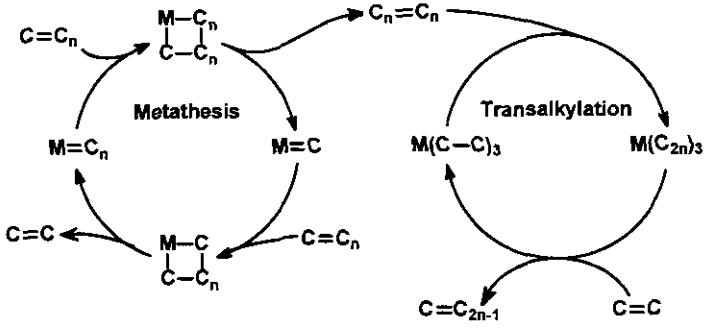
Metathesis and Transalkylation in Tandem Catalysis



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Metathesis and Transalkylation in Tandem Catalysis

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Thesis submitted in fulfilment of the requirements for the degree

PHILOSOPHIAE DOCTOR

in

CHEMISTRY

of the North-West University (Potchefstroom Campus).

Promoter: Prof. HCM Vosloo

Potchefstroom
2007

Contents

List of abbreviations

acac	Acetyl acetonate
ADMET	Acyclic diene metathesis
ATRP	Atom-transfer radical polymerization
BD or bd	Back-displacement
C=C	Ethene
$C=C_4$	1-Pentene
$C=C_5$	1-Hexene
$C=C_7$	1-Octene
$C=C_9$	1-Decene
CM	Cross metathesis
COD	Cyclooctadiene
CTC	Concurrent tandem catalysis
D or d	Displacement
DCM	Dichloromethane
GC	Gas Chromatography
Grubbs 1	First generation Grubbs catalyst
int std	Internal standard
iso1	First isomerization experiment
iso2	Second isomerization experiment
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
PhCl	Chlorobenzene
PMP	Primary Metathesis Product
RCM	Ring-closing metathesis
ROM	Ring-opening metathesis
ROMP	Ring-opening metathesis polymerization
SHOP	Shell Higher Olefin Process
SMP	Secondary Metathesis Product
ss	Stainless steel
TAA	Trialkylaluminum
T^{bd}	Back-displacement temperature

TC	Tandem catalysis
T^d	Displacement temperature
TDA	Tridecylaluminum
TEA	Triethylaluminum
THA	Trihexylaluminum
TIBA	Triisobutylaluminum
TOA	Trioctylaluminum

CHAPTER 1

General introduction

Although longer chain terminal alkenes have a wide variety of uses, such as in the production of detergents, plasticizers and lubricants and as polymerization co-monomers, only a limited number of processes are industrially applied to prepare these alkenes. Among these processes are the dehydration of natural alcohols, cracking of higher paraffins (wax cracking), and oligomerization processes such as the Ziegler process and the Shell Higher Olefin Process (SHOP).[1,2]

The basic raw material for the dehydration of alcohols is a fatty acid triglyceride, which is first converted to the methyl ester and then reduced to the primary alcohol. The alcohol is dehydrated to a terminal alkene in a catalytic vapour phase reaction at 300-450 °C over a neutral or slightly basic alumina catalyst (Figure 1.1).

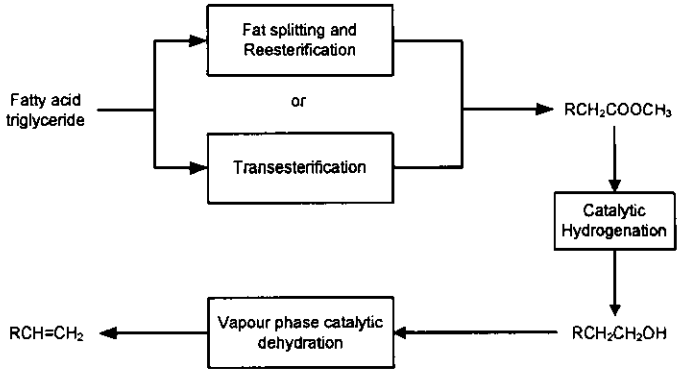

Figure 1.1: Schematic representation of the dehydration of alcohols

Thermal cracking of paraffin waxes (Figure 1.2) has been used for many years to prepare terminal alkenes (α-olefins). In order to minimize the production of ethene and propene and maximize the yield of terminal alkenes, wax cracking is conducted under somewhat milder conditions (500-600 °C for 5-15 s) compared to the production of ethene by cracking of naphtha or gas-oil. Although the chemistry of this process is quite complex, the simplified process can be seen as a radical chain mechanism in which the key step is the elimination of 1-alkene from a secondary free radical.

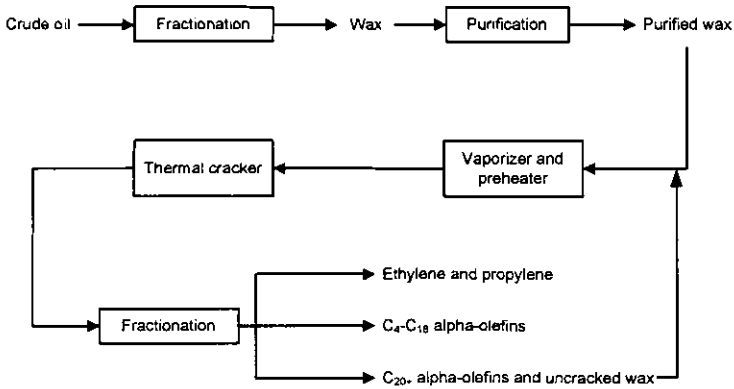

Figure 1.2: Schematic representation of wax cracking

In the Ziegler process (Figure 1.3), ethene is converted into C_4-C_{20} terminal alkenes (α-olefins) with an even number of carbon atoms. Unlike the product from the wax cracking process, the 1-alkenes that are prepared with the Ziegler process are essentially free of diene, naphthene and aromatic impurities.

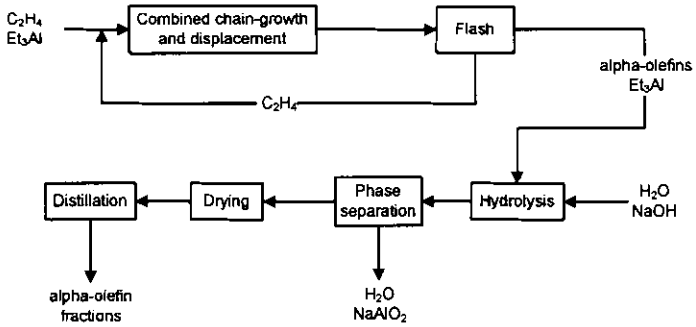

Figure 1.3: Schematic representation of the Ziegler process

The nickel-catalyzed oligomerization of ethene to prepare linear terminal alkenes on a large scale was used by Shell in the Shell Higher Olefin Process (Figure 1.4).

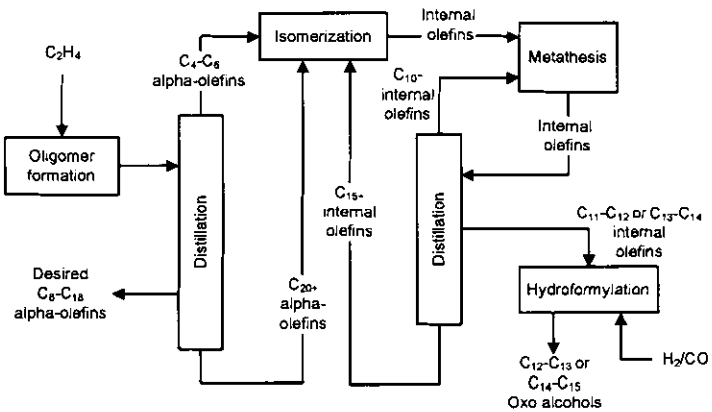

Figure 1.4: Schematic representation of the Shell Higher Olefin Process (SHOP)

SHOP involves four sequential operations, starting with ethylene oligomerization with a soluble nickel catalyst to give linear terminal alkenes. These alkenes are isomerized over a heterogeneous catalyst to internal alkenes in the second step. The third step involves a metathesis reaction, followed by a combination of isomerization, hydroformylation and hydrogenation in the last step.

Most of the commercial processes are based on ethylene oligomerization, and produce only even numbered linear terminal alkenes. The terminal alkenes that are available in South Africa however, are mostly produced from a gasification plant and Fischer-Tropsch conversion (Sasol) (Figure 1.5).

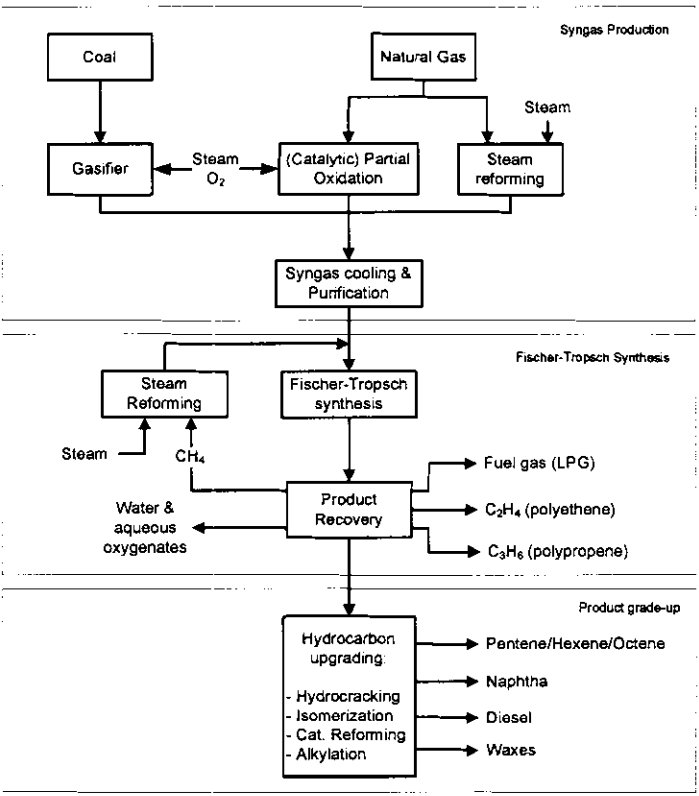

Figure 1.5: Overall process scheme for Fischer Tropsch

As can be seen in the product grade-up section, the C_5-C_8 alkene stream is distilled out in the hydrocarbon upgrading step. These alkene streams include odd-numbered terminal alkenes, making this product unique to South Africa. Since the world market is focused on even numbered terminal alkenes, there is a need to convert shorter chain (odd-numbered) terminal alkenes into the more valuable longer chain (even-numbered) terminal alkenes.

There are different catalytic routes to add value to the alkene streams available in South Africa, which consist mainly of C_5-C_8 alkenes. To increase the chain length processes such as oligomerization and metathesis can be used, followed by the conversion of an internal alkene into a terminal alkene by using an isomerization step. When different catalytic reactions are combined in one reactor, without separation steps in between, the term "tandem catalysis" is used.[3-5]

Metathesis is the reaction that is used as the first step of the tandem reactions, and converts the short chain terminal alkene starting material into a longer chain internal alkene in the presence of a transition metal catalyst.[6,7] The transalkylation reaction is based on the growth reaction that was developed by Ziegler and co-workers. In this transalkylation reaction, an internal alkene is isomerized to a terminal alkene in the presence of a trialkylaluminum compound and an isomerization catalyst, by the displacement and subsequent back-displacement of the alkyl groups of the aluminum compound.[8-10]

Although the industrial application of the transalkylation reaction was reported in patents, almost no information can be found on the reaction itself. Therefore the transalkylation reaction will be properly investigated before incorporating it in the tandem catalysis reactions.

The aim of this project is to obtain these longer chain terminal alkenes from widely available shorter chain terminal alkenes through a tandem catalysis process. In this case, the tandem catalysis experiments involve the combination of metathesis and transalkylation as well as metathesis and isomerization in one reactor resulting in the formation of longer chain terminal alkenes.

1.1 AIMS AND OBJECTIVES

The aim of this study is to make longer chain terminal alkenes by using metathesis and transalkylation or metathesis and isomerization in tandem catalysis. To achieve this, the following objectives were formulated:

- Study and optimize the metathesis reaction of short chain alkenes with Grubbs 1 as a catalyst.
- Perform the metathesis reaction with 1-pentene under optimized conditions to obtain 4-octene, the starting material for the transalkylation and isomerization experiments.
- Investigate the transalkylation reaction under different reaction conditions (temperature, reaction time, alkene:Al ratios) with different aluminum compounds and optimize it for 4-octene.
- Find a suitable and available quantitative analysis technique to determine the yield of the transalkylation reaction.
- Develop a suitable reaction setup for the transalkylation reactions that can also be used in the tandem experiments.
- Combine metathesis and transalkylation in one single reactor to obtain 1-octene by using tandem catalysis (Figure 1.6).
- Investigate the possibility of transforming the ruthenium Grubbs 1 catalyst to an isomerization catalyst *in situ*, without the addition of chemicals to induce this change, for the tandem metathesis-isomerization experiments.
- Compare the 1-octene yield and selectivity of the tandem metathesis-transalkylation reactions and the metathesis-isomerization reactions.

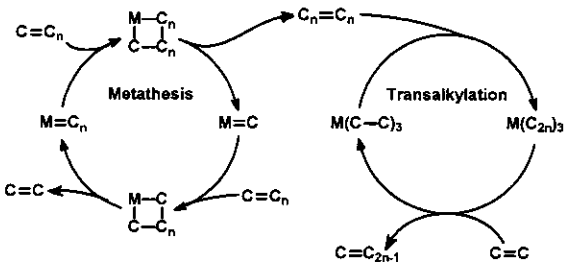

Figure 1.6: Schematic representation of tandem catalysis (hydrogen and other ligands omitted for clarity, M = metal)

1.2 STRUCTURE OF THIS THESIS

The metathesis reaction is described in **Chapter 2**, where different alkenes are used in the experiments and the metathesis reaction is optimized by varying the alkene:catalyst ratio.

The subject of **Chapter 3** is the transalkylation reaction. The displacement and back-displacement part of the transalkylation reaction are optimized and a suitable quantitative analysis method together with a stainless steel reactor setup is developed.

Chapter 4 describes two different types of tandem catalysis reactions that are both used to transform short chain terminal alkenes into longer chain terminal alkenes. In the first tandem reactions, the metathesis reaction (as described in Chapter 2) and the transalkylation reaction (Chapter 3) are combined and the tandem reaction is optimized. The 1-octene yields from these tandem reactions are then compared to the second type of tandem catalysis reactions, in which the metathesis is combined with isomerization by using the Grubbs 1 catalyst system under different reaction conditions.

Chapter 5 summarizes the conclusions of the different components of this study and reflects on the industrial importance of this research.

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CHAPTER 2

Metathesis

ABSTRACT

In this chapter the metathesis reaction of different alkenes is studied and optimized. This metathesis reaction will be used as the first step in the tandem catalysis reactions as described in Chapter 4. The Grubbs 1 catalyst showed high activity and selectivity and the obtained yields were reproducible, ranging between 45 and 64% for the primary metathesis product.

2.1 INTRODUCTION

Metathesis is the (apparent) interchange of carbon atoms between a pair of double bonds. This means that in a metathesis reaction two components react to form two new components, with no changes in oxidation number (Figure 2.1).

$$2\,CH_2{=}C_nH_{2n} \overset{\text{catalyst}}{\rightleftharpoons} C_nH_{2n}{=}C_nH_{2n} + CH_2{=}CH_2$$

Figure 2.1: Schematic representation of the metathesis reaction

The quite extraordinary nature of the alkene metathesis reaction took chemists by surprise. No one would have predicted in the 1950s or early 1960s that a reaction in which the double bond was apparently cleaved and the pieces put back together again was even remotely possible. Yet, not only is it possible, in some cases it can proceed to equilibrium within seconds.[1,2]

In industry, metathesis is one of the fundamental technologies that can be used to manipulate alkene streams. It allows manipulation of the carbon number of the streams, facilitates the preparation of higher value products and can provide alternative feed streams for other processes. A large-scale industrial process that incorporates alkene metathesis is the Shell Higher Olefin Process (SHOP), where higher linear alkenes are produced from ethene.[3] Metathesis is also used to produce compounds such as crown ethers, lactams and amino acids and in the ring-closing metathesis of dienes.[4-6]

In metathesis reactions, a distinction can be made between the primary metathesis reaction, which is the homometathesis reaction of the starting compound, side-reactions due to isomerization, and secondary metathesis reactions. The secondary metathesis reactions include cross metathesis reactions between terminal and internal alkenes and homometathesis reactions between identical alkenes.[7,8] Although cross metathesis (CM), is regarded as an unwanted side-reaction in homometathesis, studies showed that it can be used for the homologation of terminal alkenes.[9]

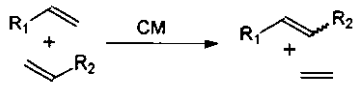

Figure 2.2: Schematic representation of CM

Other types of metathesis, which also include a metal-catalyzed redistribution of carbon-carbon double bonds are ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) and ring-opening metathesis (ROM).[10,11]

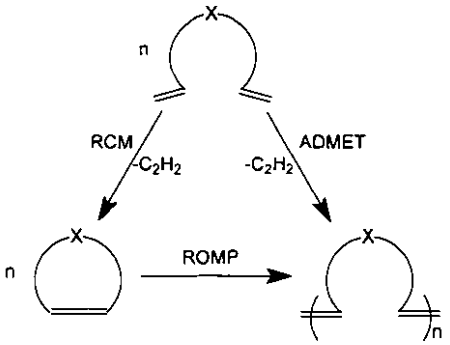

Figure 2.3: Schematic representation of various metathesis reactions

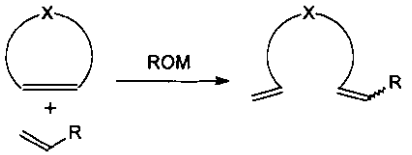

Figure 2.4: Schematic representation of ROM

These types of metathesis were thoroughly investigated and excellent results were obtained, for example with ROMP to make functional polymers.[12]

2.1.1 Metathesis catalysts

Metathesis catalysts can be divided into two categories, homogeneous catalyst systems and heterogeneous catalyst systems. In the heterogeneous systems, the catalyst and the substrate are in a different phase. Usually, the catalyst is in the solid phase, whereas the substrate will be in the gas or liquid phase. In the homogeneous systems, the catalyst and substrate are in the same phase, which usually is the liquid phase. Both homogeneous and heterogeneous systems are used

for metathesis reactions, although most research is concentrated on homogeneous systems. The main reason for this is that the homogeneous systems are more suitable for mechanistic studies.

2.1.1.a Homogeneous metathesis catalysts

Homogeneous catalysis systems play an important role on laboratory scale, where a comprehensive understanding of the metathesis process at a molecular level is required. Contrary to the ill-defined Ziegler-Natta type homogeneous catalyst systems, catalysts that are commonly used for alkene metathesis almost invariably contain a transition metal or organometallic complex and are usually well-defined.[13] These are sometimes effective by themselves, but often require the presence of a second compound (cocatalyst) and sometimes even a third compound (promoter).[14]

The systems most commonly used are based on the chlorides, oxides or other easily accessible complexes of Mo, Ru, W, Rh or Re.[15-18] Catalyzed alkene metathesis reactions are chain reactions with usually high turnover numbers.[1]

Ruthenium compounds have found wide application as catalysts for synthetic transformations in organic synthesis. The 11 different oxidation states of ruthenium make it suitable as a catalyst metal, as well as its capability to accommodate different ligands and its relative low price compared to other catalyst metals. Ruthenium catalyzed reactions include alkene metathesis, hydrogenation, oxygenation, Lewis-acid-catalyzed reactions and many more.[19,20]

Grubbs developed in the mid 1990s a ruthenium catalyst that was a breakthrough in homogeneous metathesis research (Figure 2.5).

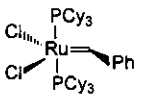

Figure 2.5: Grubbs 1 catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride)

The Grubbs catalyst is the most popular and useful metathesis catalyst known to date.[2,21-26] It combines a high activity with an excellent tolerance towards polar functional groups, which is due to the well balanced electronic and coordinative unsaturation of the Ru(III) centre.[27,28] The ruthenium complex has lower metathesis activity than the catalyst developed by Schrock based on molybdenum (Figure 2.6), but this lower intrinsic reactivity is compensated by an increased tolerance towards functional groups and a somewhat higher selectivity.

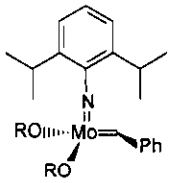

Figure 2.6: Schrock's molybdenum catalyst ($R=OC(CH_3)(CF_3)_2$)

In contrast to the Schrock catalysts, the ruthenium complexes can be used in the presence of both air and water.[3,15,22,29,30] The Grubbs catalyst is known to be active in a broad temperature range, at alkene:Ru ratios up to 100,000, with high selectivities and little or no activity for alkene isomerization.[5,14]

After the first generation Grubbs catalyst, the second generation was developed, which consisted of N-heterocyclic carbene (NHC)-ligated complexes (Figure 2.7).[31] This type of catalyst showed higher reactivity, selectivity and toleration towards functional groups.[32,33]

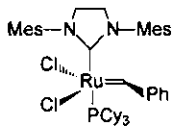

Figure 2.7: Second generation Grubbs catalyst (Grubbs 2)
[$RuCl_2(=CHPh)(PCy_3)(IMes)$]

Further investigations into functionalized ruthenium catalysts with different ligands are carried out in order to improve activity, selectivity and functional group tolerance.[34-36]

2.1.1.b Heterogeneous metathesis catalysts

In industry, mostly heterogeneous catalysts are used. These catalysts usually consist of Mo, Ru, W or Re in a high oxidation state on an inorganic support such as alumina, silica or other inert surfaces.[37] Rhenium catalyst systems received attention because of their better functionality tolerance and its ability to operate under milder reaction conditions. The advantages of hetero

geneous catalysis include easy separation of products from the catalyst, greater thermal stability and longer catalyst lifetime.[33,38,39] To be able to use heterogeneous catalysts and achieve the activity that is common to homogeneous catalysts, several studies were performed. In a particular study, a special type of supported catalyst was developed.[24] This Ru-based heterogeneous catalyst is released from the solid support during the metathesis reaction and the active species is solubilized. After the catalytic sequence, the propagating species returns to the solid support.

