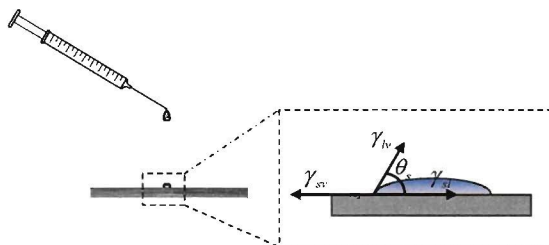


Figure 3.16 Schematic representation of the determination of the contact angle.

The drop shape will strive towards equilibrium, based on Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (3.8)$$

where

γ_{sv} interfacial tension of membrane solid and vapour phase

γ_{sl} interfacial tension of membrane solid and liquid phase

γ_{lv} interfacial tension of liquid and vapour phase

θ characteristic contact angle (°)

3.7 Reaction, separation and recycling experiments

The coupled reaction-separation and recycling procedures used in this investigation are illustrated in Figure 3.17.

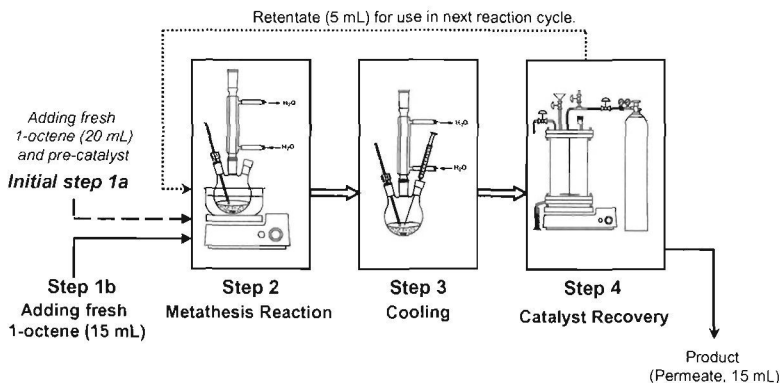


Figure 3.17 Coupled reaction-separation and recycling process, showing the different stages between reaction and OSN.

The metathesis reaction was carried out, as described in Section 3.3, in a 250 mL three-necked round-bottomed flask fitted with a condenser, thermometer and septum (see Figure 3.6). After the reaction had been completed, the post-reaction mixture (20 mL) was left to cool down to room temperature and thereafter transferred into the membrane cell (see Figure 3.10) for separation, as described in Section 3.4. The cell was pressurized to 30 bar at room temperature and the post-reaction mixture was stirred at 300 rpm to minimize the possibility of concentration polarization. The OSN process was stopped after 15 mL of the original 20 mL post-reaction mixture had passed through the membrane and the precatalyst was reclaimed. The precatalyst was reclaimed by washing out the 5 mL retentate solution left in the membrane cell, with 15 mL pure 1-octene. The 20 mL washed-out solution containing the catalyst was then transferred to the reaction flask and the reaction and OSN process were repeated. The same membrane disc was used for the repeated experiments. Luthra *et al.*^{21,22} stated that this procedure, with multiple membrane use, mimicked more closely the likely procedure which would be used industrially. Prior to each reaction, separation and recycling experiments, the cell was thoroughly washed out with pure 1-octene.

3.8 References

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4 METATHESIS - RESULTS AND DISCUSSION

Overview

In this chapter the results of the investigation into the metathesis reaction of 1-octene with different precatalysts (**HGr1**, **HGr2** and **Gr2Ph**), as well as the molecular modelling thereof, will be presented and discussed.

The chapter is subdivided into eight sections, starting in Section 4.1 with a general overview of terminology and concepts used in discussing the results. Section 4.2 presents the synthesis of a new Grubbs-type precatalyst, **Gr2Ph**. Sections 4.3, 4.4 and 4.5 describe the metathesis reaction of the precatalysts **HGr1**, **HGr2** and **Gr2Ph** with 1-octene. The effects of temperature, catalyst load and solvents on the metathesis reaction of 1-octene are also presented in these sections. Section 4.6 focuses on the theoretical description of the mechanism that describes the metathesis reaction of 1-octene with the different precatalysts by using molecular modelling. Lastly, concluding remarks are given in Section 4.7.

4.1 General considerations

4.1.1 Nature of 1-octene metathesis

The metathesis reaction of 1-octene with different Grubbs-type catalysts can produce a complex product distribution as illustrated in Figure 4.1, due to alkene isomerization, self- and cross-metathesis reactions.

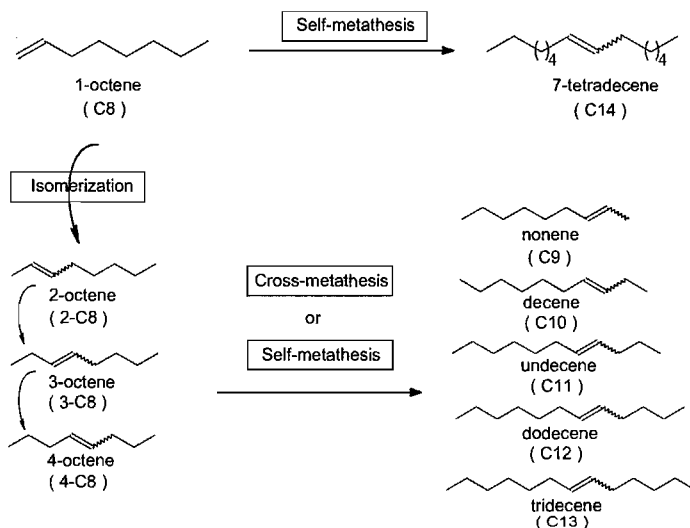


Figure 4.1 Possible reactions of 1-octene in the presence of the metathesis catalysts (only the longer chain alkenes are shown).

It is clear from Figure 4.1 that three major groups of products can be identified, namely: primary metathesis products (PMP), isomerization products (IP) and secondary metathesis products (SMP). PMP refers to the self-metathesis reaction of 1-octene to form 7-tetradecene (C₁₄), both *cis*- and *trans*-tetradecene, and ethene. IP refers to the double bond isomerization reactions of the terminal to internal alkenes (2-C₈, 3-C₈ and 4-C₈). SMP refers to the cascade of products (C₉ to C₁₃) as a result of cross-metathesis and/or self-metathesis of the isomerization products of 1-octene. These three product types PMP, IP and SMP will be used to characterize the performances of the different precatalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**), as depicted in Figure 4.2, for the metathesis reaction of 1-octene.

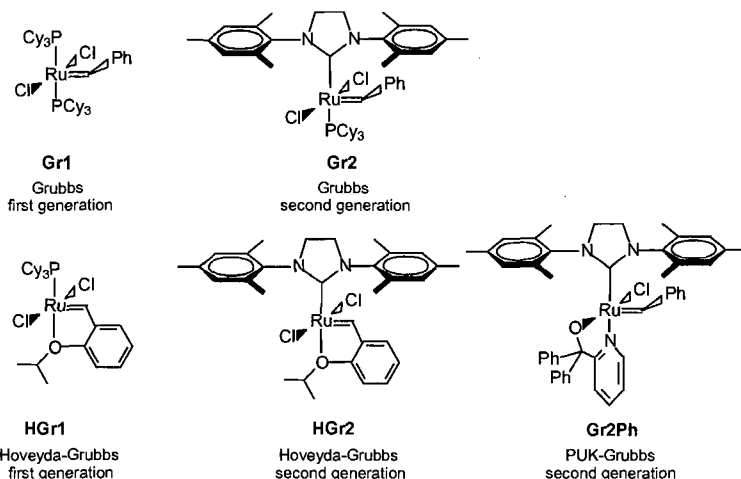


Figure 4.2 Different precatalysts applied to the metathesis reaction of 1-octene.

4.1.2 Working definitions

The standard method proposed by Grubbs and co-workers¹ for comparing and evaluating the efficiency of different catalysts with each other, will be used in this study. The reaction system will be described with respect to: product distribution (PMP, IP and SMP mol%), selectivity, activity and stability.

The selectivity can be defined as the ability of the catalyst to preferentially react with 1-octene to produce PMPs and the inability to form IPs and SMPs. The product selectivity (S) is given in Equation 4.1 as:²⁻⁴

$$S = \frac{\text{moles PMP formed}}{\text{moles (PMP + IP + SMP) formed}} \quad (4.1)$$

The activity is usually defined as the observed reaction rate at which the PMPs are formed. However, the effective turnover number (TON) is generally accepted and used in the field of metathesis to characterise the catalytic activity. The TON parameter, as defined in Equation 4.2, will be used in this study.^{5,6}

$$\text{TON} = \frac{\text{moles PMP formed}}{\text{moles precatalyst used}} \quad (4.2)$$

The stability is defined as the lifetime of the catalyst with consecutive reaction, separation and re-use before activity is completely lost.

4.1.3 Experimental error and reproducibility

The reproducibility of results (or experimental error) is extremely important in experimentation, as it helps and protects the investigator from unwitting errors and validates or confirms experimental conclusions. The experimental error for the metathesis experiments in mol% PMP, IP and SMP measurements was obtained from two different reproducibility experiments that are summarized in Table 4.1. The experimental method and procedure that was used to acquire all the metathesis reaction data with the different Grubbs-type precatalysts is described in detail in Section 3.3.

The first reproducibility experiment was done by repeating the metathesis reaction with precatalyst **Gr1** under the same conditions of 50 °C and a 1-octene/Ru molar ratio of 7000, six times at different times during the investigation.

The second reproducibility experiment was done by repeating the metathesis reaction with three different precatalyst batches of **Gr2Ph** under the same conditions of 80 °C and a 1-octene/Ru molar ratio of 7000, four times at different times during the investigation. Figure 4.3 illustrates the typical repeatable results obtained for the formation of PMP over a period of 360 minutes.

Table 4.1 Reproducibility and experimental errors of the metathesis reaction.

Reproducible experiment	C8	PMP	IP	SMP
Experiment 1				
Mean conversion ($\bar{x}$)	64.44	33.93	1.28	0.35
Standard deviation (σ)	0.85	0.68	0.38	0.08
Upper Limit	64.69	34.13	1.39	0.37
Lower Limit	64.19	33.73	1.17	0.32
95% Confidence Interval	0.50	0.40	0.22	0.05
Experiment 2				
Mean conversion ($\bar{x}$)	14.39	71.92	0.88	12.81
Standard deviation (σ)	1.90	2.05	0.29	3.01
Upper Limit	15.40	73.00	1.03	14.40
Lower Limit	13.38	70.83	0.73	11.22
95% Confidence Interval	2.02	2.17	0.31	3.19

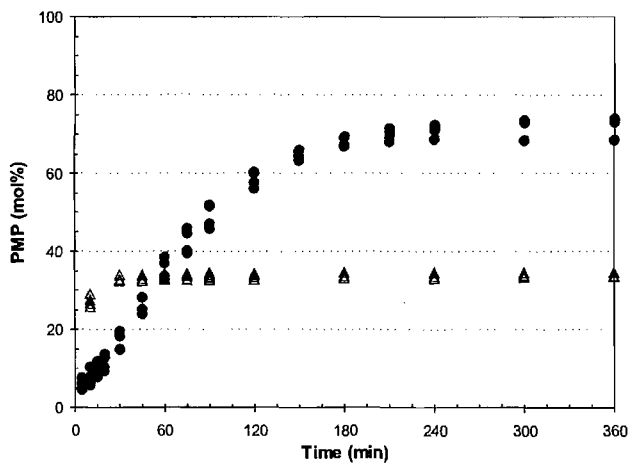


Figure 4.3 Demonstration of reproducibility with respect to PMP formation. [● Gr2Ph and △ Gr1]

4.2 Synthesis of precatalyst Gr2Ph

4.2.1 Introduction

In this Section the synthesis results of the in-house synthesized precatalyst **Gr2Ph** are discussed. Precatalyst **Gr2Ph** was prepared by stirring **Gr2** with the lithium salt (**L2**) of 2-pyridylcarbinol (**L1**) which was obtained through the reaction of **L1** with butyllithium as depicted in Figure 4.4. The detail description of the synthesis procedure is presented in Section 3.2.

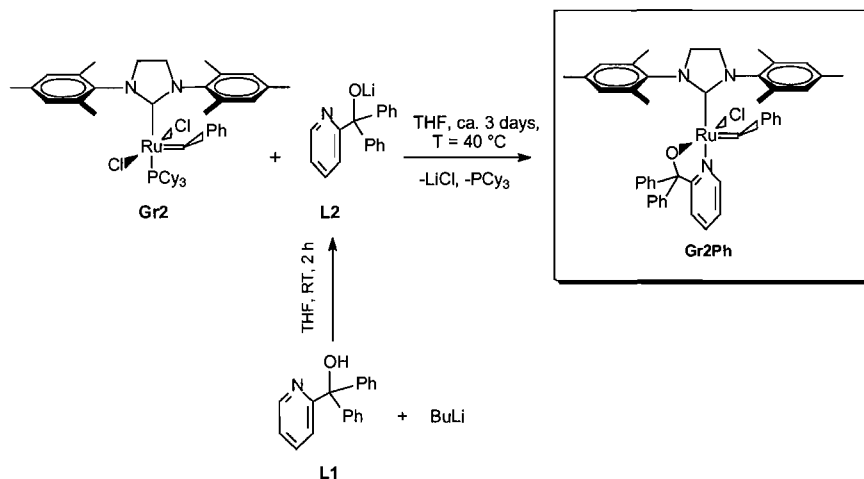


Figure 4.4 Reaction scheme of the synthesis of precatalyst **Gr2Ph**.

Five different batches were synthesized during the course of this investigation and the reproducibility of these synthesized precatalysts was tested based on (i) the precatalyst performance with 1-octene and (ii) the structural identification with NMR.

4.2.2 Synthesis results and discussion

The performance-related reproducibility was tested by carrying out four metathesis reactions under the same conditions (80°C and a 1-octene/Ru molar ratio of 7000) and comparing the response performances as shown in Figure 4.5. The experimental error was found to be approximately 3%, detail statistical analyses are presented in Table 4.1 (Experiment 2), which is evidence that the different batches of precatalysts produced consistent and repeatable results for the metathesis reaction of 1-octene.

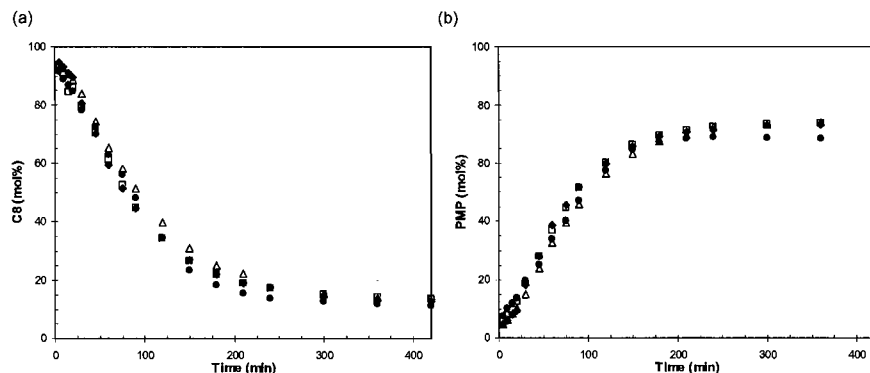


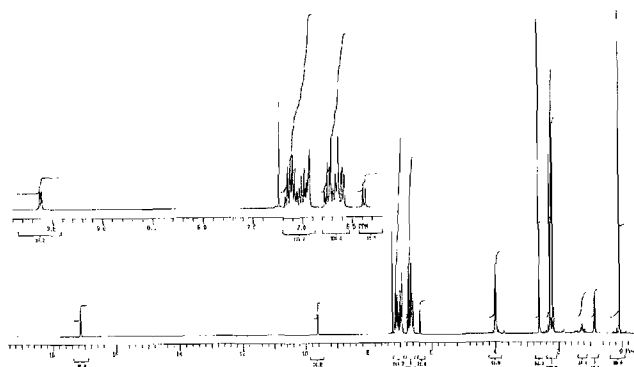
Figure 4.5 1-Octene metathesis reaction with **Gr2Ph** at a 1-octene/Ru molar ratio of 7000 with no solvent, a) 1-octene consumption and b) PMP formation.
[● Batch 1; ◆ Batch 2; △ Batch 3; □ Batch 4]

The structure-related reproducibility for the different batches of precatalysts was tested by analysing the precatalysts with ^1H and ^{31}P NMR as presented in Figure 4.6 and Figure 4.7. It is clear from Figure 4.6 that all the phosphine ligands from precatalyst **Gr2Ph** were successfully substituted with the chelated-based ligand as no ^{31}P NMR signal was observed.

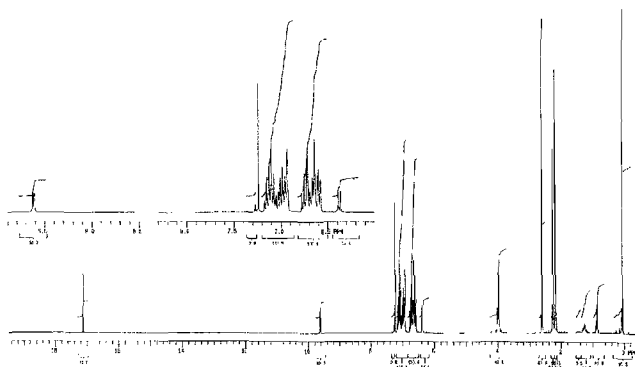


Figure 4.6 ^{31}P NMR spectrum for **Gr2Ph**.

(a)



(b)



(c)

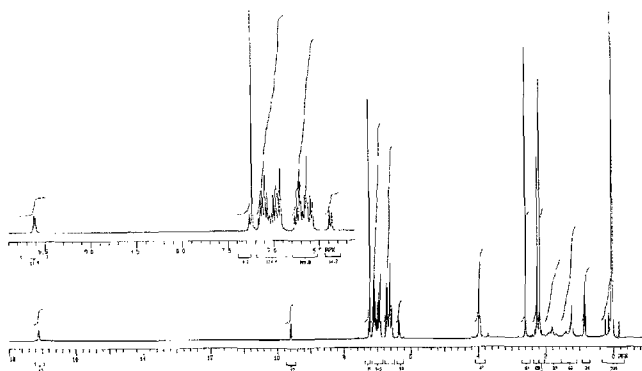
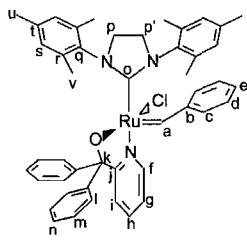


Figure 4.7 ^1H NMR spectra for the different **Gr2Ph** batches. [Batch 1 (a), Batch 2 (b) and Batch 3 (c)]

The product description, average yield and ^1H NMR chemical shifts of precatalyst **Gr2Ph** are summarized in Table 4.2 to demonstrate the successful synthesis of precatalyst **Gr2Ph**. The shelf-life of precatalyst **Gr2Ph** is also good. It was stored for seven months at room temperature without any special treatment or under any inert atmosphere. It also did not show any sign of decrease in catalytic activity as demonstrated in Figure 4.5, as well as the low experimental error of 3%.

Table 4.2 Data of synthesized precatalyst **Gr2Ph**.

Structure	Hydrogen ^a	δ^b (dpm)
	a	17.183 (s)
	c	6.43 (d)
	d	6.77 (dd)
	e	7.19 (dd)
	f	9.67 (d)
	g	7.036 (dd)
	h	7.19 (dd)
	i	6.64 (d)
	l,m,n	7.12–7.19 m (10H's)
	p/p'	4.05 (4H's)
	s/s'	6.71/6.99 (4H's)
Light-green microcrystalline powder with an average product yield of 91%.	u, v, v'	2.20; 2.30; 2.65 (18H's 3xs)

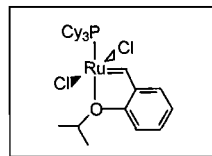
a) ^1H NMR data, 300 MHz.

b) Solvent CDCl_3 . s = singlet, d = doublet, t = triplet and m = multiplet.

4.2.3 Concluding remarks

In this Section the synthesis procedure and results obtained for the in-house precatalyst **Gr2Ph** are presented. It was found that precatalyst **Gr2Ph** could successfully be synthesized consistently for the metathesis reaction of 1-octene with a shelf-life of up to seven months.

4.3 Metathesis reaction with precatalyst HGr1



4.3.1 Introduction

In this Section the catalytic performance of precatalyst **HGr1** for the model metathesis reaction of 1-octene is evaluated. The influence of reaction temperature, precatalyst load and solvent used in the reaction environment, is evaluated with respect to selectivity and activity. Furthermore, the results are discussed from a mechanistic and a reaction engineering viewpoint; the reaction kinetics and kinetic parameters for the reaction system are determined and evaluated.

4.3.2 Experimental results and discussion

4.3.2.1 Influence of reaction temperature

The influence of the reaction temperature on the metathesis performance of precatalyst **HGr1** was investigated by varying the temperature between 30 and 100 °C. The reaction was monitored by GC/FID to determine the product distribution, as discussed in Section 3.3. The results obtained for a 1-octene/Ru molar ratio of 7000 with no solvent present, are summarized in Table 4.3, Figure 4.8 and Figure 4.9.

Table 4.3 Catalytic performance of precatalyst **HGr1** towards the metathesis of 1-octene after 420 minutes at different temperatures.
[No solvent added; 1-octene/Ru molar ratio = 7000].

Temperature (°C)	C8 (%)		PMP					
		<i>Cis-C14</i>	<i>Trans-C14</i>	Total PMP	IP (%)	SMP (%)	S (%)	TON (-)
30	44.98	6.16	20.82	53.96	0.48	0.58	98.08	3777
40	54.51	4.26	17.46	43.44	1.15	0.90	95.49	3041
50	58.56	6.76	12.42	38.36	2.68	0.39	92.58	2686
60	54.38	8.01	12.12	40.26	4.87	0.49	88.26	2818
70	47.59	7.14	12.50	39.28	12.68	0.45	74.95	2750
80	27.52	4.28	10.37	29.30	42.67	0.51	40.42	2051
90	20.92	4.89	11.84	33.47	44.57	1.03	42.33	2343
100	73.31	0.86	1.29	4.30	22.22	0.17	16.12	301

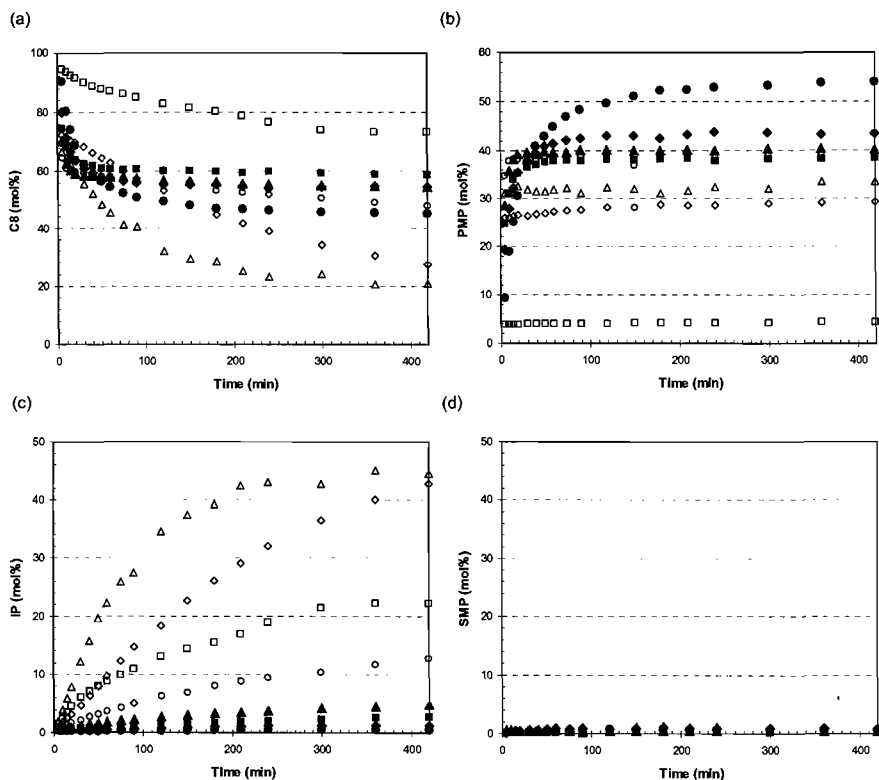


Figure 4.8 Influence of reaction temperature on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with HGr1 at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● 30 °C; ◆ 40 °C; ■ 50 °C; ▲ 60 °C; ○ 70 °C; ◇ 80 °C; △ 90 °C; □ 100 °C]

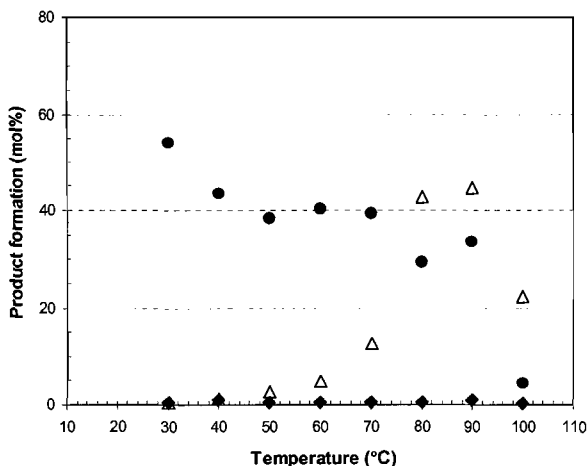


Figure 4.9 Influence of reaction temperature on the product distribution at 420 minutes for the 1-octene metathesis reaction with **HGr1** at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● PMP; △ IP; ◆ SMP]

It is clear from the results in Table 4.3 and Figure 4.8 that reaction temperature has a significant effect on the catalytic performance of precatalyst **HGr1**. As the reaction temperature increases from 30 to 50 °C, the PMP product formation decreases (~54% to 38%), while IP and SMP formations are insignificant (less than 3%). When the temperature increases above 50 °C the formation of IP starts to increase drastically and PMP formation stays relatively constant between 50 and 70 °C with a sharp decrease thereafter. No significant SMP formation is observed for the entire temperature range.

From a mechanistic viewpoint, the results indicate that two competing mechanisms are present. The one mechanism (specific for the metathesis selective of 1-octene) is preferentially observed for temperatures below 60 °C, while the other mechanism (isomerization of n-octenes) starts to occur in parallel at temperatures above 50 °C and dominates at temperatures above 70 °C. Moreover, it appears from the results that at temperatures above 90 °C, precatalyst **HGr1** starts to lose activity for metathesis and isomerization and possibly deactivates due to a high reaction temperature environment.

Similar results with regard to the formation of IP with **Gr1** and **Gr2** for the self-metathesis of 1-octene were obtained in the studies conducted by Jordaan *et al.*,² Meyer *et al.*⁷ and Lehman *et al.*⁹ Lehman *et al.*⁹ found that the isomerization process starts to occur rapidly at 60 °C

compared to 30 °C and proposed that the alkene isomerization is promoted by a decomposed catalyst. Forman *et al.*⁹ determined that the decomposition of **Gr1** starts to occur at temperatures above 50 °C and Mahahle⁴ showed that **Gr1** and **Gr2** can thermally be decomposed to hydride species. Dinger and Mol¹¹ also showed that **Gr1** and **Gr2** can form carbonyl species, which in turn are converted to the corresponding hydride species that were found to be active and selective alkene double bond isomerization catalysts.

It can thus be concluded that due to the presence of air (oxygen/CO₂) in the reaction environment, the **HGr1** precatalyst can form carbonyl species that is converted to hydrides upon reaction with terminal alkenes, which renders the **HGr1** precatalyst an active isomerization catalyst. This could be the cause of the isomerization effect of 1-octene above 50 °C through an alkyl mechanism as proposed in Figure 4.10.

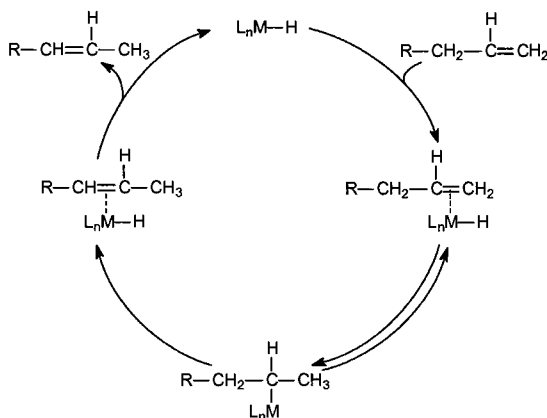


Figure 4.10 Alkyl mechanism for alkene isomerization.

From a reaction engineering point of view, two requirements are extremely important in designing any reactor, i.e. small reactor size and maximization of PMP product. Fogler¹² stated that for designing multi-reaction reactors the objective must be to minimize the formation of undesired products and to maximize the formation of the desired product, because the greater the amount of undesired product formed, the greater the cost of downstream separation processes. A reactor must, therefore, be designed in such a way that the selectivity (S) and TON, as defined in Equation 4.1 and 4.2, are maximized. From an economic standpoint, maximizing S and TON will maximize profits. The influence of reaction temperature on these two parameters for the metathesis reaction of 1-octene with precatalyst **HGr1** is given in Figure 4.11.

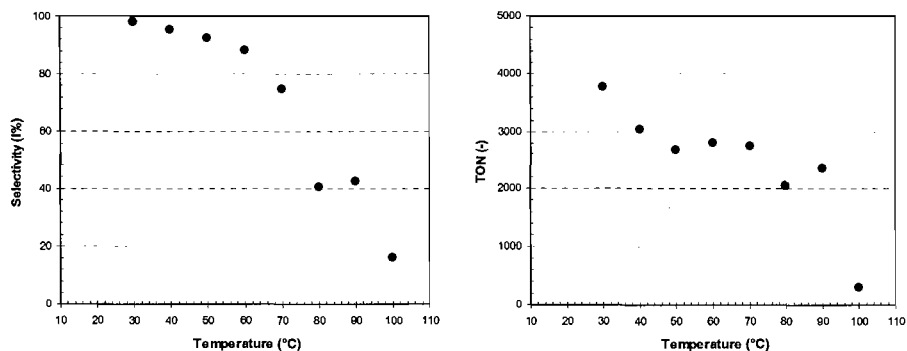


Figure 4.11 Influence of reaction temperature on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with **HGr1** at a 1-octene/Ru molar ratio of 7000 with no solvent.

It is clear from the results in Table 4.3 and Figure 4.11 that, as the reaction temperature increases the selectivity and TON decrease. It can be concluded from these results that the desired reaction temperature for designing a reactor for this reaction is at low operating temperatures, preferentially 30 °C.

4.3.2.2 Influence of precatalyst load

Ruthenium-based metathesis catalysts, such as **HGr1**, are expensive (timewise and costwise) to prepare and to use from an industrial perspective. It is, therefore, important to investigate the influence of precatalyst load on the metathesis reaction. The temperatures where the **HGr1** precatalyst gave relatively high activity, while retaining a high degree of selectivity and TON with a insignificant amount of IP and SMP products, were, in Section 4.3.2.1, found to be below 50 °C. The influence of precatalyst load (1-octene/Ru molar ratio) was, therefore, further investigated at 30 and 50 °C by varying the 1-octene/Ru molar ratio between 5000 and 14 000. The results obtained are shown in Table 4.4, Table 4.5, Figure 4.12 and Figure 4.13.

Table 4.4 Catalytic performance of **HGr1** towards the metathesis of 1-octene after 420 minutes at different precatalyst loads and 30 °C with no solvent added.

Precatalyst Load (C8/Ru molar ratio)	C8 (%)	PMP		Total PMP	IP (%)	SMP (%)	S (%)	TON (-)
		<i>Cis-C14</i>	<i>Trans-C14</i>					
5000	42.04	5.31	23.21	57.03	0.41	0.51	98.41	2852
7000	44.98	6.16	20.82	53.96	0.48	0.58	98.08	3777
9000	52.09	4.93	18.59	47.03	0.40	0.48	98.16	4232
10 000	54.59	7.56	14.73	44.58	0.57	0.26	98.16	4458

Table 4.5 Catalytic performance of **HGr1** towards the metathesis of 1-octene after 420 minutes at different precatalyst loads and 50 °C with no solvent added.

Precatalyst Load (C8/Ru molar ratio)	C8 (%)	PMP		Total PMP	IP (%)	SMP (%)	S (%)	TON (-)
		<i>Cis-C14</i>	<i>Trans-C14</i>					
5000	49.34	8.80	15.23	48.07	2.24	0.35	94.89	2403
7000	58.56	6.76	12.42	38.36	2.68	0.39	92.58	2686
9000	57.09	7.43	12.43	39.70	2.72	0.49	92.53	3573
10 000	60.47	7.29	11.14	36.87	2.29	0.37	93.28	3687
14 000	63.32	7.11	9.96	34.13	2.26	0.29	93.04	4779

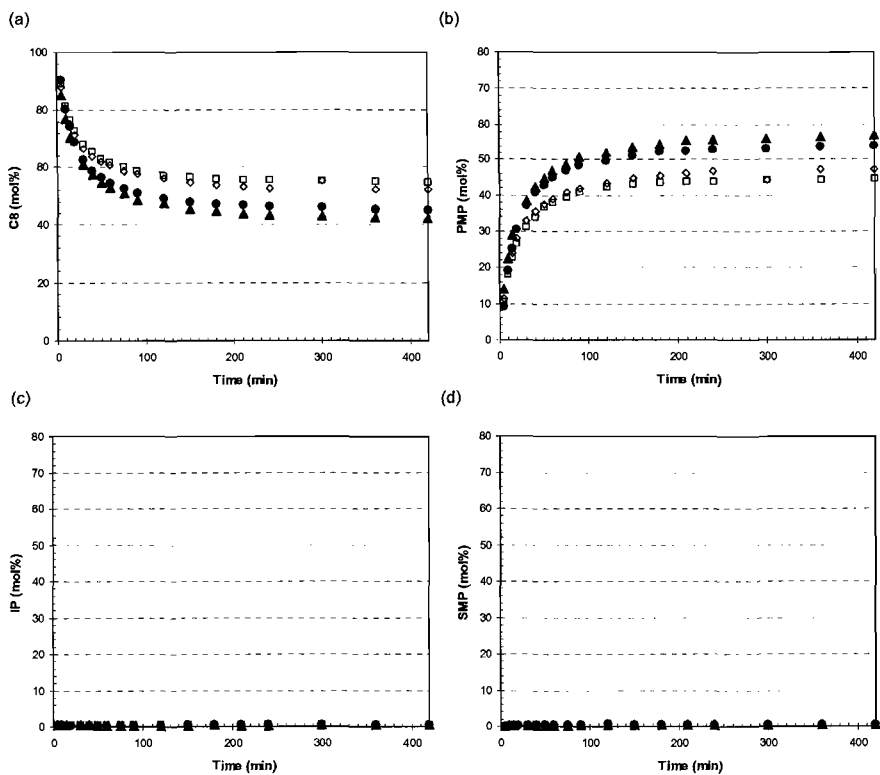


Figure 4.12 Influence of precatalyst load on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with HGr1 at 30 °C with no solvent.
[▲ 5000; ● 7000; ◇ 9000; □ 10000]

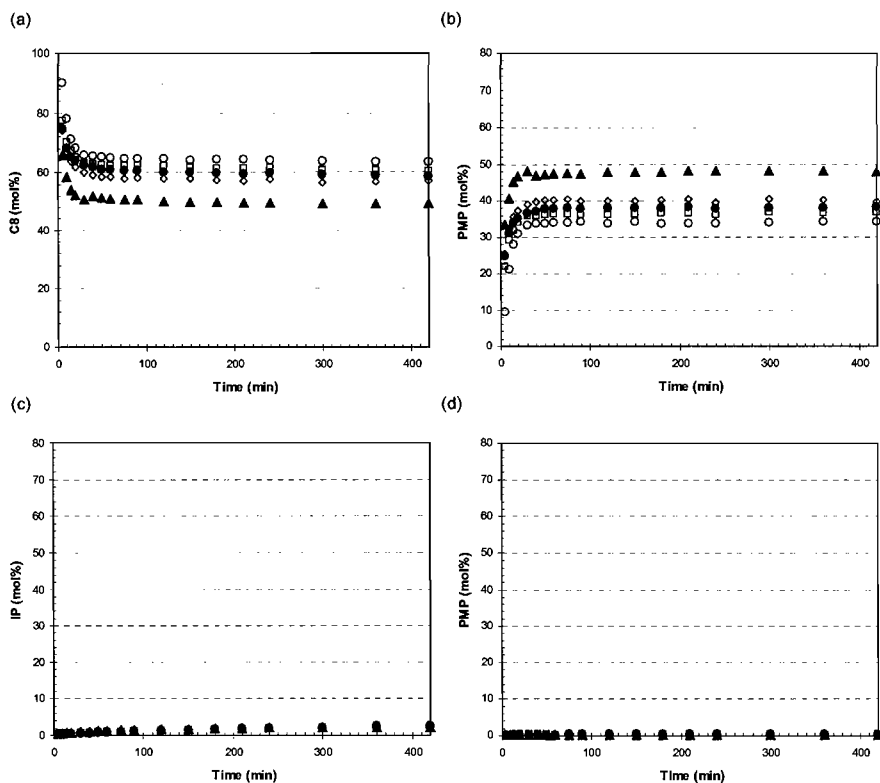


Figure 4.13 Influence of precatalyst load on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with HGr1 at 50 °C with no solvent.

[▲ 5000; ● 7000; ◇ 9000; □ 10000; ○ 14000]

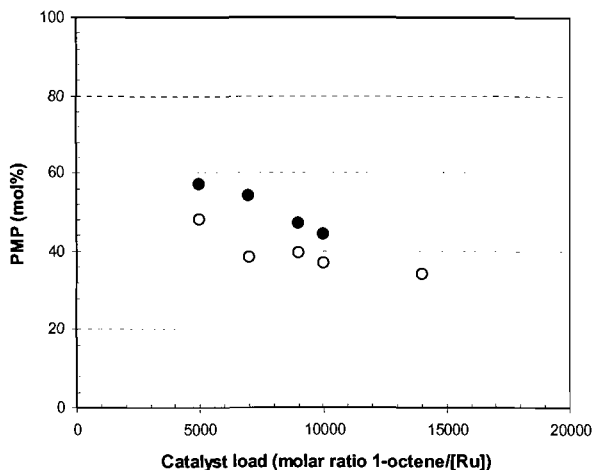


Figure 4.14 Influence of precatalyst load on the PMP formation at 420 minutes for the 1-octene metathesis reaction with HGr1.
[● 30 °C and ○ 50 °C]

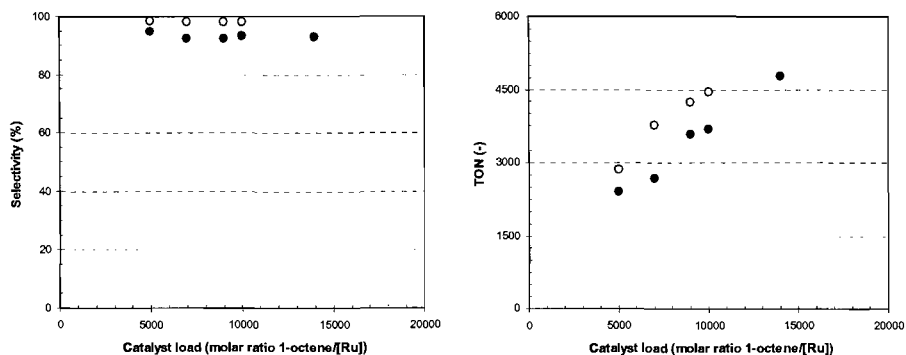


Figure 4.15 Influence of precatalyst load on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with HGr1 at ○ 30 °C and ● 50 °C with no solvent.

It appears from these results that as the precatalyst load increases (in other words a decrease in precatalyst mass) the product formation towards PMP decreases (~57% to 45% at 30 °C and 15% to 10% at 50 °C). IP and SMP formation are insignificant because of the chosen operating temperature.

The precatalyst load had no significant effect on selectivity with relatively constant values of ~98% at 30 °C and ~93% at 50 °C as shown in Figure 4.15. The precatalyst load, however, did have a linear increasing effect on the TON.

4.3.2.3 Influence of solvents

In an industrial context, alkene feed stocks derived from primary processes such as the Fischer-Tropsch¹⁸ conversion of synthesis gas often contain numerous impurities that may have the capacity to either retard or completely deactivate various homogeneous catalytic reactions.⁹ It is the aim of this Section to investigate the influence of different organic solvents on the metathesis reaction of 1-octene with HGr1. The reactions were carried out at 30 °C with a 1-octene/Ru molar ratio of 7000 as these conditions gave relatively high activity, selectivity and TON with insignificant amounts of IP and SMP being formed. The molar ratio of 1-octene/solvent was 1. The solvents used to characterize the reaction performance were selected, based on polarity with the Reichardt's E_T -scale parameter as summarized in Table 4.6. The metathesis results obtained are shown in Table 4.7.

Table 4.6 Properties of solvents used during the metathesis reaction.

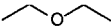
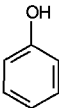
Solvent	Chemical Structure	Polarity	E_T -scale (-)	Dielectric constant (-)	Dipole-moment ($10^{-30} \times \text{C.m}$)
Toluene		Non-polar	0.099	2.38	1
Diethyl ether		Non-polar	0.117	4.20	3.8
Acetic acid		Polar Protic	0.648	6.17	5.6
Tetrahydrofuran		Polar Aprotic	0.207	7.58	5.8
Phenol		Polar Protic	-	9.90	-
Ethanol		Polar Protic	0.654	24.55	5.8
Dimethyl sulfoxide		Polar Aprotic	-	47.00	-

Table 4.7 Catalytic performance of **HGr1** towards the metathesis of 1-octene after 420 minutes for different organic solvents at 30 °C.

Solvent	C8	PMP			IP	SMP	S	TON
	(%)	<i>Cis-C14</i>	<i>Trans-C14</i>	Total PMP	(%)	(%)	(%)	(-)
Neat	44.98	6.16	20.82	53.96	0.48	0.58	98.08	3777
Toluene	53.24	8.58	14.41	45.97	0.50	0.28	98.32	3218
Diethyl Ether	65.40	6.99	9.63	33.25	1.13	0.21	96.11	2328
Acetic Acid	94.07	1.25	1.40	5.30	0.51	0.12	89.44	371
Tetrahydrofuran	92.26	1.58	1.94	7.05	0.64	0.06	91.03	493
Phenol	35.73	7.64	23.84	62.97	0.75	0.54	97.98	4408
Ethanol	96.84	0.53	0.73	2.52	0.61	0.03	79.71	176
DMSO ^[a]	-	-	-	-	-	-	-	-

[a] Dimethyl sulphoxide (DMSO): The reaction showed no metathesis activity with polar and non-polar layer separation.

It is clear from the results that the addition of organic solvents had a significant effect on the metathesis, mostly detrimental. Phenol was the only solvent that showed a beneficial effect towards the formation of PMP and TON compared to the neat reaction. These results support the findings of Forman *et al.*⁹ that showed that phenol enhanced the metathesis reaction of 1-octene with **Gr1**. Amir-Ebrahimi *et al.*¹⁰ suggested that the increased catalytic activity of **Gr1** for ROMP upon addition of phenol as solvent can be ascribed to metal to halide charge transfer. The chloride ligands in **HGr1** coordinate via phenolic hydrogen bonds to phenol, effectively resulting in a net flow of negative charge away from the ruthenium. This in turn enhances the electrophilic nature of the carbene carbon in **HGr1**, making the Ru=C bond more Lewis acidic and enhancing its reactivity toward Lewis-basic electron-rich alkenes. This charge distribution hypothesis was also verified by Forman *et al.*⁹ with molecular modelling for the metathesis system of **Gr1** and 1-octene. No clear correlation could be found between PMP formation and solvent type used. This is in agreement with what other researchers found with **Gr1** and **Gr2**.^{4,7,9}

4.3.3 Describing the reaction kinetics

4.3.3.1 Introduction

In addressing reactor sizing, it is important to describe the reaction kinetics (rate-laws) for the metathesis reaction as a reactor can only be sized once the kinetics for the specific reaction are known. The kinetic parameters for postulating a reaction rate-law for the formation of PMPs through the metathesis of 1-octene with the **HGr1** precatalyst, were obtained by using the algorithm proposed by Fogler¹² for catalytic reactor design as given in Figure 4.16 with an integral method for data analysis.

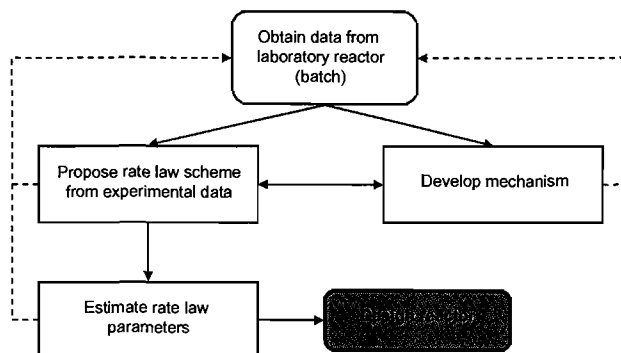


Figure 4.16 Proposed algorithm by Fogler¹² for designing catalytic reactors.

The development of a mechanism for the metathesis reaction of 1-octene with precatalyst **HGr1** is discussed in detail in Section 4.6 and the literature review with different Grubbs-type precatalysts is presented in Section 2.1.4. In Section 2.1.4 and 4.6 it is proposed that a dissociative type of mechanism is generally accepted as the preferred mechanism for describing the metathesis of 1-octene with Grubbs-type catalysts. According to Grubbs and co-workers,¹³ it appears that the dissociative mechanism for **Gr1** can be described by an empirical first-order type of rate equation. The product distribution time curves, as depicted in Figure 4.8, represent a parallel reaction type of scheme, similar to the one proposed in Figure 4.17.¹⁴ It is, therefore, proposed in this study that the metathesis reaction of 1-octene with precatalyst **HGr1** can be described by the parallel reaction scheme as postulated in Figure 4.17.

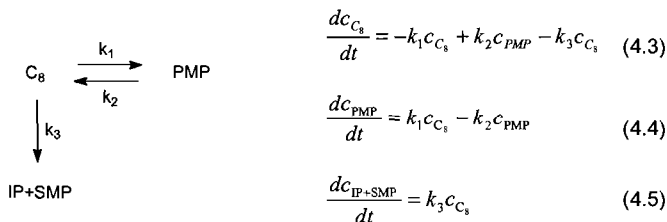


Figure 4.17 Proposed reaction scheme and elementary rate equations for the metathesis reaction of 1-octene with precatalyst **HGR1**.

The following notation is used in the three rate-law equations:

- c_{C_8} concentration of 1-octene in the reactor,
- c_{PMP} concentration of the PMPs in the reactor,
- c_{IP+SMP} concentration of the IPs and SMPs in the reactor,
- k_1 forward observed rate constant for the consumption of 1-octene in reaction 1,
- k_2 reverse observed rate constant for the formation of 1-octene in reaction 2, and
- k_3 observed rate constant for the consumption of 1-octene in reaction 3.

4.3.3.2 Calculation of observed rate constants

The value of each observed rate constant (k_1 , k_2 and k_3) for the different temperature profiles, as presented in Figure 4.8, and different precatalyst loads, as presented in Figure 4.12, was determined by regression, using the Simplex method in combination with the Runge-Kutta method to solve Equations 4.3, 4.4 and 4.5 simultaneously. The standard error of regression coefficients was determined with the Bootstrap method. Detail of the methodology and programming code can be seen in Appendix A.

The regression results are summarized in Table 4.8 for the different temperatures and in Table 4.9 for the different precatalyst loads. The predicted results compared to the observed experimental data are presented in Figure 4.18 and Figure 4.19 for the different temperatures and in Figure 4.20 for the different precatalyst loads.

Table 4.8 Observed rate constants for the metathesis reaction of 1-octene with precatalyst HGr1 at different reaction temperatures.

Temperature (°C)	Observed rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence Interval
30	$k_1 = 0.0212 \pm 0.00005$	0.00078	9.722×10^{-5}
	$k_2 = 0.0194 \pm 0.00006$	0.00099	1.223×10^{-4}
	$k_3 = 7.376 \times 10^{-5}$	1.035×10^{-5}	1.279×10^{-6}
40	$k_1 = 0.0425 \pm 0.00014$	0.00222	2.757×10^{-4}
	$k_2 = 0.0561 \pm 0.00021$	0.00335	4.155×10^{-4}
	$k_3 = 1.396 \times 10^{-5}$	1.558×10^{-5}	1.931×10^{-6}
50	$k_1 = 0.0702 \pm 0.00022$	0.00349	4.323×10^{-4}
	$k_2 = 0.1126 \pm 0.00037$	0.00600	7.439×10^{-4}
	$k_3 = 1.608 \times 10^{-4}$	1.129×10^{-5}	1.399×10^{-6}
60	$k_1 = 0.0944 \pm 0.00073$	0.01171	1.451×10^{-3}
	$k_2 = 0.1346 \pm 0.00038$	0.00608	7.541×10^{-4}
	$k_3 = 2.950 \times 10^{-4}$	1.270×10^{-5}	1.574×10^{-6}
70	$k_1 = 0.149 \pm 0.0018$	0.02916	3.614×10^{-3}
	$k_2 = 0.216 \pm 0.0022$	0.03606	4.469×10^{-3}
	$k_3 = 6.934 \times 10^{-4}$	1.881×10^{-5}	2.331×10^{-6}
80	$k_1 = 0.066 \pm 0.0016$	0.02667	3.305×10^{-3}
	$k_2 = 0.130 \pm 0.0035$	0.05629	6.976×10^{-3}
	$k_3 = 0.0024 \pm 0.0000033$	5.386×10^{-5}	6.674×10^{-6}
90	$k_1 = 0.046 \pm 0.00079$	0.01289	1.597×10^{-3}
	$k_2 = 0.054 \pm 0.00098$	0.01594	1.976×10^{-3}
	$k_3 = 4.386 \times 10^{-3}$	2.676×10^{-4}	3.316×10^{-5}
100	$k_1 = 0.0072 \pm 0.00004$	0.00071	8.818×10^{-5}
	$k_2 = 0.1137 \pm 0.00016$	0.00267	3.314×10^{-4}
	$k_3 = 8.515 \times 10^{-4}$	3.129×10^{-5}	3.878×10^{-6}

Table 4.9 Observed rate constants for the metathesis reaction of 1-octene with precatalyst HGr1 at 30 °C with different precatalyst loads.

Precatalyst load (molar ratio)	Observed rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence Interval
5000	$k_1 = 0.0231 \pm 0.00019$	0.00313	3.878×10^{-4}
	$k_2 = 0.0193 \pm 0.00010$	0.00168	2.081×10^{-4}
	$k_3 = 6.845 \times 10^{-5}$	6.439×10^{-6}	7.979×10^{-7}
7000	$k_1 = 0.0212 \pm 0.00005$	0.00078	9.722×10^{-5}
	$k_2 = 0.0194 \pm 0.00006$	0.00099	1.223×10^{-4}
	$k_3 = 7.376 \times 10^{-5}$	1.032×10^{-5}	1.279×10^{-6}
9000	$k_1 = 0.0208 \pm 0.00016$	0.00266	3.302×10^{-4}
	$k_2 = 0.0256 \pm 0.00011$	0.00181	2.244×10^{-4}
	$k_3 = 6.196 \times 10^{-5}$	6.600×10^{-6}	8.179×10^{-7}
10000	$k_1 = 0.0197 \pm 0.00073$	0.00247	3.061×10^{-4}
	$k_2 = 0.0259 \pm 0.00038$	0.00141	1.752×10^{-4}
	$k_3 = 5.804 \times 10^{-5}$	5.454×10^{-6}	6.759×10^{-7}

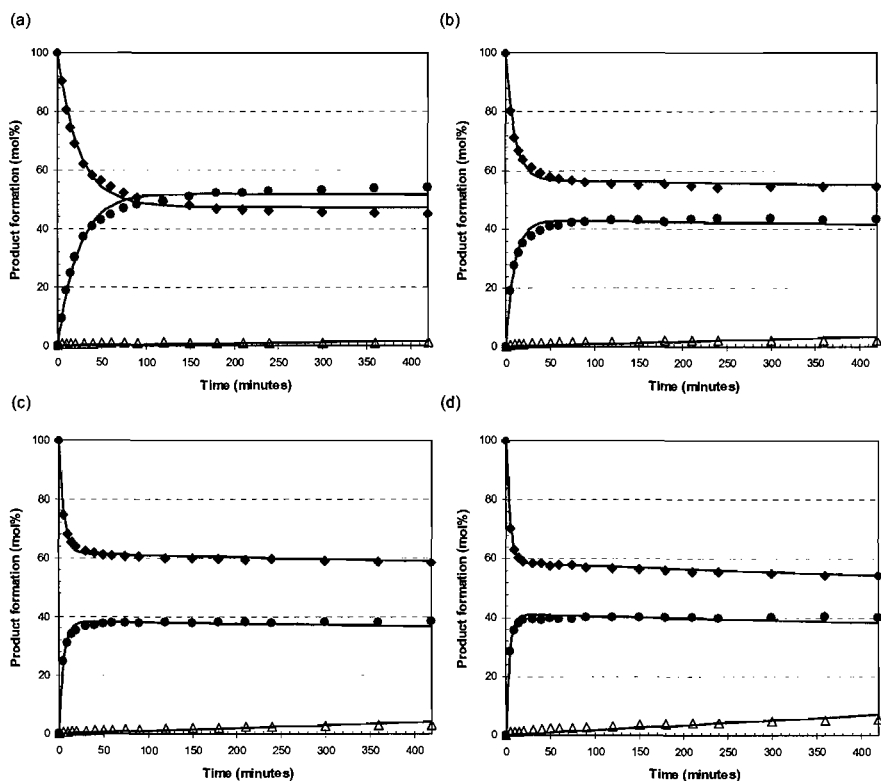


Figure 4.18 Experimental data compared to the modelled reaction scheme for the metathesis reaction of 1-octene with HGr1 at a) 30 °C, b) 40 °C, c) 50 °C and d) 60 °C. [● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

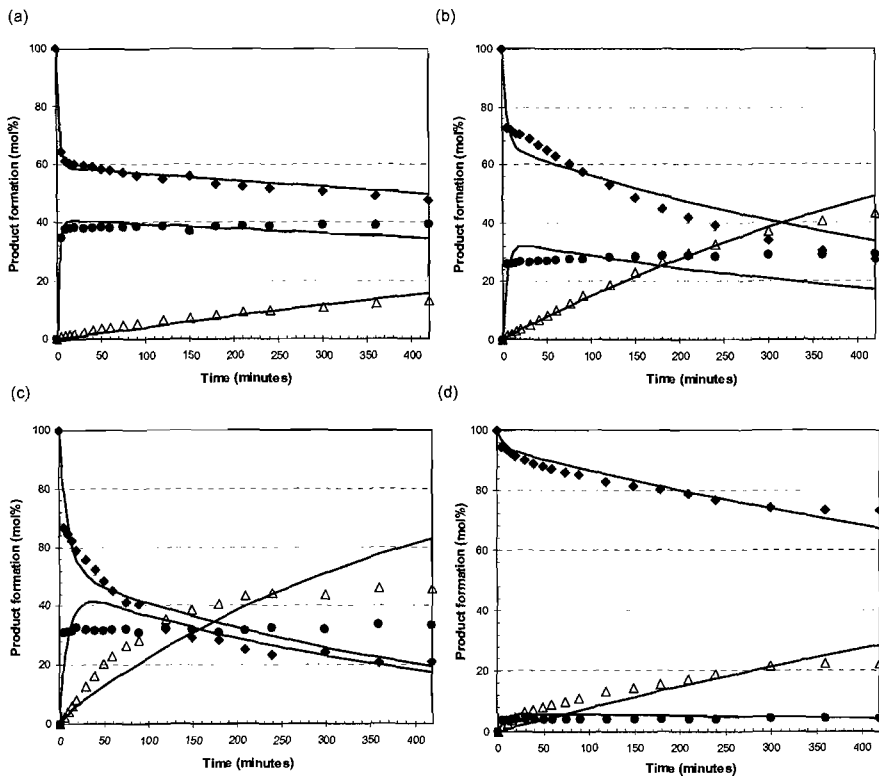


Figure 4.19 Experimental data compared to the modelled reaction scheme for the metathesis reaction of 1-octene with precatalyst HGr1 at a) 70 °C, b) 80 °C, c) 90 °C and d) 100 °C.

[● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

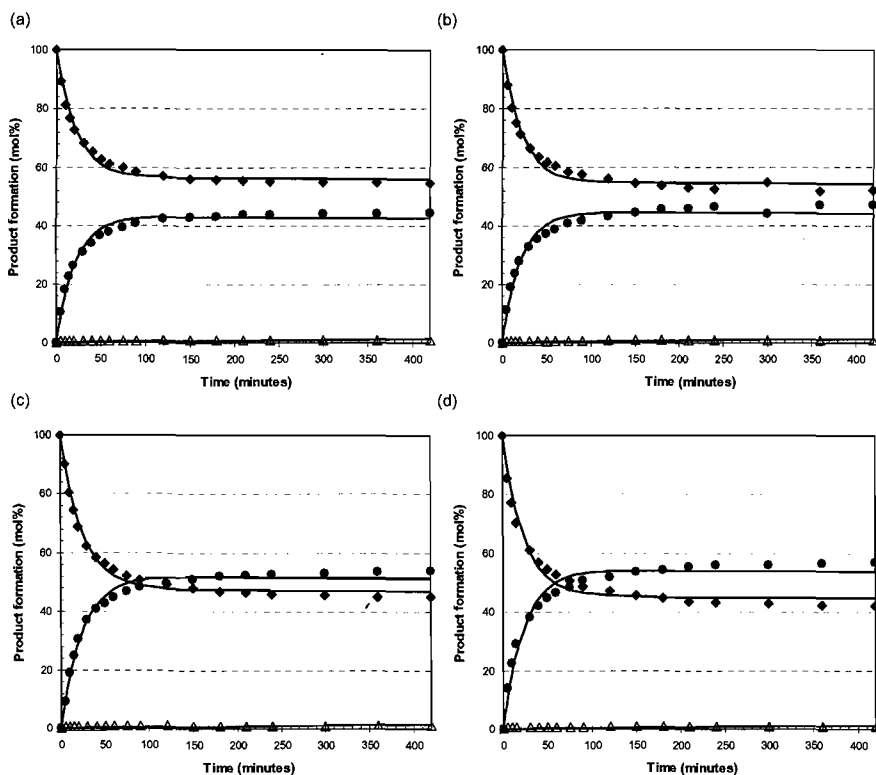


Figure 4.20 Experimental data compared to the modelled rate-laws for the metathesis reaction of 1-octene with precatalyst HGr1 for precatalyst loads of a) 10000, b) 9000, c) 7000 and d) 5 000 at 30 °C. [● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

It is clear from the results in Figure 4.18 to Figure 4.20 that the postulated rate-laws and reaction scheme as presented in Figure 4.17 (Equations 4.3, 4.4 and 4.5) with the calculated observed reaction rate constants describe the metathesis reaction of 1-octene with precatalyst HGr1 fairly accurately at the different temperatures and precatalyst loads. The proposed scheme, however, did not fully predict the experimental data correctly at higher temperatures (80 °C and 90 °C), as can be seen in Figure 4.19. Even completing different hypothesis studies with different reaction orders and reaction schemes did not significantly improve the currently proposed rate-laws and schemes. This failure at higher temperatures for the proposed scheme is probably due to the decreasing amount of PMP being formed and the increased dominance of reaction 3 at these temperatures.

4.3.3.3 Describing the observed rate constants

According to Grubbs *et al.*¹³ the observed rate constants such as calculated in Section 4.3.3.2 for an alkene metathesis reactions with precatalysts **Gr1** and **Gr2** can generally be described by a function of catalyst concentration and the dissociated phosphine ligand concentration. Grubbs *et al.*,¹³ however, did not take the influence of temperature in consideration in describing their observed rate constants. Levenspiel¹⁴ states that the temperature dependency of a reaction is determined by the activation energy and the temperature level of the reaction and can be described by an Arrhenius type of equation as depicted in Equation 4.6:

$$k_i = A_i e^{\left[\frac{-E_i}{RT}\right]} \quad (4.6)$$

where A_i is the frequency, or pre-exponential, factor, E_i is the activation energy of the reaction, R the gas constant and T the absolute temperature.

The mechanism of the metathesis reaction of 1-octene with precatalyst **HGr1** is a type of release-return mechanism with an initiation step (as discussed in Section 4.6) and not a dissociation. It is, therefore, proposed that the observed rate constants (k_1 , k_2 and k_3) as calculated in Section 4.3.3.2 and summarized in Table 4.8 and Table 4.9 can be described by a function of precatalyst concentration and temperature as given in Equation 4.7:

$$\begin{aligned} k_{obs} &= f(\text{catalyst concentration}) \times g(\text{temperature}) \\ &= k \times C_{catalyst}^{\alpha} \times e^{\left[\frac{-E}{RT}\right]} \end{aligned} \quad (4.7)$$

where k is the pseudo-frequency or pseudo-pre-exponential factor, $C_{catalyst}$ is the concentration of the precatalyst used, α is the reaction order that correlates the precatalyst influence, E is the activation energy of the reaction, R the gas constant and T the absolute temperature.

The observed rate constant parameters (k , α and E) as given in Equation 4.7 were determined by regression. The temperatures between 30 and 70 °C for all the precatalyst concentration were used. Statistica® version 8.0 with the standard nonlinear estimation methods of Levenberg-Marquardt and Gauss-Newton was used in the regression process. The regressed values of k , α and E are given in Table 4.10 and the observed versus predicted values of the observed rate constants (k_{obs}) are given in Figure 4.21. It is clear from these results that the different observed rate constants for the 1-octene metathesis reaction with precatalyst **HGr1** can fairly accurately be described by the proposed correlation of Equation 4.7 with an average Pearson correlation of 0.989.

Table 4.10 The rate constants parameter values for the metathesis reaction of 1-octene with HGr1 between 30 and 70 °C with the different precatalyst loads.

Observed rate constant	Pseudo-pre-exponential (k) ($\text{min}^{-1} \cdot \text{mmol}^{-\alpha} \cdot \text{mL}^{\alpha}$)	Reaction order (α)	Activation Energy (E) ($\text{kcal} \cdot \text{mol}^{-1}$)	Pearson square correlation (R^2)
k_1	7.771×10^4	0.25	9.47 ± 0.53	0.997
k_2	7.863×10^5	0.10	10.14 ± 1.28	0.986
k_3	2.598×10^6	0.50	14.26 ± 2.09	0.986

From the different activation energies, as given in Table 4.10, it can again be concluded that the reactor must be operated at low temperatures, as this will favour reaction 1 and the formation of PMP ($E_1 < E_2$) from an energy viewpoint. If the temperature increases, reaction 2 and reaction 3 will be favoured ($E_3 > E_1$ and $E_2 > E_1$), which correlates well with the observed results in Section 4.3.2.

The experimental results compared to postulated rate-laws and reaction scheme as presented in Figure 4.17 (Equations 4.3, 4.4 and 4.5) with the proposed observed reaction rate constants of Equation 4.7 are summarized in Figure 4.22. It is again clear from these results that the metathesis reaction of 1-octene with precatalyst HGr1 can fairly accurately be described by the modelled system of Equations 4.3, 4.4, 4.5 and 4.7.

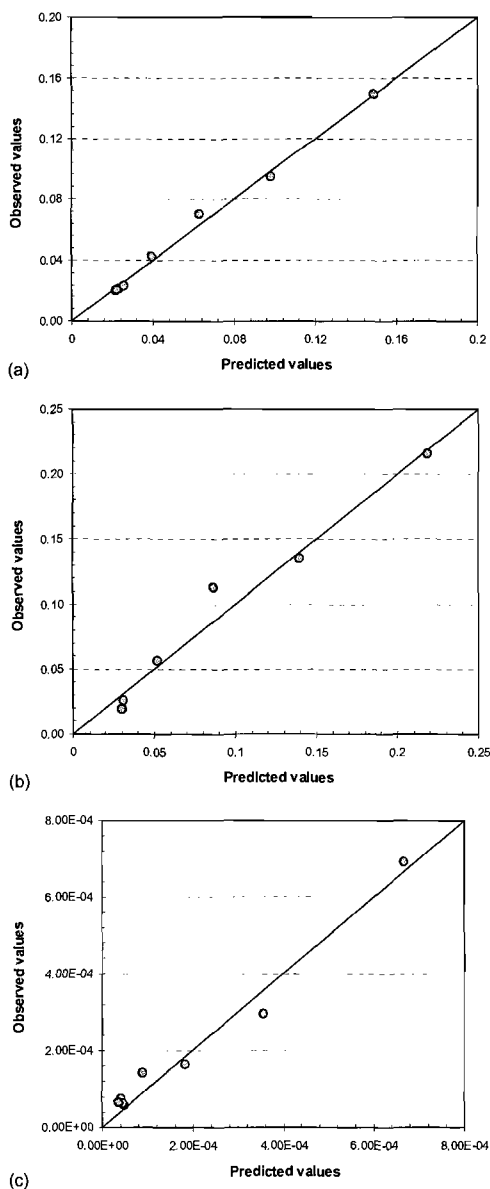


Figure 4.21 Observed rate constants values (min^{-1}) versus the regressed predicted values correlated according to Equation 4.7 for the HGr1 system between 30 and 70 °C with the different precatalyst loads. [(a) k_1 , (b) k_2 and (c) k_3]

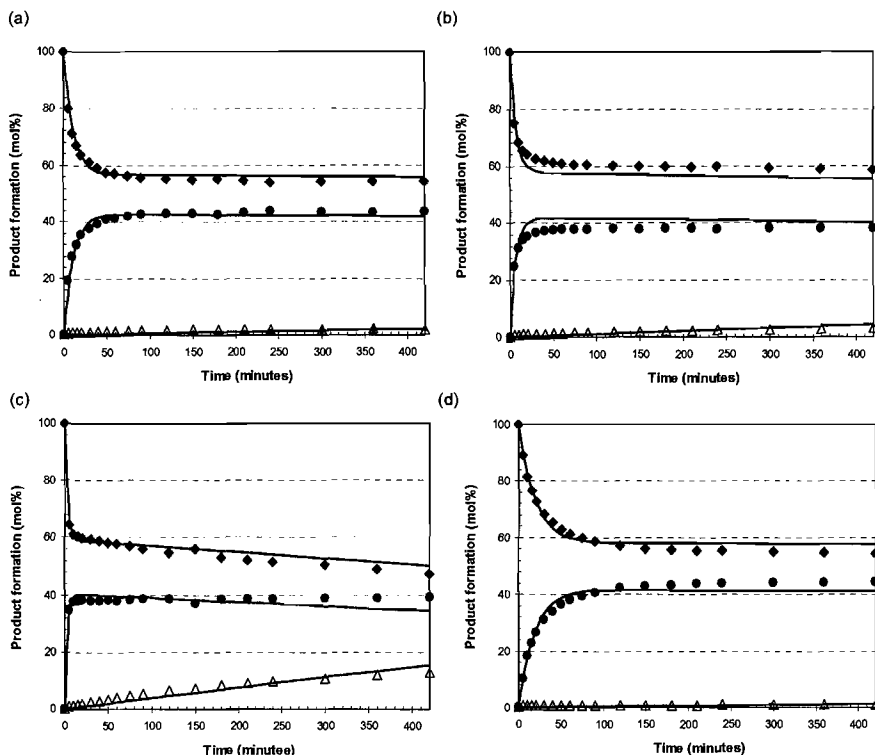


Figure 4.22 Experimental data compared to the modelled reaction scheme of Equations 4.3 to 4.5 and the proposed observed rate constants of Equation 4.7 for the metathesis reaction of 1-octene with precatalyst HGr1 at a) temperature of 40 °C and catalyst load of 7 000, b) temperature of 50 °C and catalyst load of 7 000, c) temperature of 70 °C and catalyst load of 7 000 and d) temperature of 30 °C and catalyst load of 10 000.

[● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

4.3.4 Summarized remarks about HGr1

In this Section the catalytic performance of precatalyst **HGr1** was investigated at different temperatures (30 to 100 °C), precatalyst loads (5000 to 10000 1-octene/Ru molar ratio) and in the presence of various solvents. It was found that the reaction temperature and the presence of different solvents have a significant effect on the performance of the precatalyst. At low temperatures, below 50 °C, **HGr1** showed strong metathesis activity while at higher temperatures, above 50 °C, it showed competitive metathesis and isomerization activity. A phenol-enriched reaction environment was found to be beneficial for this reaction. It is recommended that this reaction be performed at 30 °C, as these conditions showed the best activity, selectivity and TON with limited amounts of SMP and IP formation.

It was found that the reaction of 1-octene with precatalyst **HGr1** could accurately be described by the first-order reaction rate-laws as given by Equations 4.3, 4.4 and 4.5:

$$\frac{dc_{C_8}}{dt} = -k_1c_{C_8} + k_2c_{PMP} - k_3c_{C_8} \quad (4.3)$$

$$\frac{dc_{PMP}}{dt} = k_1c_{C_8} - k_2c_{PMP} \quad (4.4)$$

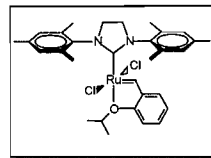
$$\frac{dc_{IP+SMP}}{dt} = k_3c_{C_8} \quad (4.5)$$

with the observed rate constant as a function of precatalyst concentration and temperature as given in Equation 4.7:

$$k_{i,obs} = k \times C_{catalyst} \times e^{\left[\frac{-E}{RT}\right]} \quad (4.7)$$

The different Arrhenius' activation energies were found in the range of 9, 10 and 14 kcal.mol⁻¹.

4.4 Metathesis reaction with precatalyst HGr2



4.4.1 Introduction

In this Section the catalytic performance of precatalyst **HGr2** for the model metathesis reaction of 1-octene is investigated. The influence of reaction temperature, precatalyst load and solvent used in the reaction environment is evaluated with respect to selectivity and activity. The results are discussed from a mechanistic viewpoint and a reaction engineering viewpoint where the reaction kinetics and kinetic parameters for the reaction system are determined and evaluated.

4.4.2 Experimental results and discussion

4.4.2.1 Influence of reaction temperature

The influence of the reaction temperature on the metathesis performance of precatalyst **HGr2** was investigated by varying the temperature between 30 and 100 °C. The reaction was monitored by GC/FID to determine the product distribution. The results obtained for a 1-octene/Ru molar ratio of 7000 with no solvent present are summarized in Table 4.11, Figure 4.23, Figure 4.24 and Figure 4.25.

Table 4.11 Catalytic performance of **HGr2** towards the metathesis of 1-octene after 420 minutes at different temperatures.
[No solvent added; 1-octene/Ru molar ratio = 7000].

Temperature	C8	PMP			IP	SMP	S	TON
(°C)	(%)	<i>Cis-C14</i>	<i>Trans-C14</i>	Total PMP	(%)	(%)	(%)	(-)
30	80.16	1.60	8.05	19.30	0.27	0.28	97.26	1351
40	71.82	2.37	11.32	27.38	0.30	0.51	97.16	1916
50	30.16	5.51	28.79	68.60	0.24	1.01	98.22	4802
60	16.43	6.37	29.70	72.13	0.84	10.61	86.30	5049
70	14.32	6.19	28.53	69.43	1.46	14.80	81.03	4860
80	7.98	6.32	29.02	70.68	1.40	19.94	76.81	4947
90	5.01	5.21	22.68	55.77	3.18	36.04	58.71	3904
100	20.72	2.09	7.69	19.55	54.20	5.53	24.65	1368

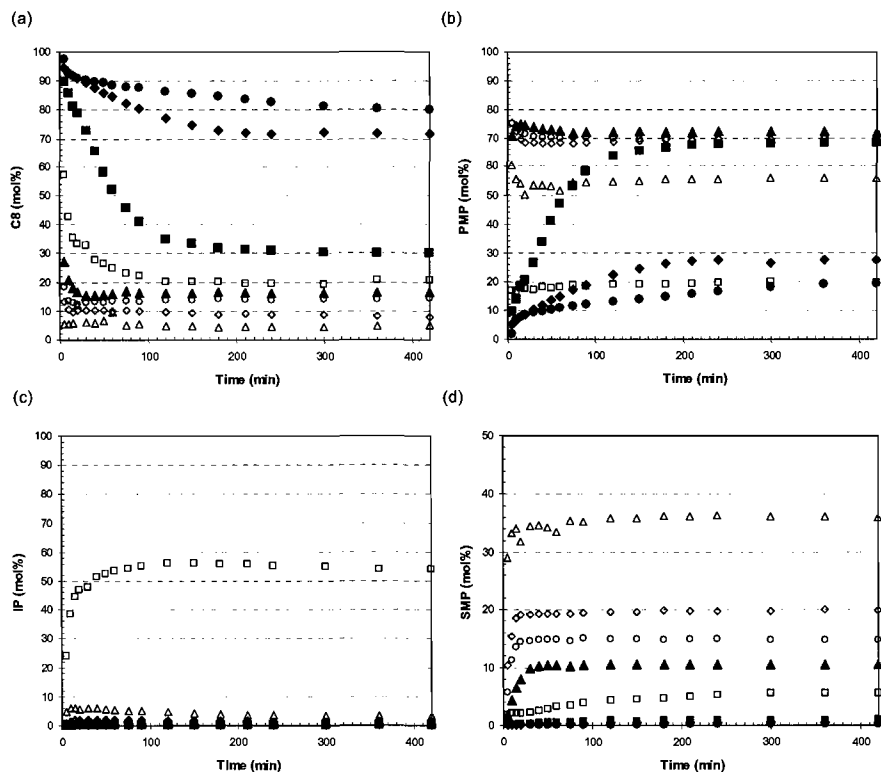


Figure 4.23 Influence of reaction temperature on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with HGr2 at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● 30 °C; ◆ 40 °C; ■ 50 °C; ▲ 60 °C; ○ 70 °C; ◇ 80 °C; △ 90 °C; □ 100 °C]

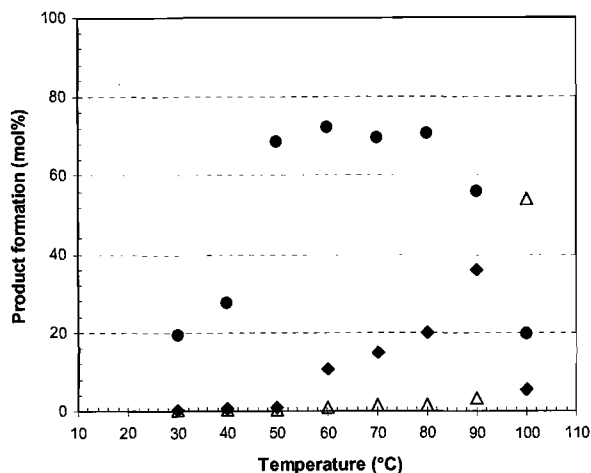


Figure 4.24 Influence of reaction temperature on the product distribution at 420 minutes for the 1-octene metathesis reaction with HGr2 at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● PMP; △ IP; ◆ SMP]

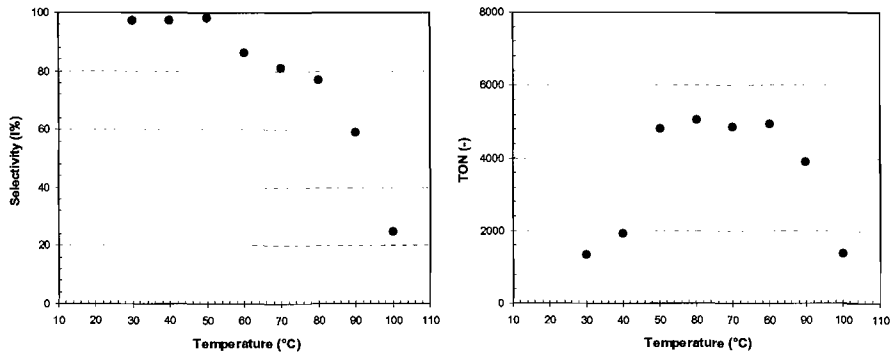


Figure 4.25 Influence of reaction temperature on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with HGr2 at a 1-octene/Ru molar ratio of 7000 with no solvent.

It is clear from the results that reaction temperature has a significant effect on the catalytic performance of precatalyst **HGr2**. As the reaction temperature increases to 50 °C, the product formation towards PMP increases (~19% to 68%), while IP and SMP formations are insignificant (less than ~1%). When the temperature increases to above 50 °C, IP and SMP formation becomes important with an exponential increase (~11% to 40%). PMP formation stays relatively constant (~70%) between 50 and 90 °C and thereafter decreases to ~19%.

The same conclusion as was found for precatalyst **HGr1** in Section 4.3 from a mechanistic viewpoint, can be drawn from the results, as given in Table 4.11, for precatalyst **HGr2**, i.e. that two competing mechanisms are present. The one mechanism is towards the selective formation of PMPs and SMPs (metathesis active mechanism) and the other is selective towards the formation of IP's (isomerization active mechanism). The isomerization active mechanism starts to occur at temperatures above 50 °C, while the metathesis active mechanism is preferentially observed for temperatures below 90 °C. Furthermore, it appears from the results that at temperatures above 90 °C, precatalyst **HGr2** starts to lose activity for metathesis and possibly deactivates due to a high reaction temperature environment. The main catalytic performance difference between precatalysts **HGr1** and **HGr2** is that precatalyst **HGr1** is only metathesis selective for 1-octene, that is precatalyst **HGr1** is only metathesis selective towards the formation of PMPs as can be seen from the results in Table 4.7 of Section 4.3. Precatalyst **HGr2** is metathesis-selective for n-octenes, that is precatalyst **HGr2** is both metathesis-selective towards the formation of PMPs and SMPs as can be seen from the results in Table 4.11. These results correlate well with other researchers' results for the metathesis of 1-octene with precatalysts **Gr1** and **Gr2**.^{8,7,3,4,9}

The selectivity stays relatively constant (~98%) from 30 to 50 °C, as can be seen from Table 4.11 and Figure 4.25, and then decreases (~68% down to ~24%). The turnover number (TON) increases up to 50 °C and then remains relatively constant (~4900) between 50 and 80 °C and decreases thereafter. In comparing the catalytic activity (measured by TON) of precatalyst **HGr1** and **HGr2** with each other, it appears that the activity is temperature-dependent. At low temperatures precatalyst **HGr1** gave a better catalytic activity performance than precatalyst **HGr2** and at higher temperatures precatalyst **HGr2** showed overall better activity than **HGr1**. It can, therefore, be concluded from these results, with respect to catalytic activity, that precatalyst **HGr2** is (at optimized conditions) a more active catalyst than precatalyst **HGr1**. Precatalyst **HGr1** is, with respect to catalytic selectivity (at optimized conditions), a more selective catalyst for PMP formation than precatalyst **HGr2**. Precatalyst **HGr1** also has the added advantage of no side metathesis reactions (SMP formation) compared to precatalyst **HGr2**. From a stability viewpoint precatalyst **HGr2** outperforms precatalyst **HGr1**, as will be discussed in Section 5.3.

It can be concluded from a reaction engineering viewpoint that the desired reaction temperature for designing a reactor must be at low temperatures, preferably 50 °C, as this temperature gave the best relative selectivity, TON and activity.

4.4.2.2 Influence of precatalyst load

The optimum reaction temperature at which precatalyst HGr2 gave high activity while retaining a high degree of selectivity and TON, with a limited amount of SMP and IP formation, was found at low temperatures, particularly 50 °C. Therefore, the influence of precatalyst load (1-octene/Ru molar ratio) was further investigated at 30 °C and 50 °C by varying the 1-octene/Ru molar ratio between 5000 and 14 000. The obtained results are presented in Table 4.12, Table 4.13 and Figure 4.26 to Figure 4.29.

Table 4.12 Catalytic performance of HGr2 towards the metathesis of 1-octene after 420 minutes at different precatalyst loads and 30 °C with no solvent added.

Precatalyst load (C ₈ /Ru molar ratio)	C8 (%)	PMP		IP (%)	SMP (%)	S (%)	TON (-)
		Cis-C14	Trans-C14				
5000	81.76	1.45	7.44	17.79	0.24	0.20	890
7000	80.16	1.60	8.05	19.30	0.27	0.28	1351
9000	90.69	0.75	3.72	8.93	0.30	0.08	804
10 000	92.04	0.66	3.13	7.59	0.28	0.09	531

Table 4.13 Catalytic performance of HGr2 towards the metathesis of 1-octene after 420 minutes at different precatalyst loads and 50 °C with no solvent added.

Precatalyst load (C ₈ /Ru molar ratio)	C8 (%)	PMP		IP (%)	SMP (%)	S (%)	TON (-)
		Cis-C14	Trans-C14				
5000	20.82	5.36	33.11	76.94	0.24	2.00	3847
7000	30.16	5.51	28.79	68.60	0.24	1.01	4802
9000	28.44	4.94	30.19	70.26	0.28	1.02	6324
10 000	34.40	5.14	27.10	64.48	0.25	0.87	6448
14 000	61.13	3.28	15.76	38.10	0.27	0.51	5334

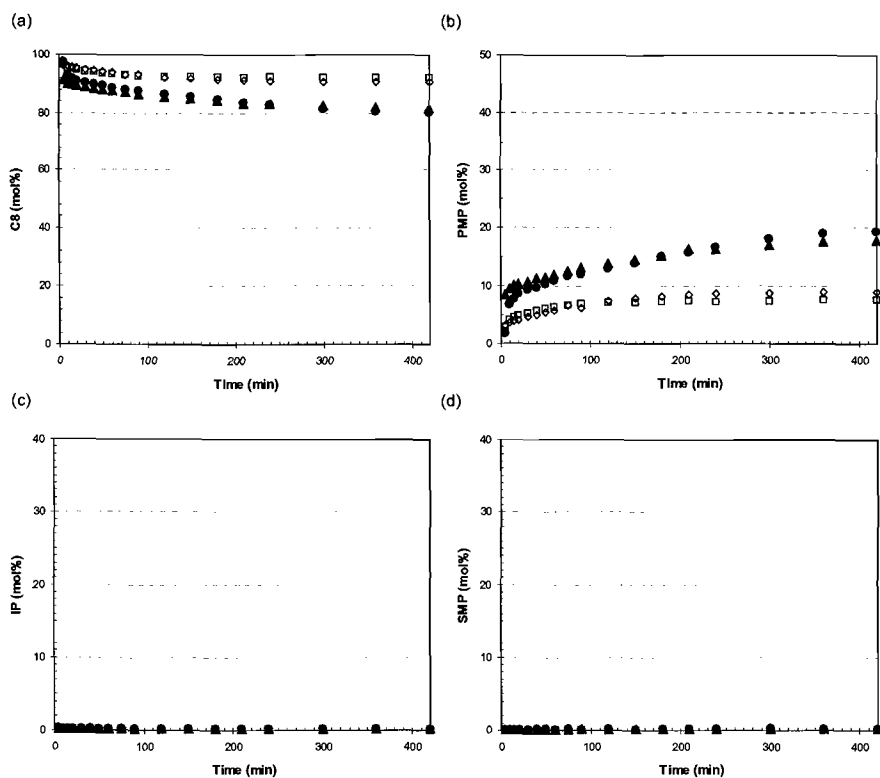


Figure 4.26 Influence of precatalyst load on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with **HGr2** at 30 °C with no solvent.
[▲ 5000; ● 7000; ◇ 9000; □ 10000]

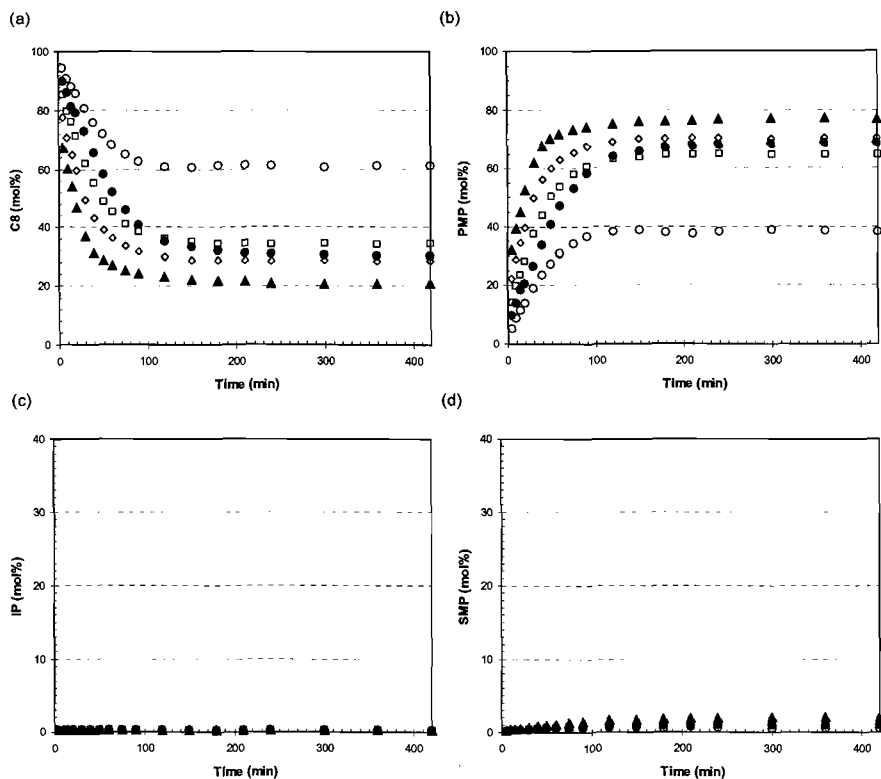


Figure 4.27 Influence of precatalyst load on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with HGr2 at 50 °C with no solvent.
[▲ 5000; ● 7000; ◇ 9000; □ 10000; ○ 14000]

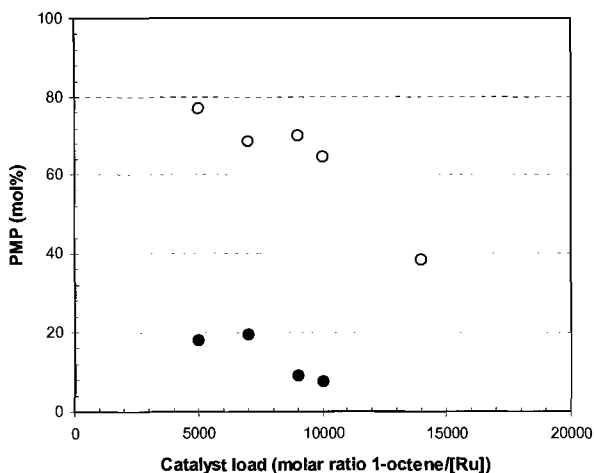


Figure 4.28 Influence of precatalyst load on the product distribution at 420 minutes for the 1-octene metathesis reaction with **HGr2**.
[● PMP at 30 °C and ○ PMP at 50 °C]

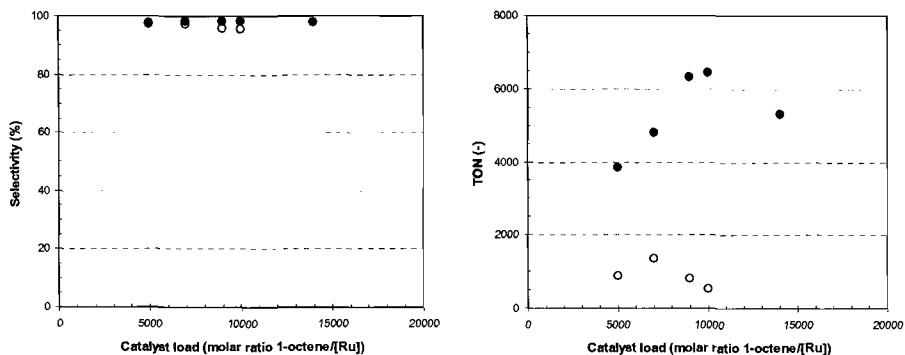


Figure 4.29 Influence of precatalyst load on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with **HGr2** at ○ 30 °C and ● 50 °C with no solvent.