2.1.2 Metathesis mechanism

The mechanism of the metathesis reaction was not understood until almost 20 years after its discovery in the mid 1950s.[40] In 1970, Chauvin proposed a mechanism that involved metal carbene and metallacycle intermediates, which has become known as the carbene mechanism and remains the generally accepted mechanism to date. He discovered that the metathesis reaction occurred by a nonpairwise metal carbene alkene exchange, which was later supported by Grubbs, who found that indeed carbene and metallacycle intermediates were formed.[12,33,41-44]

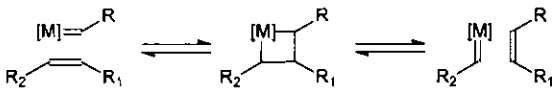

Figure 2.8: Mechanism of alkene metathesis

The principal steps of the alkene metathesis according to the Chauvin mechanism (Figure 2.8) involve a transition metal carbene that forms a π complex by coordination of an alkene. The [2+2] cycloaddition forms a metallacyclobutane, followed by a [2+2] cycloreversion and dissociation that leads to the alkene product.[45-47]

For the Grubbs catalyst systems, the proposed mechanistic pathways can be divided into an associative and dissociative mechanism (Figure 2.9).[12,35] The associative pathway involves initial binding of the alkene to form an 18-electron π complex (intermediate or transition state), followed by dissociation of phosphine (Figure 2.10).[48] The dissociative pathway proceeds by the initial loss of PCy_3 to generate a 14-electron intermediate, followed by coordination of the alkene. The rate-limiting step is believed to be the formation of the metallacyclobutane.[45] Kinetic and mechanistic studies have shown that the dissociative mechanism can be accepted as the preferred pathway.[1,32,42,48-51]

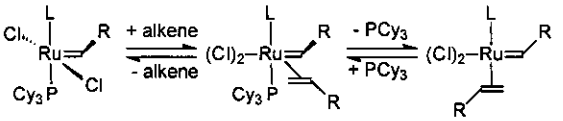

Figure 2.9: Associative pathway in alkene metathesis

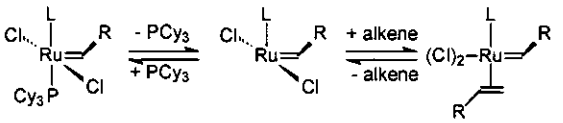

Figure 2.10: Dissociative pathway in alkene metathesis

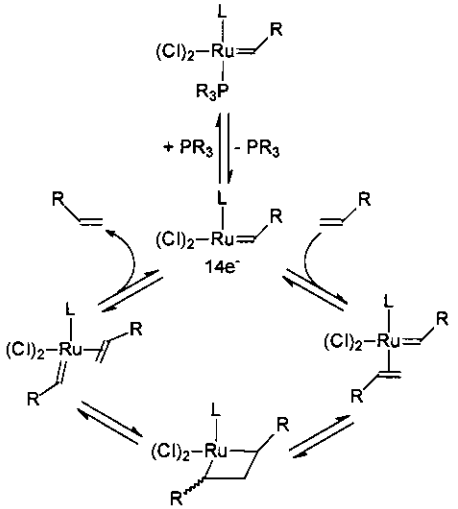

Figure 2.11: Schematic representation of dissociative pathway

When looking at the simplified schematic representation of the dissociative pathway (Figure 2.11), it can be seen that first a complex enters the catalytic cycle (initiation) by the loss of phosphine from the 16-electron benzylidene complex. The resultant 14-electron intermediate can either rebind the phosphine, or bind the alkene. Rebinding the phosphine removes the complex from the catalytic cycle, whereas reaction with the alkene (propagation) continues the catalytic cycle.

Although a lot of research has been done and there is general agreement about the mechanism, there is still a lot of discussion about the individual reaction steps. This involves the nature of the metallacyclobutane, which is considered to be either an intermediate or a transition state.[32,52] Other mechanistic aspects that have not been elucidated completely involve the determination of the actual rate-determining step and the structure of the active catalytic species.[53] Both theoretical and kinetic studies are carried out in order to find the answers to the questions that still exist with regard to the metathesis mechanism.[45,47,51,54]

Due to the extensive research considering the metathesis mechanism and the influence of different ligands on catalyst systems and metathesis activity, it was decided to concentrate this study on the optimization of the metathesis reaction to make it suitable to use as the first step in the tandem catalysis experiments.[32,41,45,47,49,51,53-56]

2.1.3 Factors influencing metathesis activity

A number of factors can influence the activity of a catalyst system.[1]

- The ratio of the different components. This usually involves the amount of catalyst relative to the amount of substrate, but also the relative amount of solvent can play a role.
- Reaction temperature. Generally it is found that activity increases when reaction temperature is increased, but the occurrence of side-reactions also plays a role in determining the optimal reaction temperature.
- Activation period and order of addition of components. This is important for systems that require the use of a cocatalyst.
- Solvent. It is important to choose a solvent with suitable properties. For example, in homogeneous systems all components have to be soluble in the chosen solvent.

To achieve the highest activity and selectivity, the optimal reaction conditions have to be determined by varying the above-mentioned factors.

2.1.4 Aims and objectives

In this project, the metathesis reaction was used as the first step in tandem catalysis experiments. The long chain internal alkenes that were prepared in the metathesis reaction from shorter chain terminal alkenes were used in the transalkylation and isomerization reactions in order to form longer chain terminal alkenes.

Metathesis 1-pentene $2\ CH_2{=}C_4H_8 \xrightarrow{\text{Grubbs1}} C_4H_8{=}C_4H_8 + CH_2{=}CH_2$

Metathesis 1-octene $2\ CH_2{=}C_7H_{14} \xrightarrow{\text{Grubbs1}} C_7H_{14}{=}C_7H_{14} + CH_2{=}CH_2$

Metathesis 1-decene $2\ CH_2{=}C_9H_{18} \xrightarrow{\text{Grubbs1}} C_9H_{18}{=}C_9H_{18} + CH_2{=}CH_2$

Figure 2.12: Schematic representation of metathesis reaction of 1-pentene, 1-octene and 1-decene with Grubbs 1 as a catalyst

Grubbs 1 was chosen as the catalyst for the metathesis reactions, because of its high selectivity towards the primary metathesis product (PMP) and relatively low price compared to the second generation Grubbs catalyst. The reaction temperature was not varied. A temperature of 30 °C was used for the reactions, because at this low temperature no significant isomerization and SMP is found. The optimal alkene to catalyst ratio was determined for 1-octene. Alkenes with different chain lengths were used in the reactions and the influence of the presence of the solvent was investigated.

2.2 EXPERIMENTAL

2.2.1 Materials

Chlorobenzene (99%) was purchased from Aldrich and dried before use by refluxing it over CaH_2. 1-Octene (97%) was obtained from Merck, passed through an activated Al_2O_3 column to remove impurities (such as peroxides) and stored under nitrogen. Grubbs 1 catalyst (Aldrich) was used as received. 1-Pentene (97%) and 1-decene (95%) were purchased from Acros and were used as received.

2.2.2 Experimental method

The general metathesis procedure that was used in this project is schematically drawn in Figure 2.13. In a typical experiment, 0.00524 g Grubbs 1 catalyst (alkene:Ru molar ratio = 1,000) was weighed and transferred to a 3 mL glass reaction vial fitted with Mininert valves (mini-reactor). The reactor was brought under nitrogen and closed, followed by the addition of 0.6 mL chlorobenzene (solvent and internal standard for gas chromatography, GC) and 1 mL 1-octene with gastight syringes. The reactor was stirred on a magnetic stirrer and kept at 30 °C in an aluminum heating block on a hot plate. A GC sample was taken for analysis at regular time intervals during the metathesis reaction.

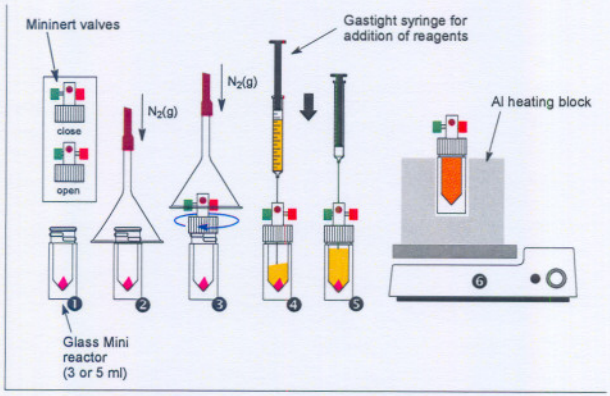

Figure 2.13: Schematic representation of metathesis procedure

Experiments were carried out with 1-pentene, 1-octene and 1-decene as the starting alkene. Generally, an alkene:Ru molar ratio of 1,000 was used for the experiments, but experiments where the ratio was varied were also performed. In some experiments, the ethene gas that was formed during the metathesis reaction was allowed to escape. To achieve this, a needle was put in the septum of the reactor during the reaction.

2.2.3 Analytical techniques

Analysis of the reaction mixture was performed on an Agilent Technologies 6850 gas chromatograph, equipped with a HP-1 column (30 m x 0.32 mm x 0.25 µm, Methyl Siloxane) and FID detector. The following analysis conditions were used:

Inlet temperature	:	300 °C
Detector temperature	:	350 °C
N_2 carrier gas flow rate	:	1.8 mL min^{-1} at room temperature
Injection volume	:	0.2 µL (manual injection)
Oven program	:	70 °C for 1 min
		70 to 200 °C at 10 °C min^{-1}
		200 °C for 1 min
H_2 gas flow rate	:	40 mL min^{-1} at room temperature
Air flow rate	:	450 mL min^{-1} at room temperature
Split ratio	:	50:1

2.2.4 Calculations

To determine the composition of the metathesis reaction mixture the internal standard method was used, with chlorobenzene (C_6H_5Cl) as the internal standard. First, the response factor (rf) of the alkene compared to the internal standard was calculated, using the following formula:

$$\frac{V_{Cn}}{V_{PhCl}} = rf \frac{A_{Cn}}{A_{PhCl}}$$

V_{Cn} = volume of alkene [mL]
V_{PhCl} = volume of internal standard [mL]
A_{Cn} = area of alkene peak (obtained from GC)
A_{PhCl} = area of internal standard peak (obtained from GC)
rf = response factor

The response factor was calculated by plotting V_{Cn}/V_{PhCl} against A_{Cn}/A_{PhCl} for solutions with different alkene:chlorobenzene ratios. The slope of the calibration curve represented the response factor. The calibration results for the different alkenes are presented in the table below.

Table 2.1: Response factors of different alkenes calculated from calibration curves with chlorobenzene as internal standard

Alkene	rf
1-pentene	1.5
1-octene	1.2
1-decene	1.2

The conversion of alkene at a certain time during the metathesis reaction was calculated using the following formula:

$$alkene\ conversion\ [mol\%] = \left(1 - \frac{n_t}{n_i}\right) \times 100$$

n_t = number of moles of alkene at time t

n_i = number of moles of alkene before reaction

The number of moles can be calculated with the following formula:

$$n = \frac{V_{Cn} \times \rho_{Cn}}{M_{Cn}} = \frac{A_{Cn} \times V_{PhCl} \times rf \times \rho_{Cn}}{M_{Cn} \times A_{PhCl}}$$

n = number of moles alkene

V_{cn} = volume of alkene [mL]

ρ_{Cn} = density of alkene [g/mL]

M_{Cn} = molar mass of alkene [g/mol]

A_{Cn} = area of alkene peak (obtained from GC)

V_{PhCl} = volume of internal standard [mL]

rf = response factor

A_{PhCl} = area of internal standard peak (obtained from GC)

The alkene conversion was then plotted against reaction time.

2.3 RESULTS AND DISCUSSION

A typical gas chromatogram of the reaction mixture after metathesis is presented in Figure 2.14. As can be seen from this graph, the different peaks are separated and suitable for quantitative analysis. Table 2.2 was composed to get an overview of possible reaction products from the metathesis reaction of 1-octene.[7,21]

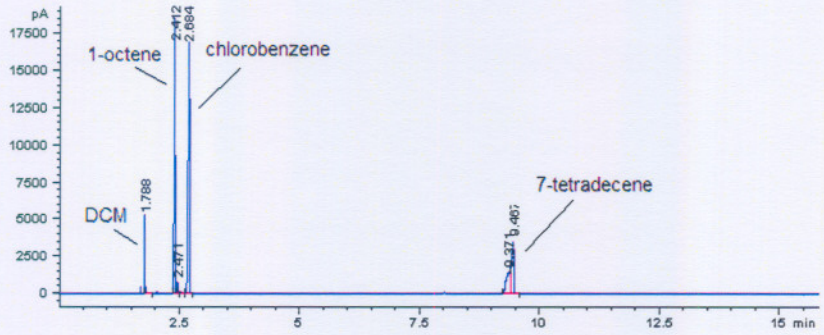

Figure 2.14: Typical gas chromatogram of the reaction mixture after metathesis of 1-octene with Grubbs 1 after 5 hours [alkene:Ru ratio = 1,000, solvent/int std = chlorobenzene, T = 30 °C]

Table 2.2: Overview of possible reaction products from the metathesis of 1-octene

	Reaction	Substrate	Products
1	Primary metathesis (PMP)[a]		
	Homometathesis[b]	C_7=C	C_7=C_7 + C=C
2	Isomerization	C_7=C	C_6=C_2
3	Secondary metathesis (SMP)[c]		
	Cross metathesis[d]	C_7=C + C_6=C_2	C_7=C_6 + C_2=C
			C_7=C_2 + C_6=C
	Homometathesis[b]	C_6=C_2	C_6=C_6 + C_2=C_2

a. Primary metathesis refers to the major metathesis reaction
b. Homometathesis refers to the metathesis reaction between the same alkenes
c. Secondary metathesis refers to the metathesis side-reactions due to isomerization
d. Cross metathesis refers to the metathesis reaction between different alkenes

As can be seen from Figure 2.14, only PMP (7-tetradecene) was formed, no SMP was detected. A little isomerization was observed, which caused the small peak right next to the 1-octene peak. The DCM peak refers to the dichloromethane, a solvent that was used to rinse the syringe between analyses.

To optimize the metathesis reaction with Grubbs 1 the alkene:Ru ratio was varied. Reactions were also carried out with different alkenes to investigate the influence of alkene chain length.

2.3.1 Different alkene:Ru ratios

1-Octene:Ru ratios of 1,000 to 100,000 were used to compare PMP yields. The analysis of the reaction mixture after the metathesis of 1-octene with Grubbs 1 with different alkene:Ru ratios showed only PMP, no SMP was detected. These results were similar to the results obtained from the metathesis reaction of 1-octene with an alkene:Ru of 1,000 (Figure 2.14), where also only PMP was detected. As can be seen from the graph displaying the PMP yield in time, the lower 1-octene:Ru ratios showed higher initial reaction rates. This was expected, since more catalyst generally results in higher yields and reaction rates.[57]

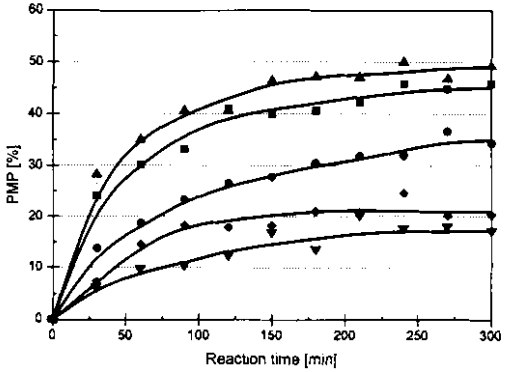

Figure 2.15: Kinetics of the metathesis reaction of 1-octene with different 1-octene:Ru ratios (1-octene:Ru = ■ 1,000; ▲ 5,000; ● 10,000; ◆ 50,000; ▼ 100,000) [Grubbs 1, solvent/int std = chlorobenzene, T = 30 °C]

The initial reaction rates were high with alkene:Ru ratios of 1,000 and 5,000, where the 5,000 was even higher than the one of 1,000. This can be due to inaccuracies in the reaction method, because the results were very close. The initial rates of the higher ratios (10,000, 50,000 and 100,000) were considerably lower and for the 50,000 and 100,000 ratios the PMP yield was only around 20%.

To compare the yields for the different alkene:Ru ratios after the metathesis reaction, the PMP yield was calculated after 5 hours.

Table 2.3: Influence of the 1-octene:Ru ratio on the PMP yield of the metathesis of 1-octene after 5 hours with Grubbs 1 [T = 30 °C, solvent/int std = chlorobenzene]

Ratio $C=C_7/Ru$	PMP [%]
1,000	45
5,000	49
10,000	35
50,000	21
100,000	17

When looking at the table, it was again confirmed that the PMP yield was increased with decreased 1-octene:Ru ratios. Although the PMP yield for a ratio of 5,000 was higher than that of 1,000, both yields were very close. When looking at yields of 50,000 and higher, it can be seen that the PMP yield dropped considerably. This could be attributed to an "overcrowding" effect of the catalyst in the relatively small reactor volume, meaning that the solution could become too concentrated. Since the PMP yield obtained from an alkene:Ru ratio of 1,000 was reproducible and sufficient for further studies, this ratio was used for the following optimization experiments.

2.3.2 Different alkene chain lengths

To investigate the influence of alkene chain length on the PMP yield in metathesis, reactions were carried out with 1-pentene, 1-octene and 1-decene. First, the metathesis reaction 1-pentene was investigated, which produced the following products (Figure 2.16). Table 2.4 summarizes the possible reaction products from the metathesis reaction of 1-pentene.

When looking at the GC analysis of the metathesis product (Figure 2.16), it can be seen that only *cis*-and *trans*-4-octene (PMP) were formed, no SMP or isomerization products were detected.

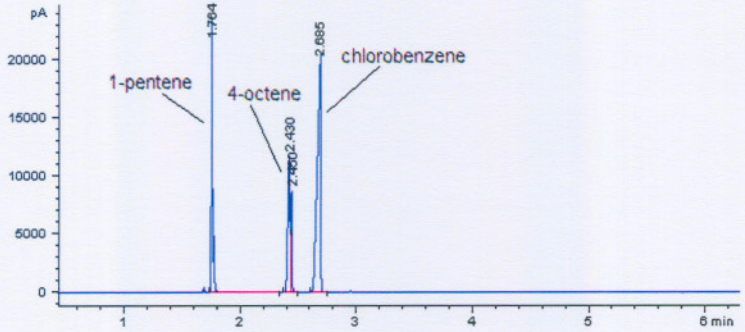

Figure 2.16: Typical gas chromatogram of the reaction mixture after metathesis of 1-pentene with Grubbs 1 after 5 hours [alkene:Ru ratio = 1,000, solvent/int std = chlorobenzene, T = 30 °C]

Table 2.4: Overview of possible reaction products from the metathesis of 1-pentene

	Reaction	Substrate	Products
1	Primary metathesis (PMP)		
	Homometathesis	C_4=C	C_4=C_4 + C=C
2	Isomerization	C_4=C	C_3=C_2
3	Secondary metathesis (SMP)		
	Cross metathesis	C_4=C + C_3=C_2	C_4=C_3 + C_2=C
			C_4=C_2 + C_3=C
	Homometathesis	C_3=C_2	C_3=C_3 + C_2=C_2

Figure 2.17 shows the product composition in time during the metathesis of 1-pentene with Grubbs 1 at 30 °C. The PMP yield (composed of 4-octene and ethene) is around 60% after 5 hours, and the 4-octene yield around 40%. As can be seen from Figure 2.17, the initial reaction rate is high, and levels out after two to three hours. After three hours the PMP yield is almost constant. The second alkene in this comparison is 1-octene, of which the analysis results were discussed in Figure 2.14 and Table 2.2. When looking at the product composition in time during the metathesis of 1-octene (Figure 2.18) it is clear that a similar pattern to that of the metathesis of 1-pentene can be found. The initial reaction rate is high and the maximum PMP yield was reached after two to three hours. The PMP yield of the metathesis of 1-octene was around 45%.

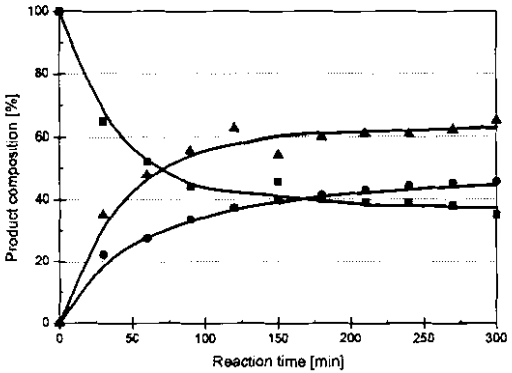

Figure 2.17: Kinetics of the metathesis reaction of 1-pentene (■ 1-pentene; ▲ PMP; ● 4-octene) [Grubbs 1, alkene:Ru ratio = 1,000, T = 30 °C, solvent/int std = chlorobenzene]

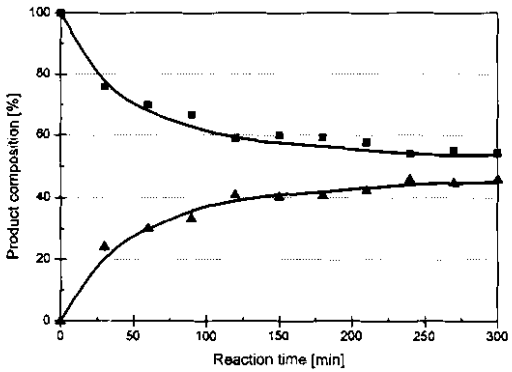

Figure 2.18: Kinetics of the standard metathesis reaction of 1-octene (■ 1-octene; ▲ PMP) [Grubbs 1 catalyst, alkene:Ru ratio = 1,000, T = 30 °C, solvent/int std = chlorobenzene]

Finally, the metathesis of 1-decene was performed under the same reaction conditions as were used for 1-pentene and 1-octene.

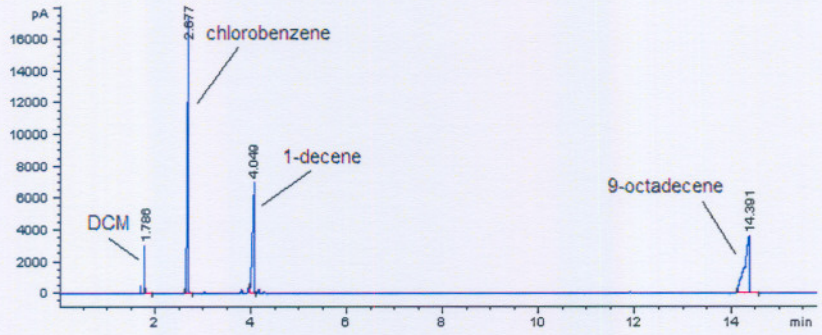

Figure 2.19: Typical gas chromatogram of the reaction mixture after metathesis of 1-decene with Grubbs 1 after 5 hours [solvent/int std = chlorobenzene, T = 30 °C]

Table 2.5 gives an overview of possible reaction products from the metathesis of 1-decene.

Table 2.5: Overview of possible reaction products from the metathesis of 1-decene

	Reaction	Substrate	Products
1	Primary metathesis (PMP)		
	Homometathesis	$C_9=C$	$C_9=C_9 + C=C$
2	Isomerization	$C_9=C$	$C_8=C_2$
3	Secondary metathesis (SMP)		
	Cross metathesis	$C_9=C + C_8=C_2$	$C_9=C_8 + C_2=C$
			$C_9=C_2 + C_8=C$
	Homometathesis	$C_8=C_2$	$C_8=C_8 + C_2=C_2$

As can be seen from Figure 2.19, only PMP (9-octadecene) was formed and no significant isomerization was observed. These results fit in with the other results that were obtained in the metathesis reactions with Grubbs 1, and confirm the selectivity of the catalyst towards PMP.[21]

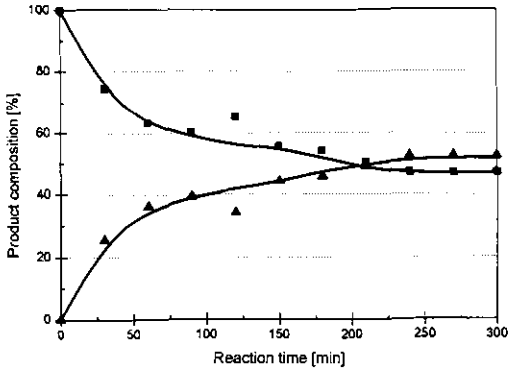

Figure 2.20: Kinetics of the metathesis reaction of 1-decene, (■1-decene; ▲ PMP) [Grubbs 1, alkene:Ru ratio = 1,000, T = 30 °C, solvent/int std = chlorobenzene]

The product composition during the metathesis of 1-decene with Grubbs 1 at 30 °C is presented in Figure 2.20. A similar pattern was observed in the metathesis of 1-pentene and 1-octene, where the initial reaction rate was high. But for 1-decene the reaction rate decreased after 1 hour, reaching the maximum PMP only after 4 hours.

Finally, the PMP yields after 5 hours for the metathesis reaction of the different alkenes were compared (Table 2.6).