It is clear from the results that as the precatalyst load increases (in other words a decrease in precatalyst mass) the product formation towards PMP decreases (~18% to 8% at 30 °C and ~77% to 38% at 50 °C). IP and SMP formation are insignificant because of the chosen operating temperatures.

The precatalyst load did not show any significant effect on selectivity with relatively constant values of ~96% at 30 °C and ~98% at 50 °C, as shown in Figure 4.29. The precatalyst load, however, did have a significant effect on TON. A different trend than precatalyst **HGr1** was observed for precatalyst **HGr2**. As the precatalyst load increases, TON also increases up to approximately a precatalyst load of 7000 for 30 °C and 10000 for 50 °C, where the TON starts to decrease. These results clearly indicate that for precatalyst **HGr2** an optimum precatalyst load with respect to TON exists at both temperatures. It is, therefore, recommended from a financial viewpoint, that the reactor be operated at a 10000 1-octene/Ru molar ratio and 50 °C.

4.4.2.3 Influence of solvents

The influence of different solvents towards the metathesis reaction of 1-octene with precatalyst **HGr2** was investigated at 50 °C and a precatalyst load of 7000. The same solvents that were used for the **HGr1** system was used for the **HGr2** system. The results obtained, are given in Table 4.14.

Table 4.14 Catalytic performance of **HGr2** towards the metathesis of 1-octene after 420 minutes for different organic solvents at 50 °C.

Solvent	C8 (%)	PMP			IP (%)	SMP (%)	S (%)	TON (-)
		Cis-C14	Trans-C14	Total PMP				
Neat	30.16	5.51	28.79	68.60	0.24	1.01	98.22	4802
Toluene	57.25	3.71	16.92	41.25	0.52	0.98	96.50	2887
Diethyl Ether	10.49	5.98	28.53	69.03	1.97	18.50	77.12	4832
Acetic Acid	94.53	0.27	0.85	2.23	3.09	0.15	40.77	156
Tetrahydrofuran	96.00	0.33	1.25	3.16	0.70	0.15	79.00	221
Phenol	87.40	1.01	4.49	11.01	1.50	0.10	87.36	771
Ethanol	90.05	0.30	0.96	2.52	6.73	0.71	25.33	177
DMSO ^[a]	-	-	-	-	-	-	-	-

[a] Dimethyl sulphoxide (DMSO): The reaction showed no metathesis activity with polar and non-polar layer separation.

It is clear from the results given in Table 4.14 that the addition of organic solvents had a significant effect on the metathesis, mostly detrimental. The same effect was observed for the **HGr1** system as discussed in Section 4.3.2.3. Furthermore, it is interesting to note that diethyl ether showed results that are comparable to that of the neat reaction. Diethyl ether significantly improves the initial activity of **HGr2**, as demonstrated in Figure 4.30, however, the diethyl ether environment also shows enhanced SMP formation (~19%). This result is very interesting and to the author's knowledge no studies relating to the metathesis activity of diethyl ether with any Grubbs-type catalyst have been undertaken.

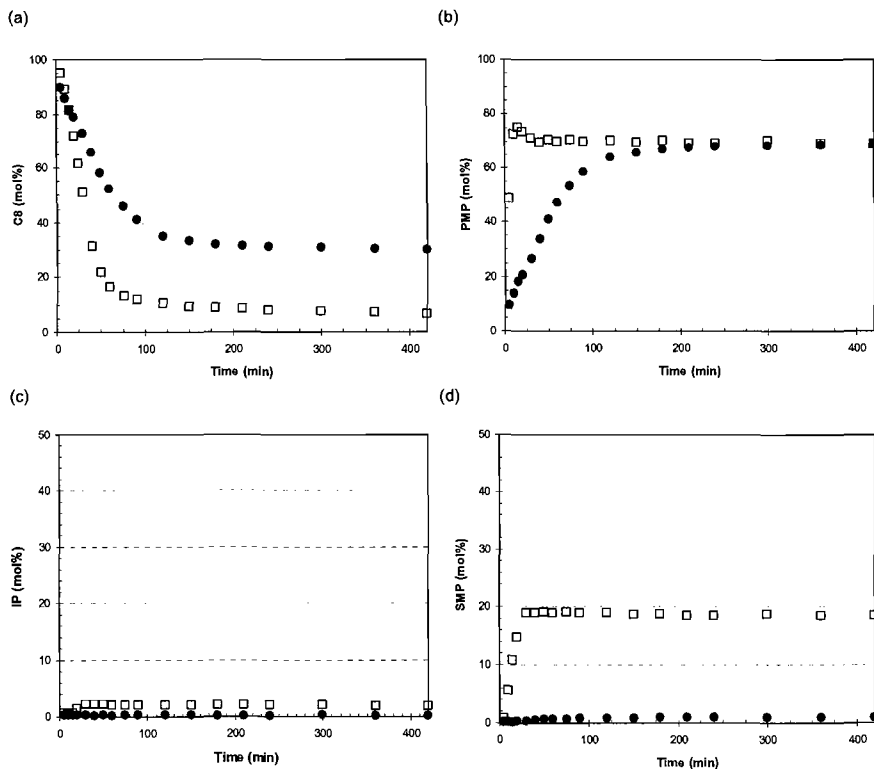


Figure 4.30 Comparison of the metathesis performances of precatalyst **HGr2** with ● neat and □ diethyl ether reaction environment on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations.

It is postulated that diethyl ether coordinates with precatalyst **HGr2**, which could lead to two main coordination effects: i) a net flow of negative charge away from the ruthenium center and ii) formation of a carbonyl-type of species that is converted to possible hydrides upon reaction with 1-octene. This net flow of negative charge away from the ruthenium center in turn enhances the electrophilic nature of the important carbene carbon in precatalyst **HGr2** by firstly increasing the initiation step of the 16-electron Ru species to the 14-electron active species and secondly making the Ru=C bond more Lewis acidic and, therefore, enhancing its reactivity towards the Lewis-basic electron-rich 1-octene that will boost the formation of PMPs. This phenomenon of increased activity and initiation is clearly indicated in the faster reaction initiation for the diethyl ether reaction environment compared to the neat reaction environment as depicted in Figure 4.30 for the formation of PMPs. The coordination of diethyl ether with species **HGr2** to possibly form a carbonyl-type of species that can be converted to hydrides in

the presence of 1-octene renders the **HGr2** species an active isomerization catalyst. This phenomenon is clearly indicated in the combined production formation of IPs and SMPs as shown in Figure 4.30 for the diethyl ether reaction environment. The dual coordination effect of diethyl ether enhances formation of PMPs firstly and secondly enhances the isomerization of 1-octene. The competitive influence of increased metathesis and active isomerization is observed in the initial high PMP formation and low IP formation but a relatively high SMP formation. It is therefore, recommended that a more detailed experimental and mechanistic study with, for example, molecular modelling, should be undertaken to explain this phenomenon from a chemistry viewpoint.

4.4.3 Describing the reaction kinetics

4.4.3.1 Introduction

In this section the reaction kinetics of the model 1-octene metathesis reaction with precatalyst **HGr2** is described and evaluated. The same method and reaction kinetics (rate-laws) that were used in describing the metathesis reaction of 1-octene with precatalyst **HGr1**, are applied to the **HGr2** system as presented in Figure 4.17 of Section 4.3.3 and re-illustrated in Figure 4.31.

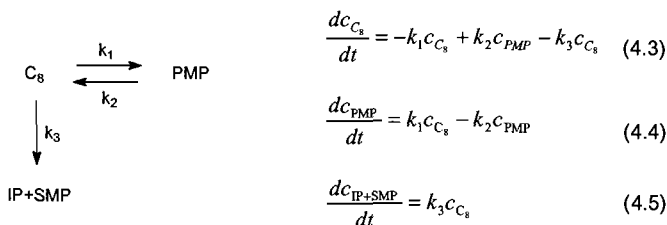


Figure 4.31 Proposed reaction scheme and elementary rate equations for the metathesis reaction of 1-octene with precatalyst **HGr2**.

The following notation is used in the three rate-law equations:

- c_{C_8} concentration of 1-octene in the reactor,
- c_{PMP} concentration of the PMPs in the reactor,
- $c_{\text{IP+SMP}}$ concentration of both IPs and SMPs in the reactor,
- k_1 forward observed rate constant for the consumption of 1-octene in reaction 1,
- k_2 reverse observed rate constant for the formation of 1-octene in reaction 2 and
- k_3 observed rate constant for the consumption of 1-octene in reaction 3.

4.4.3.2 Calculation of observed rate constants

The values of each observed rate constant (k_1 , k_2 and k_3) were determined by regression, using the *Simplex method in combination with the Runge-Kutta method to solve Equations 4.3, 4.4 and 4.5 simultaneously*. The standard error of regression coefficients was determined with the Bootstrap method. Detail of the methodology and programming code can be seen in Appendix A. The regression results are summarized in Table 4.15 for the different precatalyst loads and in Table 4.16 for the different temperatures. The predicted results compared to the observed experimental data are presented in Figure 4.32 to Figure 4.34.

Table 4.15 Observed rate constants for the metathesis reaction of 1-octene with HGr2 at 50 °C with different precatalyst loads.

Precatalyst load (molar ratio)	Observed rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence Interval
5000	$k_1 = 0.0495 \pm 0.00043$	0.00310	8.635×10^{-4}
	$k_2 = 0.0152 \pm 0.00020$	0.00140	3.908×10^{-4}
	$k_3 = 2.558 \times 10^{-4}$	3.096×10^{-5}	8.611×10^{-6}
7000	$k_1 = 0.0129 \pm 0.00005$	0.00035	9.752×10^{-5}
	$k_2 = 0.00558 \pm 0.00004$	0.00029	8.202×10^{-5}
	$k_3 = 1.107 \times 10^{-4}$	7.537×10^{-6}	2.097×10^{-6}
9000	$k_1 = 0.0313 \pm 0.0002$	0.00149	4.137×10^{-4}
	$k_2 = 0.0134 \pm 0.0001$	0.00093	2.596×10^{-4}
	$k_3 = 1.259 \times 10^{-4}$	1.419×10^{-5}	3.946×10^{-6}
10000	$k_1 = 0.0196 \pm 0.0002$	0.00052	1.442×10^{-4}
	$k_2 = 0.0104 \pm 0.0001$	0.00044	1.220×10^{-4}
	$k_3 = 1.051 \times 10^{-4}$	7.878×10^{-6}	2.191×10^{-6}
14000	$k_1 = 0.0098 \pm 0.00073$	0.00030	8.253×10^{-5}
	$k_2 = 0.0153 \pm 0.00038$	0.00056	1.556×10^{-4}
	$k_3 = 4.814 \times 10^{-5}$	4.661×10^{-6}	1.297×10^{-6}

Table 4.16 Observed rate constants for the metathesis reaction of 1-octene with precatalyst HGr2 at different reaction temperatures.

Temperature (°C)	Observed rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence Interval
30	$k_1 = 0.00241 \pm 0.00007$	0.00057	1.582×10^{-4}
	$k_2 = 0.01055 \pm 0.0005$	0.00361	1.003×10^{-3}
	$k_3 = 2.090 \times 10^{-5}$	6.498×10^{-6}	1.807×10^{-6}
40	$k_1 = 0.00408 \pm 0.000034$	0.00024	6.749×10^{-5}
	$k_2 = 0.0107 \pm 0.00012$	0.00087	2.416×10^{-4}
	$k_3 = 3.990 \times 10^{-5}$	3.888×10^{-6}	1.082×10^{-6}
50	$k_1 = 0.01288 \pm 0.00005$	0.00035	9.752×10^{-5}
	$k_2 = 0.01435 \pm 0.00004$	0.00029	8.202×10^{-5}
	$k_3 = 4.770 \times 10^{-4}$	7.537×10^{-6}	2.097×10^{-6}
60	$k_1 = 0.3329 \pm 0.00073$	0.02085	5.800×10^{-3}
	$k_2 = 0.0815 \pm 0.00038$	0.00511	1.422×10^{-3}
	$k_3 = 2.440 \times 10^{-3}$	3.251×10^{-4}	9.043×10^{-5}
70	$k_1 = 0.409 \pm 0.0048$	0.035	1.036×10^{-2}
	$k_2 = 0.091 \pm 0.0011$	0.0078	2.336×10^{-3}
	$k_3 = 4.103 \times 10^{-3}$	7.488×10^{-4}	2.229×10^{-4}
80	$k_1 = 0.329 \pm 0.0066$	0.047	0.0140
	$k_2 = 0.055 \pm 0.0017$	0.012	0.0035
	$k_3 = 0.007 \pm 0.0012$	0.008	0.0026
90	$k_1 = 0.322 \pm 0.0037$	0.027	0.0081
	$k_2 \sim 0$	0.00002	0.0006
	$k_3 = 0.238 \pm 0.0029$	0.021	0.0061
100	$k_1 = 0.0015 \pm 0.00031$	0.00224	0.0007
	$k_2 = 0.0012 \pm 0.00010$	0.00075	0.0002
	$k_3 = 0.0323 \pm 0.00061$	4.416×10^{-3}	0.0013

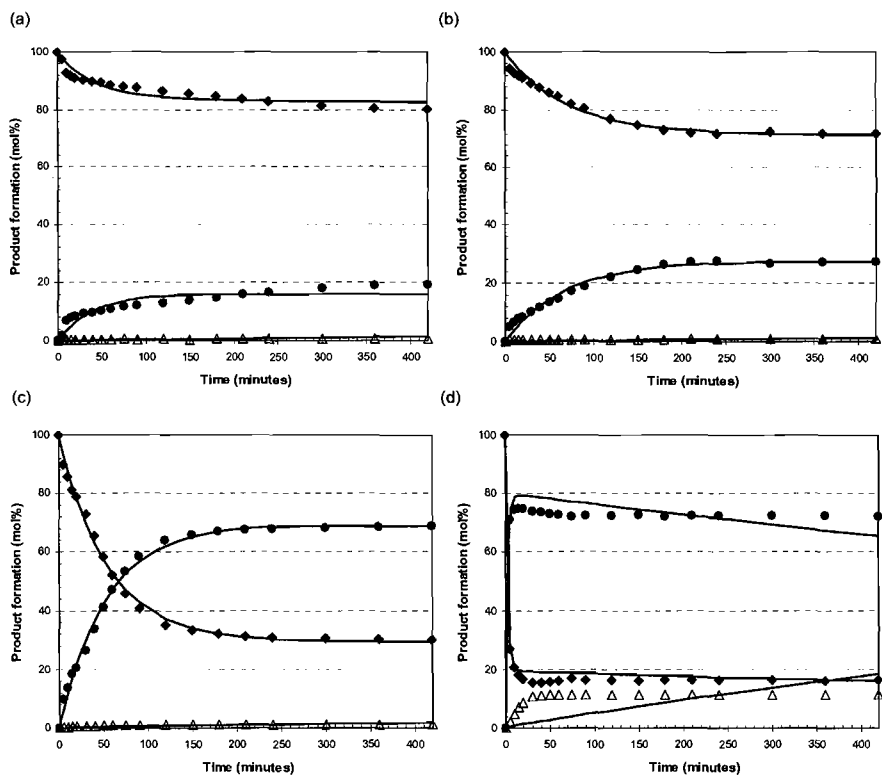


Figure 4.32 Experimental data compared to the modelled rate-laws for the metathesis reaction of 1-octene with HGr2 at a) 30 °C, b) 40 °C, c) 50 °C and d) 60 °C. [● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

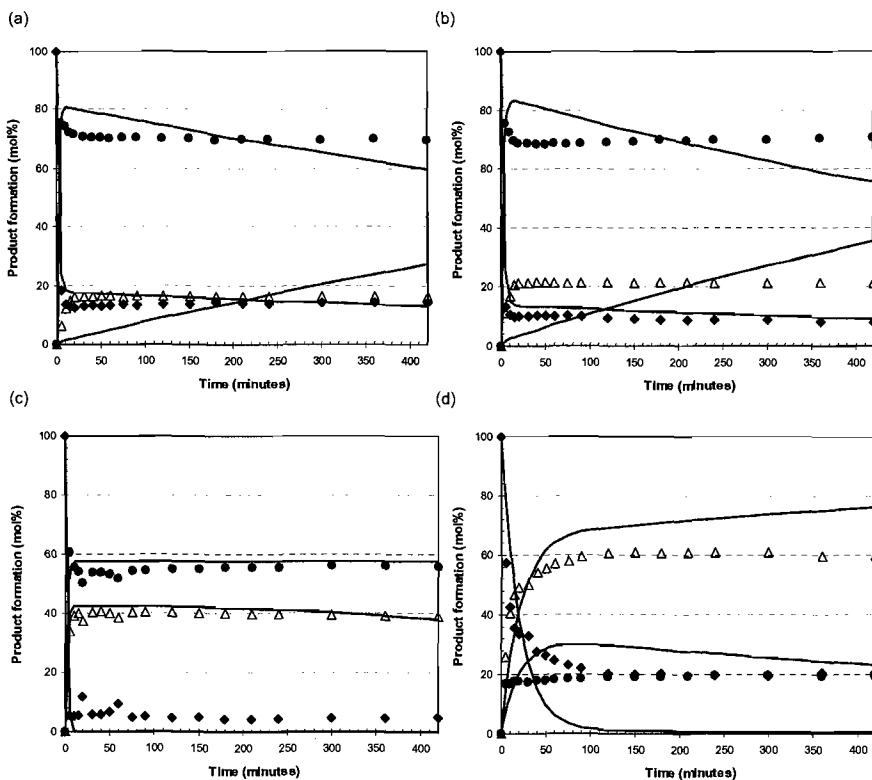


Figure 4.33 Experimental data compared to the modelled rate-laws for the metathesis reaction of 1-octene with HGr2 at a) 70 °C, b) 80 °C, c) 90 °C and d) 100 °C. [● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

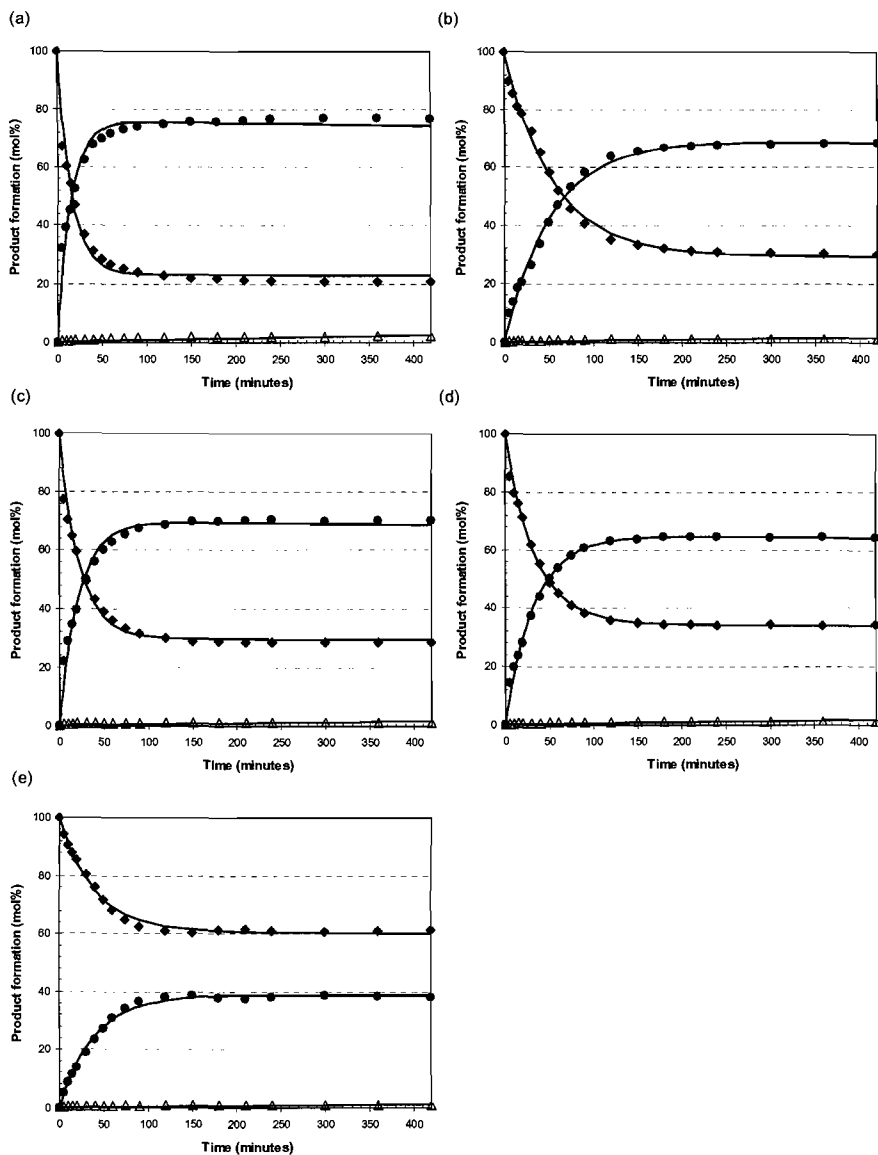


Figure 4.34 Experimental data compared to the modelled rate-laws for the metathesis reaction of 1-octene with HGr2 for a molar ratio of a) 5 000, b) 7 000, c) 9 000, d) 10 000 and e) 14 000 at 50 °C.
 [● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

It is clear from Figure 4.32 that the proposed rate-laws and reaction schemes, as presented in Figure 4.17 (Equations 4.3, 4.4 and 4.5), fit well the experimental data for the metathesis reaction of 1-octene with precatalyst **HGr2** at temperatures below 60 °C. Different hypothesis studies that include varying reaction orders and reaction schemes did not significantly improve the predicted data at temperatures above 60 °C. The primary concern of this study with regard to reaction engineering is the optimization of the formation of PMPs and, therefore, it was not further attempted to explain or better the predicted results with the experimental data above 50 °C as, in this temperature range, the formation of IPs and SMPs dominate. The kinetics of the 1-octene metathesis reaction with precatalyst **HGr2** is, therefore, only described for reaction temperatures below 60 °C.

4.4.3.3 Describing the observed rate constants

The observed rate constants (k_1 , k_2 and k_3) as calculated in Section 4.4.3.2 for temperatures below 60 °C and the different precatalyst loads as summarized in Table 4.15 and in Table 4.16, can be described as a function of catalyst concentration and temperature. This correlation is discussed in detail in Section 4.3.3 and summarized in Equation 4.7:

$$k_{i,obs} = k \times C_{catalyst}^{\alpha} \times e^{\left[\frac{-E}{RT}\right]} \quad (4.7)$$

where k is the pseudo-frequency or pseudo-pre-exponential factor, $C_{catalyst}$ is the concentration of the precatalyst used, α is the reaction order that correlates the precatalyst influence, E is the activation energy of the reaction, R the gas constant and T the absolute temperature.

The observed rate constant parameters (k , α and E) were determined by regression of the different observed rate constants with Equation 4.7. Temperatures between 30 and 60 °C for all the precatalyst loads were used. The regressed values of k , α and E are given in Table 4.17 and the observed versus predicted values are given in Figure 4.35. It is clear from these results that the different observed rate constants for the 1-octene metathesis reaction with precatalyst **HGr2** are adequately described by the proposed correlation of Equation 4.9 with an average Pearson correlation of 0.912.

Table 4.17 The rate constant parameters values for the metathesis reaction of 1-octene with precatalyst HGr2 between 30 and 60 °C with the different precatalyst loads.

Observed rate constant	Pseudo-pre-exponential (<i>k</i>) (min ⁻¹ .mmol ^{-α} .mL ^α)	Reaction order (<i>α</i>)	Activation Energy (<i>E</i>) (kcal.mol ⁻¹)	Pearson square correlation (<i>R</i> ²)
<i>k</i> ₁	1.494 x10 ¹¹	0.945	19.95 ± 3.11	0.918
<i>k</i> ₂	4.208 x10 ⁸	0.488	16.07 ± 4.55	0.905
<i>k</i> ₃	7.304 x10 ¹¹	0.934	24.28 ± 3.23	0.914

From the different activation energies as given in Table 4.17, it can again be concluded that the reactor must be operated at a relatively mild reaction temperature, as this will favour reaction 1 and hamper reaction 2 or 3 ($E_2 < E_I$; $E_3 > E_I$). The effect will be an enhancement in the formation of PMPs with little IPs and SMPs formation. If the temperature is relatively low, reaction 2 will be favoured above reaction 1 and 3, which would give low PMPs formation with little IPs and SMPs formations. This correlates well with the observed experimental results that demonstrated, for temperatures below 50 °C, a low PMP formation of up to 27% with less than 1% IP and SMP formation. At milder temperatures, around 50 °C, relatively high PMP (72%) and little IP and SMP (approximately 1%) formation was found. At higher temperatures both reaction 1 and 3 will be favoured ($E_3 > E_I$) above reaction 2 which would produce a relatively high PMP and combined IP and SMP formation. This also correlates well with the observed experimental results that showed for high temperatures, above 60 °C, IP and SMP formations of approximately 38%.

The experimental results compared to the postulated rate-laws and reaction scheme as presented in Figure 4.17 (Equations 4.3, 4.4 and 4.5) with the proposed observed reaction rate constants of Equation 4.7 are summarized in Figure 4.36. It can be seen from these results that the metathesis reaction of 1-octene with precatalyst HGr2 can reasonably be described by the modelled system of Equations 4.3, 4.4, 4.5 and 4.7.

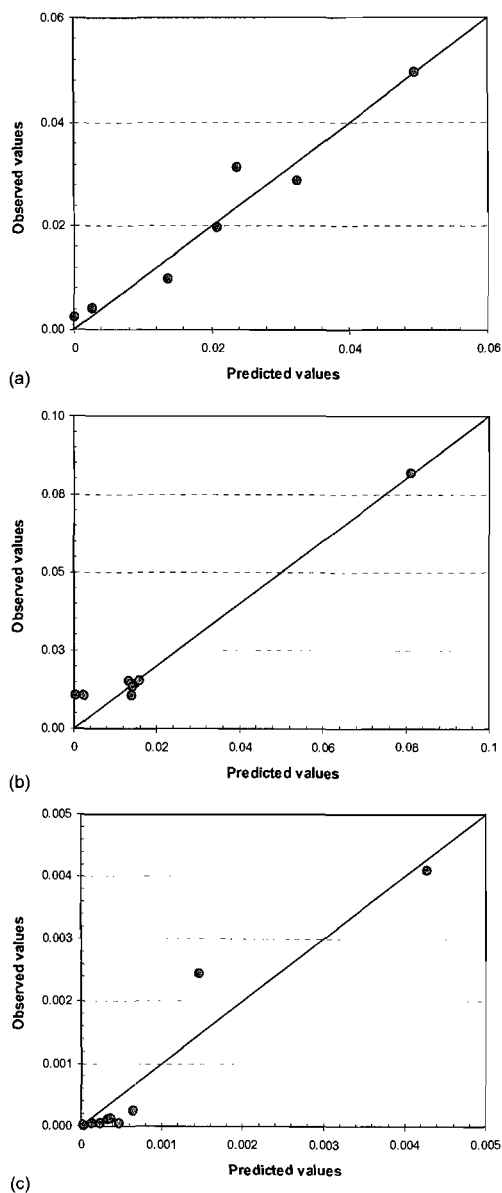


Figure 4.35 Observed rate constant values (min^{-1}) versus the regressed predicted values correlated according to Equation 4.9 for the HGr2 system. [(a) k_1 , (b) k_2 and (c) k_3]

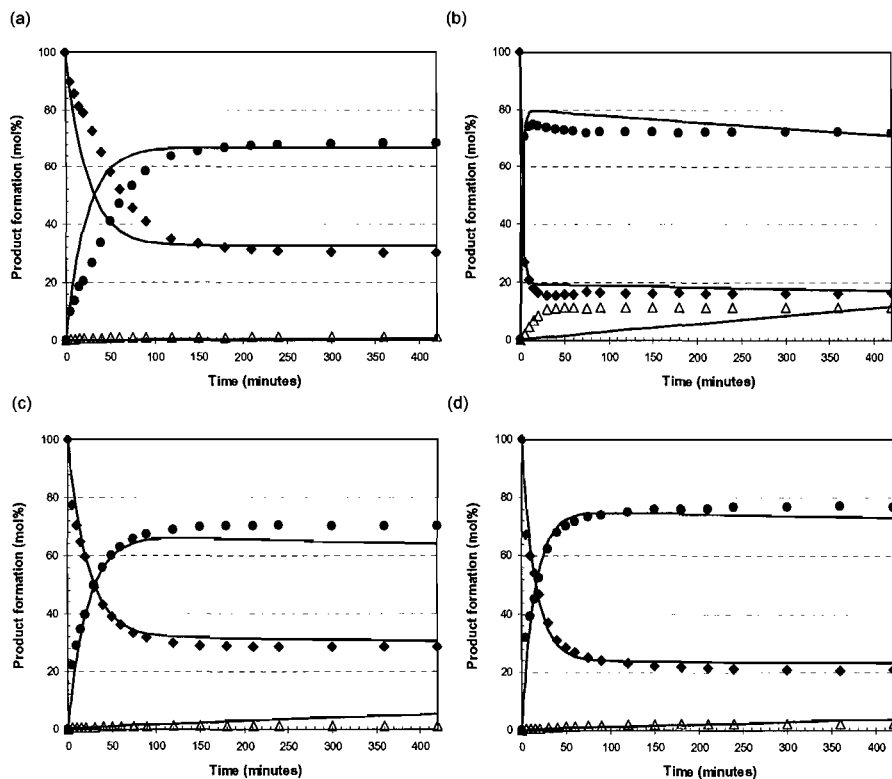


Figure 4.36 Experimental data compared to the modelled reaction scheme of Equations 4.3 to 4.5 and the proposed observed rate constants of Equation 4.7 for the metathesis reaction of 1-octene with precatalyst **HGr2** at a) temperature of 50 °C and catalyst load of 7 000, b) temperature of 60 °C and catalyst load of 7 000, c) temperature of 50 °C and catalyst load of 9 000 and d) temperature of 50 °C and catalyst load of 5 000.

[● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

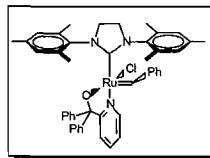
4.4.4 Summarized remarks about HGr2

In this section the catalytic performance of precatalyst **HGr2** was investigated by varying three parameters: reaction temperatures (30 to 100 °C), precatalyst loads (1-octene/Ru molar ratio between 5000 and 14000) and reaction environment with various organic solvents. It was found that these variables had a significant effect on the reaction.

Temperatures below 60 °C showed only metathesis activity while at higher temperatures competitive metathesis and isomerization activity was observed. Precatalyst **HGr2** demonstrated SMP formation compared to precatalyst **HGr1** that showed none. It is recommended that this reaction be performed at 50 °C with approximately a 1-octene/Ru molar ratio of 10000, as these conditions gave the best optimized activity, selectivity and TON with limited amount of SMP and IP forming. Precatalyst **HGr2** showed overall detrimental effects when different organic solvents were introduced to the reaction environment, with the exception of diethyl ether that showed enhanced characteristics.

The reaction kinetics for the metathesis reaction of 1-octene with precatalyst **HGr2** can accurately be described by the first-order type of reaction laws as postulated in Figure 4.17 for temperatures below 60 °C. It is recommended for future studies that a complete kinetic hypothesis investigation be undertaken to describe the reaction for temperatures above 60 °C. The activation energies for this reaction were found to be approximately 20, 16 and 24 kcal.mol⁻¹.

4.5 Metathesis reaction with precatalyst Gr2Ph



4.5.1 Introduction

In this section the catalytic performance of the in-house precatalyst **Gr2Ph** for the model metathesis reaction of 1-octene is evaluated. The influence of reaction temperature and precatalyst load is evaluated with respect to selectivity and activity. The results are discussed from a mechanistic and a reaction engineering viewpoint where the reaction kinetics and kinetic parameters for the reaction system are determined and evaluated.

4.5.2 Experimental results and discussion

4.5.2.1 Influence of reaction temperature

The influence of the reaction temperature on the metathesis performance of precatalyst **Gr2Ph** was investigated by varying the temperature between 30 and 100 °C. The reaction was monitored by GC/FID to determine the product distribution. The results obtained for a 1-octene/Ru molar ratio of 7000 with no solvent present are summarized in Table 4.18 and Figure 4.37 to Figure 4.39.

Table 4.18 Catalytic performance of precatalyst **Gr2Ph** towards the metathesis of 1-octene after 420 minutes at different temperatures.
[No solvent added; 1-octene/Ru molar ratio = 7000].

Temperature (°C)	C8 (%)	<i>Cis</i> -C14	PMP <i>Trans</i> -C14	Total PMP	IP (%)	SMP (%)	S (%)	TON (-)
30 ^[a]	100.00	-	-	-	-	-	-	-
40 ^[a]	100.00	-	-	-	-	-	-	-
50	74.45	2.23	10.16	24.79	0.29	0.47	97.01	1735
60	67.66	2.85	12.61	30.93	0.36	1.05	95.64	2165
70	51.29	4.36	18.54	45.79	0.41	2.51	94.01	3206
80	14.65	6.90	29.79	73.40	0.73	11.23	85.99	5138
90	6.74	5.75	23.48	58.46	4.09	30.71	62.68	4092
100	56.00	2.15	6.20	16.69	21.31	5.99	37.94	1168

^[a] The precatalyst showed no metathesis activity for 1-octene even after three days.

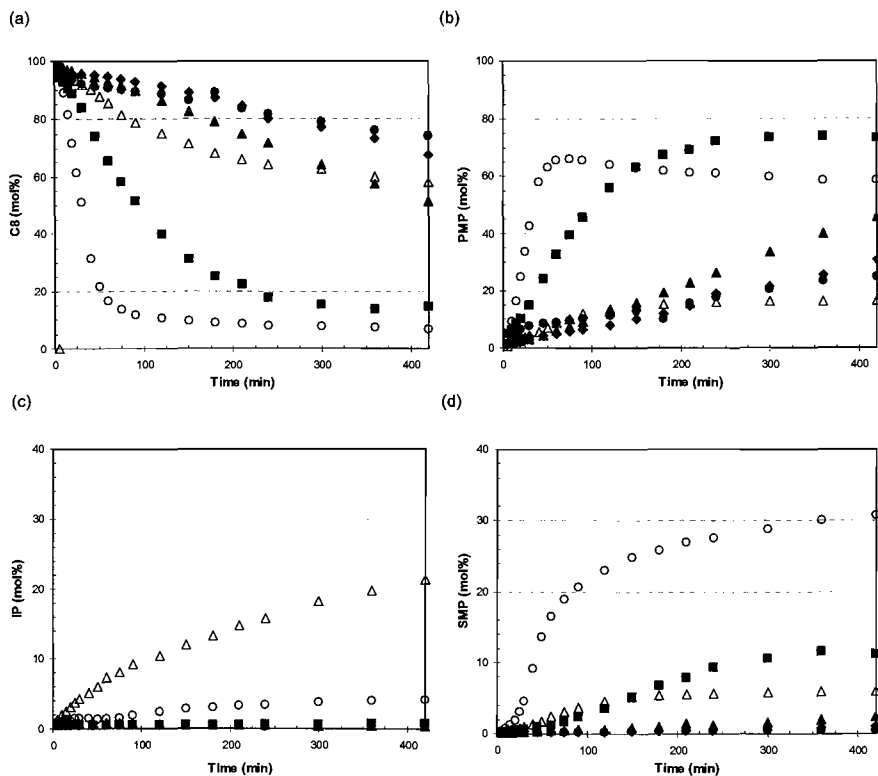


Figure 4.37 Influence of reaction temperature on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with Gr2Ph at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● 50 °C; ◆ 60 °C; ▲ 70 °C; ■ 80 °C; ○ 90 °C; △ 100 °C]

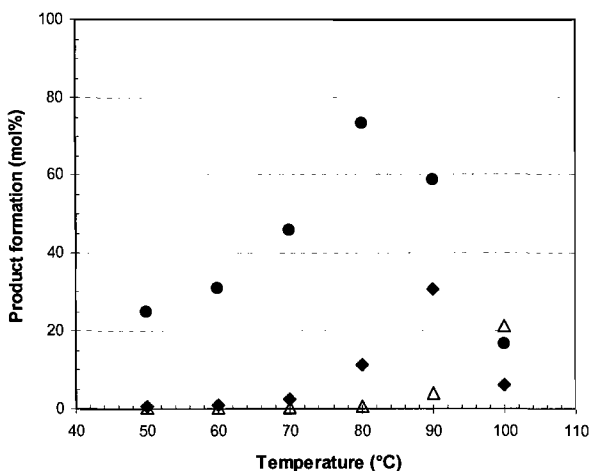


Figure 4.38 Influence of reaction temperature on the product distribution at 420 minutes for the 1-octene metathesis reaction with Gr₂Ph at a 1-octene/Ru molar ratio of 7000 with no solvent.
[● PMP; △ IP; ◆ SMP]

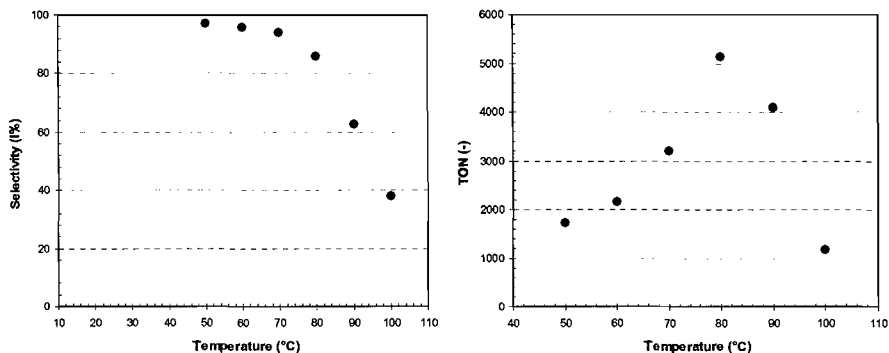


Figure 4.39 Influence of reaction temperature on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with Gr₂Ph at a 1-octene/Ru molar ratio of 7000 with no solvent.

The results demonstrate that reaction temperature has a significant effect on the catalytic performance of precatalyst **Gr2Ph**. For temperatures below 50 °C no metathesis activity was observed with precatalyst **Gr2Ph** even after three days. This is possibly due to the strong steric hindrance of the 1,1-diphenyl-1-(2'-pyridyl)methanol ligand of precatalyst **Gr2Ph** around the Ru-center that hinders the opening of the free coordination site and obstructs the coordination of 1-octene with the R=C-moiety. More energy (higher temperature) is, therefore, needed to overcome this steric obstruction. As the reaction temperature increases above 50 °C, this steric obstruction is overcome and metathesis activity is observed. As the reaction temperature increases from 50 °C up to 70 °C the product formation towards PMP increases (~25% to 46%) while IP and SMP formations are insignificant (less than ~1%). When the temperature increases above 70 °C, IP and SMP formation become notable with an exponential increase (~3% to 35%). PMP formation starts to decrease above 80 °C with the onset of a competitive isomerization mechanism.

The same dual mechanism of metathesis and isomerization, as was found for all the other Grubbs-type precatalysts investigated in this study (**Gr1**, **Gr2**, **HGr1** and **HGr2**), is observed for precatalyst **Gr2Ph**. These competitive mechanisms are dominant at different temperature ranges, as summarized in Table 4.19.

Table 4.19 Comparison of isomerization starting and optimal reaction temperatures for the different precatalysts.

Precatalyst	Isomerization starting temperature (°C) ^[a]	Optimal reaction temperature (°C) ^[b]
Gr1	70	Low (30 °C)
Gr2	60	Low (30 °C)
HGr1	50	Low (30 °C)
HGr2	60	Medium (50 °C)
Gr2Ph	80	High (80 °C)

[a] Temperature where IP+SMP formations are above 3%.

[b] Based on reactions performed between 30 and 100 °C with 1-octene/Ru molar ratio of 7000.

The first-generation Grubbs-type catalysts with the PCy₃-ligand (**Gr1** and **HGr1**) are primarily metathesis-selective and showed little secondary metathesis product formation. While the second-generation Grubbs-type catalysts with the H₂I₂Mes-ligand (**Gr2**, **HGr2** and **Gr2Ph**) are both primary and secondary metathesis-selective. The second-generation type of catalysts are, however, more temperature tolerant than the first-generation as it was further observed in Section 5.3.2 that the second-generation type of catalysts demonstrated a longer catalyst lifetime.

The selectivity of precatalyst **Gr2Ph** decreases from approximately 98% to 38% for temperatures from 50 to 100 °C, which would indicate that the preferred reaction must be operated at relatively low reaction temperatures to give a high selectivity. The TON increases exponentially from 1735 to 5138 for the temperature range 50 to 80 °C and then decreases to 1168. It is clear from the results that the maximum TON is at 80 °C, which would indicate that the preferred reaction temperature must be around 80 °C. At this temperature the highest PMP formation was observed and, therefore, 80 °C is recommended as the best operating temperature for this reaction.

4.5.2.2 Influence of precatalyst load

The influence of precatalyst load (1-octene/Ru molar ratio between 5000 and 14000) towards the metathesis reaction of 1-octene with precatalyst **Gr2Ph** was investigated at 80 °C. The results obtained are given in Table 4.20, Figure 4.40 and Figure 4.41.

Table 4.20 Catalytic performance of **Gr2Ph** towards the metathesis of 1-octene after 420 minutes at different precatalyst loads and 80 °C with no solvent added.

Precatalyst load (C8/Ru molar ratio)	C8 (%)	PMP			IP (%)	SMP (%)	S (%)	TON (-)
		<i>Cis-C14</i>	<i>Trans-C14</i>	Total PMP				
5,000	13.64	6.85	30.03	73.76	0.75	11.85	85.40	3688
7,000	14.65	6.90	29.79	73.40	0.73	11.23	85.99	5138
8,000	13.38	6.77	30.10	73.74	0.87	12.01	85.13	5899
9,000	13.77	6.80	30.21	74.01	0.67	11.54	85.83	6661
10,000	11.15	6.86	30.07	73.85	1.01	13.99	83.12	7385
14,000	16.04	6.44	29.17	71.22	0.83	11.91	84.82	9971

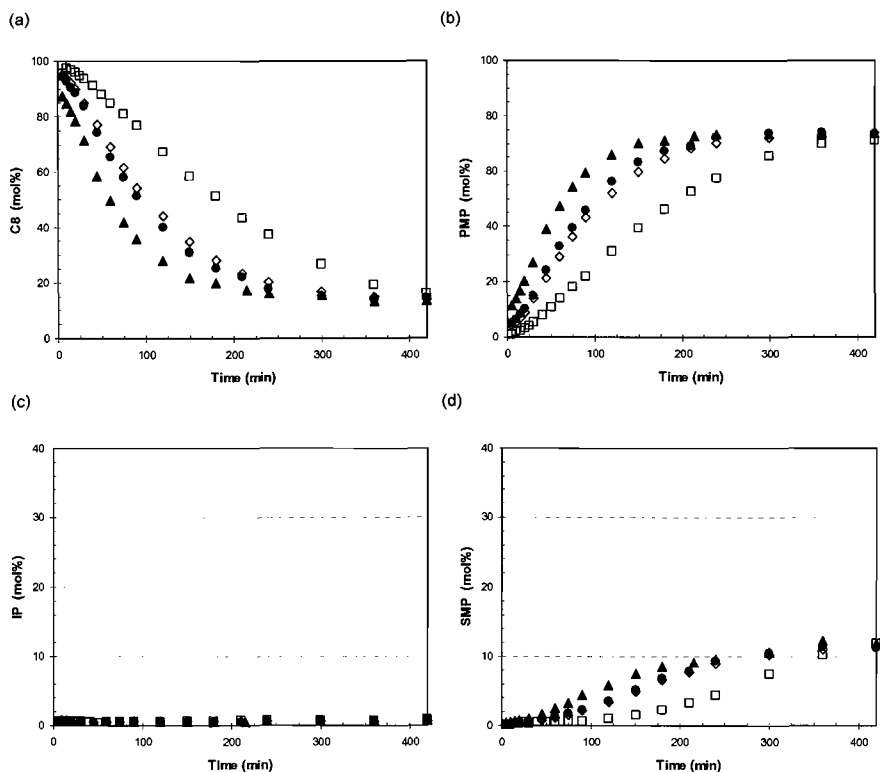


Figure 4.40 Influence of precatalyst load on (a) 1-octene consumption, (b) PMP, (c) IP and (d) SMP formations of the 1-octene metathesis reaction with Gr2Ph at 80 °C with no solvent.
[1-octene/Ru molar ratio: ▲ 5000; ● 7000; ◇ 9000; □ 14 000]

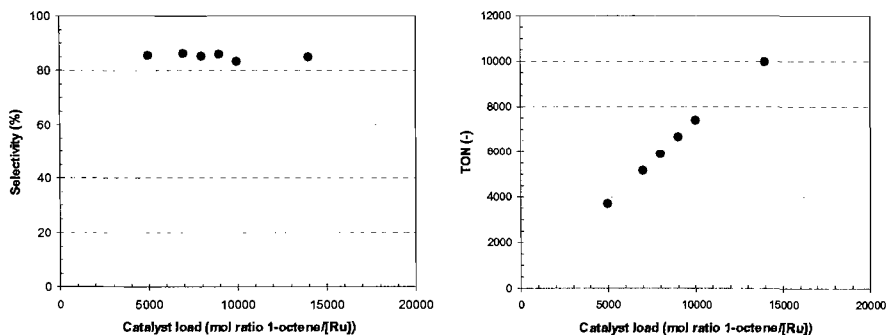


Figure 4.41 Influence of precatalyst load on selectivity and turnover number at 420 minutes for the 1-octene metathesis reaction with **Gr2Ph** at 80 °C with no solvent.

Variation in precatalyst load had no significant effect on the selectivity towards the formation of PMPs as can be seen from Figure 4.41 for the relatively constant selectivity (~98%) over the complete precatalyst load range. TON, however, increases linearly as the precatalyst load increases (in other words decreases in precatalyst mass) which indicates that a lower concentration of precatalyst gives a better formation of PMPs.

4.5.3 Describing the reaction kinetics

4.5.3.1 Introduction

In this section the reaction kinetics of the model 1-octene metathesis reaction with the in-house precatalyst **Gr2Ph** is described and evaluated. The same reaction kinetics (rate-laws), as presented in Figure 4.17, that was used in describing the metathesis reaction of 1-octene with precatalysts **HGr1** and **HGr2** is applied for the **Gr2Ph** system.

4.5.3.2 Calculation of observed rate constants

The value of each observed rate constant (k_1 , k_2 and k_3) was determined by regression using the Simplex method in combination with the Runge-Kutta method to solve Equations 4.3, 4.4 and 4.5 simultaneously. The standard error of regression coefficients was determined with the Bootstrap method. Detail of the methodology and programming code can be seen in Appendix A. The regression results are summarized in Table 4.21 for the different temperatures and in Table 4.22 for the different precatalyst loads. The predicted results compared to the observed experimental data are presented in Figure 4.42 and Figure 4.43.

Table 4.21 Rate constants for the metathesis reaction of 1-octene with Gr2Ph at different reaction temperatures.

Temperature (°C)	Rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence interval
50	$k_1 = 0.0014 \pm 0.000014$	0.00022	2.785×10^{-5}
	$k_2 = 0.000043 \pm 0.000081$	0.00131	1.627×10^{-4}
	$k_3 = 3.396 \times 10^{-5}$	1.181×10^{-5}	1.471×10^{-6}
60	$k_1 = 0.000832 \pm 0.0000009$	0.00009	1.720×10^{-5}
	$k_2 = 0.000050 \pm 0.0000035$	0.00035	6.955×10^{-5}
	$k_3 = 4.135 \times 10^{-5}$	9.521×10^{-6}	1.870×10^{-6}
70	$k_1 = 0.00134 \pm 0.0018$	0.00016	3.057×10^{-5}
	$k_2 = 1.480 \times 10^{-5}$	0.00010	1.958×10^{-5}
	$k_3 = 9.240 \times 10^{-5}$	5.065×10^{-5}	9.949×10^{-11}
80	$k_1 = 0.00722 \pm 0.000022$	0.000022	4.345×10^{-5}
	$k_2 = 0.00096 \pm 0.000019$	0.000019	3.818×10^{-5}
	$k_3 = 0.00078 \pm 3.53 \times 10^{-8}$	3.471×10^{-8}	6.943×10^{-8}
90	$k_1 = 0.0195 \pm 0.00028$	0.00289	5.678×10^{-4}
	$k_2 = 0.0028 \pm 0.00007$	0.00007	1.393×10^{-4}
	$k_3 = 0.0057 \pm 4.48 \times 10^{-11}$	4.569×10^{-10}	8.963×10^{-11}
100	$k_1 = 0.0027 \pm 0.00004$	0.00030	5.967×10^{-5}
	$k_2 = 0.0112 \pm 0.00016$	0.00063	1.231×10^{-4}
	$k_3 = 0.0011 \pm 2.45 \times 10^{-11}$	2.487×10^{-11}	4.885×10^{-11}

Table 4.22 Rate constants for the metathesis reaction of 1-octene with Gr2Ph at 80 °C with different precatalyst loads.

Precatalyst load (molar ratio)	Rate constant (min ⁻¹)	Standard deviation (σ)	95% Confidence Interval
5000	$k_1 = 0.0121 \pm 0.00014$	0.00149	2.928×10^{-4}
	$k_2 = 0.0024 \pm 0.00002$	0.00021	4.118×10^{-5}
	$k_3 = 1.903 \times 10^{-3}$	4.318×10^{-4}	8.482×10^{-6}
7000	$k_1 = 0.00722 \pm 0.000022$	0.000022	4.345×10^{-5}
	$k_2 = 0.00096 \pm 0.000019$	0.000019	3.818×10^{-5}
	$k_3 = 0.00078 \pm 3.53 \times 10^{-8}$	3.471×10^{-8}	6.943×10^{-8}
9000	$k_1 = 0.00642 \pm 0.00008$	0.00078	1.539×10^{-4}
	$k_2 = 0.00075 \pm 0.00002$	0.00020	3.933×10^{-5}
	$k_3 = 7.218 \times 10^{-4}$	3.758×10^{-5}	7.382×10^{-6}
14000	$k_1 = 0.0039 \pm 0.00004$	0.000041	8.066×10^{-5}
	$k_2 = 1.291 \times 10^{-6}$	0.000015	3.023×10^{-5}
	$k_3 = 3.556 \times 10^{-4}$	2.227×10^{-6}	4.375×10^{-7}

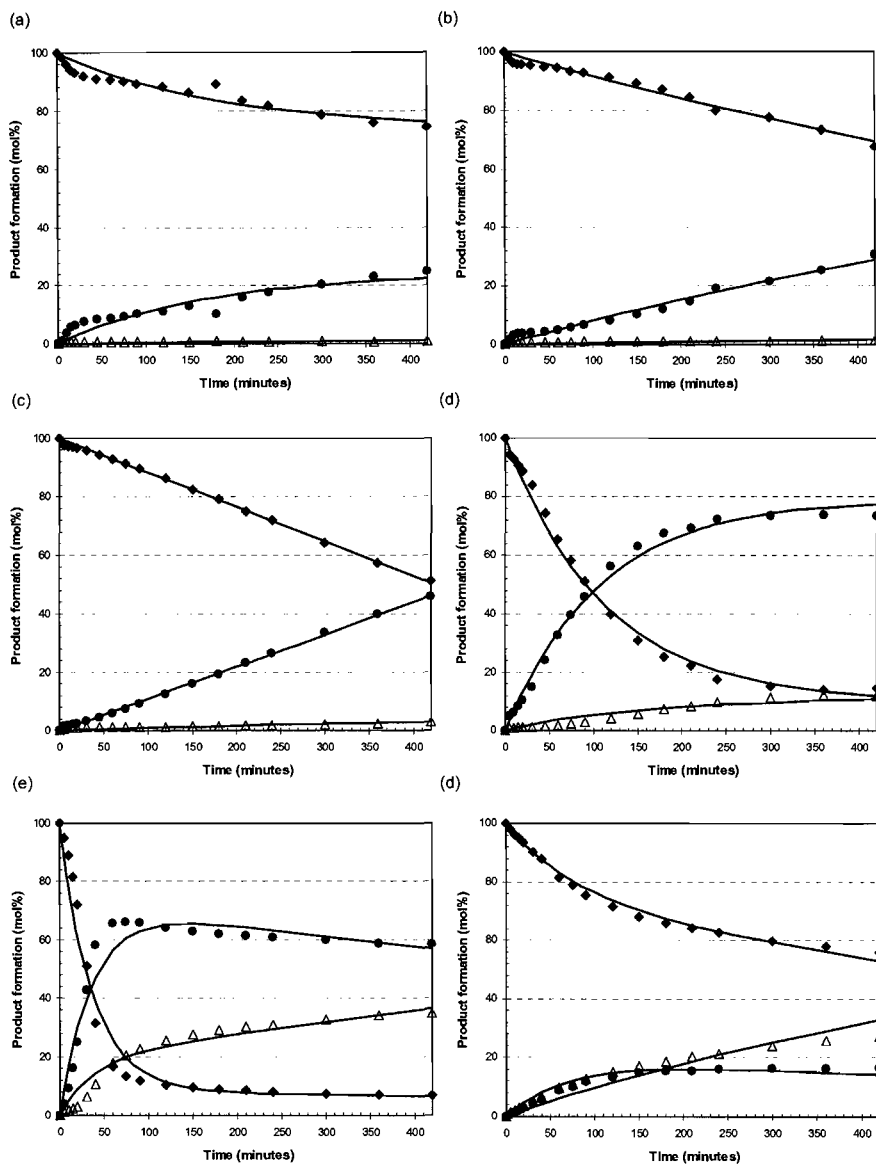


Figure 4.42 Experimental data compared to the modelled rate-laws for the metathesis reaction of 1-octene with Gr2Ph at a) 50 °C, b) 60 °C, c) 70 °C, d) 80 °C, e) 90 °C and f) 100 °C.

[● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

catalytic activity with precatalyst **Gr2Ph**, even after three days. It is thus clear from the activation energies, as given in Table 4.23, that the reaction temperature must be relatively high for reaction 1 to occur, but if the temperature is too high reactions 2 and 3 will also be favoured ($E_3 > E_2 > E_1$). The effect will be a restriction of PMP formation by reaction 2, while reaction 3 will facilitate the formation of IP and SMP. This correlates well with the experimental results that showed that as the temperature increases above 80 °C, reactions 2 and 3 start to be favoured above reaction 1. At 100 °C, for example, PMP formation was approximately 16% while the combined IP and SMP formation was 27%.

The experimental results compared to postulated rate-laws and reaction scheme as presented in Figure 4.17 (Equations 4.3, 4.4 and 4.5) with the proposed observed reaction rate constants of Equation 4.7 are summarized in Figure 4.45. It is clear from the results of Figure 4.44 and Figure 4.45 that the metathesis reaction of 1-octene with precatalyst **Gr2Ph** can fairly accurately be described by the modelled system of Equations 4.3, 4.4, 4.5 and 4.7.

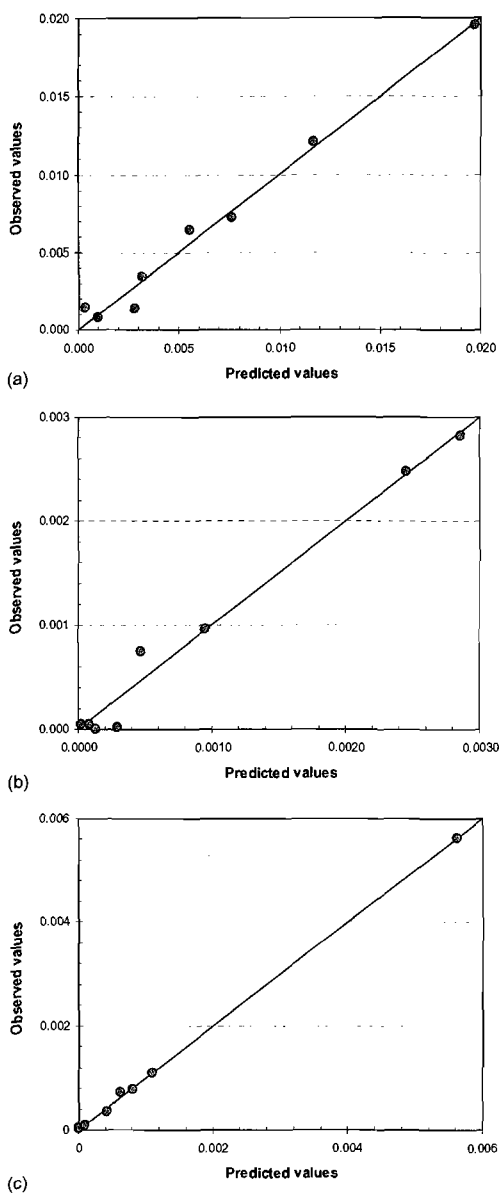


Figure 4.44 Observed rate constants values (min^{-1}) versus the regressed predicted values correlated according to Equation 4.7 for the Gr2Ph system. [(a) k_1 , (b) k_2 and (c) k_3]

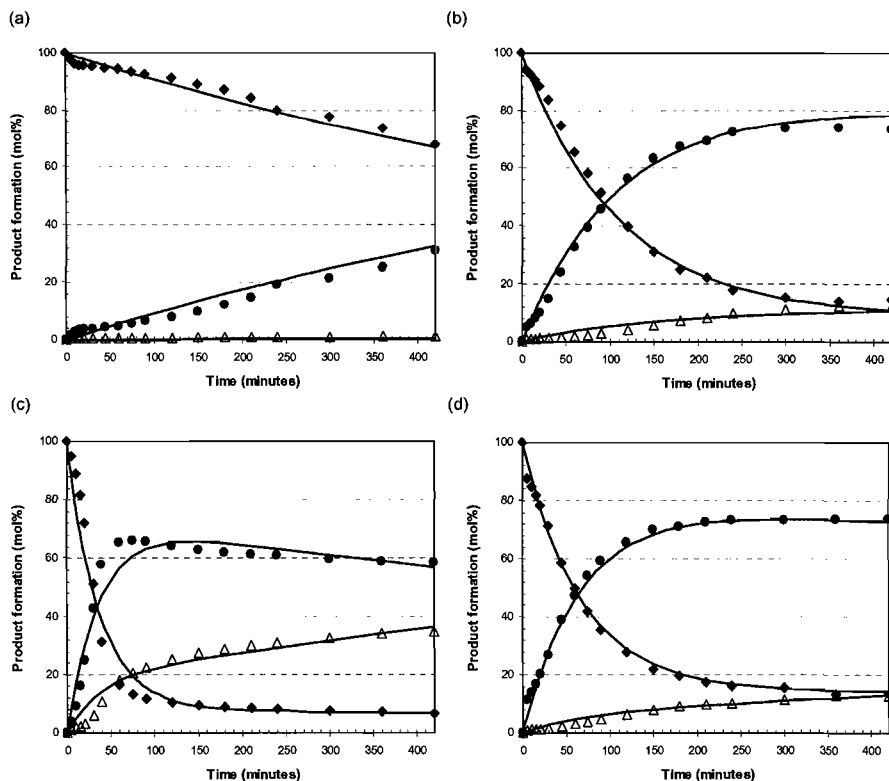


Figure 4.45 Experimental data compared to the modelled reaction scheme of Equations 4.3 to 4.5 and the proposed observed rate constants of Equation 4.7 for the metathesis reaction of 1-octene with precatalyst **Gr2Ph** at a) temperature of 60 °C and catalyst load of 7 000, b) temperature of 80 °C and catalyst load of 7 000, c) temperature of 90 °C and catalyst load of 7 000 and d) temperature of 80 °C and catalyst load of 5 000.

[● PMP formation; △ IP and SMP formation; ◆ 1-octene consumption and — modelled reaction scheme]

4.5.4 Summarized remarks about Gr2Ph

In this section the catalytic performance of the newly-developed **Gr2Ph** precatalyst was tested by varying two operating parameters: reaction temperature (between 30 and 100 °C) and precatalyst load (1-octene/Ru molar ratio between 5000 and 14000). It was found that reaction temperature had a significant effect that demonstrated metathesis activity for temperatures above 50 °C and competitive metathesis and isomerization activity for temperatures above 70 °C. Precatalyst **Gr2Ph** formed SMPs just as precatalysts **HGr2** and **Gr2** had. The preferred operating temperature was found to be 80 °C for the highest selectivity, TON, PMP formation and relatively low IP and SMP formation. Furthermore, precatalyst load showed no significant effect towards selectivity and TON. The reaction kinetics was accurately described by the three rate-laws as presented in Figure 4.17 for the different temperatures and precatalyst loads with activation energies of 24, 28 and 50 kcal.mol⁻¹.

4.6 Theoretical description of the metathesis reaction

4.6.1 Introduction

In this section the metathesis reaction of 1-octene with the three precatalysts **HGr1**, **HGr2** and **Gr2Ph** is described and evaluated from a mechanistic viewpoint by using molecular modelling and the results are compared with the experimental results reported in Sections 4.3 to 4.5.

4.6.2 Proposed mechanisms

The mechanistic pathways for the productive metathesis reaction of 1-octene with the **HGr1**, **HGr2** and **Gr2Ph** precatalysts have not recently been reported in the literature. Hoveyda and co-workers¹⁵ however, did suggest a type of release-return mechanism for the RCM reactions of acyclic dienes with the **HGr1** precatalyst. Jordaan³ also used the idea of Hoveyda's release-return mechanism to suggest a mechanistic pathway for the metathesis of 1-octene with first and second generation hemilabile ruthenium alkylidene complexes $[\text{RuCl}(\text{L})(\text{O}^{\wedge}\text{N})(=\text{CHPh})]$ $\{\text{L} = \text{H}_2\text{Mes}$ or PCy_3 and $\text{O}^{\wedge}\text{N} = 1\text{-(2'-pyridinyl)cyclohexan-1-olate}\}$, bearing a chelating pyridinyl alcoholate ligand that is similar to that of precatalyst **Gr2Ph**.

The proposed mechanism for the metathesis reaction of 1-octene with the **HGr1** or **HGr2** precatalysts, as depicted in Figure 4.46 and Figure 4.47, is based upon the mechanism suggested by Sanford *et al.*¹⁶⁻¹⁸ for **Gr1** and/or **Gr2** and was adapted to the release-return mechanism concept of Kingsbury *et al.*¹⁵

The mechanism initializes with the recoordination or release of the internal oxygen on the 16-electron Ru species **A** to create an open position active 14-electron species **B**. The activation takes place as 1-octene coordinates to the 14-electron intermediate **B** to form the π complex **C**. Complex **C** then undergoes a formal [2+2]-cycloaddition to form a metallacyclobutane ring **D** which in turn returns to a new π complex **E**. The methylidene species **F1** forms with the release of the alkene and then enters the catalytic cycle as illustrated in Figure 4.47. When the 1-octene coordinates as shown in **Cc** and **Cd**, heptylidene (**F3**, **F4**) is produced instead of the methylidene complex **F1**. The heptylidene also enters the catalytic cycle. During the catalytic cycle **F1** coordinates with 1-octene to convert either to **F3** or **F4** and produces ethene. Complexes **F3** and/or **F4** coordinates with 1-octene and converts to **F1** to produce either *cis*- or *trans*-7-tetradecene, depending on how the 1-octene coordinates with the heptylidene complex (either into **a** or out **b** of the plane). The cycle will continue to convert methylidene to heptylidene and then the heptylidene back to methylidene to produce ethene and 7-tetradecene until all the 1-octene is converted or, more likely, the catalyst has dissociated.

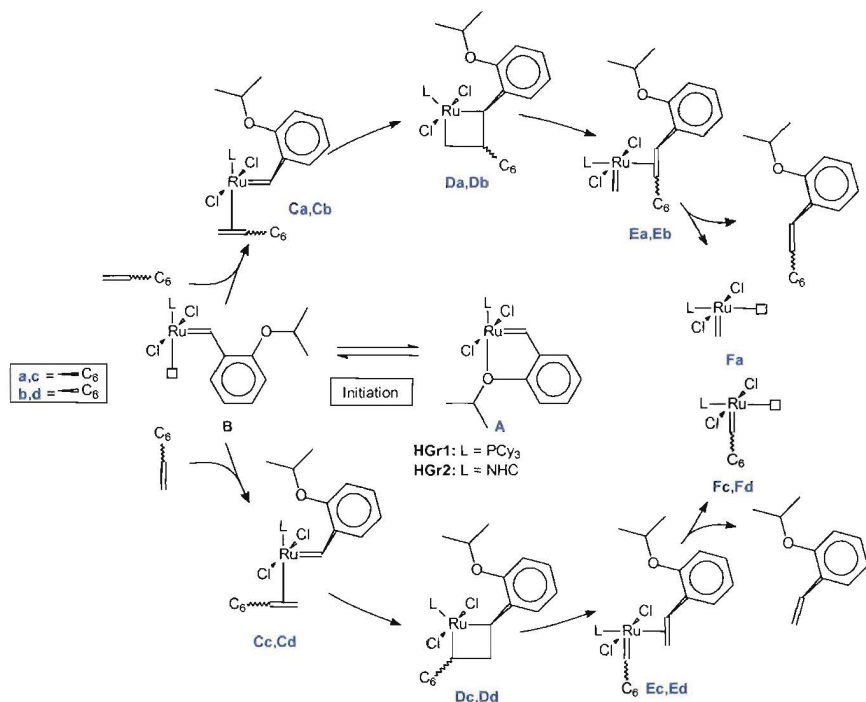


Figure 4.46 Proposed initiation and activation mechanism for the reaction of 1-octene in the presence of HGr1 and HGr2.

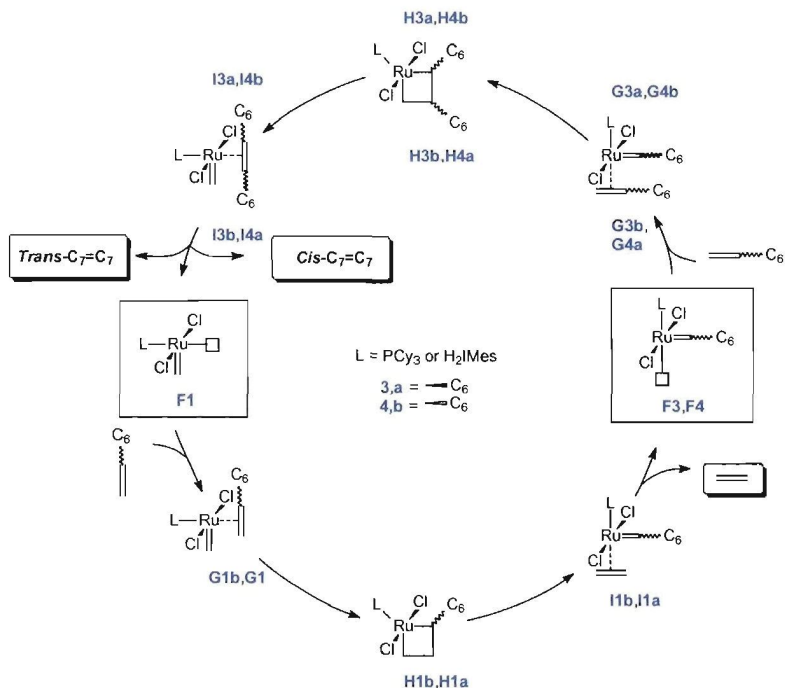


Figure 4.47 Proposed catalytic cycle for the productive metathesis of 1-octene with **HGr1** or **HGr2**.

A similar postulation can be made for **Gr2Ph** as described above for **HGr1** and **HGr2**, as summarized in Figure 4.48. The main difference between these two mechanisms is that the hemilabile ligand ($\text{O}^{\wedge}\text{N}$, as given in Figure 4.48) for **Gr2Ph**, is not dissociated or released during the activation or catalytic steps as with **HGr1** or **HGr2** that released the isopropoxystyrene (or related derivatives) to form the active catalytic species. This phenomenon of **Gr2Ph** not allowing the hemilabile ligand to be released during the activation or catalytic steps made precatalyst **Gr2Ph** thermally more stable compared to precatalysts **Gr1**, **Gr2**, **HGr1** and **HGr2**, as was described experimentally in Section 4.5. Furthermore, this phenomenon also gave precatalyst **Gr2Ph** a longer reaction lifetime, as will be described in Section 5.5.

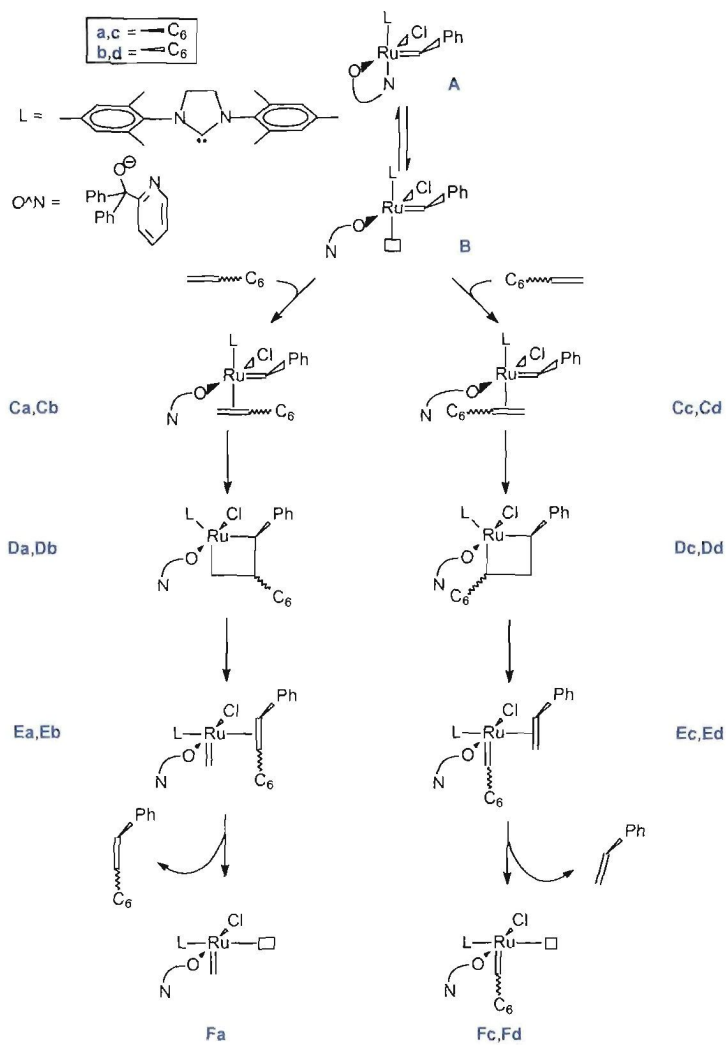


Figure 4.48 Proposed initiation and activation mechanism for the reaction of 1-octene in the presence of **Gr2Ph**.

4.6.3 Computational method used

In order to gain a deeper insight into the mechanism of precatalysts **HGr1**, **HGr2** and **Gr2Ph** for the metathesis of 1-octene, molecular modelling was used. All the computational results in this investigation were calculated by using the DMol³ DFT (Density Functional Theory) code as implemented in Accelrys Materials Studio[®] 4.2. DFT was used since it is a popular and versatile method for producing realistic geometries, relative energies and vibrational frequencies for transition metal compounds. Other authors^{2,3,9} also applied this method to Grubbs-type precatalysts.

DMol³ utilizes a basis set of numeric atomic functions, which are exact solutions to the Kohn-Sham equations for the atom. The Kohn-Sham equations are a set of eigenvalue equations within DFT. These basis sets are generally more complete than a comparable set of linearly independent Gaussian functions and have been demonstrated to have small basis set superposition errors. In this investigation a polarized split valence basis set, termed double numeric polarized (DNP) basis set has been used. All geometry optimizations employed highly efficient delocalized internal coordinates. The use of delocalized coordinates significantly reduces the number of geometry optimization iterations needed to optimize larger molecules, compared to the use of traditional Cartesian coordinates. The non-local generalised gradient approximation (GGA) functional by Perdew and Wang (PW91) was used for all geometry optimizations. The convergence criteria for these optimizations consisted of threshold values of 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å for energy, gradient and displacement convergence, respectively, while a self-consistent field (SCF) density convergence threshold value of 1×10^{-5} Ha was specified. The multiplicity was specified as auto, in order to determine the ground spin state using a spin-unrestricted calculation.

The GGA/PW91/DNP DFT calculations were carried out on a cluster with the following specifications:

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

Some of the optimized geometries were also subjected to full frequency analyses at the same GGA/PW91/DNP level of theory to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies. Transition state (TS)

geometries were obtained by transition state geometries optimizations on the GGA/PW91/DNP level of theory. This ensured the direct connection of transition states with the respective reactant and product geometries. Most of the transition structure geometries that were subjected to vibrational analyses exhibited more than one imaginary frequency in the reaction coordinate. This indicated that the structures needed to be refined and TS optimizations needed to be done. In most cases, one of the imaginary frequencies was representative of a possible transition structure and should, therefore, be investigated further. All results were mass balanced for the isolated system in the gas phase. The energy values that are given in the results are the electronic energies at 0 K and, therefore, only the electronic effects are considered in this investigation.

4.6.4 Validation of computational method

Validation of the computational method was based on two structural calculations applied to precatalyst complexes, $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-O-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$ and **HGr2**. The geometries of these two precatalysts were optimized for the lowest energies, as presented in Figure 4.49, and key calculated bond lengths and angles were compared with crystallographic data obtained by Hoveyda and coworkers^{15,20} as depicted in Table 4.24 and Table 4.25. Complex $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-O-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$ was used because Hoveyda and coworkers¹⁵ could not determine the crystallographic data for **HGr1**, and thus a structure closely resembling **HGr1** was chosen. This structure has a PPh_3 ligand instead of the classical PCy_3 ligand.

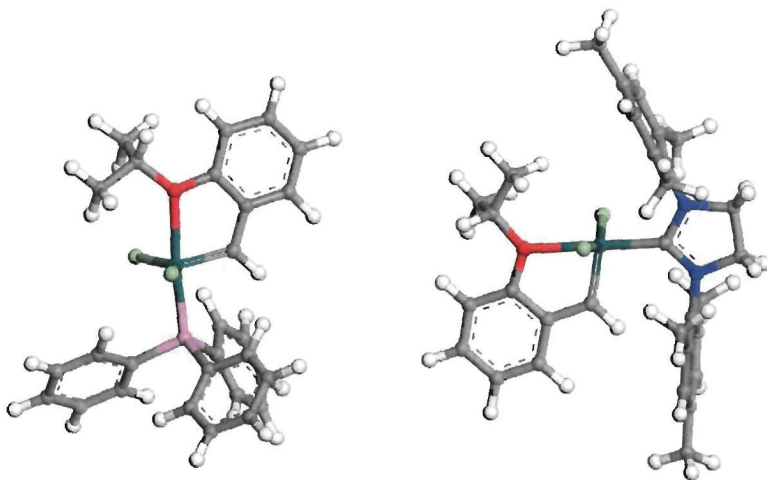
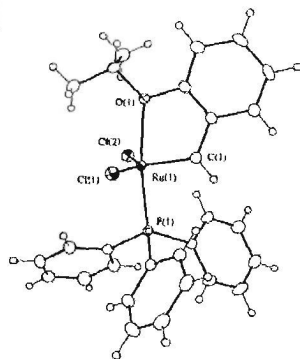


Figure 4.49 Geometrically optimized structure of complex (a) $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-O-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$ and (b) **HGr2**.

Table 4.24 DFT investigation and validation of complex $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-O-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$.

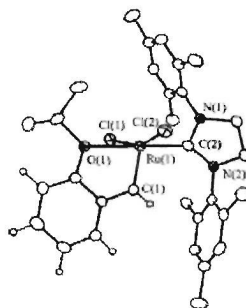
	Kingsbury <i>et al.</i> ^[a]	DFT ^[b]	% Error
Bond Lengths (Å)			
Ru(1)-C(1)	1.837(3)	1.873	1.960
Ru(1)-P(1)	2.242(8)	2.290	2.136
Ru(1)-O(1)	2.309(2)	2.339	1.299
Ru(1)-Cl(1)	2.323(8)	2.368	1.920
Ru(1)-Cl(2)	2.306(8)	2.350	1.921
Bond Angles (°)			
C(1)-Ru(1)-O(1)	79.01(11)	78.340	0.848
C(1)-Ru(1)-P(1)	93.28(10)	96.010	2.927
P(1)-Ru(1)-O(1)	172.29(5)	174.35	1.196
C(1)-Ru(1)-Cl(1)	106.99(9)	107.146	0.146
C(1)-Ru(1)-Cl(2)	106.99(9)	106.496	0.462
O(1)-Ru(1)-Cl(1)	90.81(5)	88.209	2.864
O(1)-Ru(1)-Cl(2)	88.31(6)	88.959	0.735
Cl(1)-Ru(1)-Cl(2)	145.17(3)	145.181	0.008

ORTEP diagram of $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$ thermal ellipsoids drawn at 30% probability from Kingsbury *et al.*¹⁵[a] Crystallographic data obtained from Kingsbury *et al.* Reference: 15

[b] Calculated data from this investigation on GGA/PW91/DNP DFT level of theory.

Table 4.25 DFT investigation and validation of HGr2.

	Garber <i>et al.</i> ^[a]	DFT ^[b]	% Error
Bond Lengths (Å)			
Ru(1)-C(1)	1.828(5)	1.871	2.352
Ru(1)-C(2)	1.981(5)	2.023	2.120
Ru(1)-O(1)	2.261(3)	2.352	4.025
Ru(1)-Cl(1)	2.328(12)	2.382	2.320
Ru(1)-Cl(2)	2.340(12)	2.383	1.838
C(2)-N(1)	1.351(6)	1.367	1.184
C(2)-N(2)	1.350(6)	1.360	0.741
Bond Angles (°)			
C(1)-Ru(1)-O(1)	79.3(17)	77.675	2.049
C(1)-Ru(1)-C(2)	101.5(14)	102.050	0.542
C(2)-Ru(1)-O(1)	176.2(14)	178.898	1.531
C(1)-Ru(1)-Cl(1)	100.2(15)	100.35	0.150
C(1)-Ru(1)-Cl(2)	100.1(15)	98.474	1.624
O(1)-Ru(1)-Cl(1)	86.9(9)	86.229	0.772
O(1)-Ru(1)-Cl(2)	85.3(9)	85.064	0.277
C(2)-Ru(1)-Cl(1)	96.6(12)	96.034	0.586
C(2)-Ru(1)-Cl(2)	90.9(12)	92.779	2.067
Cl(1)-Ru(1)-Cl(2)	156.5(5)	157.042	0.346
N(1)-C(2)-N(2)	106.9(4)	106.695	0.192

ORTEP diagram of HGr2, thermal ellipsoids drawn at 30% probability level from Garber *et al.*²⁰[a] Crystallographic data obtained from Garber *et al.* Reference: 20

[b] Calculated data from this investigation on GGA/PW91/DNP DFT level of theory.

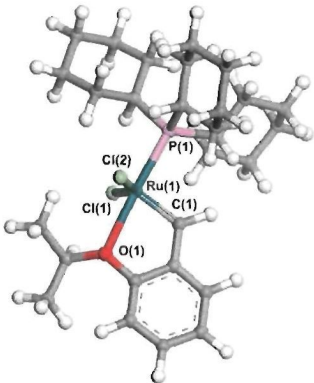
Acceptable correlations were obtained between the calculated values of this investigation and the crystallographic data of Hoveyda and coworkers,^{15,20} with an average error of 1.42% for complex $\text{Cl}_2\text{Ru}(=\text{CH}-o\text{-O-}i\text{-PrC}_6\text{H}_4)\text{PPh}_3$ and 1.37% for precatalyst **HGr2**. Furthermore, other researchers such as Jordaan^{2,3} and Forman *et al.*⁹ also used the GCA/PWS/DNP DFT level of theory for Grubbs-based systems.

4.6.5 Geometrical optimized structures of precatalysts HGr1, HGr2 and Gr2Ph

The different geometrically optimized molecular structures calculated with the GCA/PW91/DNP DFT level of theory for precatalysts **HGr1**, **HGr2** and **Gr2Ph** are summarized in Table 4.26, Table 4.27 and Table 4.28. Selected bond lengths and angles together with DFT ball and stick structures are given.

Table 4.26 DFT geometric structure of precatalyst **HGr1**.

DFT calculation ^[b]	DFT ball and stick structure
Bond Lengths (Å)	
Ru(1)-C(1)	1.860
Ru(1)-P(1)	2.343
Ru(1)-O(1)	2.394
Ru(1)-Cl(1)	2.379
Ru(1)-Cl(2)	2.358
Bond Angles (°)	
C(1)-Ru(1)-O(1)	78.877
C(1)-Ru(1)-P(1)	97.816
P(1)-Ru(1)-O(1)	176.311
C(1)-Ru(1)-Cl(1)	103.028
C(1)-Ru(1)-Cl(2)	107.324
O(1)-Ru(1)-Cl(1)	89.541
O(1)-Ru(1)-Cl(2)	84.697
Cl(1)-Ru(1)-Cl(2)	147.311



^[b] Calculated data on GCA/PW91/DNP DFT level of theory.

Table 4.27 DFT geometric structure of precatalyst HGr2.

DFT calculation^[b]

DFT ball and stick structure

Bond Lengths (Å)

Ru(1)-C(1)	1.871
Ru(1)-C(2)	2.023
Ru(1)-O(1)	2.352
Ru(1)-Cl(1)	2.382
Ru(1)-Cl(2)	2.383
C(2)-N(1)	1.367
C(2)-N(2)	1.360

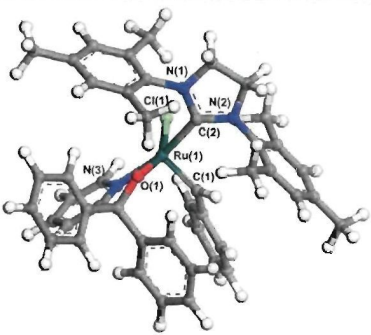
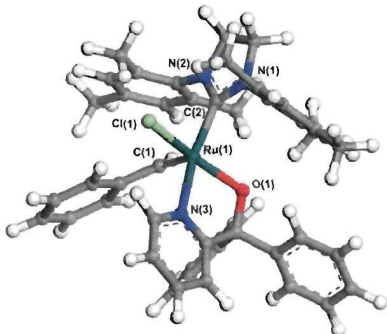
Bond Angles (°)

C(1)-Ru(1)-O(1)	77.675
C(1)-Ru(1)-C(2)	102.050
C(2)-Ru(1)-O(1)	178.898
C(1)-Ru(1)-Cl(1)	100.35
C(1)-Ru(1)-Cl(2)	98.474
O(1)-Ru(1)-Cl(1)	86.229
O(1)-Ru(1)-Cl(2)	85.064
C(2)-Ru(1)-Cl(1)	96.034
C(2)-Ru(1)-Cl(2)	92.779
Cl(1)-Ru(1)-Cl(2)	157.042
N(1)-C(2)-Cl(2)	106.695

^[b] Calculated data on GGA/PW91/ONP DFT level of theory

[b] Calculated data on GGA/PW91/DNP DFT level of theory.

Table 4.28 DFT geometric structure of Gr2Ph.