Table 2.6: Influence of alkene chain length on the PMP yield after 5 hours [Grubbs 1, alkene:Ru ratio = 1,000, T = 30 °C, solvent/int std = chlorobenzene]

	PMP [%]
$C=C_4$	62
$C=C_7$	45
$C=C_9$	52

The PMP yields after the metathesis of 1-octene and 1-decene are relatively close, which means that the influence of alkene chain length is not very clear. The PMP yield of 1-pentene is slightly higher, but this can possibly be described to the escaping of ethene gas during the reaction, caused by leaking of the mini-reactors, shifting the equilibrium to the right. Although the experiments were carried out in similar mini-reactors, small differences in for instance closing capacity of the valves might be observed. The shorter chain 1-pentene was also more volatile at the reaction temperature (30 °C) than the other two alkenes, which might also have caused differences in catalyst/alkene interactions, leading to different results.

2.3.3 Influence of solvent and equilibrium shift

The standard metathesis was performed without a solvent, using only a very small quantity of chlorobenzene as internal standard for the GC analysis. The PMP yield was compared to the PMP yield after a standard metathesis reaction (Figure 2.18).

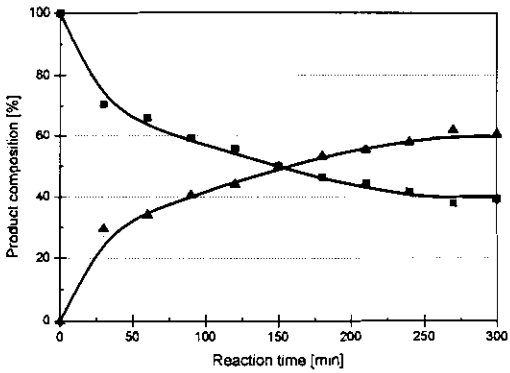

Figure 2.21: Kinetics of the metathesis reaction of 1-octene, without solvent (■ 1-octene; ▲ PMP) [Grubbs 1 catalyst, alkene:Ru ratio = 1,000, T = 30 °C, chlorobenzene = int std]

The PMP yield was higher when no solvent was used, compared to the standard metathesis reaction. This may indicate that the solvent dilutes the reaction mixture in such a way that the catalyst has less interaction with the alkene, thus resulting in lower yields.

An attempt was made to shift the equilibrium of the reaction by removing the ethene that formed during the metathesis. This was done by putting a needle in the septum of the reactor during the reaction.

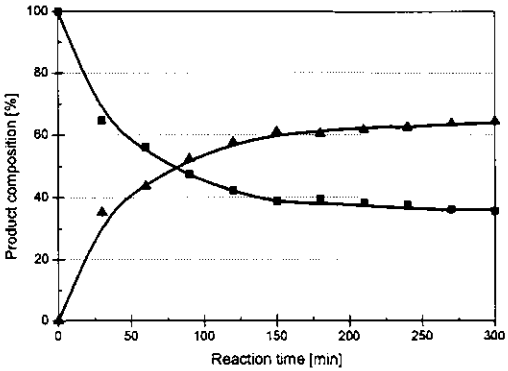

Figure 2.22: Kinetics of the metathesis reaction of 1-octene, ethene allowed to escape (■ 1-octene; ▲ PMP) [Grubbs 1 catalyst, alkene:Ru ratio = 1,000, T = 30 °C, solvent/int std = chlorobenzene]

Figure 2.22 shows an increase in PMP yield, which was as expected. It is known from literature that it is possible to shift the equilibrium towards the products if the by-product that is formed is a volatile alkene, such as ethene.[22,29,33]

Table 2.7 presents an overview of the PMP yields of the standard metathesis reaction of 1-octene, compared to the reactions without solvent and the one in which the gas was allowed to escape.

Both variations on the standard reaction method caused an increased PMP yield. The reaction in which the gas was allowed to escape, attempting to shift the equilibrium to the right showed the highest increase in PMP yield.

Table 2.7: Influence of solvent and equilibrium on the PMP yield of the metathesis of 1-octene after 5 hours [alkene:Ru ratio = 1,000, solvent/int std = chlorobenzene, Grubbs 1, T = 30 °C]

	PMP [%]
Standard	45
No solvent	60
Equilibrium shift	64

2.4 CONCLUSIONS

The metathesis reaction was performed on a small scale with good results and a reasonable understanding of the homogeneous metathesis reaction of alkenes with Grubbs 1 was developed. Grubbs 1 showed to be a suitable catalyst in these optimization reactions, since it had high activity, leading to relatively short reaction times, and high selectivity towards the primary metathesis product. At a reaction temperature of 30 °C no significant SMP or isomerization was detected.

Reproducible PMP yields were obtained from different alkenes, ranging from 45% after 5 hours for 1-octene to above 60% when 1-pentene was used or when the equilibrium of metathesis of 1-octene was shifted to the right.

It was determined that the presence of a solvent, in this case chlorobenzene, was not necessary to obtain a high PMP yield. The PMP yield for reactions without solvent even increased compared to the reactions in which a solvent was used (60% PMP compared to 45% with solvent). This can be an advantage when the reaction is scaled up, not only from a cost perspective, but also from a volume perspective. When no solvent is used, reaction volumes can be kept lower, requiring smaller reactors, or more PMP can be formed in the same size reactor.

The metathesis reaction proved to be a suitable way to produce longer chain (internal) alkenes, with high yields and relative short reaction times, making it possible to incorporate this reaction in the tandem catalysis reactions.

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CHAPTER 3

Transalkylation

ABSTRACT

The aim of the transalkylation reaction is to obtain terminal alkenes from internal alkenes by using trialkylaluminum as a catalyst. In this chapter, the chronological development of the successful reaction method and analysis of the transalkylation reaction is described, as well as the development of a stainless steel reactor to be used for the experiments. This research proves that it is possible to carry out the transalkylation in one single reactor, without the need of separation steps and with reproducible high yields.

3.1 INTRODUCTION

Alkene isomerization results in the apparent migration of the double bond along an alkyl chain and is often an undesired side-reaction in organometallic catalyzed reactions of alkenes, i.e. hydrogenation, metathesis, oligomerization and hydroformylation.[1] It is also found in a number of industrial processess as an intermediate step, such as in the SHOP process. Most isomerization reactions involve terminal-to-internal double bond isomerization, but in literature also reports of internal-to-terminal isomerization have been found.

The following observations generally apply to alkene isomerization reactions:[2]

- *Trans* alkenes are more stable than *cis* alkenes.
- Internal alkenes are more stable than terminal alkenes.
- Conjugated di- and oligoalkenes are favoured over isolated double bonds.
- Substituted (internal) alkenes with the highest degree of branching are thermodynamically favoured.
- Polar solvents accelerate the isomerization reaction.

Most catalytic isomerization reactions that are reported involve metal complexes as catalysts. Two different mechanisms are generally accepted, i.e. the metal hydride addition-elimination mechanism and the π-allyl mechanism. The first mechanism (Figure 3.1) is favoured when the catalytic species are capable of metal hydride formation. This mechanism requires external hydrogen and involves a 1,2 intermolecular hydrogen shift.

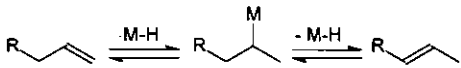

Figure 3.1: Metal hydride addition-elimination mechanism

Metals capable of π-allyl formation like Fe, Ni, Rh and Pd favour the second mechanism. This mechanism involves a 1,3 intramolecular hydrogen shift (Figure 3.2).

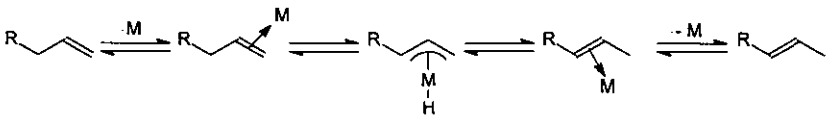

Figure 3.2: π -allyl complex mechanism

In this project, two specific types of isomerization reactions were investigated, i.e. 1-octene isomerization and transalkylation. The 1-octene isomerization was used to obtain internal alkenes that were used in the transalkylation reactions and is discussed in Paragraph 3.1.1. This isomerization reaction is an example of a terminal-to-internal type of isomerization.

The aim of this study is to add value to the short chain terminal alkenes that are widely available in South Africa by converting them into longer chain terminal alkenes. The metathesis of short chain terminal alkenes to obtain longer chain internal alkenes (Chapter 2) was used as the first step to achieve this aim. After the metathesis, a "contrathermodynamic" isomerization step is required to convert these internal alkenes into terminal alkenes.

In literature, only a few examples of internal-to-terminal double bond isomerization are mentioned. Among these are:

- Metal hydride and related catalytic systems. This category includes the Wilkinson catalyst, $(Ph_3P)_3RhCl$, which is a well known hydrogenation catalyst. This catalyst is reported to give *inter alia* terminal alkenes when an internal alkene is subjected to typical hydrogenation conditions (Figure 3.3). Metal hydrides also play a role in hydrosilylation reactions, in which isomerization takes place via the reversible formation of a metal alkyl.

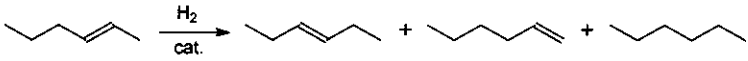

Figure 3.3: Schematic representation of the hydrogenation reaction with the Wilkinson catalyst

- Metal carbene and related catalytic systems. The primary cause of secondary metathesis product (SMP) in the metathesis reaction is double bond isomerization (Table 3.1).

Table 3.1: Overview of possible reaction products from the metathesis of 1-pentene

	Reaction	Substrate	Products
1	Primary metathesis (PMP)		
	Homometathesis	C_4=C	C_4=C_4 + C=C
2	Isomerization	C_4=C	C_3=C_2
3	Secondary metathesis (SMP)		
	Cross metathesis	C_4=C + C_3=C_2	C_4=C_3 + C_2=C
			C_4=C_2 + C_3=C
	Homometathesis	C_3=C_2	C_3=C_3 + C_2=C_2

SMP is formed as a result of cross metathesis between the original alkene and the isomer alkene. A metal carbene and metal carbene hydride mechanism was suggested to account for this observation (Figures 3.4 and 3.5).[2-4]

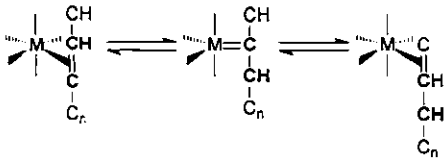

Figure 3.4: Metal carbene mechanism

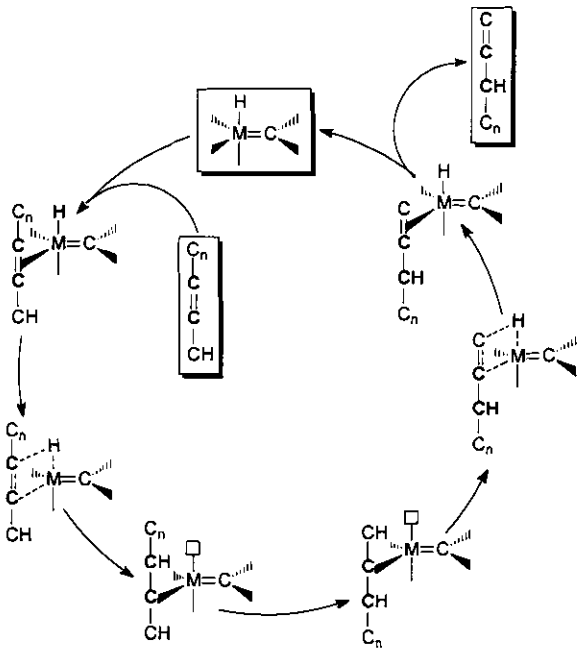

Figure 3.5: Metal carbene hydride mechanism (shown for internal-to-terminal migration)

- Other catalytic systems. Other organometallic complexes that are reported to have isomerizing properties under certain reaction conditions include Co, Cu(I), Pt chloride and Rh complexes as well as metallocenes.
- Stoichiometric methods of isomerization.[5] This type of isomerization includes aluminum catalyzed isomerizations, organoboranes and zirconocene reactions. Aluminum catalyzed isomerizations involve reactions such as alkyl growth, displacement and hydroalumination (Figure 3.6).[6-8]

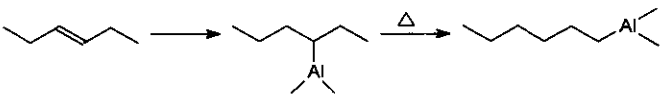

Figure 3.6: Hydroalumination and migration

Another aluminum catalyzed isomerization reaction that was reported in patents recently is the transalkylation reaction.[9,10] Based on the "Aufbau" or "growth" reaction by Ziegler[11], the reaction was modified to convert internal alkenes into terminal alkenes by means of an alkylaluminum compound and an isomerization catalyst (See Paragraph 3.1.2).

Organoboranes were used to produce terminal organoboranes from internal alkenes by heating it above 130 °C (Figure 3.7). This phenomenon makes it possible to functionalize the terminal position of the alkenes, for example by oxidation to the corresponding alcohol.[12]

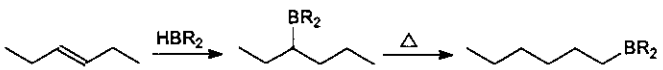

Figure 3.7: Thermal isomerization with organoboranes

Zirconium has the ability to migrate along a metal-bound polymer chain from an internal position to a terminal position, in the reaction of $Cp_2Zr(R)Cl$ with an alkene.[13] The corresponding terminal alkene can then be recovered by cleaving of the alkylzirconium

complex (Figure 3.8). In contrast to the analogous organoboron or -aluminum compounds that rearrange slowly at elevated temperatures, the migration of the metallic moieties in the case of Zr proceeds rapidly at room temperature.

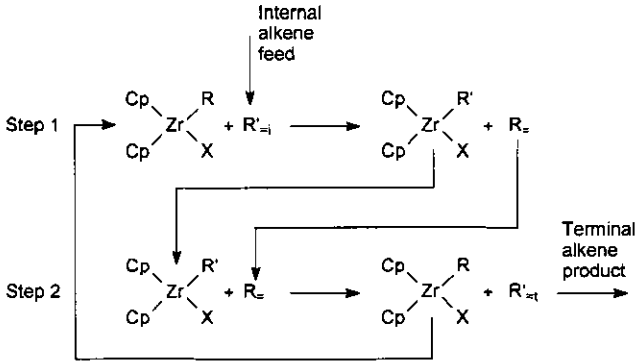

Figure 3.8: Isomerization and displacement reactions of zirconocene
($R_=$ = alkene, $R_{=t}$ = terminal alkene, $R_{=i}$ =internal alkene)

Although a number of routes were available to prepare terminal alkenes from internal ones, transalkylation was used in this study. One of the main reasons for this was that alkylaluminums are more available and accessible in industry compared to alkylboranes or the zirconium compounds. Furthermore, organoaluminum compounds are relatively cheap and show characteristic reactivity. Since aluminum is found in the earth's crust in large amounts, the environmental pollution caused by aluminum will be minimal.[14] Another important fact regarding this subject is that the majority of literature available on the transalkylation reaction consists of patents, and almost no publications have been found in the open literature. Therefore no reports have been found about the optimization of the transalkylation reaction, making it an interesting reaction to investigate.

Both isomerization reactions that were used in this project will be discussed in the next paragraphs. First, the choice of catalyst for the 1-octene isomerization is discussed in Paragraph 3.1.1. Secondly the transalkylation reaction is discussed in detail in Paragraph 3.1.2, including its history and an overview of available literature (including patents) on the subject.

3.1.1 1-Octene isomerization

Isomerization is a common reaction used to obtain internal alkenes from terminal alkenes.[15-17] Since internal octenes were used for the transalkylation reaction and 1-octene was readily available, isomerization was used to obtain internal octenes.

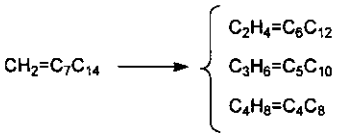

Figure 3.9: Schematic representation of isomerization of 1-octene

In literature, a wide variety of homogeneous and heterogeneous isomerization catalysts are reported.[18] This includes metal complexes such as Ni[19-28], Ni with Al as a co-catalyst,[29] Rh,[30] Ru,[31-35] Pd[36,37] and metal hydrides (i.e. Rh, Ru, Co).[38] Zeolites, such as BZSM5,[39] HZSM22, HZSM35[40] and HZSM5[41,42] are also used as heterogeneous isomerization catalysts.

HZSM5 is a protonic zeolite, which is used in industry for different reactions, such as skeletal isomerization in alkenes, xylene isomerization and cracking. Its structure is composed of SiO_2 and Al_2O_3 blocks forming rings and pores, and it reacts by means of its internal acidic hydroxyl groups that bridge between Si- and Al-substituted tetrahedral lattice sites. HZSM5 is reported to have high catalytic activity, but a low selectivity due to the occurrence of side-reactions. Cracking is one of the main side-reactions that are observed in isomerization with HZSM5, but this occurs generally at higher temperatures.[41-47] HZSM5 was chosen as the catalyst for the isomerization of 1-octene because of its high activity and selectivity, its availability and the fact that it is a heterogeneous catalyst, making separation easy.

3.1.2 Transalkylation

3.1.2.a History and development of the transalkylation reaction

Ziegler and co-workers[11] discovered in 1953 that certain combinations of transition metal and organometallic compounds converted ethene to a linear, high molecular weight polymer. A trialkylaluminum compound (such as triethylaluminum, TEA) was mostly used for this reaction, in combination with a titanium halide catalyst.

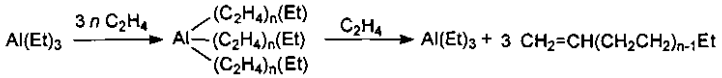

Figure 3.10: Ziegler process – growth reaction and displacement

In this "growth" reaction, the ethene is repeatedly inserted in the aluminum-alkyl bond and produces long-chain trialkylaluminums, from which long-chain primary alkenes with an even carbon number were obtained in a subsequent displacement reaction.[5,48-51] From the 1950s to the 1970s, more companies tried to exploit this growth reaction by registering their discoveries in patents. This process was realized on industrial scale by Gulf Oil,[52-54] Continental Oil[55] and Ethyl Corporation.[56]

A similar process was used by Shell, known as the Shell-higher-olefin process (SHOP).[57] In this process a series of chain lengthening and shortening steps (such as oligomerization, isomerization and metathesis) are combined to synthesize primary alkenes (Figure 3.11).[58]

The Ziegler route was also used to prepare alcohols, where the aluminum trialkyls formed after ethene insertion are oxidized by atmospheric oxygen and hydrolyzed to the corresponding alcohols (Figure 3.12).[14,57]

This process was used on industrial scale by several companies.[59,60] Continental Oil patented two different oxidation reactions of trialkylaluminum compounds, one with an oxygen containing compound and the other with an excess of an aliphatic aldehyde whereby aluminum hydroxide was a by-product.[61-63] In the oxidation and hydrolysis reaction of trialkylaluminum patented by Esso, an aluminum oxide complex was the by-product after hydrolysis with water.[64]

After Ziegler's discovery, the idea of using the trialkylaluminum compound in cooperation with an isomerizing catalyst, to obtain primary alkenes from internal alkenes was formed.[50] In this modified method, the first step, which was the chain growth step in the Ziegler method, consists of the displacement of the alkyl group on the aluminum, instead of inserting the alkene in the aluminum-alkyl bond. The alkyl on the aluminum can only be displaced by a terminal alkene, thus the need for an isomerizing catalyst.

The second step is quite similar to the second step of the Ziegler method, the displacement (in this case called the back-displacement) of the alkyl group by another alkene, setting free a primary alkene (Figure 3.13).

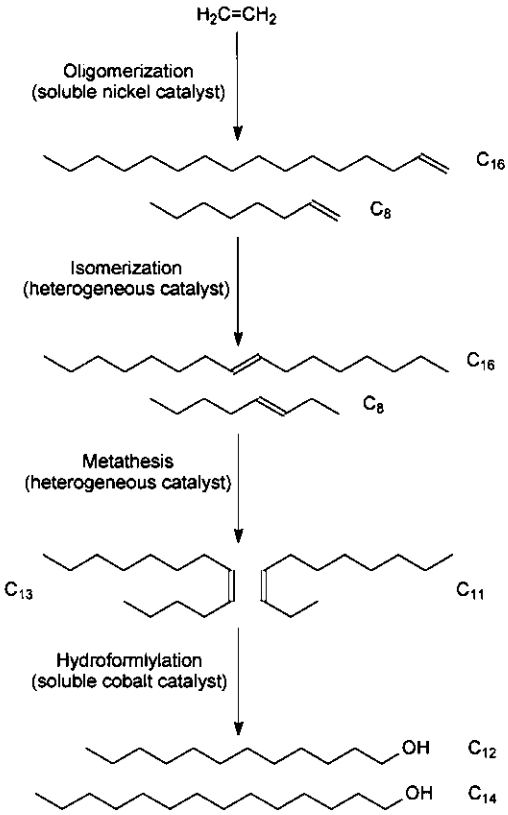

Figure 3.11: Reaction steps in the SHOP process

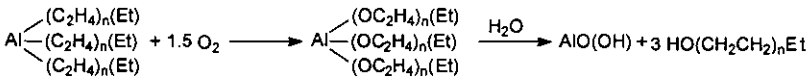

Figure 3.12: Ziegler alcohol synthesis

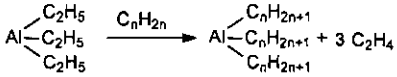

Figure 3.13: Schematic representation of the displacement of TEA with an alkene

Around the 1960s, several companies such as Ethyl Corporation,[65] Monsanto,[15,16] Henkel.[66,67] Phillips Petroleum[17] and Hercules Inc.[68] laid the basis for this method. After a long period of silence, this method was optimized with a first report in 1990 by Ethyl Corporation.[69] This publication was followed by additional patents by the same company, defining the displacement and back-displacement of trialkylaluminum, to obtain primary alkenes from internal ones.[70-72] In these patents the transalkylation reaction (displacement and back-displacement) was described.

The major change with regard to earlier patents was that the displacement reaction takes place in the presence of a catalyst, avoiding the need of extremely high temperatures (>300 °C) as is necessary in thermal displacement.[5]

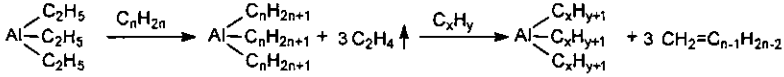

Figure 3.14: General schematic representation of the transalkylation reaction with TEA

The first part of the transalkylation reaction, the displacement, takes place with a trialkylaluminum (such as TEA) as a starting compound. The alkyl group on the aluminum is displaced by an alkene. This alkene, or a mixture of alkenes consists of internal alkenes (linear or branched), which isomerize in the presence of an isomerizing catalyst, such as a nickel compound.

Once the alkene is isomerized to a terminal alkene, it can displace the alkyl group of the aluminum. The displacing alkene should have a higher boiling point than the displaced alkene from the aluminum, because removal of the displaced alkene drives the reaction.[70]

It is favourable that the isomerization catalyst that is used also catalyzes displacement. The most suitable catalyst according to literature is a nickel compound, but also cobalt, palladium and iron compounds are reported.[5] Suitable nickel compounds include nickel(II) salts, nickel(II) carboxylates, nickel(II) acetonates and nickel(0) complexes.[69,72] The nickel catalyst can be reactivated

before the back-displacement reaction, in which it can also act as a catalyst. The mechanism of the nickel catalyzed transalkylation reaction is still poorly understood. It is believed that the catalytic active nickel species still contains at least one of the ligands that were originally bound to the nickel atom.[73]

The nickel catalyst has the tendency to catalyze undesired side-reactions, such as dimerization, chain growth and isomerization.[74] Fortunately, the rate of the side-reactions is much lower than the reaction rate of the back-displacement reaction. Therefore, with the appropriate measures, the catalyst can be deactivated after the reaction before the side-reactions become significant.