DFT calculation ^[b]		DFT ball and stick structure
Bond Lengths (Å)		
Ru(1)-C(1)	1.881	
Ru(1)-C(2)	2.089	
Ru(1)-O(1)	2.039	
Ru(1)-Cl(1)	2.428	
Ru(1)-N(3)	2.182	
C(2)-N(1)	1.364	
C(2)-N(2)	1.361	
Bond Angles (°)		
C(1)-Ru(1)-O(1)	101.156	
C(1)-Ru(1)-C(2)	96.226	
C(2)-Ru(1)-O(1)	96.848	
C(1)-Ru(1)-Cl(1)	101.599	
C(2)-Ru(1)-N(3)	167.684	
O(1)-Ru(1)-N(3)	95.495	
O(1)-Ru(1)-Cl(1)	155.306	
C(2)-Ru(1)-Cl(1)	90.105	
C(2)-Ru(1)-O(1)	96.848	
Cl(1)-Ru(1)-O(1)	155.306	
N(1)-C(2)-N(2)	106.598	

^[b] Calculated data on GGA/PW91/DNP DFT level of theory.

4.6.6 Precatalyst initiation step

It is generally accepted that the Ru-catalysed alkene metathesis reaction with **Gr1** and **Gr2** proceeds via a dissociative mechanism, which is initiated by the dissociation of a phosphine ligand from $\text{RuX}_2(\text{PR}_3)\text{L}(=\text{CHR})$ to form a 14-electron species.^{16,17,18,21} In this sense, the catalyst's initiation involves the dissociation of the base ligand (PCy_3) from both **Gr1** and **Gr2**. Furthermore, for hemilabile complexes such as **HGr1** and **HGr2** a type of release-return initiation step has been suggested¹⁵ where no phosphine dissociation takes place. This leads to the question:

Does precatalyst initiation involve the dissociation of the O-atom for the O,C-ligand with **HGr1** and **HGr2** (see Figure 4.50(a)) and the labile N-atom of the O,N-ligand (see Figure 4.51(a)) with **Gr2Ph**?

OR

Does precatalyst initiation rather involve the dissociation of the ligand L (with $\text{L} = \text{PCy}_3$ or H_2IMes) for **HGr1**, **HGr2** (see Figure 4.50(b)) and **Gr2Ph** (see Figure 4.51(b))?

Summarized electronic energies (ΔE) in kcal.mol^{-1} for these different initiation phases ("A" to "B") with **HGr1**, **HGr2** and **Gr2Ph** are given in Table 4.29.

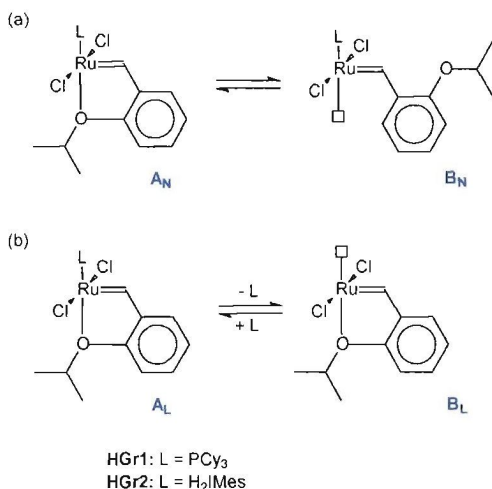
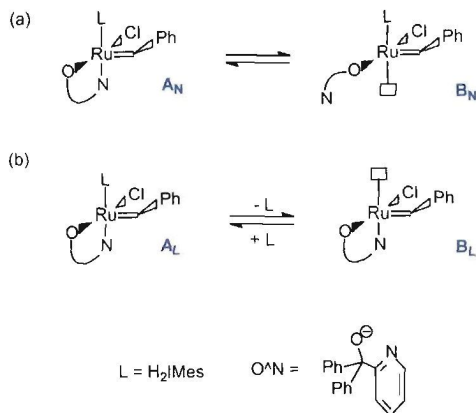


Figure 4.50 Initiation step for **HGr1** and **HGr2**.

(a) Dissociation of O-atom of the O,C-ligand and (b) Dissociation of ligand L.

**Figure 4.51** Initiation step for Gr2Ph.

(a) Dissociation of labile N-atom of O,N-ligand and (b) Dissociation of ligand L.

Table 4.29 Calculated relative electronic energies (ΔE) in kcal.mol⁻¹ for the initiation step "A" to "B" with HGr1, HGr2 and Gr2Ph.

Mechanistic sequence	HGr1	HGr2	Gr2Ph
A	0	0	0
B _N	4.10	10.23	25.13
B _L	57.57	92.61	75.72

All energies are reported relative to the respective precatalysts "A" and balanced with the energies of the free ligand where necessary.

It is clear from the results in Table 4.29 that the mechanistic sequence **A** to **B_N** is, from an electronic energy point of view, more favourable to occur than the mechanistic sequence **A** to **B_L**. The reason is that initiation step **A** to **B_N** compared to **A** to **B_L** gave the lowest electronic energies respectively for all three precatalysts. This implies that the release-return type of initiation step would preferentially occur for the metathesis reaction of 1-octene with **HGr1**, **HGr2** and **Gr2Ph** rather than the dissociation step of the L-ligand, as was found for the **Gr1** and **Gr2** systems.

The stability effect of the H_2IMes and PCy_3 -ligands for the different precatalysts can be compared based on the relative dissociation energies of the ligand, mechanistic sequence **A** to **B_L**. It is clear from these results that the second generation ligand (**HGr2** = 92.61 kcal.mol⁻¹ and **Gr2Ph** = 75.72 kcal.mol⁻¹) has a higher dissociation energy than the first generation ligand (**HGr1** = 57.57 kcal.mol⁻¹), which means that the H_2IMes -ligand is a more stable ligand than the PCy_3 -ligand. Furthermore, the results indicate that the H_2IMes -ligand with its stronger bonding

capabilities compared to the PCy_3 -ligand, has a significant effect on the initiation step of the forming complex B_N . More energy (thus higher reaction temperatures) is needed for the H_2IMes -ligand based precatalyst than the PCy_3 -ligand based precatalyst in the initiation step. This is supported by the experimental optimum reaction temperatures of 30 °C for **HGr1**, 50 °C for **HGr2** and 80 °C for **Gr2Ph**.

Since it is believed,^{3,22} and shown in Table 4.29, that the hemilabile ligands are to release a free coordination site “on demand” by competing substrates, and occupying it otherwise, the following question arises:

Does the ruthenium centre of the hemilabile complexes become coordinatively unsaturated with or without the influence of the incoming 1-octene as demonstrated in Figure 4.52 for **Gr2Ph** and Figure 4.53 for **HGr1** and **HGr2**?

This implies another mechanistic route, dominating *inter alia* an associative coordination of 1-octene prior to the release of the labile N-atom for **Gr2Ph** and the O-atom for **HGr1** and **HGr2** that could lead to different initiation energies.

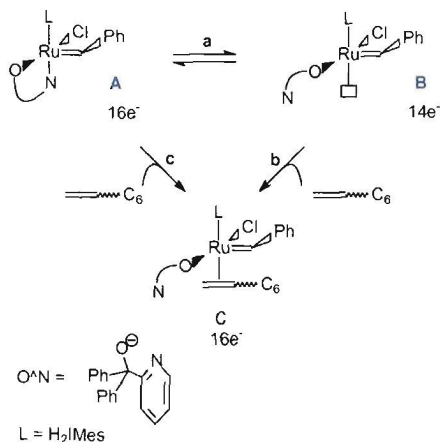


Figure 4.52 Illustration of the dissociative (pathways **a** and **b**) and the associative (pathway **c**) initiation step for the metathesis of 1-octene with **Gr2Ph**.

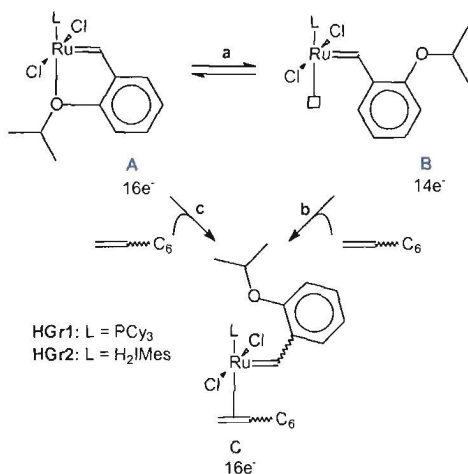


Figure 4.53 Illustration of the dissociative (pathways **a** and **b**) and the associative (pathway **c**) initiation step for the metathesis of 1-octene with HGr1 and HGr2.

It has been postulated in this study that the dissociative pathway would be energetically more favoured, as Adlhart and Chen²¹ found the dissociative pathway more favourable than the associative pathway for Gr1 and Gr2. Only the dissociative pathway could be investigated in this study, but it is recommended that in future investigations the associative pathway be investigated and compared to the results of this study.

Since ligand initiation via the release mechanism proceeds prior to the interaction of the 1-octene with the ruthenium centre, precatalyst initiation requires the formation of an unsaturated 14-electron complex **B** (as depicted in Figure 4.52 and Figure 4.53). Various orientations of the alkylidene moiety in **B** can be possible. According to Janse van Rensburg *et al.*,²³ the alkylidene moiety may be orientated either parallel or perpendicular to the Cl-Ru-X plane (X = Cl or O) for Gr1, Gr2 and hemilabile analogues. They indicated that, for the methylidene precatalyst of Gr1 and Gr2, different CH₂ orientations could account for the most stable complex, i.e. a parallel orientation of CH₂ for Gr2, and perpendicular orientation for Gr1. It was found for this study, as demonstrated in Figure 4.54, that a perpendicular orientation gave the lowest geometrically optimized energies for HGr1, HGr2 and Gr2Ph.

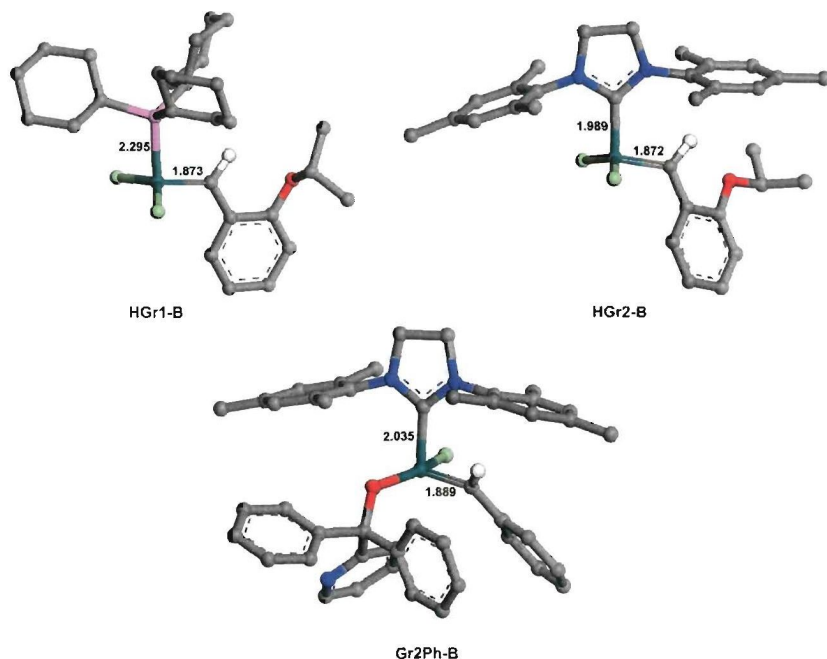


Figure 4.54 Optimized structures of **B** complexes at the lowest energy. The hydrogen atoms on the ligands are omitted for clarity and the unit of the indicated bond lengths is Angstrom units (Å).

4.6.7 Catalyst activation step

After the catalyst initiation step, as described in Section 4.7.5, 1-octene coordinates to the unsaturated intermediate species **B** to form the corresponding π -complexes **C**. Complex **C** then undergoes a formal [2+2]-cycloaddition to form a metallacyclobutane ring **D**, which in turn returns to a new π complex **E** and thereafter the methylidene or heptylidene species (**F**) forms as illustrated in Figure 4.47 for **HGr1** and **HGr2** and Figure 4.48 for **Gr2Ph**.

The coordination of 1-octene with complex **B**, was modelled where 1-octene coordinates in a parallel position to the benzylidene carbene bond (referred to as parallel coordination mode). This mode of coordination was shown to be more energetically favoured for the coordination of alkenes with precatalyst **Gr1** and **Gr2** than other modes such as alkene coordination parallel to the Cl-Ru-Cl line and perpendicular or orthogonal to the carbene.²³ Furthermore, the incoming 1-octene can enter the free coordination site of complex **B** in four pathways, as depicted in Figure 4.55.

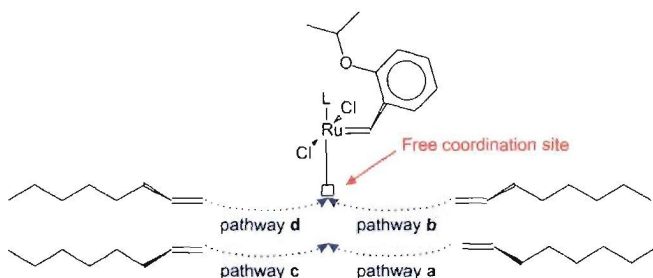


Figure 4.55 The four 1-octene coordinating modes, in a parallel position to the benzylidene carbene bond.

The different electronic energy profiles for the initiation and activation steps (complexes **A** to **F**) for all four pathways are given in Figure 4.56 and Figure 4.57 for the **HGr1** system, Figure 4.58 and Figure 4.59 for the **HGr2** system and Figure 4.60 and Figure 4.61 for the **Gr2Ph** system. The different optimized structures generated by Accelrys Materials Studio® 4.2 are given in Figure 4.62, Figure 4.63 and Figure 4.64.

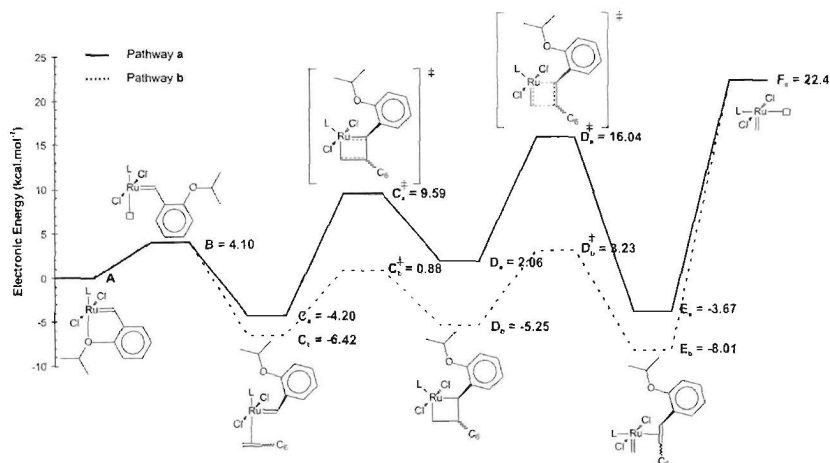


Figure 4.56 Electronic energy profiles for the initiation and activation steps of the **HGr1** system for pathways **a** and **b**.

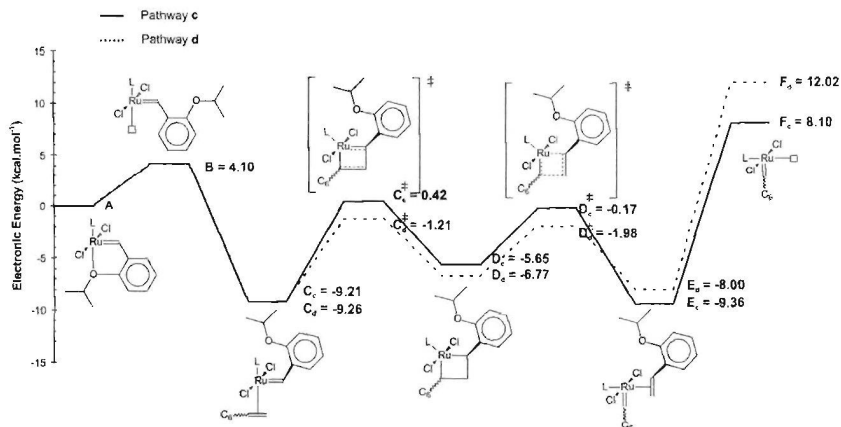


Figure 4.57 Electronic energy profiles for the initiation and activation steps of the HGr1 system for pathways c and d.

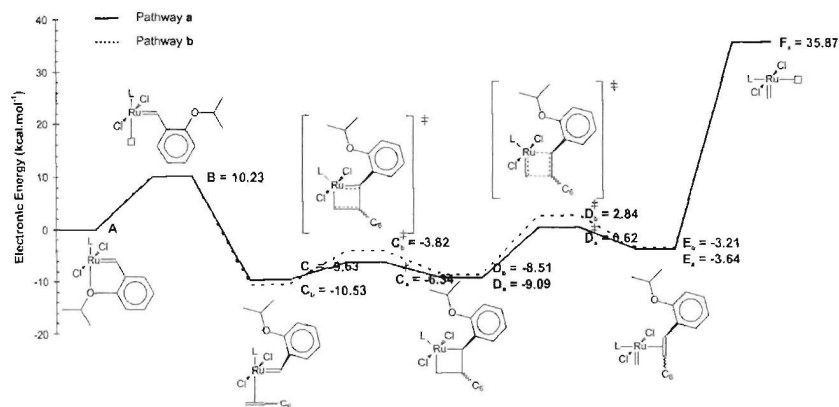


Figure 4.58 Electronic energy profiles for the initiation and activation steps of the HGr2 system for pathways a and b.

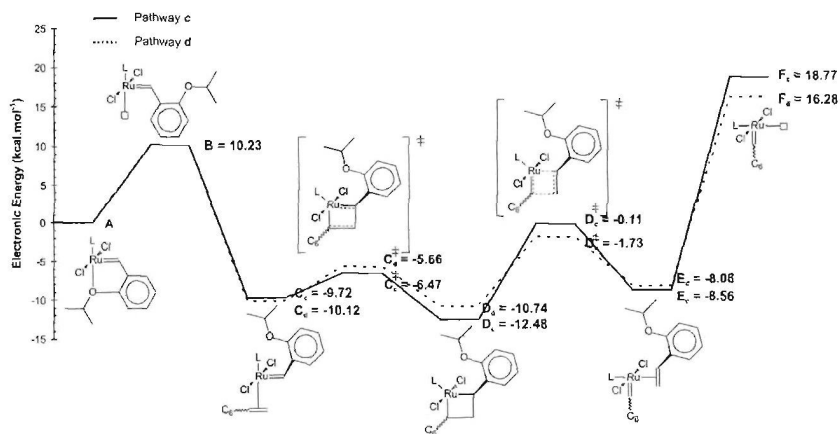


Figure 4.59 Electronic energy profiles for the initiation and activation steps of the HGr2 system for pathways c and d.

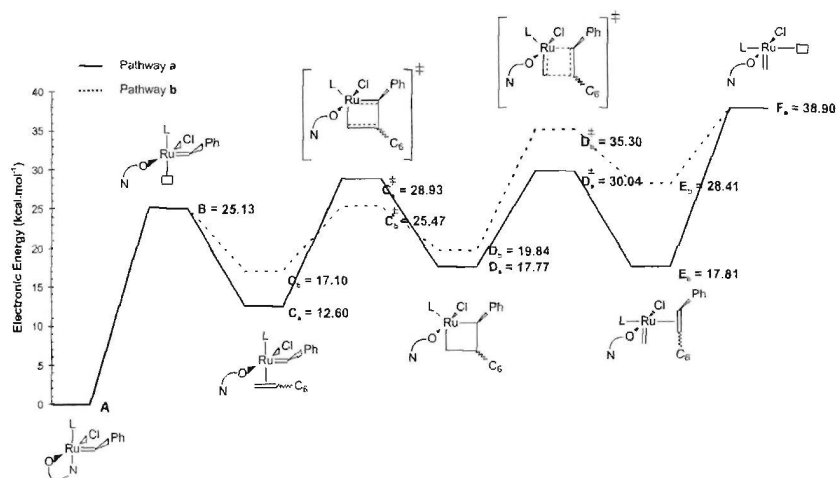


Figure 4.60 Electronic energy profiles for the initiation and activation steps of the Gr2Ph system for pathways a and b.

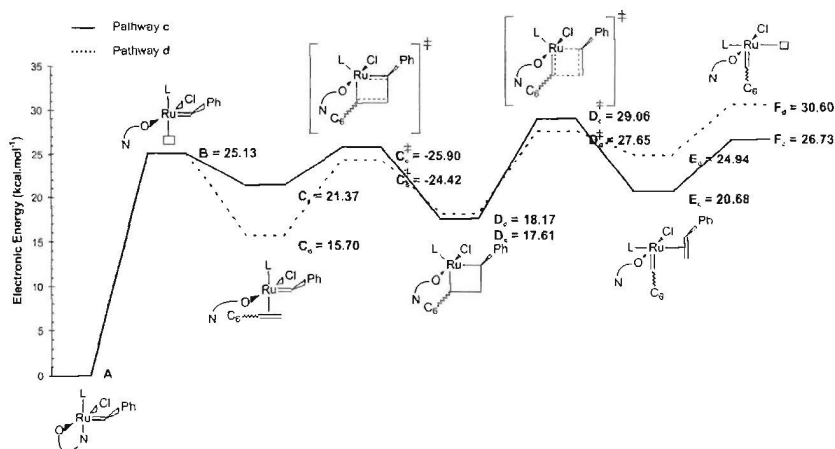


Figure 4.61 Electronic energy profiles for the initiation and activation steps of the Gr2Ph system for pathways c and d.

It is clear from the different pathway results that pathways c and d are, from an electron energy viewpoint, the most favourable pathways for all three catalysts and would preferentially be followed for the generation of 7-tetradecene. The favourable pathways of c and d are primarily due to the free rotation of the phenyl-based-rings on the alkylidene moiety, which increases the steric bulk around the Ru-centre and, therefore, obstructs coordination of 1-octene to the Ru=C-moiety in pathways a and b, but to a lesser extent for c and d. These results are in agreement with what Jordaan³ found for the Gr1 and Gr2 systems.

The rate-limiting steps and electron activation energies for the heptylidene formation and methyldiene formation are summarized in Table 4.30 for the different catalysts. The rate-limiting step for the formation of the different alkylidene species (F) with precatalysts HGr1 and HGr2 was found to be the formation step of these alkylidene species (E to F), while for precatalyst Gr2Ph the initiation step (A to B). Jordaan³ found that the decomposition step of the ruthenacyclobutane (D to E) was the rate-limiting step for precatalyst Gr1 and the ruthenacyclobutane formation step (C to D) for precatalyst Gr2.

Table 4.30 Comparison of rate-limiting steps and electron energy differences (in kcal.mol⁻¹) for the different catalyst systems.

	Gr1^[a]	Gr2^[a]	HGr1	HGr2	Gr2Ph
Rate-limiting step	D to E	C to D	E to F	E to F	A to B
Electron activation energy of rate-limiting step for heptylidene formation	25.45	31.83	17.46	27.33	25.13
Electron activation energy of rate-limiting step for methyldiene formation	31.98	44.00	20.02	39.08	25.13
Overall electron energy change from A to F	18.02	30.39	8.10	18.77	26.73
Overall electron energy change from B to F	-3.87	4.47	4.00	6.05	1.60

[a] Molecular modelling results taken from Jordaan reference 3.

According to Jordaan³ the relative stability of precatalyst **Gr1** compared to precatalyst **Gr2** can be determined from the overall electron energy change for the activation steps (**B** to **F**). It is clear from Table 4.30 that this is true for similar structural groups (same Grubbs-type catalyst) that are compared, such as **Gr1** with **Gr2** or **HGr1** with **HGr2**. For example, **HGr2** (6.05 kcal.mol⁻¹) is more stable than **HGr1** (4.00 kcal.mol⁻¹), due to the higher relative electron energy change from **B** to **F** which correlates well with the experimental results. Jordaan³ also proposed that the relative activity for the different catalysts can be determined from the comparative energy change from **A** to **F**. As given in Table 4.30, **HGr2** (18.77 kcal.mol⁻¹) is more active than **HGr1** (8.10 kcal.mol⁻¹), which also correlates well with the experimental results, as can be seen from their relative TON. However, these correlations are not effective when comparing different structural groups and ligand based catalysts as is the case when comparing **HGr1** with **Gr2Ph** or **Gr2**. It is recommended that care be taken when applying these correlations for interpretational purposes of stability and activity.

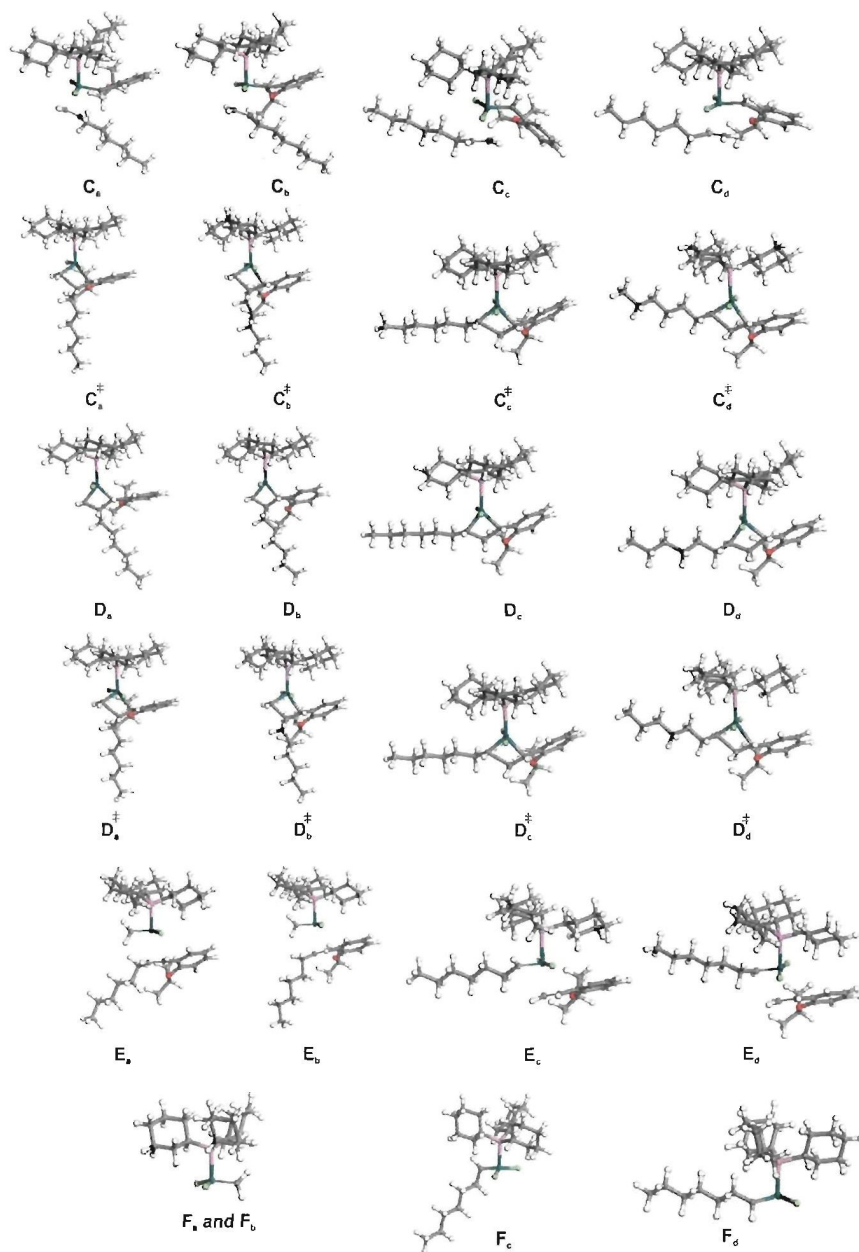


Figure 4.62 DFT optimized structures of the various HGr1 complexes.

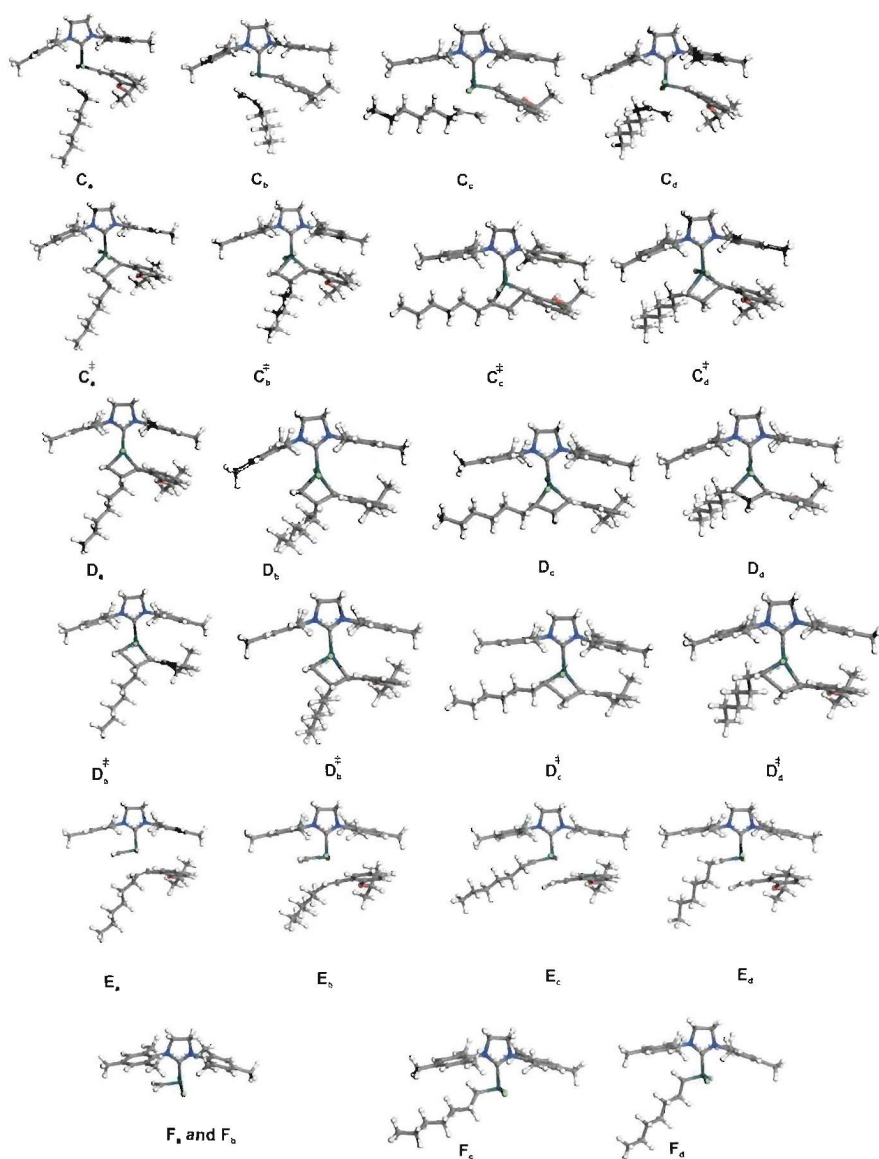


Figure 4.63 DFT optimized structures of the various HGr2 complexes.

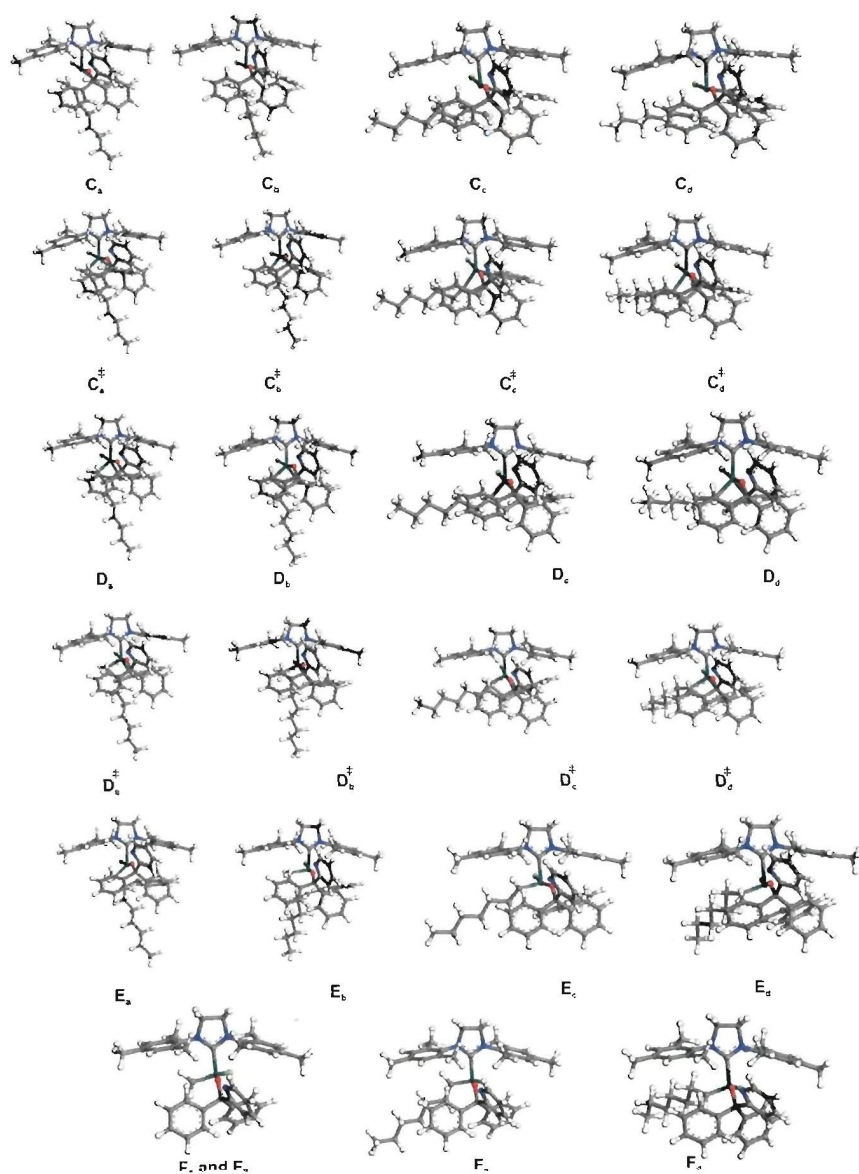


Figure 4.64 DFT optimized structures of the various Gr₂Ph complexes.

4.6.8 Summarizing remarks

In this section a theoretical understanding of the metathesis reaction of 1-octene with the three precatalysts **HGr1**, **HGr2** and **Gr2Ph** was investigated. It was postulated and demonstrated that the metathesis reaction of 1-octene with the different Grubbs-type precatalysts used in this study could be described by a type of release-return dissociative mechanism as presented in Figure 4.46 to Figure 4.48.

The proposed mechanisms and different catalytic species were further evaluated from an electron energy and structural viewpoint with molecular modelling. It was found that the theoretically modelled structures correlated extremely well with experimental crystallographic data. It was demonstrated from the theoretically modelled electron energies that the initiation step of the postulated mechanisms is favoured by the release of the O-atoms for the O,C-ligands with the **HGr1** and **HGr2** systems and the labile N-atom of the O,N-ligand with the **Gr2Ph** system. It was shown that 1-octene preferentially coordinated with a parallel coordination pathway mode that is away from the free rotated phenyl-based-rings on the alkylidene moiety. The different catalytic species PES and optimized structural diagrams were determined and provided for describing the postulated mechanisms.

It was found that the theoretically modelled overall initiation and activation electron energies from the different systems correlate well with the experimentally calculated activation energies as summarized in Table 4.31.

Table 4.31 Comparison of theoretical overall initiation and activation electron energies compared to the experimental calculated activation energies (in kcal.mol⁻¹) for the different catalyst systems.

	HGr1	HGr2	Gr2Ph
Activation energy of forward reaction for the formation of PMPs as calculated in Section 4.3 to 4.5	9.47	19.95	24.19
Overall electron energy change for the initiation and activation step for the proposed mechanisms as calculated in Section 4.6	8.10	18.77	26.73

4.7 Concluding remarks on the alkene metathesis reaction

In this chapter three main aspects were presented and discussed in detail, namely:

- 1) the synthesis results of precatalyst **Gr2Ph**,
- 2) catalytic performances of precatalysts **HGr1**, **HGr2** and **Gr2Ph** for the model metathesis reaction of 1-octene to 7-tetradecene and ethene, and
- 3) a theoretical understanding of the mechanism for the model reaction.

It was shown that precatalyst **Gr2Ph** was successfully synthesized and characterized.

It was postulated and demonstrated that the model metathesis reaction of 1-octene with the different Grubbs-type catalysts as used in this study could theoretically be described by a type of release-return dissociative mechanism.

It was further found that all three precatalysts **HGr1**, **HGr2** and **Gr2Ph** showed both metathesis and isomerization activity for the reaction with 1-octene that is strongly temperature dependent. Precatalysts **HGr2** and **Gr2Ph** showed significant secondary metathesis activity while precatalyst **HGr1** did not. It was found that the optimal reaction temperature for precatalyst **HGr1** was 30 °C, for precatalyst **HGr2** 50 °C and for precatalyst **Gr2Ph** 80 °C. The addition of different solvents to the reaction environment had an overall negative effect towards the formation of PMPs.

It was found that the reaction kinetics of the model metathesis reaction with the three precatalysts could fairly accurately be described by the first-order reaction rate-laws as given in Equations 4.3 to 4.5:

$$\frac{dc_{C_8}}{dt} = -k_1 c_{C_8} + k_2 c_{PMP} - k_3 c_{C_8} \quad (4.3)$$

$$\frac{dc_{PMP}}{dt} = k_1 c_{C_8} - k_2 c_{PMP} \quad (4.4)$$

$$\frac{dc_{IP+SMP}}{dt} = k_3 c_{C_8} \quad (4.5)$$

where the observed rate constant is a function of precatalyst concentration and temperature as given by Equation 4.7:

$$k_{r,obs} = k \times C_{catalyst} \times e^{\left[\frac{-E}{RT}\right]} \quad (4.7)$$

4.8 References

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5 ORGANIC SOLVENT NANOFILTRATION (OSN) - RESULTS AND DISCUSSION

Overview

In this chapter, all the experimental results that were obtained for the Organic Solvent Nanofiltration (OSN) process for the metathesis system of 1-octene with the different Grubbs-type precatalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**) will be presented and discussed.

The chapter is subdivided into six sections, starting in Section 5.1 with a brief introduction to the OSN process. A membrane screening process for selecting the appropriate membrane for the separation of the 1-octene and Grubbs-type metathesis system is presented in Section 5.2. In Section 5.3 the permeation and sorption performances of the STARMEMTM 228 membrane for the 1-octene metathesis system are characterized by addressing the following aspects: (i) experimental validation and reproducibility of the OSN results at steady-state operating conditions with the dead-end setup, (ii) permeation performances with pure components, (iii) permeation performances with binary-mixtures, (iv) permeation and rejection performances with post-metathesis reaction mixtures, (v) effect of pretreatment on the separation performances and (vi) sorption characteristics with pure and binary-mixtures. In Section 5.4, the OSN transport of the binary mixture of 1-octene and 7-tetradecene through the STARMEMTM 228 membrane is described by applying different transport models and variations on these models found in the literature. The main objective of this study is addressed in Section 5.5 where the separation and reusability of the different Grubbs-type precatalysts with the STARMEMTM 228 membrane are demonstrated and discussed. Concluding remarks for this chapter are given in Section 5.6.

5.1 Introduction

The separation and re-use of homogeneous catalysts, such as the ruthenium-based Grubbs-type precatalysts depicted in Figure 5.1 from their post-reaction mixtures are still unresolved challenges in the field of metathesis.

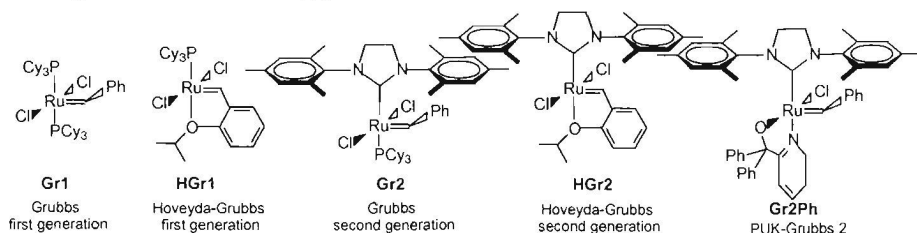


Figure 5.1 The different Grubbs-type precatalysts used in this study.

The separation of Grubbs-type homogeneous catalysts from their reaction products and solvents is difficult, requiring the use of energy-intensive and waste-generating downstream processing, such as distillation. In many cases residual inactive catalyst and catalyst decomposition fragment levels of greater than 2000 ppm remain in the product mixture after separation. From an economic point of view, in the whole chemical process the catalyst's cost is another important factor. The development of improved strategies for recovering these Grubbs-type catalysts and for removal of ruthenium decomposition by-products is, therefore, of great importance.

In this chapter, the successful separation and re-use of Grubbs-type homogeneous catalyst from the reaction mixture of 1-octene will be demonstrated and discussed, thus solving one of the key challenges in the field of alkene metathesis, as illustrated in Figure 5.2.

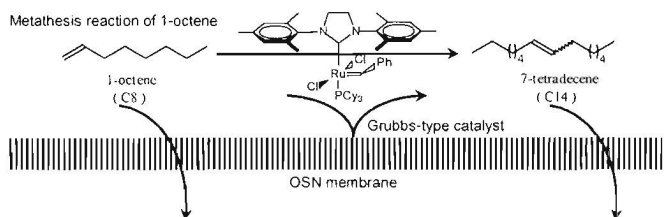


Figure 5.2 Schematic illustration of the objective with the OSN separation process.

5.2 Membrane selection

5.2.1 Introduction

The success of any industrial membrane separation process depends on three main parameters: permeation (flux), selectivity (rejection) and stability (membrane solvent resistance). For commercial application in NF there is a trade-off between flux and rejection. Although a high flux is preferred to meet flow conditions in other parts of a plant, a high rejection is more important in most NF applications. This is especially true for catalyst recovery and purification of product streams. It is thus important that care must be taken when choosing a membrane for a specific application. In this section, the selection of an appropriate membrane for separating different Grubbs-type catalysts from alkene-mixtures is given, based on the following criteria:

- high catalyst recovery with a MWCO preferably less than 500 g.mol^{-1} ,
- high permeation characteristics for hydrocarbons,
- tolerance for different organic solvent, and
- ease of handling by operator.

5.2.2 Literature evaluation

In the OSN field, polymeric membranes have been proven to be the preferred type of membranes. This field is relatively new and thus only a few solvent resistant polymeric membranes are commercially available. Some of the well-known OSN membranes commercially available are summarized in Table 5.1.

The molecular weight of the different Grubbs-type precatalysts used in this study range from 600 to 850 g.mol^{-1} which means that a membrane with an average MWCO of approximately less than 500 g.mol^{-1} will be able to reject the catalysts. Zhao *et al.*¹ showed that the Desal-5-DK membrane demonstrated low rejections (ranging from 0.146 to 0.676) towards crystal violet (MW 400) in a methanol solution. Scarpello *et al.*² found that the Desal-5 membrane showed low rejections (ranging from 0.779 to 0.841) towards a Jacobsen catalyst. Aerts *et al.*³ found a rejection of approximately 10% for a Co-Jacobsen catalyst with the Desal-5-DL membrane and ranging from 40 to 90% with a N30F membrane. It can, therefore, be concluded from these results that the Nadir and Osmonics series of membranes are not appropriate for this study.

It is clear from literature that hydrophobic type of membranes such as the MPF-50 and STARMEM™ series of membranes will give higher fluxes for non-polar components such as the hydrocarbons used in this study. The polyimide membranes of Membrane Extract Technology

(MET) have previously been used for the successful separation of different homogeneous transition metal catalysts such as the Jacobsen, Wilkinson and Pd-BINAP catalysts in several reactions ranging from the Heck reaction, Suzuki couplings to asymmetric hydrogenations with catalyst rejections varying between 92 and 100%.² White and Nitsch⁴ have shown that polyimide-based membranes such as the STARMEMTM series can successfully be used to separate light hydrocarbons from lube oil with economically viable fluxes and rejections. The STARMEMTM series of membranes were thus chosen to conduct catalyst rejection experiments in this study.

Table 5.1 Examples of commercially available solvent resistant membranes.

Membrane	Manufacturer	Material	Type	MWCO (g.mol ⁻¹)
Nadir-series	Nadir ^[a]			
N30F		PES ^[f]	hydrophilic	400
NF-PES-010		PES	hydrophilic	1000
MPF-series	Koch ^[b]			
MPF-44		PDMS ^[g]	hydrophilic	250
MPF-50		PDMS	hydrophobic	700
Desal-series	Osmonics ^[c]			
Desal-5-GE		PA ^[h]	hydrophilic	1000
Desal-5-DK		PA	hydrophilic	150-300
Desal-5-DL		PA	hydrophilic	150-300
SolSep-series	SolSep ^[d]			
SolSep-030505		-	hydrophobic	-
SolSep-169		-	-	-
SolSep-01		-	-	-
STARMEM TM -series	MET ^[e]			
ST-120		PI ^[i]	hydrophobic	200
ST-122		PI	hydrophobic	220
ST-228		PI	hydrophobic	280
ST-240		PI	hydrophobic	400

[a] Nadir Filtration GmbH, Wiesbaden, Germany;

[b] Koch Membrane Systems, Wilmington, MA, USA;

[c] GE Osmonics, Vista, CA, USA;

[d] SolSep BV, Apeldoorn, The Netherlands;

[e] Membrane Extraction Technology, London, UK.

[f] PES: Polyethersulfone [g] PDMS: Polydimethylsiloxane. [h] PA: Polyamide [i] PI: Polyimide

5.2.3 Experimental evaluation

Preliminary compatibility and permeation experiments were conducted with 1-octene and 1-tetradecene to determine which of the four commercially available STARMEM™ series of membranes (ST-120, ST-122, ST-228 and ST-240) would be best for the characterization of the OSN for the 1-octene metathesis reaction mixture. 1-Tetradecene was used in the screening experiments, rather than 7-tetradecene, due to the high cost of 7-tetradecene.

The compatibility, as described in Section 3.4.3 (a), of the different membranes for a given solvent was tested with both a visual physical stability test and suitability of the membrane to reject the catalyst and 1-octene while allowing the permeation of the products at 30 bar. The physical stability was tested by soaking the membrane in the desired solvent for at least two days and inspecting the membranes for any active-layer dissolution. A membrane was classified as visually non-stable if any active-layer dissolution was observed. A typical observation is shown in Figure 5.3 for the ST-122 membrane soaked in 1-octene. All four membranes were found to be stable for the metathesis system of 1-octene, 1-tetradecene, ethanol, water, toluene, acetone and acetic acid. These results correlate well with the manufacturer's specification sheet as given in Section 3.1.1.

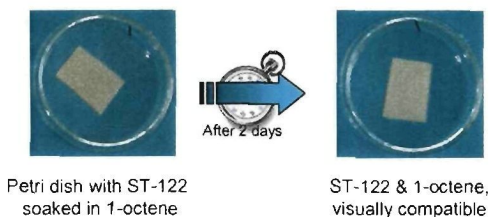
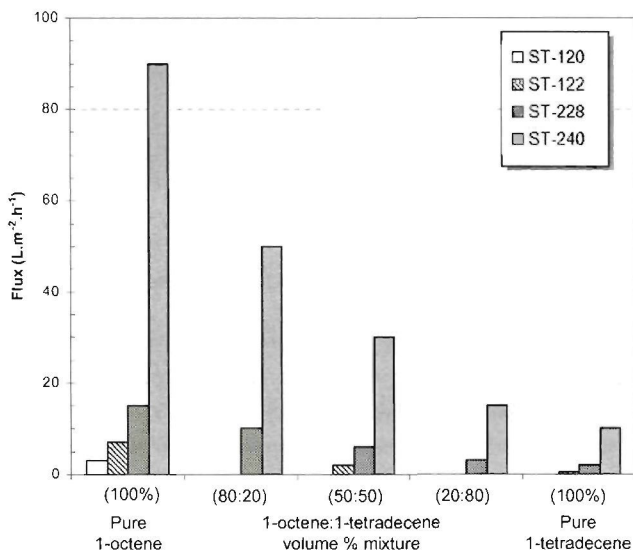


Figure 5.3 Visual stability test of membrane ST-122 in 1-octene.

The suitability or compatibility of the different membranes with the 1-octene metathesis system was evaluated by measuring component fluxes, catalyst rejection and permeate composition while varying the feed composition for the different STARMEM™ membranes. It is preferable that the PMPs for the metathesis reaction should permeate through the membrane and the substrate (1-octene) and the catalyst be rejected. The results obtained for the screening experiments done with different mixtures of 1-octene and 1-tetradecene (based on volume percentage) with each of the STARMEM™ membranes are presented in Table 5.2 and Figure 5.4. The membranes were first pretreated and broken-in with toluene according to the procedure described in Section 3.4.3 (b and c). Toluene was used as pretreatment solvent as recommended by the manufacturers.

Table 5.2 Experimental results of the screening tests with the different STARMEM™ membranes.

1-Octene volume percentage (%)	STARMEM™ membrane			
	ST-120	ST-122	ST-228	ST-240
Flux ($\text{L.m}^{-2}.\text{h}^{-1}$)				
100	3	7	15	90
80	-	-	10	50
50	-	2	6	30
20	-	-	3	15
0	0	<0.1	2	10
1-Octene in permeate (volume percentage)				
100	100	100	100	100
80	-	-	81	78
50	-	51	49	55
20	-	-	21	20
0	0	0	0	0
Catalyst Rejection (%)				
Gr1	-	>99.0	>99.0	86
Gr2Ph	-	>99.4	>99.4	85

**Figure 5.4** Permeation performances of the different STARMEM™ membranes screening tests.

It is clear from the results in Table 5.2 and Figure 5.4 that as the percentage of 1-octene in the feed increases, the total permeation flux increases exponentially for all four membranes. This phenomenon will be explained in detail in Section 5.5. At this stage, for the selection of an appropriate membrane specifically for the separation of the different Grubbs-type catalysts from the binary alkene-mixtures of 1-octene and 1-tetradecene the magnitude of the permeation flux between the different membranes is important. The relative permeation flux for the different membranes increased as follows: ST-120 < ST-122 < ST-228 << ST-240. It is obvious from the permeation results that the two membranes ST-120 and ST-122 are not suitable for the separation due their relatively low permeation performances compared to the membranes ST-228 and ST-240. Membrane ST-120 gave zero 1-tetradecene permeation for pure 1-tetradecene and a flux of $3 \text{ L.m}^{-2}.\text{h}^{-1}$ for pure 1-octene. Membrane ST-122 gave a permeation performance of less than $0.5 \text{ L.m}^{-2}.\text{h}^{-1}$ for 1-tetradecene and $7 \text{ L.m}^{-2}.\text{h}^{-1}$ for pure 1-octene. The low permeation rates were expected for the ST-120 membrane and probable for membrane ST-122 due to the membranes' relatively close MWCO (200 for ST-120 and 220 for ST-122) compared to the 1-tetradecene and 7-tetradecene molecular weights of $196.37 \text{ g.mol}^{-1}$.

It further appears from the permeation results that membrane ST-240 with the highest flux, all above $10 \text{ L.m}^{-2}.\text{h}^{-1}$, would be the preferred membrane. However, membrane ST-228 was chosen for the complete characterization of the OSN process. The main reason was that ST-228 gave better rejection performance (greater than 99%) with **Gr1** and **Gr2Ph** compared to approximately 85% for membrane ST-240. Membrane ST-228 was, therefore, selected for the OSN process in order to maximize catalyst rejection.

Therefore, according to the criteria used in evaluating which membrane to use, membrane ST-228 demonstrated to be the relatively best with:

- high catalyst recovery of greater than 99% with a MWCO of 280 g.mol^{-1} ,
- fluxes up to $15 \text{ L.m}^{-2}.\text{h}^{-1}$ for the metathesis system,
- tolerance to different organic solvents, and
- relative ease of handling with no special handling and storage requirements.

5.2.4 Concluding remarks

In this Section the selection of an appropriate membrane from a range of different commercially available polymeric membranes for the separation of Grubbs-type catalysts from alkene-mixtures was evaluated. The ST-228 membrane from MET was chosen. The ST-228 membrane performance demonstrated a relatively high permeation for 1-octene and 1-tetradecene (ranging from 2 to $15 \text{ L.m}^{-2}.\text{h}^{-1}$) with an excellent catalyst rejection of greater than 99% for precatalysts **Gr1** and **Gr2Ph**.

5.3 Separating performances of the ST-228 membrane for the 1-octene metathesis system

5.3.1 Introduction

The permeation and sorption performances of the ST-228 membrane for the metathesis system are characterized in this section. Parameters such as mixture composition (1-octene, 1-tetradecene and 7-tetradecene) used in the feed, feed operating pressure, membrane pretreat-solvent and catalyst load are varied. The effect of these parameters on the separating performances of the ST-228 membrane is evaluated with quantities such as the permeation rate (flux), catalyst rejection, solvent separation (selectivity) and degree of swelling, being measured.

5.3.2 Experimental error and reproducibility

5.3.2.1 Introduction

In this section the reliability and reproducibility of all the acquired experimental results of the OSN experiments with the dead-end apparatus are presented. The concern about using a dead-end type of setup for reliable steady-state conditions is discussed and the reproducibility and experimental error for the OSN experiments are given.

5.3.2.2 Proof of steady-state

In order to achieve a reliable representation of the ST-228 membrane separation performance during the OSN process, steady-state conditions must first be obtained where solvent permeation and catalyst rejection are not time-dependent. Whu *et al.*⁵ reported that an initial transient stage is experienced in nanofiltration membranes which lasts for about 12 hours and in that time the membranes undergo compaction. According to White and Nitsch⁴ a lined-out performance is achieved after 100 hours. Silva *et al.*⁶ also observed this phenomenon with the STARMEMTM series of membranes. They observed that a new membrane disc takes approximately three days to reach a stable solvent flux and a subsequent test with the same disc took about 1 to 2 days to stabilize. It was further found that the compaction during the transient stage was reversible. Silva *et al.*⁶ stated that the data obtained from dead-end experimental cell set-ups with experimental periods of between 1 and 3 hours may not be reliable in predicting long-term performances of a membrane.

A semi-continuous break-in-procedure, as described in Section 3.4.3 (c), demonstrated to be successful in addressing the three day unsteady fluxes, as found by Silva *et al.*⁶, and to minimize the effect of irreversible membrane compaction. All the experimental runs were conducted with this method to establish steady-state conditions. Typical observations for

acquiring steady-state fluxes are demonstrated in Figure 5.5 for 7-tetradecene at 35 bar. Five consecutive OSN runs with four depressurizing and refilling steps, as indicated by the vertical lines in Figure 5.5, were performed for the experiments. It is clear that the initial dynamic fluxes after each refilling stage have a high flux peak that after approximately 10 minutes stabilizes to the approximated steady-state flux of $0.81 \pm 0.03 \text{ kg.m}^{-2}.\text{h}^{-1}$.

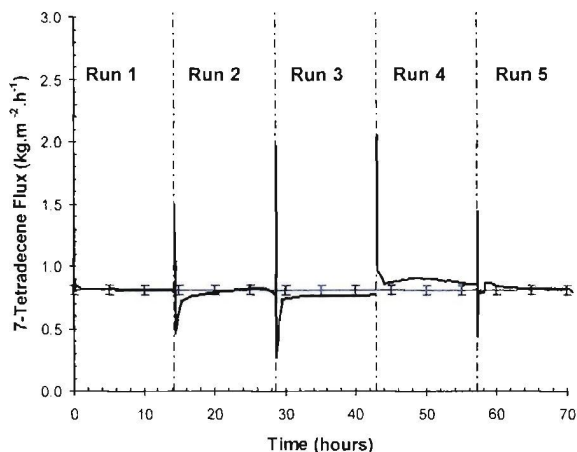


Figure 5.5 Dynamic fluxes for 7-tetradecene at 35 bar illustrating the acquisition of steady-state flux.

5.3.2.3 Experimental error

The reproducibility of results (experimental error) for the OSN process was determined by conducting at least three consecutive experimental runs for each pure component (1-octene and 7-tetradecene) at the different operating conditions (10 to 45 bars). A summary of the pure component experimental errors is presented in Table 5.3. A similar procedure was followed for the binary mixtures of 1-octene and 7-tetradecene at 30 bar, as summarized in Table 5.4. The average experimental error obtained for this study is approximately 2.9%.

Table 5.3 Repeatability and experimental errors of pure component fluxes through the ST-228 membrane.

Pressure (bar)	Total Flux (kg.m ⁻² .h ⁻¹)	Standard deviation (σ)	Confidence interval (95%)	Percentage error (%)
1-octene				
10	3.10 $\pm$ 0.05	0.039	0.09	1.52
20	6.01 $\pm$ 0.07	0.054	0.13	1.09
25	7.54 $\pm$ 0.07	0.058	0.14	0.94
30	9.19 $\pm$ 0.20	0.164	0.40	2.16
35	10.70 $\pm$ 0.22	0.145	0.45	2.08
40	12.31 $\pm$ 0.37	0.307	0.75	3.03
45	14.39 $\pm$ 0.40	0.331	0.81	2.81
1-tetradecene				
10	0.68 $\pm$ 0.04	0.045	0.08	6.02
20	1.40 $\pm$ 0.05	0.048	0.10	3.51
30	2.01 $\pm$ 0.08	0.069	0.17	4.15
40	2.62 $\pm$ 0.06	0.046	0.11	2.11
7-tetradecene				
10	0.22 $\pm$ 0.01	0.004	0.01	3.13
20	0.43 $\pm$ 0.01	0.005	0.02	1.84
25	0.54 $\pm$ 0.02	0.013	0.04	3.60
30	0.67 $\pm$ 0.03	0.023	0.06	4.19
35	0.81 $\pm$ 0.03	0.035	0.06	3.93
40	0.97 $\pm$ 0.03	0.027	0.06	3.33
45	1.06 $\pm$ 0.04	0.032	0.08	3.67

Table 5.4 Repeatability and experimental errors of binary mixtures at 30 bar.

1-Octene mass fraction (-)	Total flux (kg.m ⁻² .h ⁻¹)	Standard deviation (σ)	Confidence interval (95%)	Percentage error (%)
0.00	0.67 $\pm$ 0.03	0.023	0.06	4.19
0.10	1.00 $\pm$ 0.01	0.005	0.02	1.06
0.20	1.13 $\pm$ 0.01	0.004	0.02	0.98
0.32	1.66 $\pm$ 0.02	0.007	0.03	0.99
0.43	1.95 $\pm$ 0.03	0.012	0.05	1.39
0.50	2.42 $\pm$ 0.04	0.015	0.07	1.45
0.60	2.84 $\pm$ 0.05	0.022	0.10	1.77
0.69	3.66 $\pm$ 0.18	0.090	0.35	4.81
0.81	4.65 $\pm$ 0.09	0.039	0.18	1.91
0.92	5.78 $\pm$ 0.34	0.296	0.67	5.82
1.00	9.19 $\pm$ 0.20	0.164	0.40	2.16

5.3.2.4 Concluding remarks

In this Section the experimental results acquired for the OSN process were validated for reproducibility, and an overall average experimental error of 2.9% was found for this study. It was shown that the semi-continuous break-in-procedure, as described in Section 3.4.3 (c), could adequately be used to acquire steady-state conditions with the dead-end setup.

5.3.3 Pure solvent permeation

5.3.3.1 Introduction

In this section the permeation performance (pure solvent flux) of the ST-228 membrane is characterized and described for the substrate (1-octene), primary metathesis product (7-tetradecene) and 1-tetradecene. The effect of operating pressure, type of solvent and solvent properties is evaluated with respect to pure solvent fluxes.

5.3.3.2 Experimental results and discussion

The pure solvent fluxes of 1-octene, 1-tetradecene and 7-tetradecene at different operating pressures and room temperature are given in Table 5.3 and Figure 5.6. It is clear from Figure 5.6 that as the applied operating pressure increases in the range of 10 to 45 bar, the pure solvent fluxes for all three solvents increase linearly.

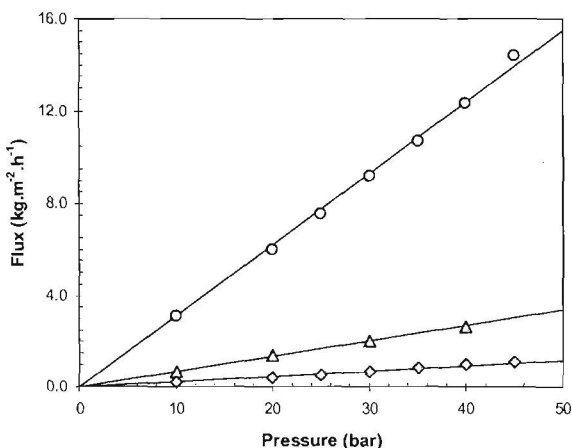


Figure 5.6 Pure solvent fluxes at different applied pressures.
[● 1-octene; ▲ 1-tetradecene; ◆ 7-tetradecene]

This linear phenomenon can be described by the classical observed relationship¹¹ of Equation 5.1

$$J_s = B(\Delta P - \Delta \Pi) \quad (5.1)$$

where J_s is the solvent flux, ΔP is transmembrane pressure and $\Delta \Pi$ is transmembrane osmotic pressure. The zero intercepts for all three solvents, as depicted in Figure 5.6, reflect the fact that $\Delta \Pi$ is negligible for pure solvent fluxes. Other researchers² also observed this linear relationship of Equation 5.1 with the STARMEMTM series of membranes in their system.

The pure solvent fluxes, as given in Figure 5.6, decrease in the order 1-octene > 1-tetradecene > 7-tetradecene at all pressures. 1-Tetradecene on average permeates three times faster than 7-tetradecene, while 1-octene permeates fourteen times faster than 7-tetradecene. The higher permeance of 1-octene relative to tetradecene was expected, due to the size differences of the molecules (MW of 196 g.mol⁻¹ for tetradecene and 112 g.mol⁻¹ for 1-octene) and the ST-228 membrane's MWCO of 280 g.mol⁻¹.

Previous studies by Machado *et al.*^{11,12} and Bhanushali *et al.*¹³ have shown that polymeric nanofiltration membrane flux depends upon certain solvent properties (viscosity, surface tension, dipole moment and Hildebrand solubility parameter), solvent structure properties (molecular size, molecular weight, solvent and molecule polarity, solvent and molecule charge) and membrane properties (surface energy, swelling, pretreatment, hydrophilicity/hydrophobicity and crosslinking). Viscosity and polarity were generally found to be the dominant properties in determining the relative magnitude of the solvent permeate fluxes. Higher solvent polarity decreased the permeate flux through a non-polar membrane, while lower solvent viscosity and surface tension increased the flux. Molecule size and structure were observed to have a relatively small influence on pure solvent flux through a polymeric membrane.^{11,12,13}

In order to explain the relative permeation difference between the three solvents some solvent properties, structure properties and solvent-membrane properties are listed in Table 5.5.

Table 5.5 Properties of 1-octene, 1-tetradecene and 7-tetradecene.

Property	1-Octene	1-Tetradecene	7-Tetradecene
<i>Solvent Properties</i>			
Viscosity (Pa.s) ^[a]	5.62x10 ⁻⁴	1.68x10 ⁻³	1.66x10 ⁻³
Density (kg.m ⁻³) ^[a]	715	775	775
<i>Solvent Structure Properties</i> (ξ)			
Molecular Weight (g.mol ⁻¹)	112.22	196.38	196.38
Equivalent molar diameter (nm) ^[b]	0.789	0.925	0.925
Effective molecular volume ($\text{\AA}^3$) ^[c]	100.9	195.1	714
Effective molecular diameter (nm) ^[d]	0.81	1.24	1.61
<i>Solvent-Membrane Properties</i>			
Swelling degree (%) ^[e]	12%	20%	20%

[a] Experimentally measured according to the method described in Section 3.6.

[b] Described by Equation 5.2.

[c] The effective molecular volume was calculated by using Material Studio.

[d] The effective molecular diameter was calculated by using Material Studio and Equation 5.3.

[e] Experimentally measured according to the method described in Section 3.5 and described in detail in Section 5.3.7.

The viscosity and density of the three solvents were experimentally measured according to the method described in Section 3.6. The equivalent molar diameter (d_m)¹⁴ is a parameter by which the size of a molecule can be described similar to the molecular weight, as given in Equation 5.2:

$$d_m = 2 \left(\frac{3V_m}{4\pi N} \right)^{\frac{1}{3}} \quad (5.2)$$

where V_m is the molar volume of the solvent and N is Avogadro's number. Every molecule is considered as equivalent to a sphere with a diameter of d_m . The equivalent molar diameter is similar to the Stokes diameter and does not take structure into account (e.g. long chained molecules are reduced to a sphere). Another parameter by which the size of a molecule can be described, is the effective molecular diameter (d_e) as proposed by van der Bruggen,¹⁴ which takes into account the long chain geometry of the different alkenes. The effective molecular diameter is calculated with the optimized geometry of a solvent molecule and Equation 5.3:

$$d_e = \frac{\pi}{4} H + \frac{D}{2} \quad (5.3)$$

where H is the height and D the base diameter, for the smallest cylinder containing the molecule as presented in Figure 5.7. A similar procedure as the effective molecular diameter proposed by van der Bruggen¹⁴ can be followed to calculate the effective molecular volume (V_e). By assuming that the molecule is cylindrical and from the height and base diameter, as shown in Figure 5.7, the effective molecular volume can be calculated.

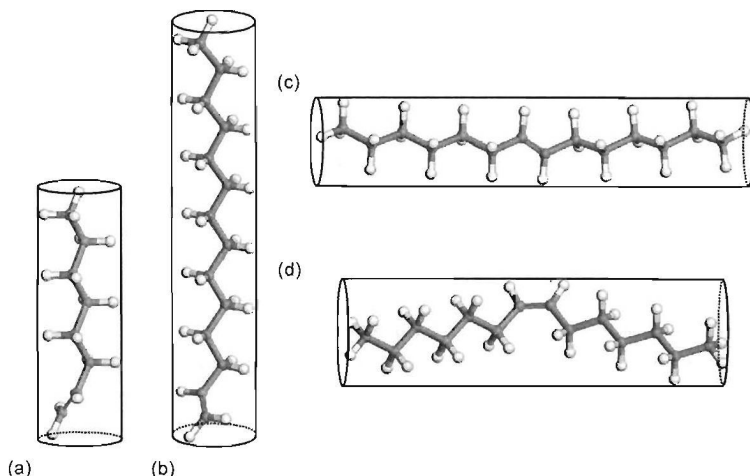


Figure 5.7 Visual representation of the optimised molecular structures of (a) 1-octene, (b) 1-tetradecene, (c) trans-7-tetradecene and (d) cis-7-tetradecene.

The swelling degree (SD) of the membrane or sorption capabilities of the solvent-membrane interaction was measured according to the method described in Section 3.5 and calculated with Equation 5.4:

$$SD = \left(\frac{M_{wet} - M_{dry}}{M_{dry}} \right) \cdot 100\% \quad (5.4)$$

where M_{dry} is the initial dried membrane mass and M_{wet} is the "wetted" membrane mass.

As discussed previously the predominant properties according to Machado *et al.*^{11,12} that account for the relative difference in permeation between solvents is the solvent viscosity and polarity. The viscosity of 1-octene (5.62×10^{-4} Pa.s) is approximately three times lower than 7-tetradecene (1.66×10^{-3} Pa.s) and 1-tetradecene (1.68×10^{-3} Pa.s) while the polarities of these three solvents are similar. Viscosity and polarity are, therefore, not the only parameters to influence the relative magnitude of the solvent permeate fluxes through the ST-228 membrane.

The combined effects of viscosity and swelling degree (12% for 1-octene and 20% for both tetradecenes) could only account for approximately 35% of the relative permeation differences between 1-octene and the two tetradecenes. This clearly indicates that the solvent and solvent-membrane properties are not the sole parameters to influence the relative magnitude of solvent permeate fluxes through the ST-228 membrane. Furthermore, in comparing the solvent and solvent-membrane properties of 1-tetradecene and 7-tetradecene, it is clear that viscosity, polarity and swelling degree of both molecules are almost identical and cannot account for the difference in fluxes.

The three times higher flux of 1-tetradecene to 7-tetradecene is well explained by the solvent structure properties such as the effective molecular volume. The effective molecular volume of 7-tetradecene ($714 \text{ \AA}^3$) is approximately three times that of 1-tetradecene ($195.1 \text{ \AA}^3$) which corresponds well with the difference in flux. It can thus be concluded that in the case of 1-tetradecene and 7-tetradecene, the difference in fluxes through the ST-228 membrane can mainly be ascribed to a difference in molecular structure. In the case of 1-octene and the two tetradecenes the combined affects of the difference in viscosity, swelling degree and structural size explain the relative difference in magnitude of the solvents through the ST-228 membrane. It can thus be concluded that the combined influences of viscosity, membrane swelling and molecular size and structure best predict the relative magnitude of the pure solvent fluxes through the ST-228 membrane.

5.3.4 Binary-mixtures permeation and separation

5.3.4.1 Introduction

In this section the permeation and separation performances of the ST-228 membrane are characterized and described for the binary mixtures of the reagent (1-octene) and main metathesis product (7-tetradecene). The effects of solvent properties and interaction-properties are evaluated with respect to the total binary flux.

5.3.4.2 Experimental results and discussion

The total binary solvent fluxes of 1-octene and 7-tetradecene at an operating pressure of 30 bar and room temperature are given in Table 5.4 and Figure 5.8. It is clear from Figure 5.8 that as the feed concentration of 1-octene increases the total flux increases exponentially. The same exponential trend was observed by Ebert *et al.*¹⁵ for solvent mixtures of ethanol and n-pentane or n-hexane.

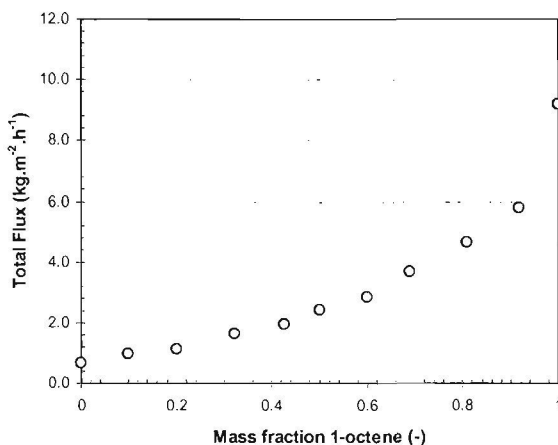


Figure 5.8 Binary solvent fluxes of 1-octene and 7-tetradecene at 30 bar.

This observed exponential trend can usually be attributed to the combined effects of viscosity, sorption and structural size, as was briefly mentioned in Section 5.3.3 for the relatively pure solvents fluxes. According to Bhanushali *et al.*¹³ the combined effects of solvent viscosity, molar volume (that is an indication of solvent size), surface tension of the solid membrane material and sorption capacity as given in Equation 5.5 would describe the permeation of any separation process fairly accurately.

$$J \propto A \propto \left(\frac{V_m}{\eta} \right) \left(\frac{1}{\phi^n \gamma_{sv}} \right) \quad (5.5)$$

Where V_m is the solvent molar volume, η is the solvent viscosity, ϕ is the sorption value for the solvent, n is an empirical constant and γ_{sv} is the surface tension or energy.

The viscosities for the binary-mixtures of 1-octene and 7-tetradecene were experimentally measured by the method discussed in Section 3.6 and are graphically presented in Figure 5.9. The Kendall and Monroe correlation,³⁴ as presented in Equation 5.6, generally shows good correlation for different hydrocarbon mixtures and was found to describe the 1-octene and 7-tetradecene system accurately with a Pearson correlation of approximately 0.997.

$$\eta_{mixture} = \left(\sum_i^n x_i \eta_i^{V_i} \right)^3 \quad (5.6)$$

where x is the mole fractions of the various pure components in the mixture and η is the viscosity of the various pure components.

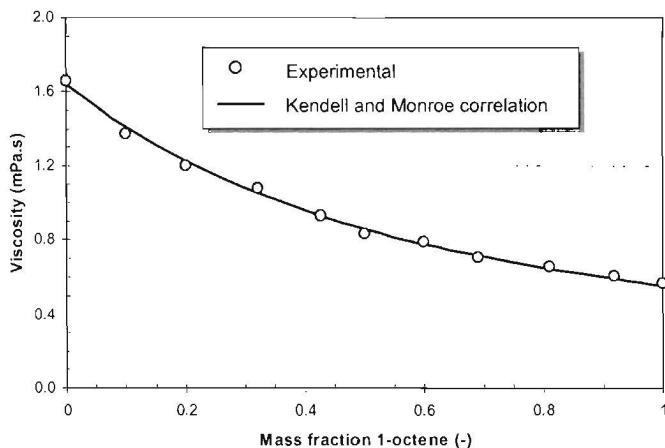


Figure 5.9 Viscosities of binary mixtures of 1-octene and 7-tetradecene at room temperature. (● Experimental; — Kendall and Monroe correlation³⁴)

The experimental sorption value is discussed in detail in Section 5.3.7. The surface tension or energy term (γ_{sv}) of the ST-228 membrane was not determined for this study. Since contact angle and surface energy are related through Young's equation, contact angles can, therefore, be used to estimate surface energies. The contact angles of the different components (1-

octene, 7-tetradecene and water) were measured by the method described in Section 3.6.3. It was found that the 1-octene and 7-tetradecene liquid droplet dispersed completely over the membrane surface and absorbed into the membrane which indicate a contact angle of approximately zero, and therefore the surface tension or energy is not expected to play a significant role.

It was found, as can be seen in Figure 5.10, that the correlation proposed by Bhanushali *et al.*¹³ in Equation 5.5 correlates well with the binary permeation fluxes of 1-octene and 7-tetradecene mixtures. The Pearson correlation is approximately 0.9654 with a small underestimation near pure 1-octene. This is possibly due to the step jump from 90% 1-octene (flux of approximately 6 kg.m⁻².h⁻¹) to pure 1-octene (flux of approximately 9 kg.m⁻².h⁻¹). It can, therefore, be concluded that the permeation of the binary-mixtures of 1-octene and 7-tetradecene through the ST-228 membrane can be described by the combined influences of viscosity, membrane swelling and molecular size and structure (such as molar volume).

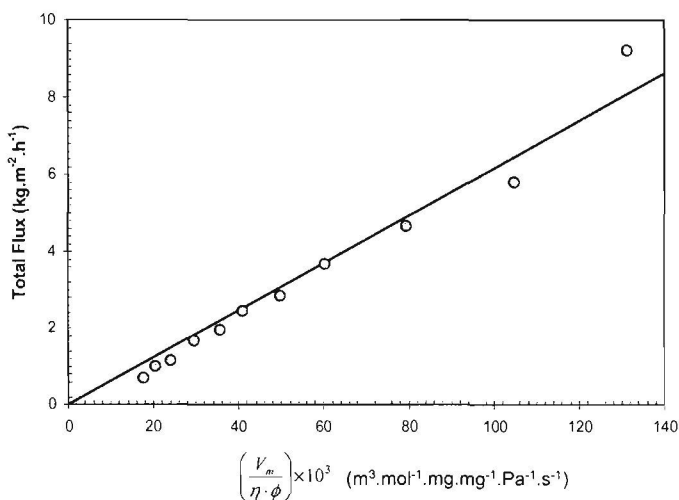


Figure 5.10 Correlation of the total binary-fluxes of 1-octene and 7-tetradecene with viscosity, molar volume and sorption.

Another useful parameter in describing the permeation of solvent mixtures such as the binary mixture of 1-octene and 7-tetradecene through a membrane, is the degree of solvent separation. The degree of solvent separation is the ratio between the composition of a solvent in the permeate and retentate. It is preferred in this study that the PMP (7-tetradecene) for the metathesis reaction should permeate through the membrane and the reagent (1-octene) and the catalyst be rejected. The binary solvent separation performance of 1-octene and 7-tetradecene for different feed compositions ranging from pure 1-octene to 7-tetradecene is given in Figure 5.11.

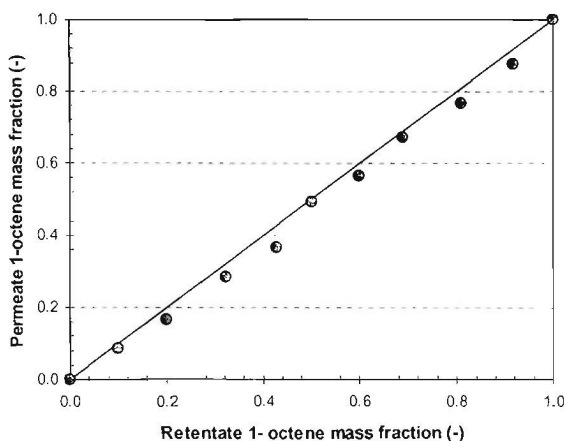


Figure 5.11 Separation curve of 1-octene and 7-tetradecene.

It was found by GC-analyses that the compositions in the permeate and retentate for the binary mixtures of 1-octene and 7-tetradecene do not vary significantly, as shown in Figure 5.11, which points to a degree of solvent separation of approximately one over the entire range. This degree of solvent separation of one indicates a preferred solvent non-separation for the 1-octene metathesis system. Solvent separation^{16,17} and non-separation⁶ have previously been reported for OSN membranes. Silva *et al.*⁶ for example found with the ST-122 membrane a non-separation performance between mixtures of methanol-toluene and toluene-ethyl acetate. This non-separation of the two solvents 1-octene and 7-tetradecene could be attributed to the ST-228 membrane's MWCO of 280, compared to 7-tetradecene's molecular weight of 196 g.mol⁻¹ and 1-octene's of 112 g.mol⁻¹. It could, therefore, be concluded that the binary mixture of 1-octene and 7-tetradecene could be considered as a pseudo single component in the separation performance of the ST-228 membrane.

5.3.5 Catalyst rejection from post-reaction mixtures

5.3.5.1 Introduction

It is preferred in this study that the different metathesis catalysts (Gr1, Gr2, HGr1, HGr2 and Gr2Ph) be retained for possible re-use by the ST-228 membrane from their post-reaction mixtures. The ability of the ST-228 membrane to retain the different metathesis catalysts from a post metathesis reaction was tested in rejection studies as described in Section 3.4.3 and characterize by the rejection (R) parameter as calculated by Equation 5.7:

$$R = \left(1 - \frac{C_P}{C_R} \right) \cdot 100\% \quad (5.7)$$

where C_P is the final concentration of catalyst in the permeate and C_R final concentration of the catalyst in the retentate.

In this Section the permeation and catalyst rejection performances of the ST-228 membrane are characterized and described for post-reaction mixtures of the 1-octene metathesis system. The influences of operating pressure and catalyst load are presented with respect to total flux and catalyst rejection.

5.3.5.2 Experimental results and discussion

The experimental results obtained for the ST-228 membrane's catalyst rejection performances are given in Table 5.6 and Figure 5.12.

Table 5.6 Rejection performances of ST-228 for the metathesis system of 1-octene and different Grubbs-type catalysts.

Precatalyst	Precatalyst feed mass (mg)	Pressure (bar)	Rejection ^[a] (-)
Gr1	17.0	20	> 0.974
Gr1	28.0	20	> 0.984
Gr1	15.4	30	> 0.971
Gr1	17.0	30	> 0.974
Gr1	22.0	30	> 0.980
Gr1	30.8	30	> 0.985
Gr1	34.3	30	> 0.987
Gr1	44.0	30	> 0.990
Gr1	17.0	40	> 0.974
Gr1	28.0	40	> 0.984
Gr2	17.0	30	> 0.974
HGr1	17.0	30	> 0.974
HGr2	17.0	30	> 0.974
Gr2Ph	28.0	30	> 0.986
Gr2Ph	17.0	40	> 0.994

^[a] Detection limit of AAS is 9 ppm. All retentate concentrations were measured the same as the corresponding feed concentrations and all the permeation concentration was measured as zero.

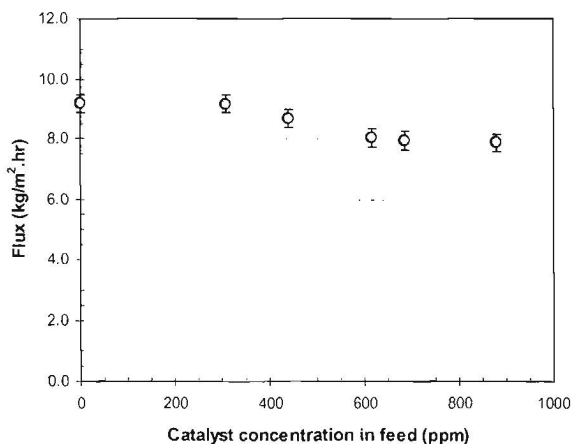


Figure 5.12 Effect of catalyst **Gr1** concentration on the total flux with the ST-228 membrane at 30 bar.

It is clear from these results that the catalyst's rejection for all the different Grubbs-type catalysts with the ST-228 membrane is approximately >97%. The high catalyst rejection with the ST-228 membrane indicates that it is possible to successfully separate the Grubbs-type catalysts from their post-reaction mixture with the OSN process.

It is clear from Figure 5.12 that as the catalyst concentration increases the total flux decreases. This decreasing effect of flux with increasing catalyst concentration is consistent with previously published data.^{2,5} A possible explanation for this phenomenon is concentration polarization or fouling. It was observed that, after a rejection experiment, small amounts of black precipitate were formed on the membrane surface, as shown in Figure 5.13.

The membrane and membrane cell were thoroughly washed out with pure 1-octene after each catalyst rejection experiment to limit fouling. Furthermore, the experiments were performed in a semi-random order. This possible indicates that fouling was partially reversible and that concentration polarization might be responsible for the observed flux decrease.

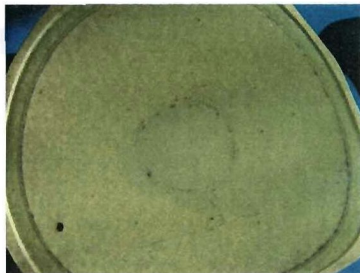


Figure 5.13 Visual illustration of the ST-228 membrane with small amounts of catalyst precipitates after the rejection studies, indicating a possible partial fouling.

5.3.6 Influence of solvents used in membrane pretreatment

5.3.6.1 Introduction

It is customary to pretreat nanofiltration membranes before use, in order to remove any unreacted residual solvents from the membrane manufacturing process. This is also true for organic systems, where membranes are pretreated prior to use to optimize its performances for a particular separation. The ST-228 membrane is supplied in a dry form with lubricating oil on top of the membrane to protect it from drying out. According to the manufacturers this preservation oil can easily be washed out with a solvent, such as toluene, by allowing the solvent to permeate at a pressure of 20 to 40 bar for at least 15 minutes. It is clear from the literature^{1,7} that this type of pretreatment has a significant effect on the membrane characteristics. For example, Zhao *et al.*¹ observed that the methanol flux varied considerable through the ST-228 membrane when treated with different solvents, ranging from 425 to 30 L.m⁻².h⁻¹.

In this Section, the effect of four different solvents used to pretreat the ST-228 membrane for the permeation performances of 1-octene, 1-tetradecene and water will be discussed. Various ST-228 membranes were pretreated with two non-polar (1-octene and toluene) and two polar (ethanol and acetic acid) solvents, according to the procedure given in Section 3.4.2.2. Some of the main properties of the four solvents are given in Table 5.7

Table 5.7 Properties of solvents used during membrane pretreatment.

Solvent	Chemical Structure	Polarity	E _r -scale (-)	Dielectric constant (-)	Dipole-moment (10 ⁻³⁰ xC.m)
1-Octene		Non-polar	-	2.1	-
Toluene		Non-polar	0.099	2.38	1
Acetic acid		Polar	0.648	6.17	5.6
Ethanol		Polar	0.654	24.55	5.8

5.3.6.2 Experimental results and discussion

The results obtained from permeating 1-octene and 1-tetradecene at pressures between 10 and 40 bar with the different pretreated ST-228 membranes are presented in Table 5.8, Figure 5.14 and Figure 5.15.

Table 5.8 Experimental results of the different pretreated membranes permeation of 1-octene and 1-tetradecene.

Component	Solvent used for pretreatment			
	1-Octene	Toluene	Acetic-Acid	Ethanol
1-Octene Flux (kg.m⁻².h⁻¹)				
10 bar	3.15 ± 0.07	3.10 ± 0.05	4.06 ± 0.08	not measured
20 bar	5.74 ± 0.23	6.01 ± 0.07	7.01 ± 0.06	4.00 ± 0.24
30 bar	8.16 ± 0.36	9.19 ± 0.20	10.21 ± 0.06	6.57 ± 0.43
40 bar	not measured	12.31 ± 0.37	not measured	10.03 ± 0.53
1-Tetradecene Flux (kg.m⁻².h⁻¹)				
10 bar	0.571 ± 0.03	0.68 ± 0.04	0.33 ± 0.02	not measured
20 bar	1.348 ± 0.04	1.40 ± 0.05	0.85 ± 0.10	0.62 ± 0.03
30 bar	2.195 ± 0.05	2.01 ± 0.08	1.12 ± 0.08	0.95 ± 0.04
40 bar	not measured	2.62 ± 0.06	not measured	1.36 ± 0.08
Water Flux (kg.m⁻².h⁻¹)				
40 bar	Not detected	Not detected	Insignificant ^[a]	0.15 ± 0.02

^[a] Small amounts of water were permeated, approximately 2g in 3 days.