To stop these side-reactions, literature reports on several methods. A catalyst poison, containing lead can be added to the reaction mixture, forming a precipitate that can be filtered off after the reaction. Acetylenic hydrocarbon compounds are also reported to be useful in these aspects. Finally, a cyclodiene, preferably 1,5-cyclooctadiene (COD) can be added.[9,10,69,70,72] A small amount of COD would catalyze isomerization, but when an amount exceeding 1 g/mg Ni is added, isomerization is inhibited.

The COD is said to produce a vinyl alkene product that has reduced isomer impurity content and can be recovered for reuse.[70] COD is reported to displace aluminum alkyls, such as TIBA, but only at higher temperatures (>145°C). This poses no problem in this project, since reactions are taking place at lower temperatures.[75-77]

Amoco[78] and Albermarle[79] also patented their version of the transalkylation reaction. Amoco looked specifically at cobalt catalysts and Albermarle focused on dialkylaluminumchlorides to replace the trialkylaluminum in the transalkylation.

Another important player in this field was BASF, who brought several patents on the market.[9,10,80-82] Their first patents consist of basically the same transalkylation reaction presented by Ethyl Corporation, but focuses on the optimization of the industrial process mainly involving recycling and separation steps. Their last patent on the transalkylation reaction involves the production of internal alkenes by means of a metathesis reaction.[10] They also investigated the possibilities of the deactivation and separation of the nickel catalyst after the reaction.[82] Other reports of this particular way to produce terminal alkenes from internal ones included di-alkylaluminum hydrides, aluminum chlorides and alkylaluminum chlorides.[15-17]

3.1.2.b Factors influencing the transalkylation reaction

A number of factors are expected to have an influence on the yield of the transalkylation reaction. Among these are:

- Catalyst to aluminum ratio (in displacement + back-displacement part)
- Choice of trialkylaluminum compound (in displacement reaction)
  → possible steric and/or electronic effects
- Displacing/back-displacing alkene → possible steric and/or electronic effects
- Reaction conditions (temperature/reaction time/pressure)
  (in displacement + back-displacement part)

To achieve the maximum yield from the transalkylation reaction, these parameters have to be varied to be able to obtain optimal reaction conditions.

3.1.3 Aims and objectives

The aim of this project is to prepare longer chain terminal alkenes from shorter chain alkenes. Chapter 2 describes how short chain terminal alkenes are converted to longer chain internal alkenes in a metathesis reaction as the first step in the tandem catalysis experiments. The transalkylation reaction was used as the second step in the tandem catalysis reactions and is used to obtain terminal octenes from internal ones. This chapter describes the investigation of the transalkylation reaction, which has not been reported in literature before.

4-Octene was used as starting material for the transalkylation reactions because this was the product from the metathesis reaction of 1-pentene as described in Chapter 2. Another reason for using the transalkylation reaction to isomerize internal octenes is that 1-octene is currently in high demand in industry and is used in a variety of reactions, one of them is as comonomer in the production of linear low-density polyethylene (LLDPE).[14,81]

The objectives are therefore:

- Use HZSM5 as a catalyst to isomerize 1-octene to provide internal octenes for the optimization of the transalkylation reaction.
- Find a suitable and available quantitative analysis technique to determine the yield of the transalkylation reaction.
- Develop a suitable reaction setup for the transalkylation reactions that can also be used in the tandem experiments.
- Investigate the transalkylation reaction under different reaction conditions (temperature, reaction time, ratios) and optimize it for 4-octene.
- Use triisobutylaluminum (TIBA) and TEA as the aluminum compounds in the transalkylation reaction.
- Use nickel acetylacetonate ($Ni(acac)_2$) as the catalyst in both isomerization/displacement and back-displacement reactions.

3.2 EXPERIMENTAL

3.2.1 Materials

A mixture of internal octenes, which consisted mainly of 2-octene was obtained from Sasol and was used as received. Chlorobenzene (99%) was purchased from Aldrich and dried before use by refluxing it over CaH_2. 1-Octene (97%) was obtained from Merck, passed through an activated Al_2O_3 column to remove impurities (such as peroxides) and stored under nitrogen. $Ni(acac)_2$ and HZSM5 catalysts, obtained from Aldrich and Sasol respectively, were used as received. Internal octenes (2-octene, 3-octene and 4-octene) were purchased from Aldrich and used as received. 1-octanol, 2-octanol, 3-octanol and 4-octanol (Aldrich) were of analytical grade and were used without further purification. Dichloromethane (Merck) was used as received. 1,5-Cyclooctadiene was purchased from Aldrich and used as received. Triethylaluminum (93%), trioctylaluminum (25wt% in hexane) and triisobutylaluminum were obtained from Aldrich and used as received. 1-Hexene (97%) was purchased from Merck und used as received. Hydrogen peroxide (Saarchem) and sulphuric acid (Aldrich) were used as received. Deuterated benzene (C_6D_6) was purchased from Aldrich and used as received. All solvents used were of analytical grade.

3.2.2 Experimental method

3.2.2.a 1-Octene isomerization

A mixture of internal octenes was obtained by heterogeneous isomerization of 1-octene with HZSM5 as a catalyst. The HZSM5 catalyst was calcined under nitrogen at 300 °C for 16 hours in a round bottom flask. After cooling down, the catalyst was used to isomerize 1-octene, where 5 grams of catalyst were used for every 100 mL octene. The reaction mixture was kept at 40-50 °C while stirring and the progress of the isomerization reaction was followed by GC.

3.2.2.b Transalkylation

The transalkylation reaction consists of two parts, the displacement part, where the alkyl group on the aluminum is replaced by the chosen alkene and the back-displacement part, where the alkyl group of the formed trialkylaluminum (TAA) is replaced again by an alkene, setting free a 1-alkene. Firstly, attempts were made to carry out the displacement reaction and analyse the product. The results will be discussed in chronological order, to make it clear how the final method was developed and how the reactor that was used for the final experiments was designed.

B1 Displacement, oxidation and hydrolysis of trialkylaluminum

B1 Displacement, oxidation and hydrolysis of trialkylaluminum – Method 1

In the first attempt to analyze the trioctylaluminum (TOA) that formed in the displacement reaction it was reacted with air and water to obtain an alcohol. The formation of a primary alcohol (in this

case 1-octanol) would be an indication of the yield of the displacement reaction. In literature there were two possible reaction paths when reacting the TOA with oxygen (from air) and water. The first reaction path (figure 3.15) shows that an aluminum complex is formed together with the alcohol.[64]

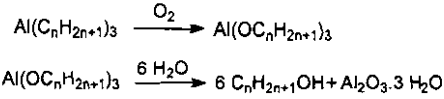

Figure 3.15: 1st possible reaction path of oxidation/hydrolysis with air/water

The second reaction path indicates that an aluminum hydroxide will form, again with the primary alcohol.[63]

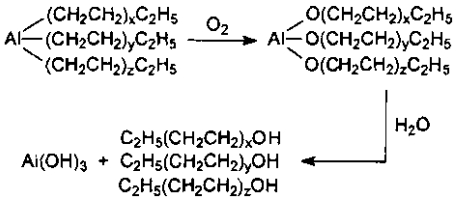

Figure 3.16: 2nd possible reaction path of oxidation/hydrolysis with air/water

In a typical experiment, a 3 mL mini-reactor was brought under nitrogen and closed with a septum. Triethylaluminum (TEA) (0.1 mL) was added to the reactor with a gastight syringe from its container, which was also placed under nitrogen. The syringe was rinsed with dichloromethane (DCM) and acetone. 1-Octene (1.8 mL) was added with a gastight syringe and the mini-reactor was kept at room temperature (25 °C) while stirring. After 2 hours the Supelco distillation setup was connected to the mini-reactor under nitrogen, and the excess 1-octene was distilled off at 160 °C. After cooling down the reactor was kept in an ice-bath and air was added with a syringe through the septum. The reaction mixture was then filtered with a Teflon syringe filter, and water was added (0.4 mL). The reaction mixture was then analyzed by GC after passing through a Teflon syringe filter.

After the experiment the reaction mixture was diluted with water, cast away on sand and disposed as chemical waste in a separate drum. The reaction was also scaled up and performed in a three-necked round bottom flask. In these experiments 1.6 mL TEA and 20 mL 1-octene were used.

B1 Displacement, oxidation and hydrolysis of trialkylaluminum – Design of stainless steel reactor, first reactor design

Since the oxidation reaction was a very exothermic reaction and trialkylaluminum compounds are known to react vigorously with both air and water, a glass flask without pressure release valve was not suitable for the experiments.[83] Therefore, a stainless steel reactor was designed.

The reactor that was designed had a volume of 150 mL, a pressure release valve and an analogue pressure meter (Figure 3.17). The temperature was monitored with an thermocouple. A heating mantle was fitted around the reactor to assure an even temperature in the reactor while it was heated on a hot plate. The reactor was also equipped with a sample inlet and two sample outlets, one for gas samples, the other for liquid samples. The liquid sample tube reached the bottom of the reactor, making it possible to obtain samples from the reactor under pressure, even when the volume of liquid that was left in the reactor was relatively small.

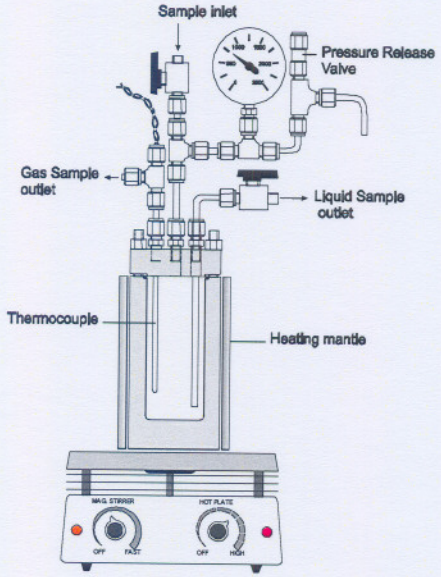

Figure 3.17: Schematic representation of first reactor model

B1 Displacement, oxidation and hydrolysis of trialkylaluminum – Method 2

The second attempt to oxidize and hydrolyze the formed TOA to obtain 1-octanol was done by reacting it with pure oxygen to form aluminumalkoxide, followed by hydrolysis with aqueous sulphuric acid. GC analysis was used to identify the 1-octanol that was formed.

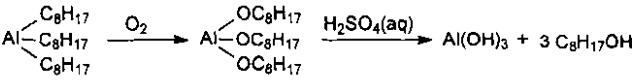

Figure 3.18: Oxidation/hydrolysis method with O_2 and H_2SO_4

In a typical experiment 20 mL 1-octene was transferred to the stainless steel reactor, which was brought under nitrogen. The trialkylaluminum (TIBA or TEA) (2 mL) was then added to the reactor with a gastight syringe. The reactor was flushed with nitrogen and the temperature was increased slowly to 100 °C on a hot plate, while stirring (magnetic stirrer). The reaction mixture was left at 100 °C for 4 to 6 hours. After cooling down the reactor the oxidation was carried out by pressurizing the reactor using oxygen while continuously stirring the reaction mixture. The reactor was depressurized and a sample was taken for analysis. For the hydrolysis, 2 mL of aqueous H_2SO_4 (10 vol%) was added to a 1 mL sample from the reactor, shaken and the top layer was analyzed by GC.

This method was also carried out with $Ni(acac)_2$ as a catalyst, where the catalyst was added to the reactor before the TAA. In later experiments, chlorobenzene (1 mL) was added to the reactor before oxidation as internal standard for the GC analysis. The optimal reaction time in displacement and the optimal oxidation time where also determined.

After the reaction, the cooled down reactor was opened, DCM was added for extra dilution and the liquid was transferred to an Erlenmeyer. The contents of the Erlenmeyer was then taken outside the building and discarded on sand. After adding water to the sand, the mixture was dried and collected in a large container, to be disposed of as chemical waste.

B1 Displacement, oxidation and hydrolysis of trialkylaluminum – Method 3

Reactor was fitted with high-pressure lines for air, nitrogen and oxygen. A gas inlet with a tube to the bottom of the reactor was also added to bubble gas through the reaction mixture. Method 3 is identical to method 2, with the only difference that during oxidation the oxygen is bubbled through the reaction mixture.

B1 Displacement, oxidation and hydrolysis of trialkylaluminum – Method 4

According to literature another way to oxidize and hydrolyze the formed TOA is to react it with hydrogen peroxide (H_2O_2) (figure 3.19). Hydrogen peroxide is known to be a widely available, efficient and relatively inexpensive oxidant, which generates no toxic by-products.[84-89]

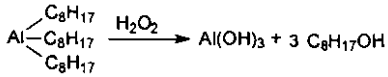

Figure 3.19: H_2O_2 method for oxidation and hydrolysis

In a typical experiment, 5 mg $Ni(acac)_2$ (0.03 mol% of the TAA), 20 mL internal octenes (Iso2) and 1 mL chlorobenzene were added to the reactor. The reactor was flushed with nitrogen and 2 mL TIBA was added with a gastight syringe. The displacement reaction was carried out at 100 °C for 3 hours. After cooling down the reaction mixture to room temperature, a sample was taken for analysis. For the oxidation and hydrolysis, 2 mL H_2O_2 was added to 1 mL of the reaction product, shaken and the top layer analyzed by GC.

B2 Pressure monitoring during displacement reaction

Since the oxidation and hydrolysis experiments were not successful as a quantitative method, another analysis method was tried. In this case, the analogue pressure meter was used to monitor the pressure during the reaction. The pressure build-up during the displacement reaction was monitored, giving an indication of the amount of isobutene gas that was formed.

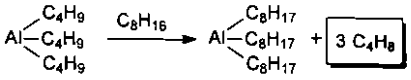

Figure 3.20: Schematic representation of displacement reaction with TIBA and octene, pressure monitoring during reaction relating to isobutene formation

Due to the influence of vapour pressures and the fact that the composition of the reaction mixture during the reaction was not completely known, the formation of isobutene could not be monitored during the reaction.

For the calculations, the pressure of the reactor after the displacement reaction at room temperature was taken. Since the starting pressure of the reactor was zero and no gas was added during the reaction, this final pressure could only be due to the isobutene gas that was formed. To verify whether the gas formed during the displacement reaction was indeed isobutene, a gas sample was taken from the reactor through the gas outlet and analyzed by GC.

General procedure

Before the reaction, the reactor was cleaned and dried. After reassembling, the reactor was filled with nitrogen. Octene was added with a gastight syringe and the reactor was flushed with nitrogen. After adding the TAA, the reactor-valve was closed, the reactor was flushed with nitrogen again and the contents were stirred continuously. The temperature was gradually increased to 100 °C and the pressure was monitored. After the reaction, the reactor was cooled down to room temperature (25 °C) and the remaining pressure was measured.

B3 Boiling off excess 1-octene between displacement and back-displacement

In an attempt to gain quantitative results in the transalkylation reaction, another method proved to be successful. In this method, the normal transalkylation reaction is performed and the excess octene is boiled off after the displacement.[56] This means that after back-displacement the amount of octene present in the reactor is equal to the total amount of octene that was displaced from the aluminum, since no octene was present in the reactor before the back-displacement.

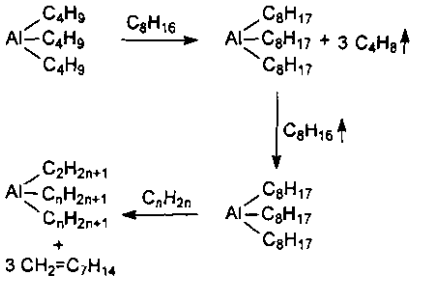

Figure 3.21: Schematic representation of transalkylation whereby excess octene is boiled off after displacement

B3 Boiling off excess octene between displacement and back-displacement – Design of stainless steel reactor, second reactor design

For this method a new stainless steel reactor was designed, with some modifications compared to the previous reactor. The tubing that was used inside the reactor and for the sample outlet has a slightly larger diameter (1/4 inch instead of 1/8 inch), to avoid clogging of the tubes by the aluminum compounds.

The new reactor was also equipped with a digital pressure meter (Wika), making the monitoring of the reactor pressure more accurate. This digital pressure meter has a pressure range of 0-16 bar with an accuracy of 0.1% and is equipped with a 12-36 V DC power supply.

Another feature on the new reactor was the septum sample inlet. This sample inlet consists of a normal outlet connection equipped with a valve and a small cap on top. This cap has a small opening, with a diameter that fits a needle. Directly underneath this cap is a rubber septum that is pierced when a needle is used to add a sample to the reactor. This inlet facilitates the injection of a liquid when the reactor is under a nitrogen atmosphere, because the reactor does not have to be opened and therefore direct contact with the outside environment and possible leakage or evaporation is prevented by the septum. When the reactor is under nitrogen, the atmosphere is not disturbed while injecting liquid with a gastight syringe. The septum is protected from high pressures with a valve, which can be closed during the reaction when the septum is not used. When the septum is used to add a sample, the reactor has to be depressurized to avoid damaging the septum. The septum can be easily replaced by simply unscrewing the cap on top of the outlet connection.

Schematically, the reactor is displayed both from the front and the back (Figure 3.23), to be able to get a proper view of all the features. On the front side, the septum sample inlet is shown (discussed above). The gas inlet (where the gas can be bubbled through the reaction mixture) and the liquid sample outlet are regulated with a 2-way valve. The third connection is the sample or gas inlet, and the connection to the digital pressure meter. The back view shows the pressure release valve, which can be set on an appropriate pressure to insure safety during the experiments. The second connection is shared between the thermocouple and the gas outlet.

General procedure

For the displacement reaction, $Ni(acac)_2$ (20 mg, 2 mol% of the TAA) was weighed and put in the reactor. Internal octenes (10 mL, 5x excess to Al) were added and the reactor was inertized with nitrogen. TIBA (1 mL) was added through the septum and the reactor was heated to 100 °C and stirred for 3 hours. After the displacement, the reactor was heated to approximately 150 °C and the octene was boiled off under nitrogen. After the octene was boiled off, the reactor was cooled down

to room temperature. Chlorobenzene (1 mL, internal standard) was added through the septum and GC analysis was used to determine the amount of octene left in the reactor after displacement.

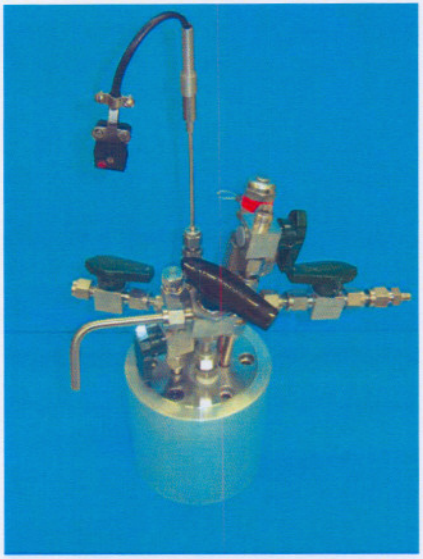

Figure 3.22: Picture of final reactor

For the back-displacement, the back-displacing alkene (for example 1-decene) was added (5x excess to Al) through the septum, and the reactor was stirred at room temperature. Samples for GC analysis were taken at certain time intervals.

For the optimization of this method, the back-displacement part was first investigated using 1-octene. Various parameters were varied, such as the amount of catalyst, back-displacing alkenes (ethene, 1-hexene and 1-decene), alkene:Al ratios and temperature.

Once the back-displacement reaction was optimized, the isomerization of the octene after the back-displacement reaction was investigated. 1,5-Cyclooctadiene (5 mL, 1.5 g/mg Ni) was added at different times to stop isomerization and thus resulting in a higher yield of 1-octene.

The total transalkylation reaction was then carried out, which was optimized by using different amounts of catalyst in both displacement and back-displacement, different temperatures and reaction times.

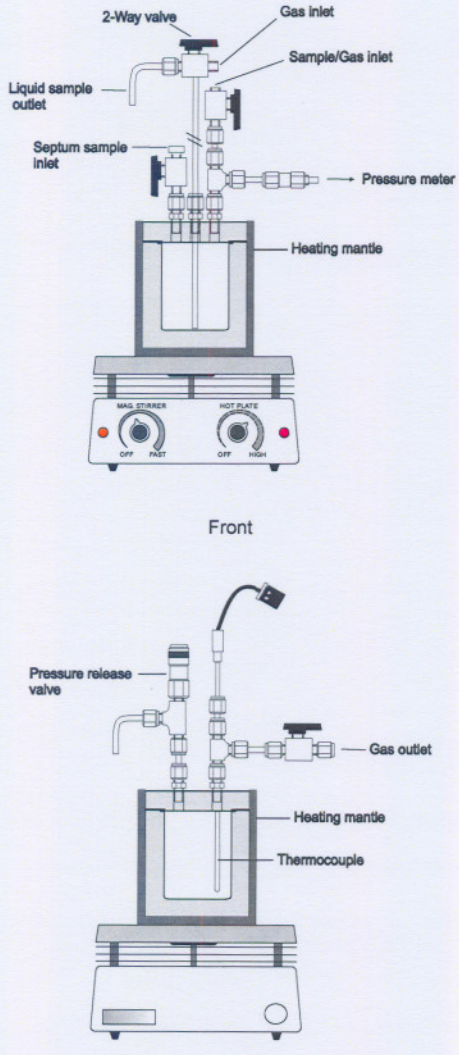

Figure 3.23: Schematic representation of final reactor for transalkylation reactions

3.2.3 Analytical techniques

3.2.3.a GC analysis

Analysis of the reaction mixture was performed on an Agilent Technologies 6850 gas chromatograph, equipped with a HP-1 column (30 m x 0.32 mm x 0.25 µm, Methyl Siloxane) and FID detector. The following analysis conditions were used:

Inlet temperature	:	280 °C
Detector temperature	:	300 °C
N_2 carrier gas flow rate	:	2 mL min^{-1} at room temperature
Injection volume	:	0.2 µL (manual injection)
Oven program	:	50 °C for 4 min
		50 to 255 °C at 20 °C min^{-1}
		255 °C for 2 min
H_2 gas flow rate	:	40 mL min^{-1} at room temperature
Air flow rate	:	450 mL min^{-1} at room temperature
Split ratio	:	50:1

3.2.3.b Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR, ^{13}C-NMR and ^{27}Al-NMR analysis of the alkylaluminum compounds in deuterated benzene (C_6D_6) were attempted on a Varian Gemini 300 spectrometer. Analysis by ^{27}Al-NMR would allow insight in the reaction mechanism, by showing the state of the aluminum as a result of the alkyl groups present at different times during the reaction. ^{1}H-NMR and ^{13}C-NMR would provide information on the alkyl groups, for instance to see which and how many of the alkyl groups were connected to the aluminum. Unfortunately the starting aluminum compounds (TEA/TIBA) could not be detected with this spectrometer and as a result no NMR data could be obtained from the reaction.

3.2.4 Calculations

3.2.4.a Displacement, oxidation and hydrolysis of trialkylaluminum

After the displacement, oxidation and hydrolysis the amount of 1-octanol was determined to calculate the amount of alkyl groups that were displaced from the aluminum. This amount corresponds to the amount of octene that reacted. To be able to determine the amount of 1-octanol after hydrolysis by GC analysis, the response factor (rf) of 1-octanol compared to the internal standard had to be determined. Chlorobenzene (C_6H_5Cl) was used as the internal standard, and the response factor was determined by using the following formula:

$$\frac{V_{C8OH}}{V_{PhCl}} = rf \frac{A_{C8OH}}{A_{PhCl}}$$

V_{C8OH} = volume of 1-octanol [mL]
V_{PhCl} = volume of internal standard [mL]
A_{C8OH} = area of 1-octanol peak
A_{PhCl} = area of internal standard peak

The response factor was calculated by plotting V_{C8OH}/V_{PhCl} against A_{C8OH}/A_{PhCl} for solutions with different 1-octanol:chlorobenzene ratios. The slope of the calibration curve represented the response factor. The calculated response factor for 1-octanol was 0.7.