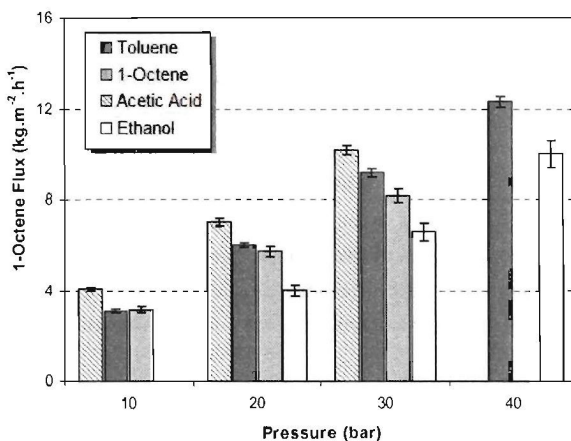


Figure 5.14 1-Octene permeate flux through the different pretreated ST-228 membranes.

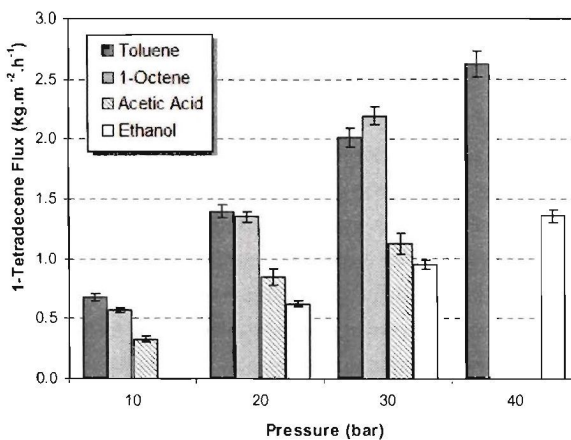


Figure 5.15 1-Tetradecene permeate flux through the different pretreated ST-228 membranes.

It is clear from Figure 5.14 and Figure 5.15 that as the applied pressure increases, the permeation of 1-octene and 1-tetradecene also increases according to the classic linear trend² observed, as discussed in Section 5.5.2 and Equation 5.1. It can, therefore, be concluded that the use of different pretreated solvents had no significant effect on the classical linear response when the applied pressure was varied.

It is, however, clear from the results that the use of different pretreated solvents has a significant effect on the permeation rate of 1-octene and 1-tetradecene through the ST-228 membrane. The 1-octene permeation rate, as given in Figure 5.14, decreases with pretreated solvent in the order of acetic acid > toluene > 1-octene > ethanol. The 1-tetradecene permeation rate, as given in Figure 5.15, decreases in the order of pretreated solvent: toluene > 1-octene > acetic acid > ethanol. It appears from these results that the non-polar pretreated solvents (toluene and 1-octene) give relatively higher overall permeation rates for 1-tetradecene and 1-octene compared to the polar pretreated solvents (acetic acid and ethanol). The only exception to this observation is the permeation of 1-octene with an acetic acid pretreated membrane.

Garcia *et al.*⁸ and Jirjis^{9,10} suggested that the effect of pretreatment is a gradual change in polarity of the membrane. As ST-228 is a hydrophobic type of membrane, non-polar components such as 1-tetradecene and 1-octene will preferentially permeate through the membrane. This is true, as it was found in this study and by Zhao *et al.*¹ that if the ST-228 membrane is pretreated with a non-polar solvent, such as toluene or 1-octene, then zero water flux is observed. However, if the ST-228 membrane is pretreated with a polar solvent such as ethanol a non-zero water flux is observed and the permeation rates for 1-tetradecene and 1-octene decreases by approximately 50% and 30%, respectively. This phenomenon can be ascribed to the change in polarity of the membrane due to the solvent used in the pretreated process. The solvent could be forming chemical bonds or interacting with the membrane, resulting in a chemical stability of the membrane towards the solvent with a similar surface tension and energy. The more polar pretreated solvent changes the polarity of the ST-228 membrane to a less hydrophobic membrane and, therefore, introduces a resistance against mass transport for the non-polar permeating components, due to the high surface tension between the non-polar component and the membrane. It is, therefore, recommended that, for optimal permeating performance, the solvent used to pretreat the membrane must have approximately the same polarity as the permeating components.

5.3.7 Sorption characteristics

5.3.7.1 Introduction

In this section the sorption characteristics of the ST-228 membrane are evaluated with respect to the amount of pure and binary-mixture of the reagent (1-octene) and main metathesis product (7-tetradecene) absorbed.

5.3.7.2 Experimental results and discussion

Swelling of the membrane occurs when polymeric membranes are used. The liquid, in contact with the membrane, dissolves into it and causes membrane swelling. Swelling tends to alter the membrane properties and generally leads to higher permeability and lower solvent selectivity. The swelling ratio (M_{∞}) and swelling degree (SD) are used interchangeably to describe the swelling and solvent-membrane interaction of the membrane. The degree of swelling or sorption capabilities of the solvent-membrane interaction is defined as the amount of equilibration solution sorbed in the membrane ($M_{wet} - M_{dry}$) compared to the mass of the unswollen membrane (M_{dry}), i.e. the swelling degree is the mass % uptake at equilibrium:

$$SD = \left(\frac{M_{wet} - M_{dry}}{M_{dry}} \right) \cdot 100\% \quad (5.8)$$

where M_{dry} is the initial dried membrane mass and M_{wet} is the "wetted" membrane mass.

The swelling ratio (M_{∞}) is the amount of solution absorbed in the membrane when equilibrium between the mixture and the membrane is obtained, compared to the initial mass of the membrane:

$$M_{\infty} = \left[\frac{M_{wet} - M_{dry}}{M_{dry}} \right] \quad (5.9)$$

The experimental swelling ratio as measured by the method described in Section 3.5 and calculated by using Equation 5.8 is given in Figure 5.16 for the binary system of 1-octene and 7-tetradecene with the ST-228 membrane.

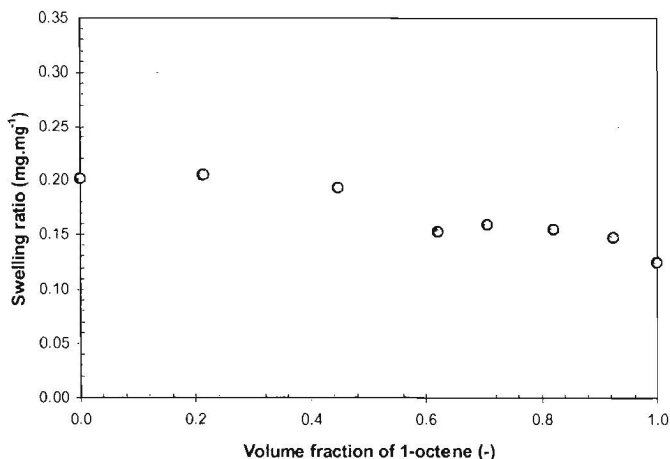


Figure 5.16 Swelling ratio for mixtures of 1-octene and 7-tetradecene with a ST-228 membrane.

It is clear from Figure 5.16 that the swelling ratio decreases as the 1-octene concentration increases. This decrease of the swelling ratio parameter with an increase in 1-octene concentration suggests that the ST-228 membrane is preferentially swollen by 7-tetradecene.

In order to gain further insight into the sorption characteristics of the ST-228 membrane with the binary system of 1-octene and 7-tetradecene, the solvent-polymer interaction parameter, χ , as described by the Flory-Rehner theory and given in Equation 5.11 for pure solvents, will be used. The membrane can be considered as a swollen gel or a network with crosslinks caused by crystalline regions, chain entanglements or Van der Waals interactions. The swelling behaviour of such a network can be expressed by the Flory-Rehner theory and the free energy change, ΔG , involved in the mixing of the pure solvent with the initially pure polymer, consists of two parts: the free energy of mixing, ΔG_M , and the elastic free energy, ΔG_{el} :

$$\Delta G = \Delta G_M + \Delta G_{el} \quad (5.10)$$

At swelling equilibrium, $\Delta G = 0$, and from the Flory-Rehner theory for pure-solvent and/or polymer-nonsolvent with small amounts of nonsolvents in the membrane:

$$\chi_{i3} = -\frac{[\ln(1 - \phi_3) + \phi_3]}{\phi_3^2} \quad (5.11)$$

where χ_{i3} is an interaction parameter for the pure component i in the polymer (membrane) and ϕ_3 the volume fraction of the polymer (membrane) in the polymer-penetrant mixture.

The dimensionless parameter χ is, therefore, determined by the energies that characterize the interactions between the pairs of polymer segments, pair of penetrant molecules and one polymer segment with one penetrant molecule. As this interaction between polymer and penetrant increases, the amount of liquid inside the polymer increases and χ decreases. It is well-known that when χ is large (>2), the solvent-membrane interaction is small, but strong solvent-membrane interactions exist for small values ($0.5 < \chi < 2.0$).³³ The calculated solvent-membrane interaction parameter for 7-tetradecene is 1.26 and for 1-octene is 1.58 which suggests that the ST-228 membrane has a relatively higher affinity for 7-tetradecene than for 1-octene. Furthermore, the low values of the interaction parameter (between 0.5 and 2) indicate that solvent-membrane interaction has a significant influence on the permeation rates, as was observed in Section 5.3.3 and 5.3.4.

5.3.8 Concluding remarks

The permeation and sorption performances of the ST-228 membrane for the 1-octene metathesis system were characterized in this section. It was found that the combined influences of viscosity, membrane swelling and molecular size and structure (such as the equivalent molar diameter, effective molecular volume etc.) best described the relative magnitude of the pure solvent fluxes through the ST-228 membrane. It was further found that the permeation rate for the 1-octene metathesis system could be described by a similar proposed correlation of Bhanushali *et al.*¹³ as given in Equation 5.5:

$$J \propto A \propto \left(\frac{V_m}{\eta \times \phi^n} \right) \quad (5.5)$$

The binary system of 1-octene and 7-tetradecene also demonstrated a preferentially non-solvent-separation. A greater than 97% rejection was obtained for all the Grubbs-type catalysts with the ST-228 membrane and an increase in catalyst concentration affected a decrease in the permeation rate. It was shown that the ST-228 membrane preferentially absorbed 7-tetradecene with a 20% swelling degree compared to a 12% for 1-octene.

5.4 Modelling of binary mixture through the ST-228 membrane

5.4.1 Introduction

Levenspiel³⁰ made the following comment regarding modelling in chemical engineering:

“May I end up by suggesting the following modeling strategy: always start by trying the simplest model and then only add complexity to the extent needed. This is the \$10 approach, or as Einstein said, ‘Keep things as simple as possible, but not simpler’.”

In view of this comment it is, therefore, the aim of this section to describe the transport of the binary mixtures (1-octene and 7-tetradecene) for the OSN process with the \$10 approach. The modelling strategy will start with the classical simple models of Pore-flow (Hagen-Poiseuille) and Solution Diffusion as described in detail in Section 2.4 and summarized in Equations 5.12 and 5.13. Thereafter, adjustment of these models and complexity will be added to the extent needed, in order to fairly accurately predicting the binary fluxes of 1-octene and 7-tetradecene through the ST-228 membrane.

$$N_v = -\frac{d_{pore}^2}{32l\eta} \frac{\varepsilon}{\tau} \Delta p \quad (5.12)$$

where d_{pore} is the diameter of the pore in the membrane, ε is the porosity of the membrane, τ is the tortuosity factor of the membrane, l length of membrane thickness, η is the viscosity of the mixture, Δp is the pressure in Pa and N_v is the total volume flux.

$$n_1 = P_{L,m}^{mass} \left(\omega_{1,f} - \frac{n_1}{n_1 + n_2} \exp \left\{ -\frac{V_1 \Delta p}{RT} \right\} \right) \quad (5.13a)$$

$$n_2 = P_{2,m}^{mass} \left(\omega_{2,f} - \frac{n_2}{n_1 + n_2} \exp \left\{ -\frac{V_2 \Delta p}{RT} \right\} \right) \quad (5.13b)$$

where n_i is the mass flux of component i , $\omega_{i,f}$ is the mass fraction of species i , R is the gas constant, T is the temperature in K, Δp is the pressure in Pa, V_i is the molar volume of species i and P_i^{mass} is the mass permeability parameter for component i ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$).

5.4.2 Pore-flow models

In order to model the system with the pore-flow model of Hagen-Poiseuille (Equation 5.12), the parameters: porosity, tortuosity, thickness and pore size diameter of the membrane are required. As these parameters were not experimentally determine, two models, or approaches, were used in describing these parameters. The two models (named HP-1 and HP-2) were based on the proposed idea of Silva *et al.*⁶ as discussed in detail in Section 2.4.

The permeability term $\left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix}$ in Equation 5.12 is determined by the physical properties of the membrane and when the ST-228 geometry remains constant, i.e. if there is no membrane compaction or membrane swelling then this term should be independent of solvent mixtures used. This concept was used by Silva *et al.*⁶ for the one-parameter HP model, called HP-1, as given in Equation 5.14:

$$N_v = \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix} \cdot \frac{1}{\eta} \Delta p \quad (5.14)$$

It was found that the derived values for the permeability term $\left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix}$ in Equation 5.14 for the pure components differ from each other with pure 1-octene equal to 6.581×10^{-16} m and 7-tetradecene equal to 1.311×10^{-16} m. Silva *et al.*⁶ also found this deviation for their system of methanol, toluene and ethyl acetate with the ST-122 membrane and used the arithmetic average of these specific permeabilities for the HP-1 model. The permeability term for this study was, therefore, calculated with the arithmetic average of the two pure components values.

For the two-parameter Hagen-Poiseuille model, called HP-2, Silva *et al.*⁶ incorporated the idea that the physical properties of the membrane change with the solvent due to different solvent-polymer interactions, i.e. different degrees of swelling. For this an approximate approach was used to describe the term $\left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix}$ for the solvent mixtures by considering a concentration average of the pure solvent values, i.e. going back to Equation 5.12, assuming no viscous selectivity and a linear pressure profile inside the membrane the relation as given in Equation 5.15 is obtained by using the two pure solvent parameters to describe the total flux of the binary mixture:

$$N_v = \frac{\Delta p}{\eta} \left\{ \bar{V}_1 \cdot c_{1,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right) + \bar{V}_2 \cdot c_{2,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right) \right\} \quad (5.15)$$

where d_{pore} is the diameter of the pore in the membrane, ε is the porosity of the membrane, τ is the tortuosity factor of the membrane, η is the viscosity of the mixture, Δp is the pressure in Pascal, $\bar{V}_i$ is the molar volume of species i and N_v is the total volume flux.

The predicted values of the two pore-flow models (HP-1 and HP-2) compared to the experimental data are presented in Figure 5.17.

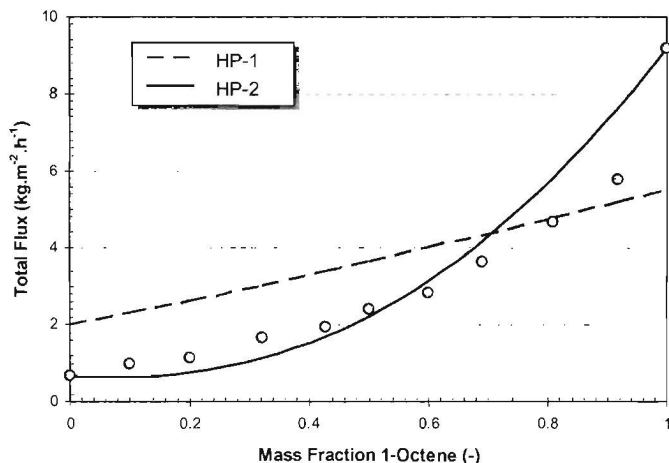


Figure 5.17 Comparison of the experimental flux data of 1-octene/7-tetradecene through the ST-228 membrane at 30 bar and at 25 °C with predicted pore-flow models.

It is clear from these results that the one-parameter model (HP-1) poorly predict the experimental data, while the HP-2 model provides a much better prediction. The reason for the predictive failure of the HP-1 model can be attributed to the fact that the HP-1 model use only viscosity as the dependent parameter in describing the transport through the membrane and no membrane-solvent interaction is considered. Model HP-2, however, indirectly takes into account that the permeability change due to membrane-solvent interaction, such as the swelling difference of 1-octene and 7-tetradecene with the ST-228 membrane. It is shown in Section 5.3.3 that the combined effects of the viscosity, sorption and structural size describe the relative difference in magnitude of 1-octene and 7-tetradecene best. It appears, therefore, that a three-parameter model with viscosity, sorption and solvent volume will describe this system more accurately.

5.4.3 Solution-Diffusion model

The solution-diffusion model as proposed by Silva *et al.*⁶ (Equation 5.13a and 5.13b), called SD-1, and discussed in detail in Section 2.4, was used to model the binary mixture of 1-octene and 7-tetradecene. It is clear from Equations 5.13a and 5.13b that the SD-1 model is also effectively a two-parameter model as the permeability for each solvent is needed to solve the equations. In this study the mass permeability terms of Equations 5.13a and 5.13b for 1-octene and 7-tetradecene were assumed to be independent of composition and determined by the pure solvent flux data. The mass permeability terms of Equations 5.13a and 5.13b for pure 1-octene was calculated as $0.01466 \text{ kg.m}^{-2}.\text{s}^{-1}$ and $0.000698 \text{ kg.m}^{-2}.\text{s}^{-1}$ for pure 7-tetradecene. The predicted values of the SD-1 model and HP-2 compared to the experimental data are presented in Figure 5.18.

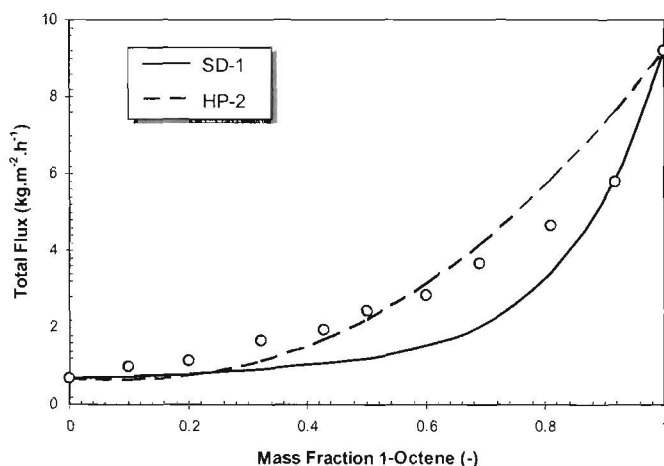


Figure 5.18 Comparison of the experimental flux data of 1-octene/7-tetradecene through ST-228 (at 30 bar applied pressure and at 25 °C) and the calculated values by the solution-diffusion and Hagen–Poiseuille two-parameter model.

It is clear from Figure 5.18, that the SD-1 model underestimates the experimental data. Silva *et al.*⁶ also observed (with no explanation) this underestimation for the binary mixture of ethylacetate and toluene. A possible reason for this underestimation can be because it is assumed in the SD-1 model that the permeability terms of 1-octene and 7-tetradecene are independent of composition.

Another empirical solution-diffusion-based model presented by Bhanushali *et al.*¹³ (Equation 5.16) combines different approaches of existing models by introducing four parameters: the solvent viscosity, the molar volume V_m (as a measure of the molecular size), the surface tension of the solid membrane material and a sorption value (as a measure for membrane-solvent interactions).

$$J \propto A \propto \left(\frac{V_m}{\eta} \right) \left(\frac{1}{\phi^n \gamma_{sv}} \right) \quad (5.16)$$

where V_m is the solvent molar volume, η is the solvent viscosity, ϕ is the sorption value for the solvent and n is an empirical constant and γ_{sv} is the surface tension or energy.

As the surface tension and surface energy of the ST-228 membrane was not determined for this study, the γ_{sv} term was neglected, as discussed in Section 5.3.4. Furthermore, a model called SD-2 based on the four-parameter model of Bhanushali *et al.*¹³ (Equation 5.16) and the HP-2 model (Equation 5.15) is proposed as given in Equation 5.17.

$$N_V = \frac{\Delta p}{\eta \cdot \phi^n} \left\{ \bar{V}_1 \cdot c_{1,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right) + \bar{V}_2 \cdot c_{2,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right) \right\} \quad (5.17)$$

where d_{pore} is the diameter of the pore in the membrane, ε is the porosity of the membrane, τ is the tortuosity factor of the membrane, η is the viscosity of the mixture, Δp is the pressure in Pascal, V_i is the molar volume of species i , N_V is the total volume flux and n an empirical constant. The symbol ϕ in Equation 5.17 is the sorption value or swelling ratio (M_∞) as defined and described in Section 5.3.7 (Equation 5.5 and 5.18). The sorption value (ϕ) correlates the interaction between the membrane and solvent as defined by Equation 5.18:

$$\phi = \left(\frac{M_{wet} - M_{dry}}{M_{dry}} \right) \quad (5.18)$$

where M_{dry} is the initial dried membrane mass and M_{wet} is the “wetted” membrane mass. The experimental sorption characteristics of ST-228 with the binary mixtures of 1-octene and 7-tetradecene are discussed in detail in Section 5.3.7. The empirical constant n was determined with regression to be approximately 3 for the 1-octene/7-tetradecene system.

The predicted values of the SD-1 model and the proposed SD-2 model are compared to the experimental data as presented in Figure 5.19. It is clear from these results that both models

SD-1 and SD-2 describe the transport of the binary-mixtures of 1-octene and 7-tetradecene in the same way, which implies that the permeability parameters in Equation 5.13a and 5.13b are equal to: $P_{i,m}^{mass} = \frac{\bar{V}_i}{\eta \cdot \phi^n} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)$. This correlates well with the finding of Bhanushali *et al.*¹³ that

stated that the permeability parameter is proportional to the molar volume and inversely proportional to the viscosity and sorption-parameter, see Equation 5.16. It is possible that the underestimation of both models SD-1 and SD-2 is due to the fact that no solvent-solvent structural size interaction parameter is used in describing the transport as discussed in Section 5.3 for the binary mixtures.

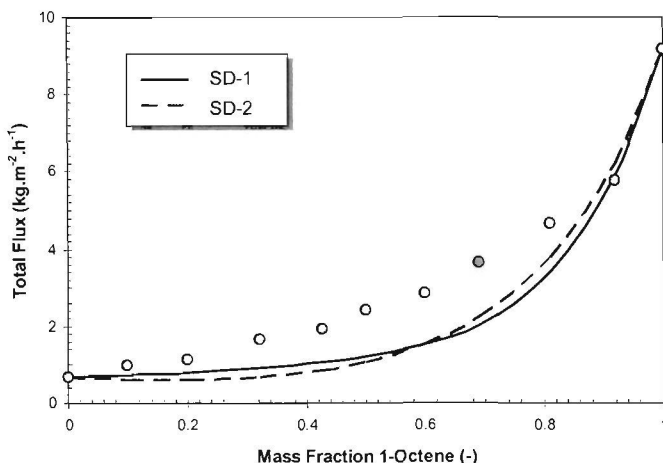


Figure 5.19 Comparison of the experimental data of 1-octene/7-tetradecene flux through ST-228 (at 30 bar applied pressure and at 25 °C) and the calculated values by the solution-diffusion (SD-1) and proposed solution-diffusion (SD-2) models.

5.4.4 Adapted Hagen–Poiseuille and solution-diffusion model

It is shown in Section 5.3.3 and 5.3.4 that the combined effects of the viscosity, sorption and structural size (not merely the molar volume) describe the relative difference in magnitude of 1-octene and 7-tetradecene best. It is therefore, proposed in this study that the transport of 1-octene/7-tetradecene through the ST-228 membrane will more accurately be described by the

permeability parameter $P_{i,m}^{mass} = \frac{\bar{V}_i}{\eta \cdot \phi^n} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)$ as derived for model SD-2 and an additional

structural sizing fraction parameter (f) that estimates solvent-solvent structural interactions. This

idea of a sizing fraction parameter is based on the fact that 1-octene is approximately seven times smaller than 7-tetradecene on a cylindrical volume basis and two times smaller on a diameter basis which implies that 1-octene must permeate faster than 7-tetradecene. Furthermore, it is possible for the fast permeating molecule to facilitate the slow permeating molecule in permeating faster and *visa versa*.

The structural sizing fraction is the ratio between the solvent structural sizing quantity and the mixtures as defined by Equation 5.19:

$$f_1 = \frac{\xi_1}{\xi_{mix}} = \frac{\xi_1}{x_1 \cdot \xi_1 + x_2 \cdot \xi_2} \quad (5.19a)$$

$$f_2 = \frac{\xi_2}{\xi_{mix}} = \frac{\xi_2}{x_1 \cdot \xi_1 + x_2 \cdot \xi_2} \quad (5.19b)$$

where ξ_1 and ξ_2 represents a structural sizing quantity of the pure solvents 1-octene and 7-tetradecene and ξ_{mix} represents the mixtures structural sizing quantity. The structural size quantity can range from the molecular weight, molar volume, equivalent molecular volume, equivalent molar diameter, effective molecular diameter, stokes diameter, etc. Four examples of calculated ξ -values for the pure solvents of 1-octene, 1-tetradecene and 7-tetradecene are given in Table 5.5 and discussed in Section 5.3.3. The mixtures structural size quantity (ξ_{mix}) was calculated with a linear mixing rule due to the cylindrical nature of 1-octene and 7-tetradecene, as visually illustrated in Figure 5.7.

By introducing the structural sizing fraction into model SD-2, Equation 5.20 called model SD-3 is given as:

$$N_p = \frac{\Delta p}{\eta \cdot \phi^n} \left\{ f_1 \bar{V}_1 c_{1,m} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)_1 + f_2 \bar{V}_2 c_{2,m} \left(\frac{\epsilon d_{pore}^2}{32l\tau} \right)_2 \right\} \quad (5.20)$$

where f_i is the structural sizing fraction to correlate solvent-solvent sizing interaction as given in Equation 5.19.

The predicted values of three different SD-3 structural fraction models based on 1) equivalent molecular volume, 2) effective molecular diameter and 3) equivalent molar diameter are compared to the experimental data as presented in Figure 5.20. It is clear from these results that the structural size quantity or structural sizing fraction has a significant effect on the predicted trends. The structural sizing fractions of equivalent molecular volume, for example, overestimate the experimental data while the diameter fractions (equivalent molar and effective molecular) give better predictions. Furthermore, the results show that the transport of the binary mixture of 1-octene and 7-tetradecene through the ST-228 membrane can accurately be

described by the newly developed SD-3 model that incorporates equivalent molar diameter as the structural sizing fraction.

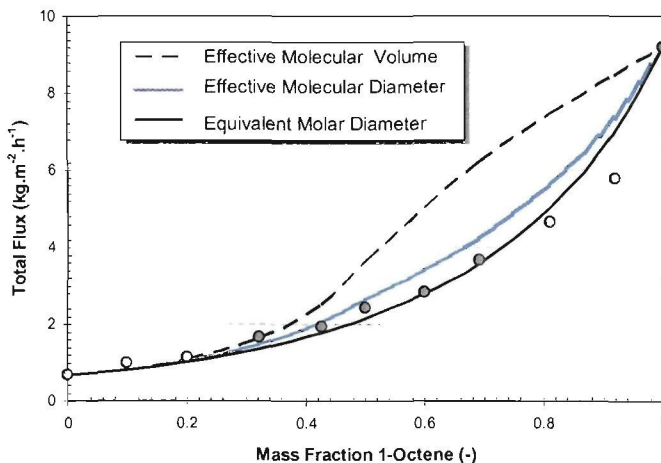


Figure 5.20 Comparison of the experimental data of 1-octene/7-tetradecene flux through ST-228 (at 30 bar applied pressure and at 25 °C) and the calculated values with different structural fraction SD-3 models.

5.4.5 Concluding remarks about the different models

Three literature-based models (one and two Hagen–Poiseuille models and a solution-diffusion model) and a newly developed model that incorporates structural solvent-solvent interaction were used to describe the transport of the binary mixtures of 1-octene and 7-tetradecene through the ST-228 membrane. The different models with their Pearson square correlations for predicting the experimental data are summarized in Table 5.9.

It was found that the HP-2 model fairly accurately described the experimental data compared to the SD-1 model that underestimated the data. The newly-developed transport model (SD-3 with solvent-solvent structural sizing interaction fractional parameter) provided an improved model fit, compared to the best literature model, HP-2, as can be seen in Figure 5.21. The experimental error variance compared to the predicted model values was reduced by about approximately 6% for SD-3 with structural sizing interaction parameter compared to the best literature model, HP-2.

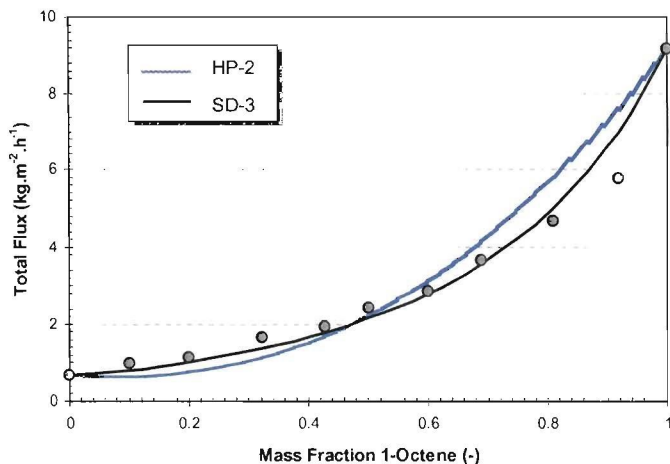


Figure 5.21 Comparison of the experimental data of 1-octene/7-tetradecene flux through ST-228 (at 30 bar applied pressure and at 25 °C) and the calculated values with HP-2 and the newly developed structural fraction SD-3 model for the equivalent molar diameter.

These results indicate that the predominant parameters that influence the transport of the 1-octene metathesis system through ST-228 are: solvent properties (viscosity) $\gg$ membrane-solvent interaction property $\left(\left(\frac{\varepsilon d_{pore}^2}{32\ell\tau} \right)_{mix} \right) >$ solvent-solvent structural properties. Furthermore,

from a model complexity view-point, it can be concluded that the HP-2 model adequately describes the transport, even though the newly developed SD-3 model has a 6% better correlation. It is possible to predict with a 90% accuracy the permeation of the 1-octene metathesis system by using only the pure solvent data.

Table 5.9 Comparison of the different transport models used in this study.

Transport Model	Equation	Description	Pearson square correlation (R ²)
HP-1	$N_v = \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix} \cdot \frac{1}{\eta} \Delta p$	$\left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_{mix}$ parameter was calculated from the arithmetic average of the two pure components.	0.849
HP-2	$N_v = \frac{\Delta p}{\eta} \left\{ \bar{V}_1 \cdot c_{1,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_1 + \bar{V}_2 \cdot c_{2,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_2 \right\}$	Silva <i>et al.</i> ³ two-parameter Hagen-Poiseuille model	0.956
SD-1	$n_1 = P_{1,m}^{mass} \left(\omega_{1,f} - \frac{n_1}{n_1 + n_2} \exp \left\{ -\frac{V_1 \Delta p}{RT} \right\} \right)$ $n_2 = P_{2,m}^{mass} \left(\omega_{2,f} - \frac{n_2}{n_1 + n_2} \exp \left\{ -\frac{V_2 \Delta p}{RT} \right\} \right)$	Silva <i>et al.</i> ³ solution-diffusion based model.	0.950
SD-2	$N_v = \frac{\Delta p}{\eta \cdot \phi^n} \left\{ \bar{V}_1 \cdot c_{1,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_1 + \bar{V}_2 \cdot c_{2,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_2 \right\}$	Combination of Bhanushali <i>et al.</i> ⁹ model and Silva <i>et al.</i> ³ two-parameter Hagen Poseuille model.	0.956
SD-3	$N_v = \frac{\Delta p}{\eta \cdot \phi^n} \left\{ f_1 \bar{V}_1 c_{1,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_1 + f_2 \bar{V}_2 c_{2,m} \left(\frac{\varepsilon d_{pore}^2}{32l\tau} \right)_2 \right\}$	Adaptation of SD-2 with incorporation of a solvent-solvent structural sizing parameter.	0.982

5.5 Coupled reaction-separation and re-use process

5.5.1 Introduction

The main objective of this investigation is to show that it is possible to process a post-reaction mixture (metathesis reaction of 1-octene with different Grubbs-type precatalysts) by OSN in order to isolate the products in the permeate and retain the catalyst in the retentate. This allows for possible re-use of the catalyst into successive reaction-OSN cycles as depicted in Figure 5.22 and described in Section 3.7.

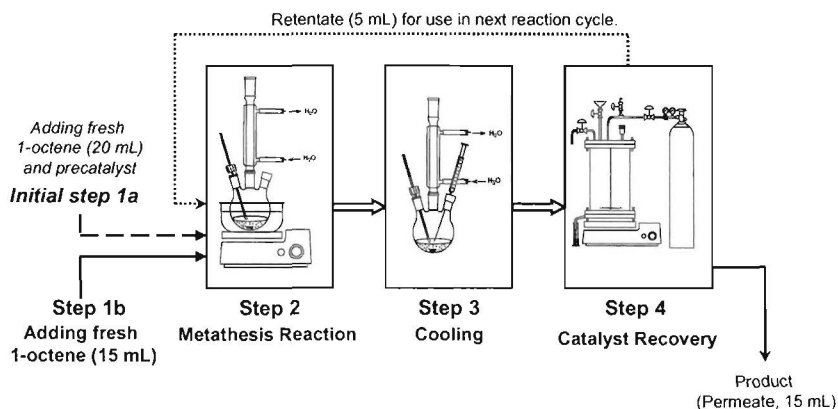


Figure 5.22 Schematic diagram of the reaction-OSN coupled process.

This coupled reaction-separation and recycling process as illustrated in Figure 5.22 aims at improving cumulative catalyst turnover number (TON) as the catalyst, loaded only in the first cycle (Step 1a), is re-used for successive reaction-OSN cycles. The post-reaction mixture (Step 2) is cooled down to room temperature (Step 3) and directly processed by OSN (Step 4), without the need for catalyst heterogenization or biphasic extraction. The OSN process provides for a neat isolation of the product that is potentially free or has lower levels of ruthenium contamination. As this methodology is applied in this study for the first time for the metathesis reaction of 1-octene with different Grubbs-type catalysts, the limitations and challenges are identified and presented in this Section.

5.5.2 Experimental results and discussion

The coupled reaction-separation and recycling processes as illustrated in Figure 5.22 were applied to all five Grubbs-type catalysts (**Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph**). The reaction conditions of Step 2 for the different catalytic systems were taken as the optimal reaction temperatures for the specific catalytic system with a catalyst load of 7000, as summarized in Table 5.10. The reaction times (τ) was approximately when steady-state conversion was attained.

Table 5.10 Reaction conditions of the different catalytic systems

Precatalyst	Reaction temperature (°C)	Reaction time for first cycle (hours)
Gr1	30	≈ 3.5
Gr2	30	≈ 3.5
HGr1	30	≈ 6.5
HGr2	50	≈ 6.5
Gr2Ph	80	≈ 6.5

Catalysts **Gr1**, **Gr2**, **HGr1** and **HGr2** showed no significant catalytic activity after the first separating step. This observation of no catalytic activity was possibly due to the relatively short catalyst lifetime of these catalysts for the metathesis reaction of 1-octene. Forman *et al.*¹⁹ found that the catalysts **Gr1** and **Gr2** demonstrated short catalyst lifetimes of less than three hours for the metathesis of 1-octene. Wijkens *et al.*²⁰ also studied the separation and re-use of a Grubbs-type complex, as shown in Figure 5.23, which was immobilised on a carbosilane support. The classical RCM reaction of diethyl diallyl malonate to diethyl-3-cyclopentene dicarboxylate was used. Wijkens *et al.*²⁰ observed that their catalyst could not be separated in an active form and theorized that the lack of catalytic activity of their catalyst was possibly due to deactivation by the MPF-60 membrane surface. It was proposed by Wijkens *et al.*²⁰ that the surface of the MPF-60 membrane used in their study deactivated the catalyst and that the separation and re-use via membrane technology would only be successful if more stable organic nanofiltration membranes were available.

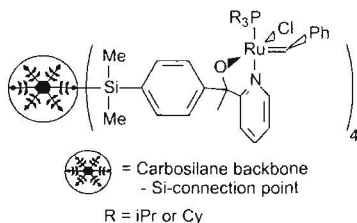


Figure 5.23 Grubbs-type catalyst used by Wijdens *et al.*²⁰

In this study it is shown that it is not the lack of stability of organic nanofiltration membrane (although stability is highly sought after), but indeed the short catalyst lifetimes that prevent the successive re-use of Grubbs-type catalysts after separation. It was found in this study that the catalyst stability with respect to reaction lifetime with the OSN process for the metathesis of 1-octene with the different precatalysts are in the order: **Gr1** < **Gr2** < **HGr1** < **HGr2** << **Gr2Ph** as summarized in Figure 5.24.

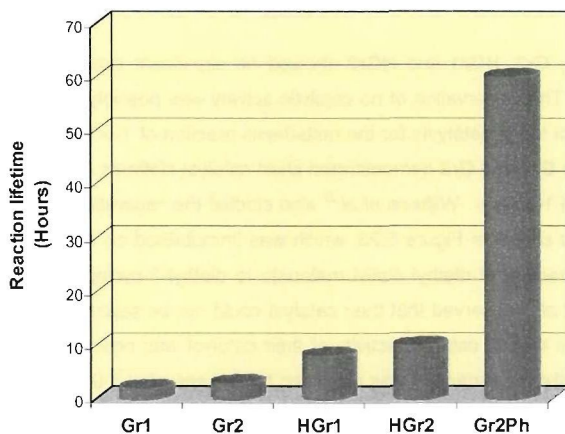


Figure 5.24 Reaction lifetimes for **Gr1**, **Gr2**, **HGr1**, **HGr2** and **Gr2Ph** for the metathesis of 1-octene.

All the Grubbs-type catalysts used in this study could be recovered and separated from their post-reaction mixtures with OSN, although some of them were not in an active form. The rejection characteristics of the ST-228 membrane for the different Grubbs-type catalysts were studied at catalyst concentrations ranging from 340 to 1400 ppm as summarized in Table 5.11. The ST-228 membrane performed well, showing catalyst rejections of approximately > 97% for

all the different Grubbs-type catalysts. The permeate measurements were all below the detection range of 9 ppm for the AAS and the retentate measurements were all within experimental error of the original loaded catalyst concentration as discussed in Section 5.3.5.

Table 5.11 Separation performances of ST-228 for the metathesis system of 1-octene and different Grubbs-type catalysts.

Precatalyst	Precatalyst concentration (ppm)	Pressure (bar)	Rejection (-)
Gr1	340	20	> 0.974
Gr1	560	20	> 0.984
Gr1	340	30	> 0.974
Gr1	560	30	> 0.984
Gr1	340	40	> 0.974
Gr1	560	40	> 0.984
Gr2	340	30	> 0.974
HGr1	340	30	> 0.974
HGr2	340	30	> 0.974
Gr2Ph	625	30	> 0.986
Gr2Ph	1400	40	> 0.994

Other studies²¹⁻²⁹ proposed several methods for recovering the different ruthenium based complexes from their post-reaction mixtures. Use of biphasic extraction, various scavengers, such as lead tetra-acetate,²⁴ DMSO or phosphine additives²⁵ (including supported phosphines)^{26,27} were found to reduce the ruthenium content in the post-reaction mixture to between 200 and 1 200 ppm. Even two cycles of chromatography followed by twelve hours of incubation with activated charcoal showed only ppm-levels less than 100²⁸. Another innovative method involved the use of tagged catalysts, which could easily be separated from untagged products by a phase-transfer event (precipitation or liquid-liquid partition).²⁹ Michrowska *et al.*¹⁸ showed that a Grubbs-type catalyst could easily be separated after reaction by deposition on silica gel to 83 ppm. It was found in this study that the OSN separation method with the ST-228 membrane could purify a post reaction-mixture of a 1-octene metathesis system with the different Grubbs-type catalysts to levels below 9 ppm.

The in-house synthesized precatalyst **Gr2Ph** showed the longest active reaction lifetime and was, therefore, used in further experiments to demonstrate the coupled reaction-separation-recycling and re-use of a Grubbs-type catalyst for the 1-octene metathesis reaction. The results of the coupled reaction-separation and recycling process are summarized in Figure 5.25.

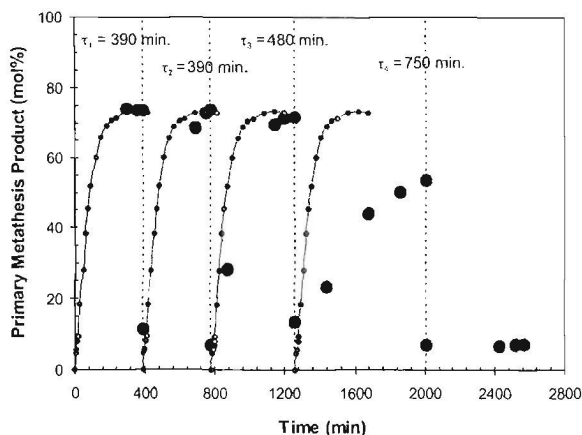


Figure 5.25 Coupled reaction-separation process using OSN to recover and re-use the catalyst for the metathesis of 1-octene with a **Gr2Ph** catalyst.

Five reaction and four separation steps, as indicated by the vertical lines (τ) in Figure 5.25, were consecutively performed until the catalyst showed almost no activity in metathesizing 1-octene. It is clear from these results that a decrease in catalytic activity can be observed during the different reaction cycles. The first three reaction cycles reached their steady-state standard conversion of approximately 73 mol% primary metathesis products of 7-tetradecene and ethylene, whereas the last two reaction cycles demonstrated a substantial decrease in the amount of PMPs being formed. The steady-state conversion for the last two cycles was found to be 54% and 7%. The reaction time (τ) to reach steady-state conversion also increased from 390 min for the first cycle to 750 min for the fourth cycle. The last reaction was stopped after 520 min when it appeared that no more primary metathesis product formed. This phenomenon is ascribed to the deactivation of the catalyst and not to the incomplete rejection of the catalyst or the membranes surface. It is shown, as summarized in Table 5.11, that the ST-228 membrane completely rejected all the Grubbs-type catalyst. It is also shown in Section 5.2 that the ST-228 membrane was completely stable in the presence of the catalyst and solvents used in this study. It can thus be concluded that the decrease in PMPs formed with repeated reaction-recovery-recycling and re-use cycles was mainly due to the deactivation of the Grubbs-type catalyst with time. This finding was confirmed by Aerts *et al.*³ who also observed that a decrease in catalyst activity was the primary cause of a decrease in conversion and ee for the hydrolytic kinetic resolution of 1,2-epoxyhexane catalyzed by the Co-Jacobsen catalyst. It was thus demonstrated that OSN could be successfully used to recover and re-use Grubbs-type catalysts such as **Gr2Ph** in the field of metathesis. The coupled reaction-separation and

recycling cycles increased the TON from 1400 for a single pass reaction to 5500 for the overall consecutive reaction-separation steps.