The amount of 1-octanol that was determined after hydrolysis was used to determine the yield of the displacement reaction. The yield in this case was defined as the amount of 1-octanol after hydrolysis compared to the maximum amount of 1-octanol that could have been formed when all available alkyl groups of the aluminum compound were displaced with 1-octene. A 100% yield would mean that all alkyl groups of the aluminum were displaced by 1-octene.

To calculate the yield, the following formula was used:

$$Yield\ [\%] = \frac{n\ C_8OH(t)}{n\ C_8OH(\max)} \times 100$$

In which:

$$n\ C_8OH(t) = \frac{V_{C8OH} \times \rho_{C8OH}}{M_{C8OH}} = \frac{A_{C8OH} \times V_{PhCl} \times rf \times \rho_{C8OH}}{M_{C8OH} \times A_{PhCl}}$$

And:

$$n\ C_8OH(\max) = \frac{3 \times V_{TAA} \times \rho_{TAA}}{M_{TAA}}$$

n = number of moles
ρ_{C8OH} = density of octanol [g/mL]
M_{C8OH} = molar mass of octanol [g/mol]
V_{TAA} = volume of trialkylaluminum compound [mL]
ρ_{TAA} = density of trialkylaluminum compound [g/mL]
M_{TAA} = molar mass of trialkylaluminum compound [g/mol]

3.2.4.b Pressure monitoring during displacement reaction

The amount of isobutene gas that was formed during the displacement reaction was calculated from the final pressure in the reactor. After calculating the amount of isobutene gas, the yield of the reaction could be determined. A 100% yield would mean that all alkyl groups of the aluminum were displaced by 1-octene.

$$Yield\ [\%] = \frac{n\ iC_4}{n\ iC_4(\max)} \times 100$$

Where:

$$n\ iC_4(g) = n_{tot} - n_{N2}$$

n_{tot} = number of moles gas in reactor after reaction
n_{N2} = number of moles nitrogen before reaction

$$n_{tot} = \frac{P \times V}{R \times T}$$

P = final pressure in reactor [Pa]
V = volume of gas in reactor [m^3]
R = gas constant [J/mol·K]
T = temperature [K]

$$n_{N2} = \frac{V_{N2}}{V_m} = \frac{V_{reactor} - V_{liquid}}{V_m}$$

V_{N2} = volume of nitrogen [m^3]
V_m = molar volume of ideal gas [m^3]
$V_{reactor}$ = volume of reactor [m^3]
V_{liquid} = volume of liquid in reactor [m^3]

And:

$$n\ iC_4(\max) = 3 \times n\ TAA = \frac{3 \times V_{TAA} \times \rho_{TAA}}{M_{TAA}}$$

3.2.4.c Boiling off excess octene between displacement and back-displacement

The yield of the experiments was defined in the results as "Octene [%]", meaning the amount of octene that was recovered after back-displacement compared to the maximum amount of octene that could have been obtained when all alkyl groups of the aluminum compound were replaced. To calculate the amount of octene present in the reaction mixture after back-displacement, the response factor of octene relative to the internal standard (chlorobenzene) was determined with GC analysis, using the following equation:

$$\frac{V_{C8}}{V_{PhCl}} = rf \frac{A_{C8}}{A_{PhCl}}$$

V_{C8} = volume of octene [mL]
A_{C8} = area of 1-octene peak

After plotting plotting V_{C8}/V_{PhCl} against A_{C8}/A_{PhCl} for solutions with different C_8:PhCl ratios, the response factor was calculated by determining the slope of the calibration curve. The response factor of octene was 1.2.

To calculate the yield (or octene %) from the GC results after the reaction, the following formula was used:

$$Octene\ [\%] = \frac{n\ C_8(t)}{n\ C_8(\max)} \times 100$$

In which:

$$n\ C_8(t) = \frac{V_{C8} \times \rho_{C8}}{M_{C8}} = \frac{A_{C8} \times V_{PhCl} \times rf \times \rho_{C8}}{M_{C8} \times A_{PhCl}}$$

And:

$$n\ C_8(\max) = \frac{3 \times V_{TAA} \times \rho_{TAA}}{M_{TAA}}$$

ρ_{C8} = density of octene [g/mL]
M_{C8} = molar mass of octene [g/mol]

3.3 RESULTS AND DISCUSSION

3.3.1 1-Octene isomerization

To monitor the isomerization of 1-octene over an HZSM5 catalyst, GC analysis was used, and samples were taken at regular time intervals. Since the isomerization was very slow, the temperature was increased after 1 day with 10 °C to 50 °C to speed up the reaction. Isomerization of 1-octene was performed twice during this study (iso1 and iso2 respectively), both with HZSM5 as a catalyst.

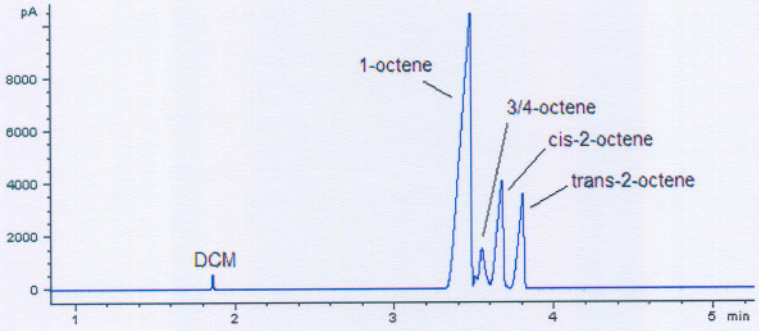

Figure 3.24: Typical gas chromatogram of the product mixture obtained during the isomerization of 1-octene (iso2) in the presence of HZSM5 after 4 days at 50 °C

The gas chromatogram shows that the peaks of the internal octenes are clearly distinguishable and therefore the exact composition of the reaction product could be calculated. The DCM peak refers to the dichloromethane, a solvent that was used to rinse the syringe between analyses. The compositions of both the isomerization products after 4 days, as well as the composition of the internal octenes mixture that was obtained from Sasol are given in the table below. These three octene mixtures were used in the transalkylation reactions.

The isomerization reaction with HZSM5 resulted in a mixture of internal octenes, with 1-octene still the main component. In both cases the isomerization went as far as 3- and 4-octene, although only a small amount of 4-octene was identified. The Sasol mixture mainly consisted of 2-octene, mixed with 1-octene and little 3-octene.

Table 3.2: Product composition of internal octenes

	Iso1 [%]	Iso2 [%]	Sasol mix [%]
1-octene	65	67	29
2-octene	32	27	69
3-octene	2	5	2
4-octene	1	1	0

3.3.2 Transalkylation

The results of the different methods that were used in the transalkylation reaction are discussed in chronological order, starting with displacement, oxidation and hydrolysis of TAA (a), followed by pressure monitoring during displacement (b) and finally boiling of excess octene between displacement and back-displacement (c).

3.3.2.a Displacement, oxidation and hydrolysis of trialkylaluminum

After hydrolysis, the reaction product was analyzed with GC. A typical GC graph of the reaction product is presented in Figure 3.25, in which the 1-octanol peak is clearly visible.

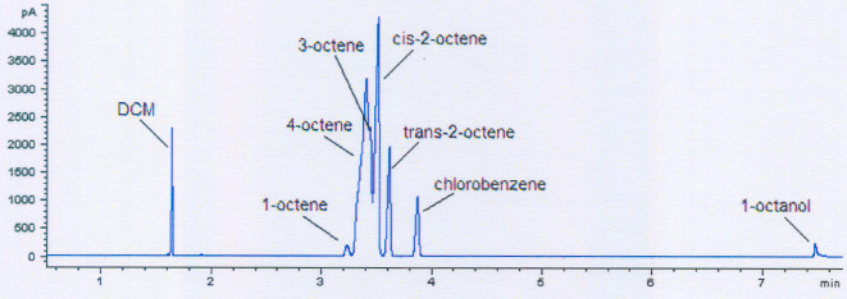

Figure 3.25: Typical gas chromatogram of reaction product after oxidation and hydrolysis

Method 1

As was discussed in Paragraph 3.2.2 B1, two possible reaction paths of trialkylaluminum in oxidation and hydrolysis were reported in literature.

$$Al(C_nH_{2n+1})_3 \xrightarrow{O_2} Al(OC_nH_{2n+1})_3$$

$$2\ Al(OC_nH_{2n+1})_3 \xrightarrow{6\ H_2O} 6\ C_nH_{2n+1}OH + Al_2O_3.3\ H_2O$$

Figure 3.26: 1st possible reaction path of oxidation/hydrolysis with air/water

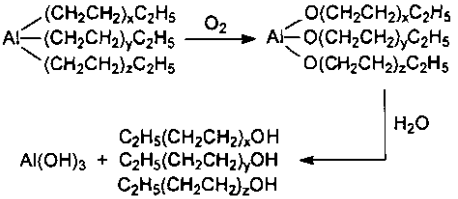

Figure 3.27: 2nd possible reaction path of oxidation/hydrolysis with air/water

Both reaction paths show the formation of a primary alcohol. Therefore, the reaction product was analyzed by GC and the amount of alcohol was determined.

Because of the formation of a gel during hydrolysis, the analysis of the reaction mixture was very difficult. Only a small amount of liquid could be recovered by filtration and analyzed by GC. The formation of a gel could be due to the reaction of aluminum with water, forming $Al(OH)_3$ or $Al_2O_3.3\ H_2O$.

No 1-octanol was detected after hydrolysis, which could mean that the oxidation and hydrolysis was not successful under these reaction conditions or that the displacement reaction did not take place. The GC analysis of the experiments that were carried out on a slightly larger scale in the three-necked round bottom flask also showed no 1-octanol.

Since the oxidation step was very exothermic, the reaction setup proved to be unsuitable for the experiments. Furthermore, the mini-reactors and the Supelco distillation setup were not totally airtight, making the results unreliable. Therefore, a stainless steel reactor with a pressure release

valve was developed, and further experiments were performed with this new setup. Other oxidation and hydrolysis methods, as well as other analysis possibilities had to be explored.

Table 3.3: Displacement of TEA with 1-octene, oxidation with air and hydrolysis with water in 3 mL mini-reactor with Supelco distillation setup

TEA [mL]	1-octene [mL]	Reaction time [d] [h]	T [°C]	GC-detection of 1-octanol
0.1	1.8	2	25	No
0.1	1.8	2	25	No
0.1	1.8	2	25	No
0.2	1.8	4	25	No

Method 2

In this method, the temperature of the displacement reaction was 100 °C, and the oxidation was carried out with oxygen instead of air at higher pressure. This was possible with the high-pressure lines fitted on the reactor.

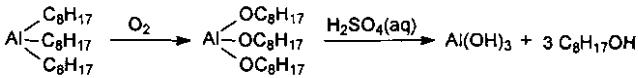

Figure 3.28: Oxidation/hydrolysis method with O_2 and H_2SO_4

The GC analysis of the reaction products was difficult in this method as well, since a gel formed during hydrolysis, indicating the formation of $Al(OH)_3$. In three cases, the GC analysis showed 1-octanol, indicating that the displacement reaction took place (Table 3.4). These were all experiments were TIBA was used; no 1-octanol was detected in the experiments with TEA. Since the excess 1-octene present after the displacement was not distilled off, a reference experiment was carried out, which proved 1-octene did not oxidize and hydrolyse under the current reaction conditions. This points out that the 1-octanol detected after hydrolysis was in fact formed from the octene that displaced the alkyl group of the aluminum.

Table 3.4: Qualitative analysis of 1-octanol after displacement of TIBA and TEA with 1-octene in stainless steel reactor, oxidation with O_2 for 6 hours under pressure, hydrolysis with H_2SO_4

TIBA [mL]	TEA [mL]	1-octene [mL]	$Ni(acac)_2$ mol% to Al	Reaction time [d] [h]	T [d] [°C]	GC-detection of 1-octanol
2	-	20	-	4	100	Yes
2	-	20	-	4	100	No
2	-	20	0.03	5	100	Yes
2	-	20	0.03	5	100	Yes
-	2	20	0.03	6	100	No

To be able to get quantitative results, an internal standard (chlorobenzene) was added before oxidation. Samples were taken at regular time intervals, to monitor the reaction progress as a function of time. The yield was calculated in such a way that a 100% yield would mean that the 1-octanol detected corresponds to the maximum amount of 1-octene that could have reacted with the aluminum compound.

Table 3.5: Determination of optimal oxidation time after displacement of TIBA with internal octenes (Iso1) at 100 °C for 7 hours in a stainless steel reactor, with 0.03 mol% $Ni(acac_2)$ catalyst, oxidation with O_2 under pressure, hydrolysis with H_2SO_4

Oxidation time [h]	Amount of octene reacted [%]
0	0.5
1	3.5
2	5.3
3	6.0
4	6.0
5	6.3
24	3.8
Direct ox	2.6

As can be seen from this table, the yield was very low, even after 24 hours. This could indicate that the displacement reaction did not proceed until the full extend, or that the yield of the oxidation and hydrolysis reaction was very low. The yield after oxidation was compared to the yield of direct oxidation, where a sample was taken and a large amount of oxygen was directly injected in the liquid. This method also showed a relatively low yield.

When looking at the graph of oxidation time vs. yield, it was determined that an oxidation time of 3 hours was sufficient for further experiments.

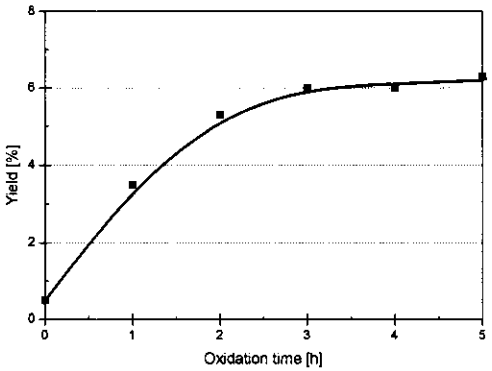

Figure 3.29: Determination of optimal oxidation time after displacement of TIBA with internal octenes (Iso1) at 100 °C in a stainless steel reactor, with 0.03 mol% Ni(acac$_2$) catalyst, oxidation with O_2 under pressure (2 bar), hydrolysis with H_2SO_4 (■ 1-octanol)

After determining the optimal oxidation time, the displacement reaction was investigated. As can be seen from the results in Table 3.6, the yield did not change significantly with different displacement reaction times. This may indicate that the displacement reaction takes place within one hour and the maximum yield is reached, or the slight variations are only to be attributed to the oxidation and hydrolysis step, which does not proceed to completion. The different internal octenes mixtures showed no significant differences in yield, which was expected, since both mixtures had a high 1-octene content. The 1-octene present in the mixture would displace the alkyl group of the aluminum first, since no double bond isomerization was required.

Table 3.6: Results of quantitative analysis of 1-octanol after different duration of displacement reactions at 100 °C of TIBA with internal octenes (Iso1/Sasol mix) in stainless steel reactor, with 0.03 mol% $Ni(acac)_2$ catalyst, oxidation with O_2 for 3 hours under pressure, hydrolysis with H_2SO_4, chlorobenzene as internal standard

TIBA [mL]	Iso1 [mL]	Sasol mix [mL]	Reaction time [d] [h]	Amount of octene reacted [%]
2	20	-	1	4.6
2	20	-	2	4.2
2	-	20	1	5.8
2	-	20	2	4.1

Method 2+3+4

The yield from the standard reaction as mentioned above was compared to the yield obtained from slightly different methods. Firstly, method 2 was used, in which the pressure was released during the displacement reaction, letting the possibly formed isobutene gas escape. Method 3 involved the bubbling of the oxygen through the liquid reaction mixture, made possible by the fitment of a gas inlet tube reaching to the bottom of the reactor. Finally, method 4 was performed, whereby H_2O_2 was used in the oxidation and hydrolysis step.

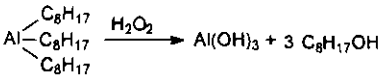

Figure 3.30: H_2O_2 method for oxidation and hydrolysis

The results from these experiments are presented in Table 3.7.

As can be seen from these results, methods 2 and 3 showed almost the same yield. The yield of method 4, where H_2O_2 was used was higher, indicating that this oxidation/hydrolysis method was more successful. The oxidation with oxygen is reported in literature to have generally lower yields than oxidations where hydrogen peroxide was used. This is attributed to the fact that the use of oxygen is often difficult to control and only one of the two oxygen atoms is known to be productive in the oxidation.[87,89]

Table 3.7: Results of quantitative analysis of 1-octanol after displacement reaction at 100 °C of TIBA with internal octenes (Iso1/Sasol mix) in stainless steel reactor, with 0.03 mol% $Ni(acac)_2$ catalyst, oxidation and hydrolysis, chlorobenzene as internal standard

TIBA [mL]	Iso1 [mL]	Sasol mix [mL]	Oxidation method	Reaction time [d] [h]	Oxidation time [h]	Amount of octene reacted [%]	Method
2	-	20	3	2	3	4.1	2
2	-	20	3	2	3	4.5	2 – P released
2	20	-	4	3	1.5	5.8	3
2	20	-	5	3	-	9.0	4

Summary of results of oxidation and hydrolysis method

The different methods that were used to oxidize and hydrolyze the trialkylaluminum that was formed during the displacement reaction all showed very low yields. It is not clear whether these low yields are due to the low yield of the displacement reaction or that the yield of the oxidation and hydrolysis step was not 100%. Therefore, another analysis method was investigated, which involved the monitoring of the pressure during the displacement reaction.

3.3.2.b Pressure monitoring during displacement reaction

The isobutene gas that was expected to form during the displacement of TIBA with octene would result in an increase in reactor pressure, since the reaction takes place in a closed system. This pressure was monitored during and after the reaction by measuring the pressure in the reactor with an analogue pressure meter.

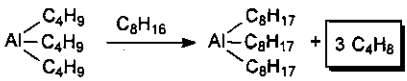

Figure 3.31: Schematic representation of displacement reaction with TIBA and octene, pressure monitoring during reaction relating to isobutene formation

The conditions of the experiments in which the pressure was monitored during the reaction are displayed in the table below. Six types of reactions with different parameters were carried out.

Table 3.8: Reaction parameters of displacement reactions during which the pressure was monitored

	1-octene [mL]	TIBA [mL]	TEA [mL]	$Ni(acac)_2$ [mol% to Al]	Molar ratio C_8:Al
1	25	2	-	-	20
2	25	-	-	-	-
3	20	2	-	-	16
4	20	4	-	-	8
5	20	-	2	-	9
6	20	2	-	0.03	16

During experiment 1 a relatively large pressure increase was observed. To get an idea of the influence of the vapour pressure of 1-octene on the total pressure with increasing temperature, experiment 2 was carried out with only 1-octene (Figure 3.32). The pressure obtained in this experiment was considerably lower, and since this could not only be due to the vapour pressure of TIBA, which was a very small quantity, it could be assumed that indeed isobutene was formed in the reaction.

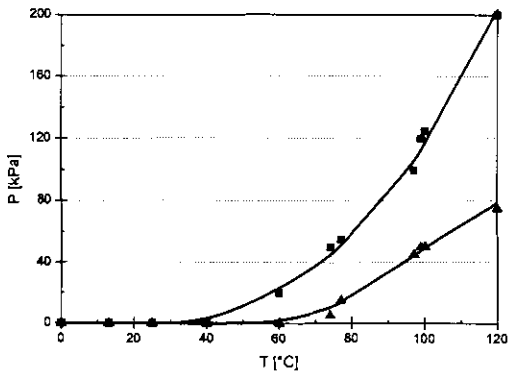

Figure 3.32: Pressure at various temperatures during displacement of TIBA with 1-octene (■ experiment 1; ▲ experiment 2)

The pressure increase with time for experiments 3-6 is given in Figure 3.33. As can be seen from this graph, the pressure is higher for the reaction with TEA (experiment 5) and the one with catalyst (experiment 6). The pressure in experiment 4 is a bit higher than in experiment 3, this could be due to the fact that in experiment 4 more TIBA was used, increasing the vapour pressure.

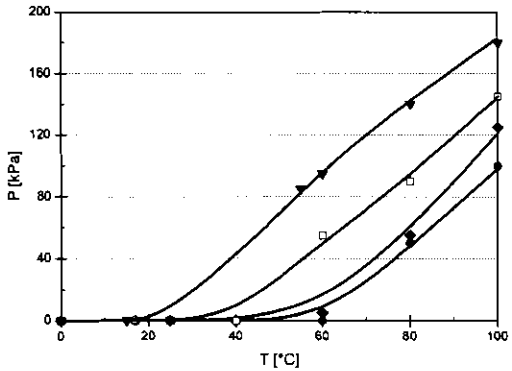

Figure 3.33: Pressure at various temperatures during displacement of TIBA/TEA with 1-octene (◆ experiment 3; ● experiment 4; □ experiment 5; ▼experiment 6)

GC analysis of the gas sample that was taken from the reactor after the displacement reaction of TIBA and 1-octene showed a large peak at 1.86 min (Figure 3.34). This was confirmed to be isobutene by a reference sample from a gas cylinder. This proved that indeed isobutene was formed during the reaction, indicating that the displacement reaction took place.

The calculations that were performed are based on readings with an analogue pressure meter, which is not very accurate; therefore the results can only be a rough indication. Since a lot of factors play a role, the calculation of the amount of alkyl groups that was displaced from the gas pressure is quite complicated. The vapour pressures of octene and the TAA increase with increasing temperature, and it is a closed volume. The exact composition of the liquid reaction mixture is not known during the reaction, and therefore the amount of octene reacting over time cannot be calculated.

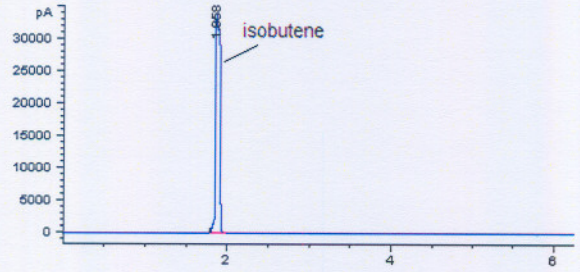

Figure 3.34: Results of GC analysis of gas formed during displacement of TIBA with 1-octene

However, the total amount of octene that displaced isobutene or ethene on the aluminum during the reaction could be calculated. Since the reactor pressure before the reaction at room temperature (25 °C) was 0 and the reactor showed an increased pressure at room temperature after the reaction, this pressure could be attributed to the isobutene that was formed. Since it is a simplified approach, the vapour-liquid equilibrium data of octene, isobutene, ethene, nitrogen and TAA were left out of the calculation, as well as any dissolved isobutene. Therefore, with this final pressure reading, an indication could be given of the percentage of alkyl groups that was displaced during the reaction.

Table 3.9: Calculation of displaced alkyl groups during displacement of TIBA/TEA with 1-octene (see table 3.7 for reaction parameters)

	Final P [kPa]	Gas formed [kmol]	Yield [%] (= % Alkyl groups displaced)
1	20	1.033	4.4
3	20	1.073	4.5
4	25	1.321	2.8
5	70	3.758	8.6
6	45	2.416	10.2

With this method, very low yields were calculated. This could be due to the low yield of the displacement reaction, indicating that the reaction conditions were not optimal. Another possibility could be that the pressure readings were not accurate enough, or that the reactor had a small leak, resulting in a lower final pressure. The yield, or % alkyl groups displaced was calculated in such a way that a 100% yield would mean that the octene displaced all alkyl groups on the aluminum, since the octene was in excess over the aluminum compound. Experiment 5, performed with TEA, showed a higher yield, which corresponds with observations during the reactions, in which TEA reacts more violently than TIBA. The yield from experiment 6 is slightly higher, which could indicate that the catalyst indeed had an influence on the reaction.

Summary of results of pressure monitoring method

From the results of this analysis method it can be concluded that the displacement reaction indeed took place. The yield was higher when TEA was used instead of TIBA, and also the addition of a nickel catalyst increased the yield. Unfortunately, the yields were relatively low. Since it was not clear whether this was caused by the low yield of the displacement reaction or that this analysis method was not accurate enough, other possible analysis methods had to be explored.

3.3.2.c Boiling off excess octene between displacement and back-displacement

This method involves boiling off the residual octene after the displacement reaction, prior to the back-displacement reaction.

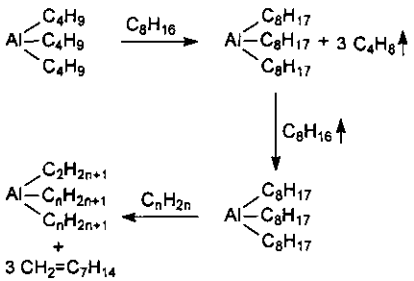

Figure 3.35: Schematic representation of transalkylation whereby excess octene is boiled off after displacement

The reaction mixture after back-displacement was analyzed by GC (Figure 3.36).

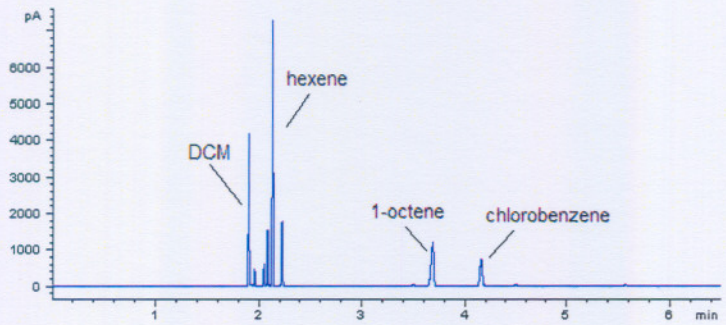

Figure 3.36: Typical gas chromatogram of the reaction product after back-displacement

After the displacement, the excess octene was boiled off, confirmed by GC that no octene was left and the back-displacement reaction was performed with 1-hexene. Both displacement and back-displacement were performed with a 5-fold excess of alkene to the aluminum (500 mol%). The first experiments performed with this method showed promising results.

Table 3.10: Octene yield after displacement of TIBA with internal octenes (iso2) [100 °C, 3 h, 0.03 mol% $Ni(acac)_2$] and back-displacement with 1-hexene [25 °C, chlorobenzene = int std]

Time	Octene [%]
5 min	2
1 hour	3
4 days	45

After these first experiments it was decided to optimize this method, with some alterations to the initial method. Due to the fact that the reactor was not equipped for distillation, a small amount of octene was left after the boiling off procedure. Attempts to boil off the total amount of octene were unsuccessful, as the results proved to be inaccurate and not reproducible. This could be due to

other components being boiled off together with the octene due to the small volume of liquid in the reactor at the end of the boiling off procedure.

To make sure the amount of octene calculated after the back-displacement was only the amount of octene that was displaced from the aluminum, an extra GC analysis was performed before starting the back-displacement. This way a correction was done for the octene that could not be boiled off. When the excess octene was not boiled off after displacement, the yields were considerably lower and not reproducible, indicating that the GC analysis might not be accurate enough to determine the slight increase in octene after back-displacement when a large amount of octene was still present. The octene yield corresponds with the total amount of octene that was displaced from the aluminum (which was corrected for the amount of octene that was left after the boiling off step) and includes any octene that might have isomerized after it was released from the aluminum. The optimization experiments were started with an investigation of the back-displacement reaction. After optimizing this part, the total transalkylation reaction could be optimized.

Back-displacement

Initial back-displacement reactions were performed for longer periods of time, until it was clear that the maximum yield was reached after approximately 2 hours. Since the increase in yield thereafter was relatively small, the experiments were carried out for 2 hours. To compare the yields after back-displacement, the yields after 2 hours of reaction time were taken into account, regardless of whether the reaction carried on for longer. Firstly, different back-displacing alkenes were used, with or without the $Ni(acac)_2$ catalyst, the results of which are presented in the table below.

Table 3.11: Octene yield after 2 hours after back-displacement of TOA with different alkenes with and without catalyst [2 mol% $Ni(acac)_2$, T = 25 °C, 5x excess alkene to Al]

Alkene	Octene [%] with catalyst	Octene [%] without catalyst
C=C	87	58
$C=C_5$	90	76
$C=C_9$	93	69

From these results it can be seen that the yields were higher when catalyst was added. To compare the octene yield in time during back-displacement of the different back-displacing alkenes for the experiments with catalyst, the octene yield for the back-displacement reaction was plotted as a function of time in Figure 3.37.

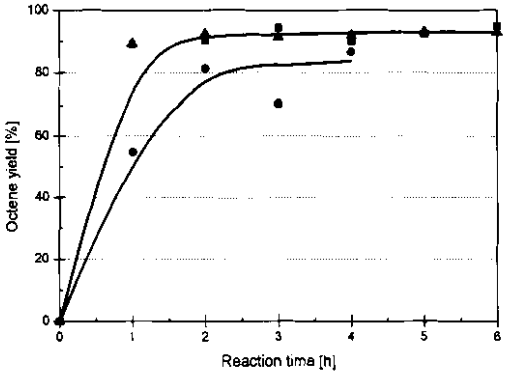

Figure 3.37: Octene yield after back-displacement of TOA with different alkenes with catalyst (■ 1-hexene; ▲ 1-decene; ● ethene) [2 mol% $Ni(acac)_2$, T = 25 °C, 5x excess alkene to Al]

As can be seen from this graph, the results for both hexene and decene were almost the same. When using ethene, which is a gas, the amount that was used could not be measured accurately, resulting in a lower and less reproducible yield.

Figure 3.38 shows the octene yield as a function of time during the back-displacement of TOA using different alkenes without catalyst.

This graph shows that the results of the back-displacement without catalyst were more scattered, and also lower. This indicated that indeed the presence of the $Ni(acac)_2$ catalyst was necessary for this part of the transalkylation reaction.

The results for 1-decene were most reproducible in the experiments with and without catalyst, and since the tridecylaluminum compound was expected to be the most stable of the three possible aluminum compounds after back-displacement, 1-decene was chosen as the back-displacing alkene for the optimization experiments. The influence of the amount of catalyst used in the back-displacement reaction was investigated next.

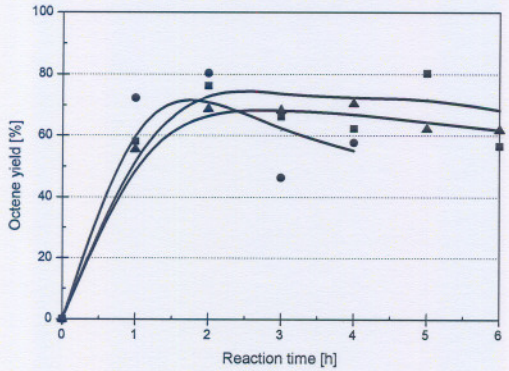

Figure 3.38: Octene yield after back-displacement of TOA with different alkenes without catalyst (■ 1-hexene; ▲ 1-decene; ● ethene) [T = 25 °C, 5x excess alkene to Al]

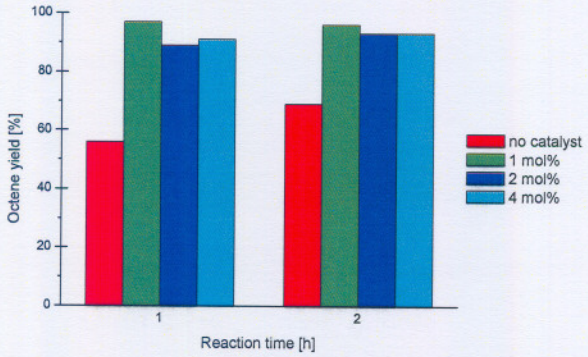

Figure 3.39: Octene yield after back-displacement of TOA with 1-decene, different amounts of catalyst [T = 25 °C]

As can be seen from Figure 3.39, the yield for the experiment without the catalyst was lower, confirming again that a catalyst is needed for the back-displacement reactions. When looking at the results after 2 hours of back-displacement, the experiment where 1 mol% catalyst was used had the highest yield. The yield did seem to stay relatively constant above 1 mol%, indicating that 1 mol% of $Ni(acac)_2$ would be sufficient. The octene yield after back-displacement was also close to 100%, which meant that this reaction step was operating under almost ideal reaction conditions.

Table 3.12: Octene yield after 2 hours after back-displacement of TOA with 1-decene, different mol% catalyst [T = 25 °C]

Mol% catalyst	Octene [%]
0	69
1	96
2	93
4	93

To investigate the influence of temperature and the 1-decene to aluminum ratio, more experiments were performed.

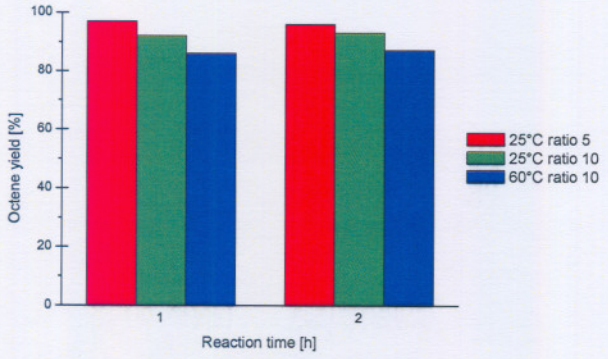

Figure 3.40: Octene yield after back-displacement of TOA with 1-decene at different back-displacement temperatures and decene:Al ratios [1 mol% $Ni(acac)_2$]

The yields of the different experiments were relatively close, as can be seen from Figure 3.40. When comparing the octene yields after 2 hours, the following results were obtained:

Table 3.13: Octene yield after 2 hours after back-displacement of TOA with 1-decene (different temperature and ratios)

T [°C]	Ratio decene:Al	Octene [%]
25	5	96
25	10	93
60	5	87

When the temperature was increased, the yield decreased slightly. Increasing the 1-decene to Al ratio also seemed to decrease the yield slightly, but no significant change was observed. Therefore the following experiments were performed at 25 °C with a 1-decene to Al molar ratio of 5.

To prevent the rapid isomerization of the octene that was displaced from the TOA, 1,5-cyclooctadiene (COD, 5 mL) was added as an isomerization-inhibiting agent. This compound was added at different times after the addition of TOA to the reactor, to determine the optimal procedure.

Table 3.14: Isomerization of 1-octene after back-displacement reaction, different addition times of 1,5-cyclooctadiene compared to standard reaction [2 hour d, T = 25 °C, 1.5 g COD/mg Ni]

Time [min]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
No COD	2	10	41	47
t = 0	100	0	0	0
t = 1	72	0	1	27
t = 5	72	1	3	25

These results indicate that without COD, the isomerization after 2 hours was quite significant, leaving only 2% 1-octene in the reaction mixture. When the COD was added together with the TOA, the isomerization was stopped and only 1-octene was detected. When the COD was added after the TOA, the isomerization already occurred, leaving 72% 1-octene after the back-

displacement. Therefore, the optimal time to add the COD to the reaction mixture was together with the TOA.

Displacement and back-displacement

After optimizing the back-displacement reaction, the total transalkylation reaction was performed. Optimization experiments were started with 1-octene, followed by experiments with internal octenes. First, different $Ni(acac)_2$ catalyst concentrations were used for the displacement (d) of TIBA with 1-octene, followed by back-displacement (bd) of the formed TOA with 1-decene.

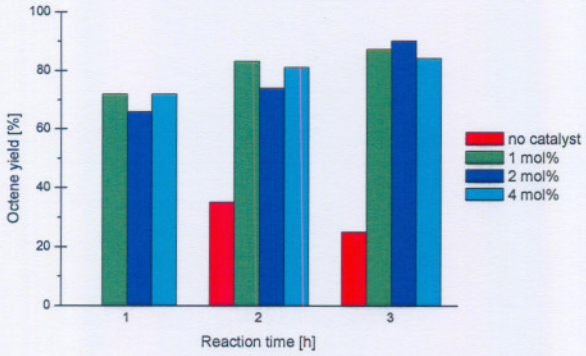

Figure 3.41: Octene yield after displacement of TIBA with 1-octene and back-displacement with 1-decene, different amounts of catalyst in the displacement reaction [1hour d, T^d = 100 °C, T^{bd} = 25 °C, 5x excess alkene to Al, 1 mol% $Ni(acac)_2$ bd]

From Figure 3.41 it becomes clear that the yield was considerably lower when no catalyst is used in the displacement reaction. The yields of the reactions with 1,2 and 4 mol% catalyst are all relatively close.

The influence of temperature on the displacement reaction was investigated in another set of experiments. For these experiments, no catalyst was added for the back-displacement step.

The experiment that was performed at 100 °C showed a lower yield, indicating that the reaction proceeded better at lower temperatures.

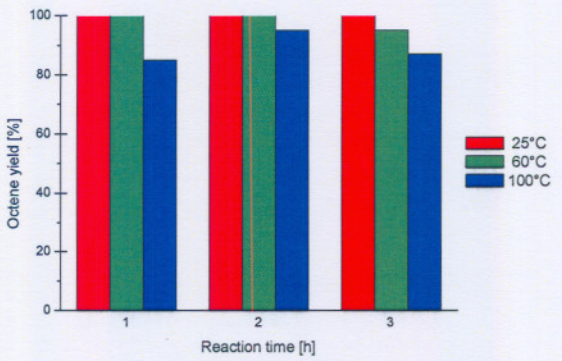

Figure 3.42: Octene yield after displacement of TIBA with 1-octene and back-displacement with 1-decene at different temperatures for the back-displacement reaction [1 mol% cat d, 1 hour d, no cat bd, T^{bd} = 25 °C]

Summarizing the results and comparing the yield after 2 hours of back-displacement, it is clear that the best results were obtained in the experiments where no extra catalyst was added for the back-displacement reaction. This indicates that the catalyst might be still active after displacement, since the back-displacement experiments showed that a certain amount of catalyst was necessary in the back-displacement to obtain these high yields.

Table 3.15: Octene yield after displacement of TIBA with 1-octene and back-displacement of TOA with 1-decene [1 hour d, T^{bd} = 25 °C, 2 hour bd]

T^d [°C]	mol% catalyst d	mol% catalyst bd	Octene [%]
100	4	1	81
100	2	1	74
100	1	1	83
100	0	1	35
100	1	0	95
60	1	0	100
25	1	0	100

Since no increase in yield was observed at higher catalyst concentrations, the use of 1 mol% catalyst in displacement seemed optimal. The yield was very high even at lower temperatures, indicating that for the displacement of TIBA with 1-octene a temperature of 25 °C was sufficient.

After optimizing the transalkylation reaction with 1-octene it was performed with 4-octene under the optimized reaction conditions. In these experiments it became clear that the present reaction conditions were not optimal for internal octenes, and more optimization experiments were carried out.

Table 3.16: Octene yield after displacement of TIBA with 4-octene and back-displacement of TOA with 1-decene at 25 °C for 2 hours at different conditions [no cat bd]

T^d [°C]	Mol% catalyst d	Reaction time d	Octene [%]
25	1	1	8
25	4	3	36
25	4	1	0
100	4	3	65
100	1	3	82

When performing the transalkylation reaction with 4-octene under the optimized reaction conditions obtained with 1-octene, the yield was only 8%. The reason for this could be that the double bond of the 4-octene has to shift to the primary position (isomerization to 1-octene) in order for the octene to bind to the aluminum, thus displacing the alkyl group.

Therefore the catalyst concentration as well as the reaction time was increased, which resulted in a yield of 36%. The next experiment, where only the catalyst amount was increased, proved that the reaction time had been the yield-increasing factor. Meaning that a catalyst amount of 1 mol% was sufficient, only that a longer reaction time was needed to isomerize all the octene and let it bind to the aluminum. Furthermore, the yield increased when the temperature of the displacement reaction was increased to 100 °C, resulting in an octene yield of 82%.

After optimizing the reaction conditions of the transalkylation for 4-octene, the reaction was also performed with 2-octene and 3-octene.

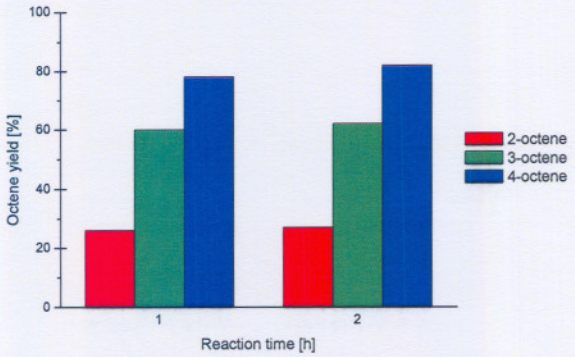

Figure 3.43: Octene yield after displacement of TIBA with different internal octenes and back-displacement with 1-decene [d 3 hours, T^d = 100 °C, 1 mol% cat; bd no cat, T^{bd} = 25 °C]

As can be seen from Figure 3.43, the yields of the transalkylation reaction with different internal alkenes were not the same. The yields of the transalkylation reactions for the different internal alkenes after 2 hours of back-displacement are presented in the table below.

Table 3.17: Octene yield in time after displacement of TIBA with different internal octenes and back-displacement of TOA with 1-decene [T^d = 100 °C, 3 hour d, 1 mol% cat^d, 2 hour bd at 25 °C]

	Octene [%]
2-octene	27
3-octene	62
4-octene	82

The yield for 4 octene is 82%, whereas the experiments where 2- or 3-octene was used had lower yields. This could be due to the fact that the reaction conditions were optimized for 4-octene. The main objective was to get the best yield for 4-octene, since this is the product of the metathesis reaction, and will be used as the displacing alkene in the tandem catalysis reactions.

Summary of results of the boiling off excess octene method

This method proved to be successful in obtaining quantitative results for the transalkylation reaction, and optimization of both the displacement and the back-displacement steps could be carried out. The results show that the optimized reaction conditions were optimal for 4-octene. Since 4-octene is the starting compound for the transalkylation reaction in the tandem catalysis experiments, this method and reaction conditions will be used in the tandem catalysis experiments. The stainless steel reactor (final design, Figure 3.22 and 3.23) that was developed for the experiments proved to be suitable for this type of reactions. With this reactor it was possible to carry out the experiments in a safe way, in a closed volume and with all necessary fittings and valves that were needed to perform the reactions.

3.4 CONCLUSIONS

Heterogeneous isomerization of 1-octene was successfully carried out with HZSM5 as a catalyst. The products were analyzed with GC, which proved to be a useful analysis method to determine the exact composition of the internal octenes. Around 35% of the 1-octene was isomerized to internal octenes, and the isomerization proceeded up to 4-octene. Although the isomerization proceeded slower than expected, the yield after 4 days was high enough and provided a mixture of internal octenes that was suitable to be used as starting material in the transalkylation reactions.

Three different analysis methods were used to determine the extent of the transalkylation reaction.

- The oxidation and hydrolysis of the reaction product after the displacement reaction showed that the displacement reaction took place. Attempts to obtain reliable and reproducible quantitative results by using this method were not successful, since the oxidation and hydrolysis step did not appear to proceed to completion.
- Reactor pressure monitoring during the displacement reaction also proved that the reaction took place, but this method was not sufficiently accurate to produce quantitative results. The results did show that the use of a $Ni(acac)_2$ catalyst increased the yield of the reaction.
- When the excess octene was boiled off between displacement and back-displacement it was possible to obtain reproducible, quantitative results. Therefore, this method was used to optimize the transalkylation reaction.

The back-displacement reaction was optimized by using different back-displacing alkenes (ethene, 1-hexene and 1-decene), different amounts of catalyst, temperatures and alkene:Al ratios. The octene yield was considerably higher when $Ni(acac)_2$ was used as a catalyst. The octene yields for reactions where 1-hexene or 1-decene were used as the back-displacing alkene were both higher

than when ethene was used. Since ethene is a gas, it was difficult to monitor the exact amount of ethene that was added to the reaction mixture, making the experiments less reproducible. Back-displacement reactions with 1-decene provided the most reproducible yields, therefore 1-decene was chosen as the back-displacing alkene.

The highest octene yields were obtained when the back-displacement was carried out at 25 °C with 1 mol% $Ni(acac)_2$ catalyst (relative to the Al). A reaction time of 2 hours proved to be sufficient to obtain the maximum yield.

COD was suitable in stopping the isomerization of the back-displaced alkene when the COD was added together with TOA in the back-displacement reaction. The octene product consisted of 100% 1-octene when COD was added together with TOA, compared to only 2% 1-octene that was left in the reaction mixture when no COD was added.

After determining the optimal reaction conditions for the back-displacement reaction, the transalkylation reaction was carried out and again optimal reaction conditions (temperature, amount of catalyst, reaction time) were determined.

The displacement and back-displacement reactions were optimized by using 1-octene, obtaining the highest octene yield when the displacement reaction was carried out at 25 °C for 1 hour with 1 mol% catalyst, followed by back-displacement with 1-decene at 25 °C for 2 hours without catalyst. After obtaining a 100% yield with 1-octene, the transalkylation reaction was carried out with 4-octene. Since the octene yield for 4-octene was considerably lower than when 1-octene was used, the reaction was optimized again to obtain a higher yield. It became clear that for displacement reactions with an internal octene a higher reaction temperature and longer reaction times were required. This was to be expected, since the double bond in 4-octene has to be shifted to the terminal position. The double bond of 1-octene is already in the terminal position, allowing it to immediately displace an alkyl group of the trialkylaluminum. The highest octene yields after back-displacement were obtained when the displacement reaction was carried out for 3 hours at 100 °C with 1 mol% catalyst, followed by 2 hours of back-displacement at 25°C without the addition of extra catalyst.

Optimization of the transalkylation reaction for 4-octene lead to an 82% yield, where after the reaction was also carried out with 2-octene and 3-octene. The octene yields after back-displacement for 2- and 3-octene were 27% and 62% respectively. The yields for 2- and 3-octene were lower than for 1- and 4-octene. The reason for this could be that in the case of 1-octene and 4-octene, the reaction was optimized for this particular octene, whereas the results obtained for 2- and 3-octene were the result of a reaction under conditions that were optimized for 4-octene. Since

only 4-octene will be used as a starting material for the transalkylation reactions in the tandem experiments and high yields were obtained with 4-octene, there was no need to optimize the reaction further for 2- and 3-octene.

The results obtained in these experiments increase the understanding of the transalkylation reaction and prove that it is possible to carry out this reaction on a small scale in a stainless steel reactor. The transalkylation reaction is applied in industry on a large scale, but no reports have been found about the optimization of reaction conditions. The industrial applications as described in the patents also mention recycle streams and the use of multiple reactors for the separation and reaction steps.[9,78,79] The results presented in this chapter prove that it is possible to carry out the displacement reaction in a single reactor, without separation steps in between, and that high and reproducible reaction yields can be obtained.

The development of the stainless steel reactor that was used in the transalkylation experiments was a multi-step process, starting with the first reactor design and adapting it to the specific reaction conditions and safety issues involving the transalkylation reaction. The final reactor is a reactor that is not only suitable for this type of reactions but can be used in other types of reactions as well. The reactor made it possible to perform the experiments in a safe way, with all necessary inlet and outlet tubes, valves and fittings.