5.5.3 Concluding remarks

It is demonstrated in this section that it is possible to successfully separate different Grubbs-type catalysts from their post-reaction mixtures with the OSN process. The OSN process for recovery of Grubbs-type catalyst by far outperformed other processes such as biphasic extraction (<200 ppm), activated charcoal (<100 ppm) and silica gel extraction (<83 ppm) by lowering the ruthenium content in the post reaction mixtures to below 9 ppm. It was also found that it is possible to separate a Grubbs-type catalyst such as **Gr2Ph** in an active form for consecutive re-use that improves the overall TON. It was thus proven that the biggest challenge in the metathesis field of separation, recovery or purification of the homogeneous catalyst from the post-reaction mixture is solved with the OSN process.

5.6 Concluding remarks on OSN

In this chapter it is shown that the challenge of separating and reusing Grubbs-type catalysts from their post-reaction mixtures in the field of metathesis for the model reaction of 1-octene was solved by using the membrane technique of organic solvent nanofiltration.

The STARMEM™ ST-228 membrane from MET was found to be a suitable OSN-membrane for the separating process of the 1-octene metathesis system. Relatively moderate fluxes were found for the 1-octene metathesis components through the ST-228 membrane that ranged from 0.2 to 15 kg.m⁻².h⁻¹. The rejection performance of the ST-228 membrane was excellent with an average catalyst rejection of > 97% for all the different Grubbs-type catalyst used in this study. It was found that the binary system of 1-octene and 7-tetradecene is a non-solvent-separation system and that the ST-228 membrane preferentially absorbs 7-tetradecene than 1-octene.

Two pore-flow-based models (HP-1 and HP-2) and three solution-diffusion based models (SD-1, SD-2 and SD-3) were used to describe the transport of the binary mixtures of 1-octene and 7-tetradecene through the ST-228 membrane. It was found that the newly developed SD-3 model that incorporated a structural solvent-solvent interaction parameter best described the separation of the binary mixtures of 1-octene and 7-tetradecene through the ST-228 membrane. From a model complexity view-point the two-parameter HP-2 model adequately described the transport, even though the newly developed SD-3 model had a 6% better correlation. The predominate parameters that influenced the transport of the 1-octene metathesis system through the ST-228 membrane was found to be solvent properties (viscosity) >> membrane-solvent interaction property (such as sorption) > solvent-solvent structural properties.

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6 CONCLUSIONS AND RECOMMENDATIONS

Engineering is the art or science of making practical.

(Samuel C. Florman)

Overview

In this chapter, the main conclusions drawn from this investigation are presented in Section 6.1 with recommendations for future studies in Section 6.2. The chapter concludes with Section 6.3 by presenting some peer reviews and submitted contributions and research awards that emanated from this investigation.

6.1 Conclusions

6.1.1 Main objective

In this thesis it was demonstrated that the membrane separating technique of Organic Solvent Nanofiltration (OSN) was successful in separating different Grubbs-type catalysts (**Gr1**, **Gr2**, **HGr2**, **HGr2** and **Gr2Ph**) from their post-reaction mixtures for the model reaction of 1-octene to 7-tetradecene and ethene as illustrated in Figure 6.1.

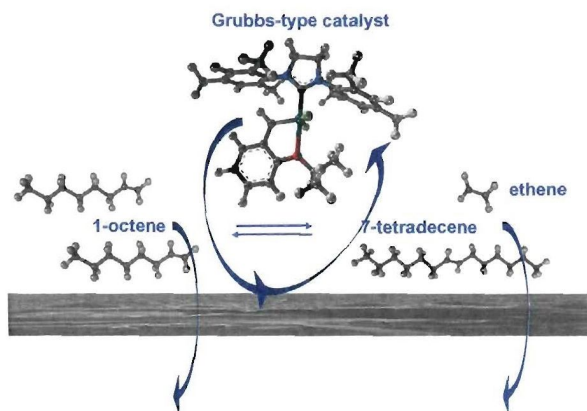


Figure 6.1 Illustration of main objective: Separation and re-use of Grubbs-type catalyst for the 1-octene metathesis system.

In terms of purity, it was found that the OSN technique could purify and remove ruthenium-based complexes from their post-metathesis-reaction mixtures below 9 ppm for the model system. This finding outperforms other¹⁻⁷ separation protocols and methods for the purification of ruthenium-based complexes from their post-reaction mixtures in the field of metathesis, such as the biphasic extraction method that reduces the ruthenium-based complexes only to between 200 and 1 200 ppms. Even two cycles of chromatography followed by twelve hours of incubation with activated charcoal showed only ppm-levels of less than 100. The separating technique proposed by Michrowska *et al.*¹ with the deposition on silica gel could only separate Grubbs-type catalysts to 83 ppms.

In terms of re-usability, it was shown that a Grubbs-type catalyst such as the **Gr2Ph** precatalyst could be separated *in an active form* for recycling and consecutive re-use, as summarized in Figure 6.2. The TON for the model reaction was increased from 1400 for a single pass reaction to a cumulative value of 5500 after five consecutive cycles.

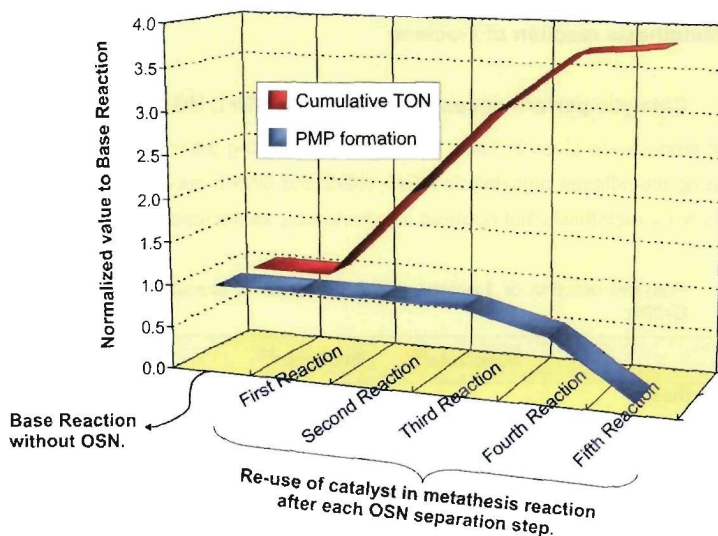


Figure 6.2 Graphical summary of the main OSN results that illustrate the successful separation and re-use (up to five cycles) of a Grubbs-type catalyst for the model 1-octene metathesis reaction.

This research, therefore, clearly demonstrates that the technique of OSN is a feasible solution to one of the major drawbacks in the field of metathesis, namely catalyst separation and re-use.

6.1.2 Synthesis of precatalyst Gr2Ph

It was demonstrated in this research that a viable solution to the disadvantage of short catalytic lifetimes in the field of metathesis can be solved with the catalytic synthesizing concept of modifying and binding the dissociating ligand and anionic ligand with a bidentate O,N-chelated Schiff base ligand on the second generation Grubbs precatalyst. This design concept was applied and illustrated with the synthesis of precatalyst **Gr2Ph**. Precatalyst **Gr2Ph** was successfully synthesized several times with demonstrated shelf-life of up to seven months.

In terms of catalyst reaction lifetime, precatalyst **Gr2Ph** demonstrated catalytic activity in the model metathesis reaction of 1-octene for the formation of PMPs up to approximately *three* days, compared to other Grubbs-type catalysts such as **Gr1**, **Gr2**, **HGr1** and **HGr2** that showed only a maximum catalytic activity of approximately *ten* hours.

6.1.3 Metathesis reaction of 1-octene

6.1.3.1 Catalytic performances of precatalysts HGr1, HGr2 and Gr2Ph

A mixture of products, as given in Table 6.1, was formed during the metathesis reaction of 1-octene by using the different precatalysts **HGr1**, **HGr2** and **Gr2Ph** due to alkene isomerization and self- and cross-metathesis that occurred simultaneously as the reaction proceeded.

Table 6.1 Possible reaction of 1-octene in the presence of precatalysts **HGr1**, **HGr2** and **Gr2Ph**.

Reaction	Substrate ^[a]	Products ^[a]	
Primary metathesis			
<i>Self-metathesis</i>	$C=C_7$	$C_7=C_7 + C=C$	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>Thereafter cross-metathesis</i>	$C=C_6 + C_2=C_5$	$C=C_2 + C=C_5 + C_2=C_6 + C_5=C_6$	
	$C=C_6 + C_3=C_4$	$C=C_3 + C=C_4 + C_3=C_6 + C_4=C$	
	$C_2=C_5 + C_3=C_4$	$C_2=C_3 + C_2=C_4 + C_3=C_5 + C_4=C$	
	Etc.	Etc.	
<i>Self-metathesis</i>	$C_2=C_6$	$C_2=C_2 + C_6=C_6$	
<i>Thereafter self-metathesis</i>	$C=C_6$	$C=C + C_6=C_6$	
	$C=C_5$	$C=C + C_5=C_5$	
	$C=C_4$	$C=C + C_4=C_4$	
	Etc.	Etc.	

^a. Hydrogens are omitted and geometrical isomers not shown for simplicity.

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

In terms of product formation, the first generation catalysts (**Gr1** and **HGr1**) gave higher PMP selectivity with insignificant amounts of SMP formation compared to the second generation catalysts (**Gr2**, **HGr2** and **Gr2Ph**) that showed significant amounts of SMP formation. All the catalysts demonstrated IP formation that is temperature dependent.

In terms of activity, it was found that the second generation catalysts generally showed higher TON compared to the first generation catalysts and the activation energies of the first generation catalysts were relatively lower than the second generation catalysts. The relative reaction rates were also observed to be faster for the first generation catalysts compared to the

second generation catalysts. These phenomena were attributed to the more stable N-heterocyclic carbene (NHC) ligand used in the second generation catalysts compared to the tricyclohexylphosphine (PCy₃) ligand used in the first generation catalysts. The use of the NHC-ligand demonstrated an increase in catalyst lifetime, thermal stability and activity compared to the PCy₃-ligand. The main concluding catalytic performances of the different catalysts are summarized in Table 6.2.

Table 6.2 Summarized catalytic performances.

Precatalyst	Optimum Temperature ^[a]	Formation of IPs ^[b]	Formation of SMPs ^[b]	Relative activity ^[c]	Relative life-time ^[d]
Gr1	Low (30 °C)	✓ (>70 °C)	×	2801	≈2
Gr2	Low (30 °C)	✓ (>60 °C)	✓ (>60 °C)	5337	≈3
HGr1	Low (30 °C)	✓ (>50 °C)	×	4458	≈8
HGr2	Medium (50 °C)	✓ (>60 °C)	✓ (>60 °C)	6448	≈10
Gr2Ph	High (80 °C)	✓ (>70 °C)	✓ (>70 °C)	7385	≈60

^{a.} Temperature where the highest selectivity and PMP formation are observed at a catalyst load of 7000.

^{b.} Temperature where more 3% starts to form at a catalyst load of 7000.

^{c.} TON values at optimum temperature and catalyst load of 10000.

^{d.} Time in hours measured of catalytic activity for PMP formation at catalyst load of 7000 with consecutive separation and re-use.

6.1.3.2 Reaction Mechanism

It was shown that the different Grubbs-type catalysts for the model reaction of 1-octene demonstrated both metathesis and isomerization catalytic activity that could be supported by the two competing mechanisms as illustrated in Figure 6.3 with precatalyst **Gr2Ph**:

- Metathesis Dissociated based release-return mechanism.
- Isomerization Alkyl based isomerization mechanism for n-octenes.

6.1.3.3 Reaction Kinetics

It was found that the metathesis reaction of 1-octene with the different precatalysts could fairly accurately be described by the first-order reaction rate-laws as given by Equations 6.3, 6.4 and 6.5:

$$\frac{dc_{C_8}}{dt} = -k_1 c_{C_8} + k_2 c_{PMP} - k_3 c_{C_8} \quad (6.3)$$

$$\frac{dc_{PMP}}{dt} = k_1 c_{C_8} - k_2 c_{PMP} \quad (6.4)$$

$$\frac{dc_{IP+SMP}}{dt} = k_3 c_{C_8} \quad (6.5)$$

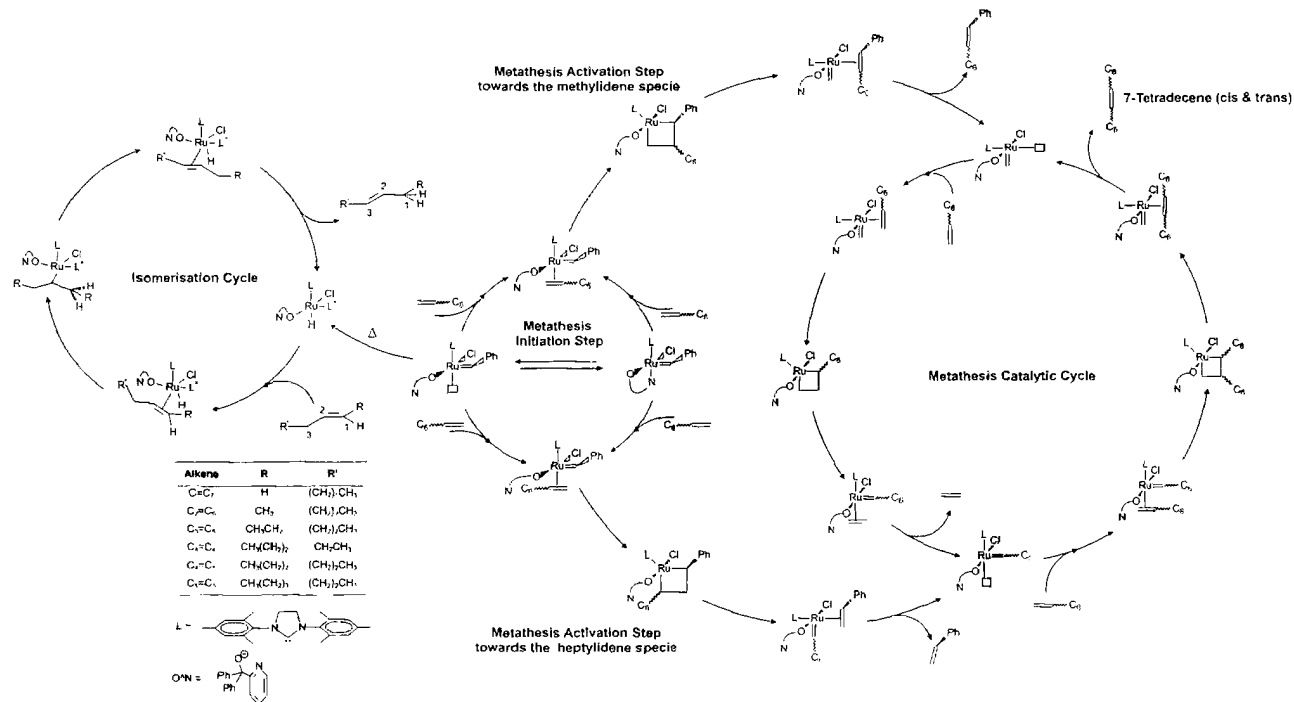


Figure 6.3 Proposed metathesis and isomerisation mechanism for the reaction of 1-octene in the presence of Gr2Ph.

6.1.4 Organic Solvent Nanofiltration (OSN)

It was found that the STARMEM™ ST-228 membrane from MET⁸ was a suitable OSN membrane for separating the 1-octene metathesis system. The characterization performances of the ST-228 membrane were found to be:

- In terms of permeation Moderate fluxes ranging from 0.2 to 15 kg.m⁻².h⁻¹.
- In terms of catalyst rejection Average catalyst rejection of > 97% for all the different Grubbs-type catalysts used in this research.
- In terms of solvent separation Non-solvent separating system.
- In terms of sorption Membrane ST-228 demonstrated relatively higher affinity and absorption capabilities for 7-tetradecene than for 1-octene.

The predominant parameters that influenced the transport of the 1-octene metathesis system through the ST-228 membrane were found to be solvent properties (viscosity) >> membrane-solvent interaction properties (such as sorption) > solvent-solvent structural properties (such as molar volume or effective molecular volume). The relationship between these parameters and the permeation rate (flux) was found to be described by the correlation in Equation 6.1:

$$\text{Permeation Rate} \propto \left(\frac{1}{\text{viscosity}} \right) \times \left(\frac{1}{\text{sorption}^n} \right) \times (\text{molar volume}) \cdot (\text{sizing parameter}) \quad (6.1)$$

In terms of describing the transport of the binary mixtures of 1-octene and 7-tetradecene through the ST-228 membrane theoretically it was found that:

- It was possible to predict the permeation by using only the pure solvent data with accuracy above 90%.
- The pore-flow based mechanism described the 1-octene system better than a solution-diffusion based mechanism.
- A newly developed model as given in Equation 6.2, based on the two-parameter Hagen-Poiseuille idea of Silva *et al.*⁹ with the incorporation of a structural solvent-solvent interaction parameter best described the transport.

$$N_i = \frac{\Delta p}{\eta \cdot \sigma^n} \left(f_1 \bar{V}_1 c_{1,m} \left(\frac{ed^2}{32l\tau} \right)_1 + f_2 \bar{V}_2 c_{2,m} \left(\frac{ed^2}{32l\tau} \right)_2 \right) \quad (6.2)$$

- From a model complexity viewpoint the two-parameter Hagen-Poiseuille model with a Pearson-correlation of 0.956, adequately described the transport, even though the newly developed model of Equation 6.2 gave slightly better predictions ($R^2 = 0.982$).

6.2 Recommendations for future research

The next step would be to do a full OSN investigation into different metathesis systems, especially pharmaceutical systems, as these systems require ruthenium impurities of less than 10 ppm, as it was shown in this study that the OSN process can accomplish this purity for the petrochemical system of 1-octene. This study can then be used to do a full economic evaluation of the possible implementation of the OSN process in the field of metathesis and furthermore, to determine what is the economic resistance to using the process in industry.

6.3 Contribution and awards from this study

The use of Organic Solvent Nanofiltration, especially in the field of metathesis, is a novel idea that has the possibility of being both economically profitable and environmentally friendly. This idea is now beyond the point of a scientific curiosity and it is important to bridge the gap between science and sustainable industrial implementation. To do this, researchers will need to firstly know how large this gap is and secondly what the real unresolved challenges in the two fields are. It is, therefore, the author's opinion that this thesis contributes to introducing a better understanding of this gap and will give rise to new ideas and approaches of how to cross this gap. The following contributions to the research community emanated from this study:

- Percy van der Gryp, Sanette Marx, Manie Vosloo. Separation of a Homogeneous Catalyst from an alkene metathesis reaction by using Nanofiltration. Conference Proceedings of CATSA, South Africa, November 2007.
 - Percy van der Gryp, Sanette Marx, Manie Vosloo. Separation of Grubbs-type precatalysts with organic solvent nanofiltration. Conference Proceedings of the International Symposium on Homogeneous Catalysis, Florence, Italy, July 2008.
 - Percy van der Gryp, Dennis de Vlieger, Sanette Marx, Margaritha Jordaan and Hermanus C. M. Vosloo. Separation and re-use of a chelated Grubbs-type precatalyst for the metathesis of 1-octene. Submitted for publication: *Adv. Synth. Catal.* (2008).
 - Micromeritics medal for best poster presentation at the 2006 CATSA conference.
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APPENDIX A – COMPUTER PROGRAMS

Overview

In this appendix all the computer programs written for this investigation, specifically to solve the three differential rate law equations, are presented. Section A.1 describes the Runge-Kutta method, Section A.2 the Simplex method and Section A.3 the Bootstrap method. The general philosophy applied for each program with a summarized flow diagram and the Delphi (Visual Pascal) language codes are given.

A.1 Runge-Kutta method

A.1.1 Background and algorithms

A variety of methods to approximate the solutions to initial-value problems for numerically solving ordinary differential equations, systems of differential equations, and certain partial differential equations are found, ranging from Euler's to Adams-Bashforth's, etc.¹ In this study the classic Runge-Kutta method of order 4 is used.

The Runge-Kutta technique makes use of the Taylor expansion of the function on the right-hand side of the differential equation, f . The 4th order Runge-Kutta is obtained by expanding an expression that involves only four function evaluations. Deriving this expression requires solving a system of equations involving 12 unknowns. Once the algebra has been performed, the method has the following simple representation:¹

$w_0 = \alpha$, initial condition value.

$$k_1 = h \cdot f(t_i, w_i)$$

$$k_2 = h \cdot f\left(t_i + \frac{h}{2}, w_i + \frac{1}{2} \cdot k_1\right)$$

$$k_3 = h \cdot f\left(t_i + \frac{h}{2}, w_i + \frac{1}{2} \cdot k_2\right)$$

$$k_4 = h \cdot f(t_{i+1}, w_i)$$

for each $i = 0, 1, \dots, N-1$.

(A.1)

Methods to solve systems of differential equations are generalizations of the methods for the single equation. Consider the m th-order system with the form:

$$\frac{du_1}{dt} = f_1(t, u_1, u_2, \dots, u_m),$$

$$\frac{du_2}{dt} = f_2(t, u_1, u_2, \dots, u_m),$$

...

$$\frac{du_m}{dt} = f_m(t, u_1, u_2, \dots, u_m).$$

(A.2)

with $a \leq t \leq b$ and the initial conditions $u_1(a) = \alpha_1, u_2(a) = \alpha_2, \dots, u_m(a) = \alpha_m$.

The object is to find m functions $u_1, u_2, \dots, u_m$ that satisfy the system of differential equations together with all the initial conditions. It is generalized in the following steps:

1. Let an integer $N > 0$ be chosen and set $h = \frac{b-a}{N}$. Partition the interval $[a, b]$ into N

subintervals with the mesh points

$$t_j = a + j \cdot h \quad \text{for each } j = 0, 1, \dots, N \quad (\text{A.3})$$

2. Using the notation w_{ij} for each $j = 0, 1, \dots, N$ and $i = 0, 1, \dots, m$ to denote an approximation to $u_i(t_j)$. For the initial conditions, set

$$w_{1,0} = \alpha_1, \quad w_{2,0} = \alpha_2, \quad \dots, \quad w_{m,0} = \alpha_m. \quad (\text{A.4})$$

3. Calculate the different k -values for each $i = 1, 2, \dots, m$.

$$\begin{aligned} k_{1,i} &= h \cdot f_i(t_j, w_{1,j}, w_{2,j}, \dots, w_{m,j}) \\ k_{2,i} &= h \cdot f_i\left(t_j + \frac{h}{2}, w_{1,j} + \frac{1}{2} \cdot k_{1,1}, w_{2,j} + \frac{1}{2} \cdot k_{1,2}, \dots, w_{m,j} + \frac{1}{2} \cdot k_{1,m}\right) \\ k_{3,i} &= h \cdot f_i\left(t_j + \frac{h}{2}, w_{1,j} + \frac{1}{2} \cdot k_{2,1}, w_{2,j} + \frac{1}{2} \cdot k_{2,2}, \dots, w_{m,j} + \frac{1}{2} \cdot k_{2,m}\right) \\ k_{4,i} &= h \cdot f_i(t_j + h, w_{1,j} + k_{3,1}, w_{2,j} + k_{3,2}, \dots, w_{m,j} + k_{3,m}) \end{aligned} \quad (\text{A.5})$$

Note that all the values of $k_{l,i}$ must be computed before $k_{l+1,i}$ can be.

4. Combining these values gives:

$$w_{i,j} = w_{i,j} + \frac{1}{6} [k_{1,i} + 2 \cdot k_{2,i} + 2 \cdot k_{3,i} + k_{4,i}] \quad \text{for each } i = 1, 2, \dots, m. \quad (\text{A.6})$$

The Runge-Kutta method is summarized in the flow diagram presented in Figure A.1.

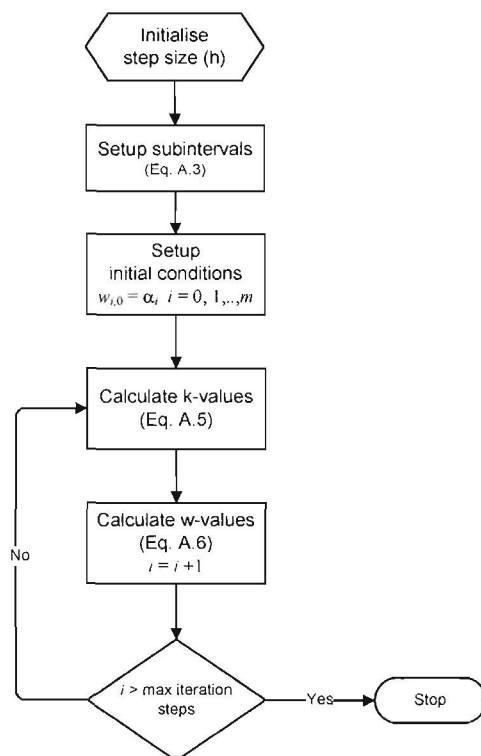


Figure A.1 Flow diagram of the Runge-Kutta method for systems of equations.

A.1.2 Delphi codes

```

procedure Runge(xm : Array of Double);
var
  w : array[0..4,1..3005] of double;
  t : array[1..3005] of double;
  h, time : double;
  y0 : array[0..4] of double;
  i,eq,k, maxi : integer;
  ii : integer;
  k1, k2, k3, k4 : array[0..4] of double;
begin
  i := 1;

  h := 0.25; {stap groote}
  maxi := round(420/h)+1; {aantal iteraties in 420 minute}
  eq := 3; {aantal equations}

  y0[1] := 1; {Begin waarden, grens waarden}
  y0[2] := 0;
  y0[3] := 0;

  for i := 1 to maxi do
  begin
    w[1,i] := 0;
    w[2,i] := 0;
    w[3,i] := 0;
  end;

  For k := 1 to eq do
  begin
    w[k,1] := y0[k];
    k1[k] := 0;k2[k] := 0;k3[k] := 0;k4[k] := 0;
    t[1] := 0;
  end;

  k := 0;

  For i := 2 to maxi do
  begin
    t[i] := t[i-1]+h;

    k1[1] := h*f1(t[i-1],w[1,i-1],w[2,i-1],w[3,i-1],xm);
    k1[2] := h*f2(t[i-1],w[1,i-1],w[2,i-1],w[3,i-1],xm);
    k1[3] := h*f3(t[i-1],w[1,i-1],w[2,i-1],w[3,i-1],xm);

    k2[1] := h*f1(t[i-1]+0.5*h,w[1,i-1]+0.5*k1[1], w[2,i-1]+0.5*k1[2], w[3,i-1]+0.5*k1[3],xm);
    k2[2] := h*f2(t[i-1]+0.5*h,w[1,i-1]+0.5*k1[1], w[2,i-1]+0.5*k1[2], w[3,i-1]+0.5*k1[3],xm);
    k2[3] := h*f3(t[i-1]+0.5*h,w[1,i-1]+0.5*k1[1], w[2,i-1]+0.5*k1[2], w[3,i-1]+0.5*k1[3],xm);

    k3[1] := h*f1(t[i-1]+0.5*h,w[1,i-1]+0.5*k2[1], w[2,i-1]+0.5*k2[2], w[3,i-1]+0.5*k2[3],xm);
    k3[2] := h*f2(t[i-1]+0.5*h,w[1,i-1]+0.5*k2[1], w[2,i-1]+0.5*k2[2], w[3,i-1]+0.5*k2[3],xm);
    k3[3] := h*f3(t[i-1]+0.5*h,w[1,i-1]+0.5*k2[1], w[2,i-1]+0.5*k2[2], w[3,i-1]+0.5*k2[3],xm);

```



```

k4[1] := h*f1(t[i],w[1,i-1]+k3[1], w[2,i-1]+k3[2], w[3,i-1]+k3[3],xm);
k4[2] := h*f2(t[i],w[1,i-1]+k3[1], w[2,i-1]+k3[2], w[3,i-1]+k3[3],xm);
k4[3] := h*f3(t[i],w[1,i-1]+k3[1], w[2,i-1]+k3[2], w[3,i-1]+k3[3],xm);

w[1,i] := w[1,i-1] + 1/6*(k1[1]+2*k2[1]+2*k3[1]+k4[1]);
w[2,i] := w[2,i-1] + 1/6*(k1[2]+2*k2[2]+2*k3[2]+k4[2]);
w[3,i] := w[3,i-1] + 1/6*(k1[3]+2*k2[3]+2*k3[3]+k4[3]);

if t[i] = v1[k] then
begin
  w1[k] := w[1,i];
  w2[k] := w[2,i];
  w3[k] := w[3,i];
  k := k+1;
end; {if}

end; {for}
end;
```

A.2 Simplex method

A.2.1 Background and algorithms

Today, there are abounding amounts of non-linear regression programs commercially available with multifunctionalite etc. However, these products have some shortcomings and are usually not suitable for specialized applications such as needed for this study. Three main disadvantages are:

- They cannot solve systems of equations.
- The input function must be in a certain form.
- They cannot solve equations with differentials or integrals.

In this study, the simplex method is used to determine the non-linear regression constants of the three differential rate law equations. The simplex method was developed by Nelder and Mead² and is based on the comparison of the objective function values at the $(n + 1)$ vertices of a general simplex (in n dimensions) and moving the simplex towards the optimum point.³ This movement is achieved by three basic operations, summarized by Koekemoer⁴ as:

1. Reflection: x^h is replaced by:

$$x^r = 2 \cdot x^0 - x^h \quad (\text{A.7})$$

2. Contraction: The simplex is contracted:

$$x^c = 0.5 \cdot x^h + 0.5 \cdot x^0 \quad (\text{A.8})$$

3. Expansion: x^r is expanded in the direction along which a further improvement of the function value may be expected:

$$x^e = 2 \cdot x^r - x^0 \quad (\text{A.9})$$

The following notation is used in the equations:

x^h : This is the vertex corresponding to the highest value of the objective function:

$$M(x^h) = \max_i (x^i), \quad i = 1, 2, \dots, (n + 1) \quad (\text{A.10})$$

x^e : This is the vertex with the second highest value of M .

x^l : This is the vertex with the lowest value of M .

x^0 : This is the centroid of all x^i except $i = h$, given by Equation A.11

$$x^0 = -\frac{1}{n} \sum_{i=1}^{n+1} x^i \quad (\text{A.11})$$

The first step is to estimate a minimum $x^j = (x_1, x_2, \dots, x_n)$. The next step is to form an initial simplex, using two auxiliary values p_n and q_n :

$$\begin{aligned} p_n &= \frac{\sqrt{n+1}-1+n}{n \cdot \sqrt{2}} \cdot S \\ q_n &= \frac{\sqrt{n+1}-1}{n \cdot \sqrt{2}} \cdot S \end{aligned} \quad (\text{A.12})$$

where S is a scaling factor (the estimate for x^j is usually used). The $n+1$ vertices of a regular simplex with edge of length S are given by:

$$\begin{aligned} x^1 &= (x_1, x_2, \dots, x_n)^T, \\ x^2 &= (p_n + x_1, q_n + x_2, q_n + x_3, \dots, q_n + x_n)^T, \\ x^3 &= (q_n + x_1, p_n + x_2, q_n + x_3, \dots, q_n + x_n)^T, \\ x^4 &= (q_n + x_1, q_n + x_2, p_n + x_3, \dots, q_n + x_n)^T, \\ &\dots \\ x^{n+1} &= (q_n + x_1, q_n + x_2, q_n + x_3, \dots, p_n + x_n)^T. \end{aligned} \quad (\text{A.13})$$

The construction of the initial simplex assures that its vertices span the full n -dimensional space. To test for convergence, the standard deviation of the function at the $(n+1)$ vertices of the current simplex is compared with some preselected tolerance $\zeta > 0$:

$$\left[\sum_{i=1}^{n+1} \frac{\{M(x^i) - M(x^0)\}^2}{n} \right]^{\frac{1}{2}} \leq \zeta \quad (\text{A.14})$$

The process is terminated if Equation A.14 is satisfied.

A flow diagram of the simplex method as used in this study is presented in Figure A.2.

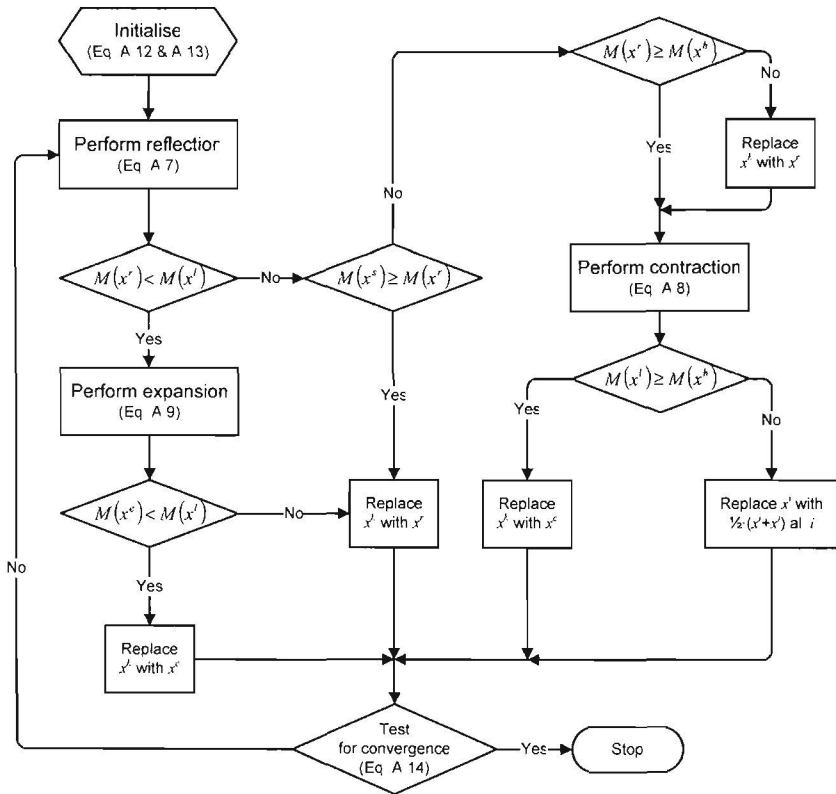


Figure A.2 Flow diagram for the Simplex method.

A.2.2 Delphi codes

```

procedure Simplex;
Const
  sc = 250;
  sx0 = 100; sy0 = 100;
Var
  i,j : integer;
  High, Sec, low, sum, tsi : Double;

begin
  Repeat

    High := 0;
    Sec := 0;
    low := M(x[0]);
  
```

```

l := 0;
i := 0;
Repeat
  IF M(x[i]) > high then
    Begin
      high := M(x[i]);
      h := i;
      i := -1;
    End
  Else
    If (M(x[i]) > sec) and (M(x[i]) < high) then
      Begin
        sec := M(x[i]);
        s := i;
        i := -1;
      end
    Else
      If M(x[i]) < low then
        Begin
          low := M(x[i]);
          l := i;
          i := -1;
        end;
      i := i+1;
    Until i > n+1;

```

{Calculate centerpoint without h}

```

for i := 0 to n do
  Begin
    sum := 0;
    for j := 0 to (n+1) do
      If j <> h then
        sum := sum + x[j,i];
      x0[i] := sum/(n+1);
    end;

```

{Perform reflection}

```

for i := 0 to n do
  begin
    xr[i] := 2*x0[i] - x[h,i];
  end;

```

If M(xr) < M(x[l]) then

{yes}

Begin

{Expansion}

For i := 0 to n do

begin

xe[i] := 2*xr[i] - x0[i];

end;

If M(xe) < M(x[l]) then

Begin

```

    for i := 0 to n do
        x[h,i] := xe[i];
    End
Else
    Begin
        for i := 0 to n do
            x[h,i] := xr[i];
        end;
    End

Else
{no}
    Begin
        If M(x[s]) >= M(xr) then
            Begin
                for i := 0 to n do
                    x[h,i] := xr[i];
                end
            End
        Else
            Begin
                If M(xr) < M(x[h]) then
                    {no no. 2}
                    Begin
                        for i := 0 to n do
                            x[h,i] := xr[i];
                        End;
                    {Contraction}
                    for i := 0 to n do
                        begin
                            xc[i] := 0.5*x[h,i] + 0.5*x0[i];

                        end;

                    If M(xc) < M(x[h]) then
                        Begin
                            for i := 0 to n do
                                x[h,i] := xc[i];
                            End
                        Else
                            Begin
                                for j := 0 to (n+1) do
                                    for i := 0 to n do
                                        x[j,i] := 0.5*(x[j,i]+x[l,i]);
                                    End;
                                End;
                            End;
                        End;
                    End;

                tsi := 0;
                for j := 0 to (n+1) do
                    tsi := tsi + sqr (M(x[j])-M(x0));
                tsi := sqrt (tsi/(n+1));
                Until (tsi < con) ;

            end;

```

A.3 Bootstrap method

A.3.1 Background and algorithms

In this study the bootstrap method is used to determine the standard errors and confidence intervals (level) for the results obtained from the non-linear simplex regression method (see Section A.2). The bootstrap method is one of a larger class of statistical methods that resample from the original data set and are thus called resampling procedures.⁵ There are numerous variations on this method and the Efron's version in combination with the Monte Carlo approximation will be used.⁵ The method is as summarized in Figure A.3 and as follows:

1. Generate a bootstrap sample of size n (where n is the original sample size) with replacement from the empirical distribution. Detail discussion of this step is presented below.
2. Compute the values of interest by using the bootstrap sample in place of the original sample.
3. Repeat steps 1 and 2, k times.

The procedure for bootstrapping the residuals of a regressing is as follows:⁵

Take a general regression model:

$$y_i = f(x, c_i) + \varepsilon_i \quad (\text{A.15})$$

The functions $f(x, c_i)$ are of known form and may depend on a fixed vector of covariates c_i . The vector x is a $p \times 1$ vector of unknown parameters and ε_i the errors of each data point. The value of x is usually calculated by minimizing the distance measure with the least squares method (see Section A1 and A.2):

$$M(y, x, c) = \sum_{i=1}^n [y_i - f(x, c_i)]^2 \quad (\text{A.16})$$

By taking $x' = \{x \text{ such that } M \text{ is minimized}\}$ the parameter estimation of x is acquired. The residuals are obtained by Equation A.17.

$$\varepsilon'_i = y_i - f(x', c_i) \quad (\text{A.17})$$

Thereafter, bootstrapping the residuals $\hat{y}_i^*$ for $i = 1, 2, \dots, n$ where $\hat{y}_i^*$ are obtained by sampling independently (that is randomly) from $\hat{y}_i$. A bootstrap sample data set can then be generated by using $\hat{y}_i^*$ and $f(x', c_i)$:

$$y_i^* = f(x', c_i) + \varepsilon_i^* \quad \text{for } i = 1, 2, \dots, n \quad (\text{A.18})$$

Form each of the bootstrap data set (y^*) , $x^* = \{x \text{ such that } M \text{ is minimized}\}$ can be obtained (step 2 of the Monte Carlo approximation).

The procedure is repeated k times (step 3 of the Monte Carlo approximation) and the variance and confidence interval of x is approximately the same as the variance and confidence interval of x^* .

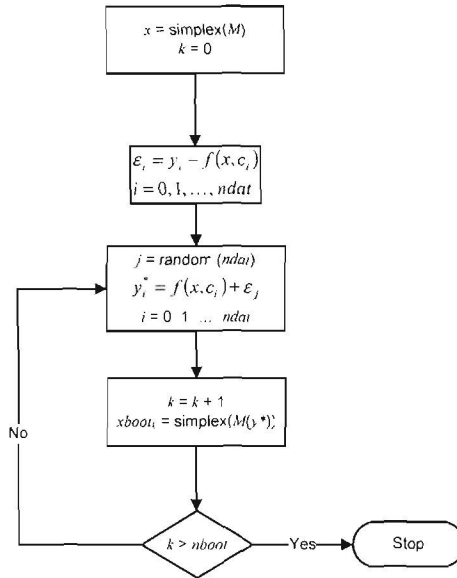


Figure A.3 Flow diagram of the Bootstrap method.

A.3.2 Delphi codes

```
procedure TForm1.BootstrapClick(Sender: TObject);
```

```
Var
```

```
  i, j, k : Integer;
```

```
begin
```

```
  For i := 0 to ndat do
```

```
    Begin
```

```
      w1m[i] := w1[i];
```

```
      w2m[i] := w2[i];
```

```
      w3m[i] := w3[i];
```

```
      epsi1[i] := v2[i] - w1[i];
```

```
      epsi2[i] := v3[i] - w2[i];
```

```
      epsi3[i] := v4[i] - w3[i];
```



```

end;

x0r := x0;
Randomize;
For k := 0 to nboot do
  Begin
    For i := 0 to ndat do
      Begin
        j := Random (ndat);

        v2[i] := w1m[i] + epsi1[j];
        v3[i] := w2m[i] + epsi2[j];
        v4[i] := w3m[i] + epsi3[j];
      end;

      x[0,0] := x0[0];
      x[0,1] := x0[1];
      x[0,2] := x0[2];

      p := (sqrt (n+2) - 1 + (n+1))/((n+1)*sqrt(2))*Sf;
      q := (sqrt (n+2) - 1)/((n+1)*sqrt(2))*Sf;

      For i := 1 to n+1 do
        For j := 0 to n do
          Begin
            If i = (j+1) then
              x[i,j] := p+x[0,i]
            Else
              x[i,j] := q+x[0,i];
            end;
          end;

          Simplex;
          For i := 0 to n do
            xboot[i,k] := x0[i];
          end;
        }k}

    {Calculate standard deviation}
    for i := 0 to n do
      SE[i] := StdDev (xboot[i]);

      {Save data to file}
      AssignFile(datfile, 'c:\percy\boot_terug.txt');
      Rewrite(datfile);
      writeln(datfile, 'Nr. '+chr(9)+'k1'+chr(9)+'k2'+chr(9)+'k3');
      For i := 0 to nboot do
        begin
          writeln(datfile, inttostr(i+1)+chr(9)+floattostr(xboot[0,i])+chr(9)+floattostr(xboot[1,i])+chr(9)+
            floattostr(xboot[2,i]));
        end;

        writeln(datfile);

```

```
writeln(datfile,'Stdev:'+chr(9)+floattostr(SE[0]));  
writeln(datfile,'Stdev:'+chr(9)+floattostr(SE[1]));  
writeln(datfile,'Stdev:'+chr(9)+floattostr(SE[2]));  
  
closefile(datfile);  
  
label4.Caption := floattostr (SE[0]);  
label5.Caption := floattostr (SE[1]);  
label6.Caption := floattostr (SE[2]);  
  
end;
```

A.4 References

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2. Nelder, J.A. and Mead, R., *Computer Journal*, 1965, 7, 308.
3. Jacoby, S.L.S., Kowalik, J.S. and Pizzo, J.T., **Iterative methods for nonlinear optimization problems**, Englewood Cliffs : Prentice-hall, 1972.
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