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CHAPTER 4

Tandem Catalysis

ABSTRACT

In this chapter two different tandem sequences were investigated to prepare longer chain terminal alkenes from short chain terminal alkenes. For the first tandem process the metathesis reaction, as described in Chapter 2, and the transalkylation from Chapter 3 were combined. It was found that it was indeed possible to combine metathesis and transalkylation in a tandem process and reasonable high and reproducible yields were obtained. The second tandem process involved metathesis and an isomerization step where the same Grubbs 1 catalyst was used for both reaction steps. It was concluded that indeed an increase in temperature induced the formation of the hydride species without the addition of other compounds, although the 1-octene yields were very low. The 1-octene yield and selectivity of the metathesis-transalkylation sequence and the ruthenium-catalyzed metathesis-isomerization tandem reaction were compared. It was found that the overall yield and selectivity for the metathesis-transalkylation was higher and that it was indeed possible to obtain longer chain terminal alkenes in a tandem process.

4.1 INTRODUCTION

Tandem catalysis involves the combination of multiple reactions in one synthetic operation, with minimum workup or change in conditions.[1,2] The concept "tandem" is generally used to refer to reactions that occur parallel, one behind another, alongside each other, or an association of events working towards the same goal.[3] Tandem methodology provides excellent tactics to combine different concurrent or sequential processes in productive single operation employing one or several catalysts. Tandem catalysis poses a challenge for chemists to find conditions that allow for the controlling of reactivity and selectivity in each step, but also presents a number of opportunities to improve chemical transformations. The advantage of tandem catalysis is that intermediates do not have to be stable enough for isolation, because they are quickly transformed by a subsequent reaction. The yield losses associated with the isolation and purification of intermediates in multi-step processes can be avoided, and reaction times are considerably reduced.[1,4,5] The application of tandem reactions to generate and then destroy harmful chemicals *in situ* also presents environmental and safety advantages.

4.1.1 Classification of tandem reactions

The terminology that is used to classify the different types of tandem catalysis reactions is not consistent, which makes it difficult to distinguish between the different reaction mechanisms. According to literature, reactions that are not considered tandem catalysis are for example one-pot reactions involving isolated catalytic events, where the second catalyst is added only after the first catalytic transformation is complete.

The term tandem catalysis is reserved to describe coupled catalyses in which sequential transformation of the substrate occurs via two (or more) mechanistically distinct processes. Tandem catalysis is defined to have all catalytic species, whether masked or apparent, present from the start of the reaction, and is also referred to as concurrent tandem catalysis.[1,6]

One of the recent and most accepted types of classifications of tandem catalysis reactions, as reported in literature, will be discussed here.[6] In this particular classification, three distinct types of tandem reactions are mentioned.

- Orthogonal tandem catalysis (Figure 4.1), where there is a mutual independence of the different catalytic cycles that operate simultaneously, with non-interfering catalysts.

- Auto-tandem catalysis (Figure 4.2) refers to two or more mechanistically distinct catalyses promoted by a single catalyst precursor. Both cycles occur spontaneously and simultaneously by cooperative interaction of the various species, which are present at the outset of the reaction.

- Assisted tandem catalysis (Figure 4.3) is a term used to identify the reactions in which a single catalyst species carries out different transformations that are triggered by the addition of a further reagent to evoke a change in mechanism.

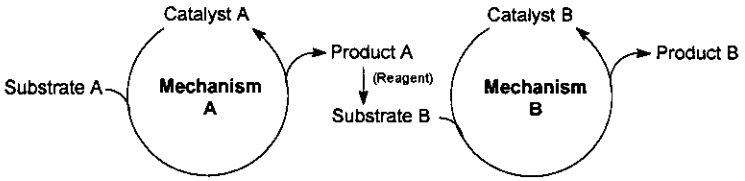


Figure 4.1: Schematic illustration of orthogonal catalysis

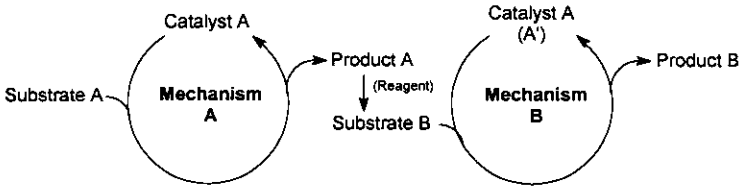


Figure 4.2: Schematic illustration of auto-tandem catalysis

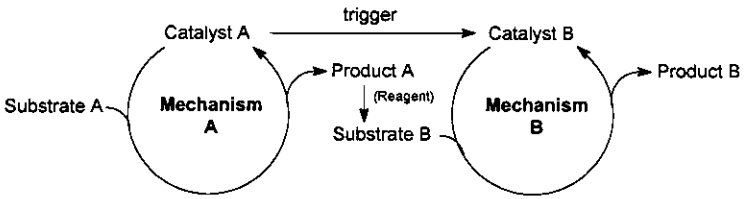


Figure 4.3: Schematic illustration of assisted tandem catalysis

A variety of names are used to refer to the different types of tandem reactions, such as domino reactions, cascade reactions, sequential transformations, consecutive reactions and zipper reactions.[7]

Domino and cascade reactions often require a complex substrate with predetermined functionalities.[1] Domino reactions are defined as processes involving two or more bond-forming transformations that take place under the same reaction condition without adding additional reagents and catalysts, and in which subsequent reactions result as a consequence of the functionality in the previous step. In domino reactions, there are two aspects that define the usefulness of the process, the bond-forming efficiency (the number of bonds that are formed in one sequence) and the increase in structural complexity (structure economy).[8,9] Cascade reactions lead to an increase in molecular complexity by combining a series of reactions on one synthetic operation.[10]

4.1.2 Catalysts in tandem reactions

Catalysts are traditionally designed and optimized to mediate a single reaction, but with the increasing demand for more efficient synthetic processes, catalysts that are capable of catalyzing multiple reactions (sometimes by an *in situ* transformation) or are compatible with other catalysts to perform sequential reactions are developed.[11] Different catalyst materials have been reported to be successful in tandem catalysis; among them are the transition metals.[12-14] The homogeneously catalyzed tandem reactions where transition metals are used prove to be valuable in organic synthesis because they are effective, selective and require only mild reaction conditions.[2]

4.1.3 Tandem reactions involving metathesis

Different combinations of catalytic reactions where metathesis is involved are reported (Figure 4.5), for example metathesis-hydrogenation,[15] intramolecular ring-opening/ring-closing metathesis,[16] metathesis-Heck coupling,[17] CM-hydrogenation,[18] tandem RCM-Kharasch addition[5] and metathesis-isomerization.[19] Metathesis catalysts generally have high activity and excellent tolerance for many common functional groups, which makes them suitable for use in tandem reactions.[1] Other examples of tandem reactions where no metathesis step was involved include combinations of hydroformylation,[2] Heck-reactions[9] and many others.

Combinations of homogeneous and heterogeneous reactions in tandem catalysis have been investigated. An example of such a reaction is the ruthenium catalyzed homogeneous metathesis-heterogeneous hydrogenation in the synthesis of polymers, for example telechelic polyethylene (Figure 4.4). In this reaction sequence, a silica gel is added after the metathesis to act as a support for the catalyst residue in the hydrogenation step. This conversion to a heterogeneous system facilitates the removal of catalyst and the isolation of the reaction products after the reaction.[15]

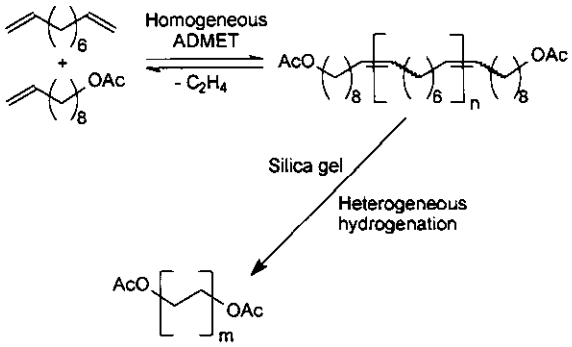


Figure 4.4: Schematic illustration of a combination of homogeneous ADMET and heterogeneous hydrogenation in the synthesis of telechelic ester-functionalized polyethylene

A cascade process that involves three different transition metal catalysts (Figure 4.6) in the same vessel was also reported in literature.[20] In this case, the first step of the tandem process was the palladium-catalyzed oxidation of alcohols, followed by the rhodium-catalyzed methylenation and finally the ruthenium-catalyzed RCM to provide cyclic alkenes with a 70% yield.

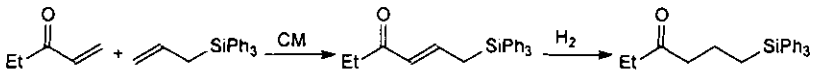
Another example of a three-step tandem process whereby a ruthenium catalyst was used is the ROMP/atom-transfer radical polymerization (ATRP)/hydrogenation in the preparation of functional polymers. In this report, the ROMP and ATRP steps are catalyzed by the same di-functional ruthenium complex, which is subsequently transformed into a hydrogenation catalyst upon addition of hydrogen.[11]

4.1.4 Tandem catalysis to obtain longer chain terminal alkenes

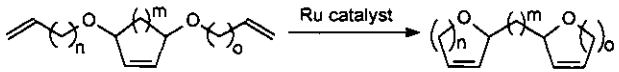
The aim of this project is to obtain longer chain terminal alkenes from shorter chain terminal alkenes. To be able to achieve this aim, two different types of tandem reactions were investigated, metathesis followed by transalkylation and metathesis followed by an isomerization step catalyzed by the ruthenium species that was used in the metathesis reaction.

4.1.4.a Metathesis and transalkylation

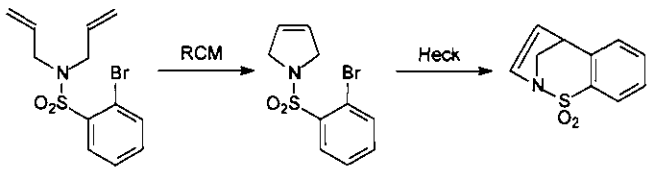
For the first type of tandem reactions, the metathesis reaction (Chapter 2) and the transalkylation reactions (Chapter 3) were combined in a tandem catalysis process (Figure 4.8).



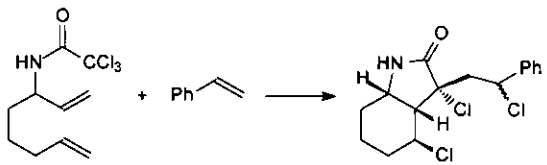
CM-Hydrogenation



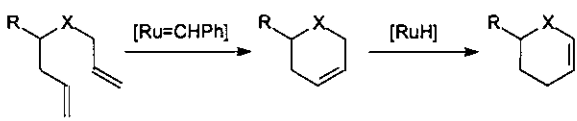
ROM-RCM



RCM-Heck coupling



RCM-Kharasch addition



RCM-Isomerization

Figure 4.5: Schematic illustration of tandem catalytic reactions that involve metathesis

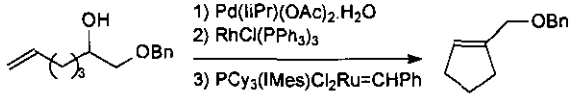


Figure 4.6: Schematic illustration of cascade process involving three different transition metal catalysts

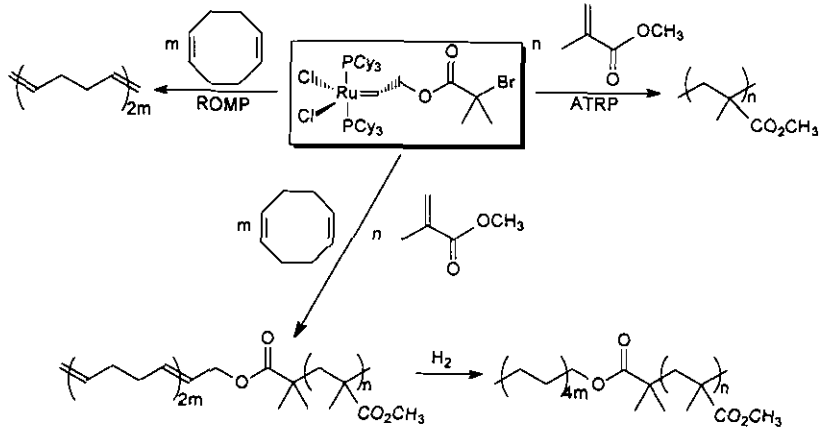


Figure 4.7: Schematic illustration of a three-step tandem process with a single ruthenium catalyst

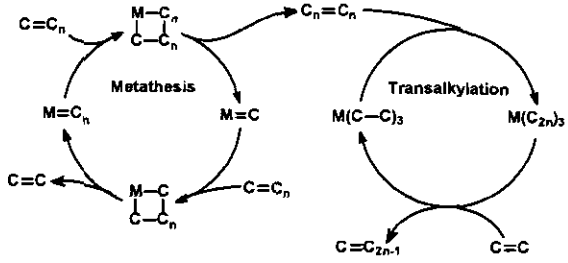


Figure 4.8: Schematic representation of metathesis and transalkylation in tandem catalysis (hydrogen and other ligands omitted for clarity, M = metal)

The metathesis-transalkylation reaction was described in literature as a method to synthesize terminal alkenes by combining isomerization metathesis and isomerization transalkylation. So far, the only industrial application of this process was described by BASF in patents.[21-23] This industrial process involves different reaction vessels, recirculation and separation steps (Figure 4.9). The commercial application of tandem catalysis in this particular process has not been reported to date.

For this industrial process, a C_4-C_{10} alkene fraction is used for the isomerizing metathesis (40-100 °C, 30-35 bar), followed by the separation of the product stream by chain length in 4 different fractions. The lower fractions and the fraction that contains the higher carbon numbers (which are higher than the desired number) are recycled in the isomerizing metathesis reactor. The fraction that contains the alkenes with the desired carbon number is subjected to a transalkylation reaction (displacement) with trialkylaluminum (TAA) under isomerizing conditions. The TAA that was formed in the transalkylation reaction is reacted with an alkene (back-displacement) to liberate a 1-alkene corresponding to the TAA that was formed in the displacement reaction.

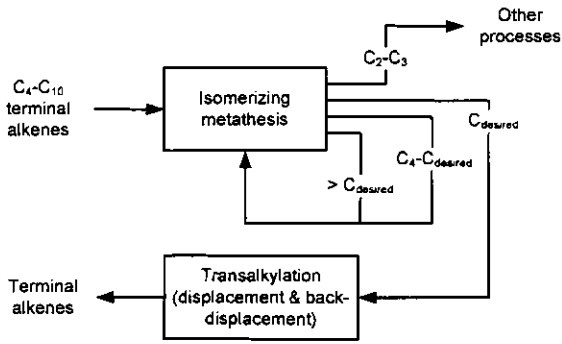


Figure 4.9: Simplified schematic representation of BASF process

The catalysts that were used for the reactions consisted of a mixture of heterogeneous catalysts with different elements from various groups of the periodic table on a support such as SiO_2, MgO, γ-Al_2O_3 or B_2O_3. Different aluminum compounds were used in the reactions, with an alkene:Al ratio between 1:1 and 50:1.

The same type of process to prepare linear alkenes was earlier described by Conoco, but this process involved an intricate combination of growth, separation, recirculation, distillation, metathesis, isomerization and displacement steps (Figure 4.10).[24]

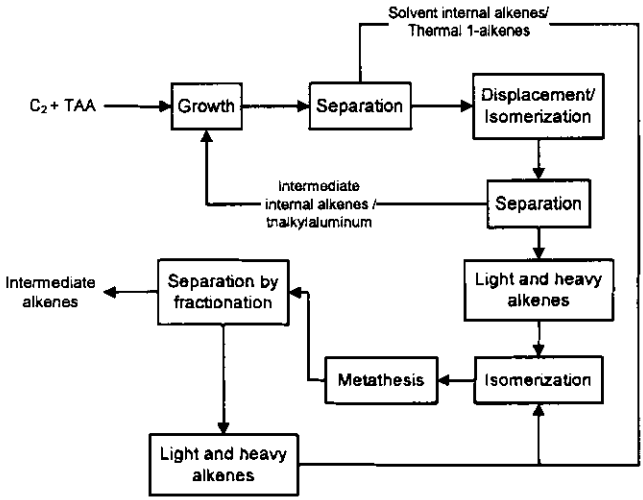


Figure 4.10: Simplified schematic representation of Conoco process

Since opinions about what classifies as a tandem catalysis reaction vary, it is not exactly clear in which category the metathesis-transalkylation sequence falls. According to literature, this particular combination can either be referred to as sequential tandem catalysis or assisted tandem catalysis.[1,6] Even though some reports classify this reaction not as a tandem process, the transalkylation reaction in itself could be described as a tandem process, since different mechanistic reactions (displacement, isomerization and back-displacement) are taking place without addition of catalyst or reaction components during the reaction.

4.1.4.b Metathesis and isomerization

Another method to obtain longer chain terminal alkenes is to combine metathesis and isomerization in a tandem catalysis fashion. Although isomerization is usually a side-reaction in metal-catalyzed reactions, it can be used to convert internal alkenes to terminal alkenes when there is a proper understanding of the reaction mechanism.[25-28]

In contrast to the well-established metathesis tandem reactions, such as the ring-opening/ring-closing cross-metathesis sequence where all of the steps are catalyzed by a ruthenium carbene species, metathesis/non-metathesis reactions require a change in the nature of the catalytic active species, which may be induced by the addition of appropriate reagents to the reaction mixture after the completion of the metathesis step.[27]

Investigations in the isomerization activity of metathesis catalysts were reported in literature. It was found that with Grubbs 1 metathesis was favoured below 70°C and no isomerization took place.[29] It was also reported that after metathesis, the decomposed ruthenium catalyst becomes quite efficient as an isomerization catalyst, although the exact mechanism was not completely understood yet.[26,30]

These findings lead to an investigation into the mechanism whereby the ruthenium is transformed from a metathesis catalyst into an isomerization catalyst. One of the focus points was to determine whether alkene isomerization was promoted by the metathesis catalyst itself, by decomposition products or by impurities from the catalyst synthesis.[4] According to literature, a ruthenium hydride or dihydride complex is responsible for alkene isomerization, which is also a good hydrogenation catalyst.[31] Since both internal and external alkenes undergo isomerization, the possibility that the methylidene complex is solely responsible for the observed alkene isomerization was excluded.[25] Studies by McGrath and Grubbs[32] confirmed the role of the hydride species in alkene isomerization. They investigated and compared the two established pathways for transition metal catalyzed alkene isomerization, the π-allyl metal hydride mechanism and the metal hydride addition-elimination mechanism.

In the metal hydride addition-elimination mechanism (Figure 4.11), which is the most prevalent mechanism of the two, the free alkene coordinates to a kinetically long-lived metal hydride species. Subsequent insertion into the metal-hydride bond yields a metal alkyl. The initial metal hydride is regenerated by formation of a secondary metal alkyl followed by β-elimination, yielding isomerized alkene. Since the formation of the primary alkyl is thermodynamically favoured, non-productive addition-elimination of the alkene through formation of and subsequent β-elimination from a primary metal alkyl occurs to great extent.

The π-allyl hydride mechanism (Figure 4.12) is the less commonly observed pathway for alkene isomerization. In this mechanism, the free alkene coordinates to a transition metal fragment that does not have a hydride ligand. A π-allyl metal hydride is formed by oxidative addition of an activated allylic C-H bond to the metal. The coordinated hydride is transferred to the opposite end of the allyl group, yielding the isomerized alkene.

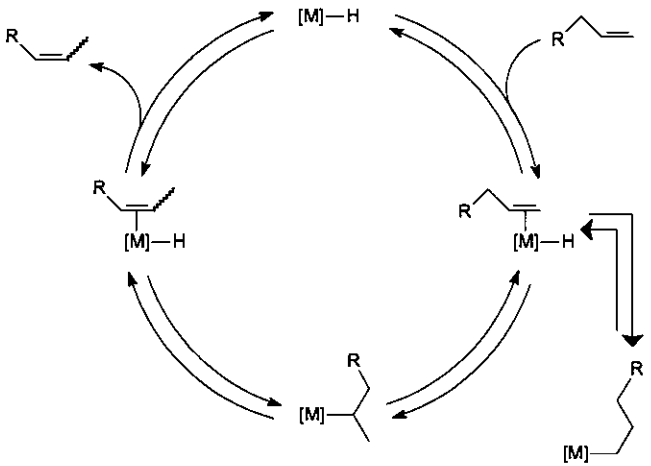


Figure 4.11: Schematic representation of the metal hydride addition-elimination mechanism

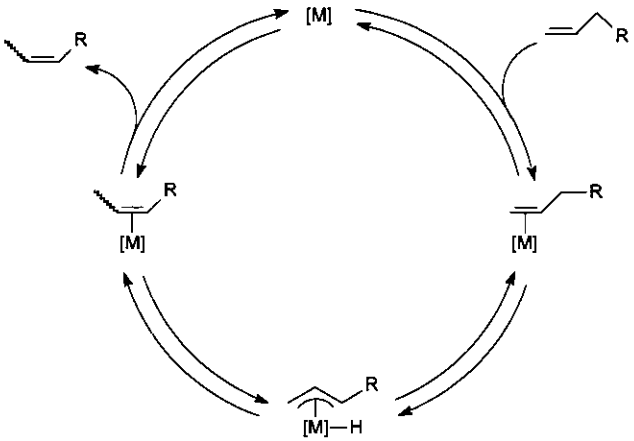


Figure 4.12: Schematic representation of the π-allyl metal hydride mechanism

If all steps in both mechanisms would be truly reversible, eventual equilibration to a thermodynamic mixture of alkenes is observed. Two differences make these two mechanisms distinguishable through labelling studies.

- First, the π-allyl hydride mechanism is a formal 1,3-hydrogen shift, whereas the metal hydride addition-elimination mechanism involves a 1,2-hydrogen shift. In the 1,3-hydrogen shift, a hydrogen in the allylic position undergoes a metal-mediated transfer to a terminal position (in a terminal alkene). The 1,2-hydrogen shift involves the formation of a primary metal alkyl and β-elimination of a different hydrogen. The 1,2-hydrogen shift is completed by readdition of the metal hydride to the alkene to yield a secondary metal alkyl, followed by appropriate β-elimination.

- Second, the π-allyl hydride mechanism is intramolecular. In this mechanism, a single substrate molecule is rearranged by the metal and released as product. In the intermolecular metal hydride addition-elimination mechanism the hydrogen atoms from one substrate molecule are transferred to the catalyst and then to another substrate molecule.

Although several studies were dedicated to determine which of the two proposed pathways is favourable, the findings are not conclusive, but there is certainty about the involvement of the hydride species in the isomerization reactions.

Since it was found that the ruthenium hydride was responsible for the isomerization activity, several investigations were carried out to get insight in possible reaction paths for converting the ruthenium catalyst to its hydride species.

It was found that additions of (a primary or secondary) alcohol and substoichiometric amounts of a base to a metathesis reaction induce *in situ* conversion of the metathesis-active carbene catalyst to an isomerization-active hydride species.[19] The source of the hydride atom was investigated and it was found that the hydride was formed *via* a non-catalytic alcohol dehydrogenation pathway followed by decarbonylation.[33,34]

Another investigation of the reaction mechanism showed that when secondary alcohols were used, the ruthenium hydride complex was formed by beta-hydride elimination of a ruthenium-alkoxide. It was assumed that addition of a secondary alcohol and a base to a completed metathesis reaction should induce the conversion of a Ru-carbene to a Ru-hydride species. It was also reported that secondary alcohols proved to be more effective in converting the ruthenium catalyst into its hydride species than primary alcohols.[27]

Another way to convert the ruthenium to its hydride species is the addition of hydrogen at room temperature and atmospheric pressure.[12,27,35] A combination of the hydrogen atmosphere with the addition of an alcohol (and in some cases also a base) was also reported to be an efficient way to obtain the hydride complex.[13,36] It was also found that in some cases, heating induced the decomposition of the ruthenium complex, thereby forming the hydride species.[28,34]

This tandem reaction would be classified as sequential (concurrent) tandem catalysis, or assisted tandem catalysis, since the second step involves a change of the catalyst by an external influence (trigger).[1,6]

4.1.5 Aims and objectives

In this chapter, two different tandem catalysis sequences are investigated and optimized in order to obtain longer chain terminal alkenes, where after the overall 1-octene yield and selectivities for both tandem sequences will be compared.

4.1.5.a Metathesis and transalkylation

- Use the optimized reaction conditions from Chapter 2 and 3 and investigate the possibility of combining metathesis and transalkylation in a tandem process.
- Scale up of the metathesis reaction from a mini-reactor to the 150 mL stainless steel reactor.
- Carry out and optimize the tandem reactions by using 1-pentene as a starting material for the metathesis step and different trialkylaluminum compounds and back-displacing alkenes to obtain 1-octene.

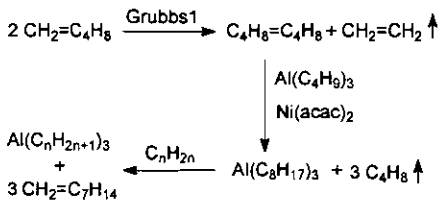


Figure 4.13: Schematic illustration of tandem catalysis reaction, metathesis and transalkylation

4.1.5.b Metathesis and isomerization

- Investigate the possibility of transforming the ruthenium Grubbs 1 catalyst to an isomerization catalyst *in situ*, without the addition of chemicals to induce this change, for the tandem metathesis-isomerization experiments.
- Use 1-pentene as the starting compound in the metathesis reactions and use the isomerization step to obtain 1-octene from the 4-octene that was formed in the metathesis step.
- Optimize the metathesis-isomerization reaction by varying reaction time and temperature and alkene:Ru ratios.

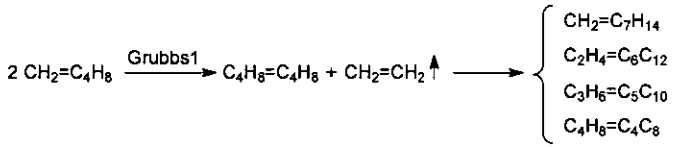


Figure 4.14: Schematic illustration of tandem catalysis reaction, metathesis and isomerization

4.2 EXPERIMENTAL

4.2.1 Materials

A mixture of internal octenes, which consisted mainly of 2-octene was obtained from Sasol and was used as received. Chlorobenzene (99%) was purchased from Aldrich and dried before use by refluxing it over CaH_2. 1-Octene (97%) was obtained from Merck, passed through an activated Al_2O_3 column to remove impurities (such as peroxides) and stored under nitrogen. Grubbs 1 (Aldrich) and $Ni(acac)_2$ (Aldrich) catalysts were used as received. Internal octenes (2-Octene, 3-octene and 4-octene) were purchased from Aldrich and used as received. Dichloromethane (Merck) was used as received. 1,5-Cyclooctadiene (COD) was purchased from Aldrich and used as received. Triethylaluminum (93%), trioctylaluminum (25wt% in hexane) and triisobutylaluminum were obtained from Aldrich and used as received. 1-Hexene (97%) was purchased from Merck und used as received. All solvents used were of analytical grade.

4.2.2 Experimental method

4.2.2.a Metathesis and transalkylation

The metathesis reaction that was investigated in Chapter 2 and the transalkylation part from Chapter 3 were combined in a tandem catalysis reaction. Both parts of the tandem catalysis reaction were thoroughly investigated, and therefore the optimized reaction conditions could be used.

General procedure

The metathesis was performed at 30 °C overnight, with a 1-pentene:Ru ratio of 1,000 and chlorobenzene as internal standard in a 150 mL stainless steel reactor (Chapter 3, Figure 3.23). The 4-octene yield was determined using GC analysis. After the metathesis, the reactor was opened, 1 mol% $Ni(acac)_2$ catalyst was added and the reactor was closed and brought under nitrogen. After adding TEA or TIBA (5x excess 4-octene to Al), the reactor was heated to 100 °C. After stirring at 100 °C for 3 hours, the reactor was heated to 150 °C to boil off the excess octene under nitrogen. After cooling the reactor down to room temperature, chlorobenzene was added as internal standard and GC analysis was performed to determine the amount of octene that was left in the reactor. Subsequently, 1-alkene (ethene, 1-hexene or 1-decene, 5x excess over Al) and 1,5-cyclooctadiene (1.5 g/mg Ni) were added through the septum, and the reactor was stirred at 25 °C for 2 hours. GC samples were taken for analysis every hour. For the experiments where ethene was used as the back-displacing alkene, the gas was bubbled through the reaction mixture, and left stirring for 30 minutes and analyzed by GC. This procedure was repeated and the reaction mixture was stirred again for 30 minutes, and analyzed by GC.

4.2.2.b Metathesis and isomerization

For the metathesis reaction the standard metathesis of 1-pentene as described in Chapter 2 was used. The second step of this tandem catalysis reaction involved the isomerization of the metathesis product, 4-octene, and was performed with Grubbs 1 as a catalyst. The results from these tandem catalysis experiments are compared to the tandem catalysis reactions involving metathesis and transalkylation.

General procedure

Metathesis of 1-pentene was performed at 30 °C for 3 hours with a 1-pentene:Ru ratio of 1,000. The reaction was performed in a 3 or 5 mL mini-reactor, as well as in the stainless steel reactor (Chapter 3, Figure 3.23). After the metathesis, the isomerization reaction was carried out with different amounts of catalyst, various reaction times and different temperatures.

4.2.3 Analytical techniques

Analysis of the reaction mixture was performed on an Agilent Technologies 6850 gas chromatograph, equipped with a HP-1 column (30 m x 0.32 mm x 0.25 µm, Methyl Siloxane) and FID detector. The following analysis conditions were used:

Inlet temperature	:	280 °C
Detector temperature	:	300 °C
N_2 carrier gas flow rate	:	2 mL min^{-1} at room temperature
Injection volume	:	0.2 µL (manual injection)
Oven program	:	50 °C for 4 min
		50 to 255 °C at 20 °C min^{-1}
		255 °C for 2 min
H_2 gas flow rate	:	40 mL min^{-1} at room temperature
Air flow rate	:	450 mL min^{-1} at room temperature
Split ratio	:	50:1

4.2.4 Calculations

The first part in the tandem catalysis reactions for both metathesis and transalkylation and metathesis and isomerization is the metathesis reaction of 1-pentene. To determine the composition of the metathesis reaction mixture the internal standard method was used, with chlorobenzene (C_6H_5Cl) as the internal standard.

First, the response factor (rf) of 1-pentene compared to the internal standard was calculated, using the following formula:

$$\frac{V_{C5}}{V_{PhCl}} = rf \frac{A_{C5}}{A_{PhCl}}$$

V_{C5} = volume of pentene [mL]
V_{PhCl} = volume of internal standard [mL]
A_{C5} = area of pentene peak (obtained from GC)
A_{PhCl} = area of internal standard peak (obtained from GC)

The response factor was calculated by plotting V_{C5}/V_{PhCl} against A_{C5}/A_{PhCl} for solutions with different pentene:chlorobenzene ratios. The slope of the calibration curve represented the response factor, which was 1.5 for 1-pentene.

The conversion of pentene at a certain time during the metathesis reaction was calculated using the following formula:

$$pentene\ conversion\ [mol\%] = \left(1 - \frac{n_t}{n_i}\right) \times 100$$

n_t = number of moles of 1-pentene at time t
n_i = number of moles of 1-pentene before reaction

The number of moles of 1-pentene (n) can be calculated with the following formula:

$$n = \frac{V_{C5} \times \rho_{C5}}{M_{C5}} = \frac{A_{C5} \times V_{PhCl} \times rf \times \rho_{C5}}{M_{C5} \times A_{PhCl}}$$

ρ_{Cn} = density of 1-pentene [g/mL]
M_{Cn} = molar mass of 1-pentene [g/mol]

4.2.4.a Metathesis and transalkylation

The second part of this tandem catalysis experiment is the transalkylation reaction. For the transalkylation, the yield was defined "Octene [%]", meaning the amount of octene that was recovered after back-displacement compared to the maximum amount of octene that could have been obtained when all alkyl groups of the aluminum compound were replaced. The composition of internal octenes (isomerization) was determined by GC analysis.

To calculate the amount of octene present in the reaction mixture after back-displacement, the response factor of octene relative to the internal standard (chlorobenzene) was determined with GC analysis, using the following equation:

$$\frac{V_{C8}}{V_{PhCl}} = rf \frac{A_{C8}}{A_{PhCl}}$$

V_{C8} = volume of octene [mL]
A_{C8} = area of 1-octene peak

After plotting plotting V_{C8}/V_{PhCl} against A_{C8}/A_{PhCl} for solutions with different C_8:PhCl ratios, the response factor was calculated by determining the slope of the calibration curve. The response factor of octene was 1.2.

To calculate the yield (or octene [%]) from the GC results after the reaction, the following formula was used:

$$Octene\ [\%] = \frac{n\ C_8(t)}{n\ C_8(\max)} \times 100$$

In which:

$$n\ C_8(t) = \frac{V_{C8} \times \rho_{C8}}{M_{C8}} = \frac{A_{C8} \times V_{PhCl} \times rf \times \rho_{C8}}{M_{C8} \times A_{PhCl}}$$

And:

$$n\ C_8(\max) = \frac{3 \times V_{TAA} \times \rho_{TAA}}{M_{TAA}}$$

V_{TAA} = volume of trialkylaluminum compound [mL]
ρ_{TAA} = density of trialkylaluminum compound [g/mL]
M_{TAA} = molar mass of trialkylaluminum compound [g/mol]

4.2.4.b Metathesis and isomerization

For the metathesis and isomerization tandem catalysis reactions the metathesis product was isomerized under different reaction conditions. After the reaction, the composition of the internal octenes was determined with GC analysis.

4.3 RESULTS AND DISCUSSION

4.3.1 Metathesis and transalkylation

The 4-octene yield of the metathesis of 1-pentene was on average around 21%. Compared to the yields obtained in Chapter 2, it was clear that the 4-octene yields of the metathesis step in the tandem reactions were lower. The reason for this could be that the reaction conditions were not identical, since the experiments in Chapter 2 took place in the 3 mL mini-reactor and the experiments described in this chapter were performed on a larger scale, without solvent in the stainless steel reactor.

Since the metathesis reaction for the tandem sequence was carried out overnight, the deactivation of the Grubbs 1 catalyst could also have played a role, since deactivation means that no new carbene species are formed and metathesis activity decreases. Reports in literature suggest that the Grubbs catalyst only deactivates at extended reaction times, but estimated and calculated half-life times for this catalyst vary.[29,30,37,38]

The metathesis and transalkylation reaction was performed with TIBA and TEA and different back-displacing alkenes, to compare the yields. The octene yield in time during back-displacement (bd) after metathesis and displacement (d) is displayed below.

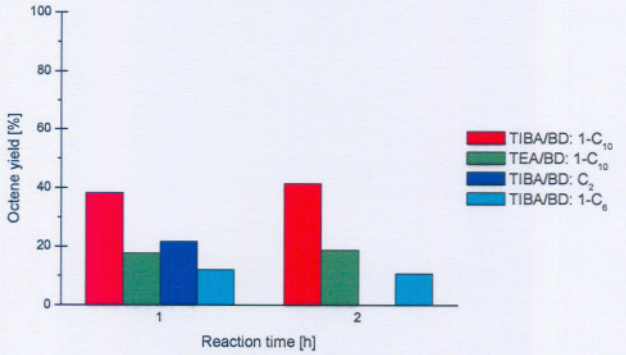


Figure 4.15: Octene yield in time during back-displacement for tandem catalysis experiments [meta: 30 °C overnight, 1-pentene:Ru = 1,000; d: 3 hours, T^d = 100 °C, 1 mol% $Ni(acac)_2$; bd: 2 hours, T^{bd} = 25 °C; chlorobenzene int std, 5x excess alkene to Al]

As can be seen from Figure 4.15, the best results were obtained for the TIBA/1-C_{10} combination, which was also used in the optimization steps in Chapter 3. The results with TEA were lower, which is in agreement with the results that were obtained in Chapter 3, where the transalkylation reaction was investigated. When 1-hexene or ethene was used as the back-displacing alkene, lower yields were observed.

These results are consistent with the yields that were obtained in Chapter 3, where the transalkylation reaction was investigated with the same back-displacing alkenes. 1-Decene was the alkene that produced the highest yield, both in the tandem experiments and when only the transalkylation reaction was performed.

The octene yield in time during back-displacement from the tandem catalysis reaction with TIBA and 1-decene was also compared to the yield from the transalkylation reaction (no metathesis, start with 4-octene, marked as D-BD) and the yield from the back-displacement reaction of TOA with 1-decene (Figure 4.16). Since no extra catalyst was added in the tandem catalysis sequence for the back-displacement, also the results from the back-displacement of TOA without catalyst were added.

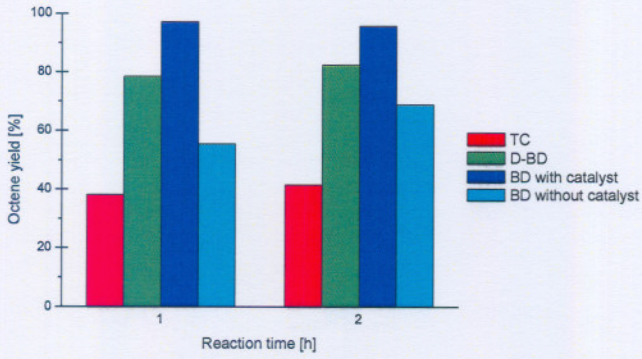


Figure 4.16: Comparison of octene yield in time during back-displacement for tandem catalysis experiments and separate displacement and back-displacement reactions for TIBA with 1-decene [meta: 30 °C overnight, 1-pentene:Ru = 1,000; d: 3 hours, T^{d} = 100 °C, 1 mol% $Ni(acac)_2$; bd: 2 hours, T^{bd} = 25 °C; chlorobenzene int std, 5x excess alkene to Al]

From Figure 4.16 it becomes clear that the octene yield in back-displacement decreased with each additional reaction step. This may be caused by the interaction of the different catalysts, or the presence of unreacted components, influencing the next reaction.

For the tandem catalysis experiments, the octene yield was around 40%. When the transalkylation reaction was performed with 1-decene as the back-displacing alkene a yield of around 80% was obtained. This means that the metathesis reaction indeed has influence on the transalkylation reaction. Possibly the Grubbs catalyst has interaction with the nickel catalyst that was used in the displacement reaction. It may also be possible that the unreacted pentene that was left after the metathesis reaction also displaces the TIBA, thus decreasing the octene yield after back-displacement.

When only the back-displacement reaction was performed (with catalyst), the yield was above 95%, whereas the back-displacement without catalyst only had a yield around 70%. This is consistent with the results that were obtained in Chapter 3. Although the nickel catalyst is added in the displacement reaction, it is still active for the back-displacement part. This can be concluded from the lower yield obtained in the back-displacement reaction without catalyst compared to the yield of the transalkylation reaction.

The octene yield from the tandem catalysis experiments where TIBA and ethene were used were compared to the separate back-displacement experiments where also ethene was used as the back-displacing alkene.

Since the ethene was bubbled through the reaction mixture, the reaction time that is displayed in Figure 4.17 is not accurate. The ethene gas was bubbled through for a short time (2-3 minutes), after which the reactor was stirred at 25 °C. Then the ethene line was opened again and the procedure was repeated.

Although it was difficult to compare the yields for tandem catalysis and back-displacement reactions, the results did show that the yields obtained when only the back-displacement reaction was carried out were considerably higher than the tandem catalysis yield. The same trend was observed for the experiments where 1-decene was used as the back-displacing alkene. This indicates that compounds present from metathesis and displacement might interfere with the reaction.

Finally, the same comparison was made for the tandem catalysis reactions with TIBA and 1-hexene with the corresponding separate back-displacement reactions, which can be found in the Figure 4.18. In this case, the same pattern was observed.

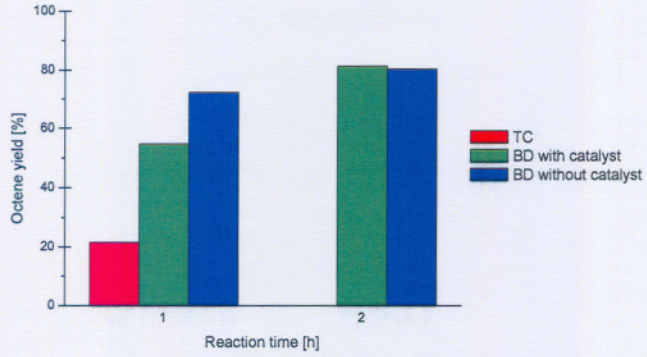


Figure 4.17: Comparison of octene yield in time during back-displacement for tandem catalysis experiments and separate back-displacement reactions for TIBA with ethene [TC: meta: 30 °C overnight, 1-pentene:Ru = 1,000; d: 3 hours, T^{d} = 100 °C, 1 mol% $Ni(acac)_2$; bd: 2 hours, T^{bd} = 25 °C; chlorobenzene int std, 5x excess alkene to Al; BD: T = 25 °C]

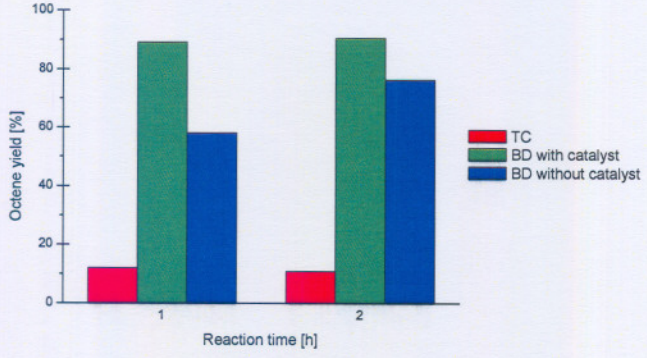


Figure 4.18: Comparison of octene yield in time during back-displacement for tandem catalysis experiments and separate back-displacement reactions for TIBA with 1-hexene [TC: meta: 30 °C overnight, 1-pentene:Ru = 1,000; d: 3 hours, T^{d} = 100 °C, 1 mol% $Ni(acac)_2$; bd: 2 hours, T^{bd} = 25 °C; chlorobenzene int std, 5x excess alkene to Al; BD: 6 hours T = 25 °C]

The tandem catalysis yield for 1-hexene was even lower than when 1-decene was used. Again, the yields for the back-displacement reaction were much higher than the tandem catalysis yields. The octene yields after back-displacement for the different tandem catalysis experiments can be found in the table below.

Table 4.1: Results of tandem catalysis experiments after back-displacement [meta: 30 °C overnight, 1-pentene:Ru = 1,000; d: 3 hours, T^{d} = 100 °C, 1 mol% Ni(acac)$_2$; bd: 2 hours, T^{bd} = 25 °C, 1.5 g COD/mg Ni; chlorobenzene int std, 5x excess alkene to Al]

Displacement	Back-displacement	Octene	Isomerization [%]			
		[%]	1-octene	2-octene	3-octene	4-octene
TIBA	1-C_{10}	41	95	1	4	0
TEA	1-C_{10}	19	97	1	2	0
TIBA	1-C_2	22	94	2	4	0
TIBA	1-C_6	11	96	2	2	0

As was also observed, the highest octene yield was obtained when TIBA was used in the displacement reaction and 1-decene as the back-displacing alkene. The tridecylaluminum compound was expected to be the most stable of the possible trialkylaluminum products after back-displacement, which could explain the higher yield. Reactions with TEA were expected to have a lower yield, which was consistent with results obtained from the transalkylation experiments (Chapter 3, Table 3.3 and 3.4). The isomerization could be kept under control by adding the COD compound before back-displacement (1.5 g COD/mg Ni), resulting in a high 1-octene percentage in the product mixture.

The effectiveness of the COD compound was determined by comparing the isomerization that took place during the back-displacement with different reaction conditions.

Table 4.2: Isomerization of 1-octene after back-displacement reaction

Exp	1-octene	2-octene	3-octene	4-octene
	[%]	[%]	[%]	[%]
Std D+BD exp, no COD	2	10	41	47
Optimized BD – TOA with 1-C_{10}	100	0	0	0
Tandem catalysis – TIBA with 1-C_{10}	95	1	4	0

When no COD was used, the isomerization was quite high, which left only a small amount of 1-octene in the product. The isomerization after tandem catalysis was slightly higher than when the back-displacement was performed separately, but the octene product contained a high percentage of 1-octene (95%). Since the composition of the reaction mixture in tandem catalysis was not the same as for the separate back-displacement reaction due to the presence of other catalysts and unreacted compounds, this could have affected the isomerization inhibiting mechanism of COD.

Summary of results of metathesis-transalkylation tandem catalysis experiments

The metathesis-transalkylation tandem catalysis reactions were performed with 1-pentene as starting alkene in the metathesis reaction and TIBA and TEA as aluminum compounds in the transalkylation reaction with different back-displacing alkenes. The best 1-octene yields were obtained when TIBA was used with 1-decene as back-displacing alkene. This corresponds to the trend that was observed in Chapter 3, when the transalkylation reaction was investigated. Isomerization after back-displacement was effectively inhibited by the addition of 1,5-cyclooctadiene during back-displacement. It was also observed that the overall yield of the reaction decreased with every additional reaction step that was added to the reaction sequence.

4.3.2 Metathesis and isomerization

In these tandem catalysis reactions, an attempt was made to combine metathesis and isomerization to obtain longer chain terminal alkenes. Starting with the standard metathesis of 1-pentene (30 °C, 3 hours, 1-pentene:Ru ratio = 1,000) to yield 4-octene, the isomerising step was investigated further. In some cases, the experiments were carried out in the mini-reactor as well as in the stainless steel reactor (ss), to be able to evaluate scale effects. Firstly, after the metathesis reaction the isomerization was carried out at 30 °C with the addition of extra Grubbs 1 catalyst.

Table 4.3: Isomerization of 4-octene at 30 °C for 3 hours after metathesis of 1-pentene in mini-reactor

Ratio $C=C_x/Ru$ Meta	Ratio $C=C_x/Ru$ Iso	PMP [%]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
1000	1000	80	0	0	25	75
1000	1000 + $Ni(acac)_2$	85	0	0	0	100

From these results it became clear that this temperature was not suitable for isomerization. Almost no isomerization took place, but the high metathesis yield indicated that at these conditions,

metathesis was favoured. The addition of the $Ni(acac)_2$ catalyst together with the Grubbs catalyst seemed to stop isomerization completely.

When the isomerization was carried out at higher temperatures (120 °C) with the addition of extra Grubbs after metathesis, there was still metathesis in the second reaction step, but after 24 hours some isomerization was observed.

Table 4.4: Isomerization of 4-octene at 120 °C after metathesis of 1-pentene in mini-reactor

Ratio $C=C_x/Ru$ Meta&Iso	Reaction time [h]	PMP [%]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
1000	3	85	0	0	32	68
1000	24	90	0	3	35	62

Isomerization at 150 °C showed more 1-octene and 2-octene, but overall, less 4-octene had reacted (see Table 4.5). The results from both the stainless steel reactor and the mini-reactor showed a lower PMP yield and more isomerization, indicating that at higher temperatures isomerization was favoured. The results from the stainless steel reactor show a higher metathesis yield but almost the same amount of isomerization. Since the shape of the reactors and the scale on which the experiments were performed are not equal, the results were expected to show differences.

Table 4.5: Isomerization of 4-octene at 150 °C for 3 hours after metathesis of 1-pentene

Ratio $C=C_x/Ru$ Meta&Iso	Reactor	PMP [%]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
1000	mini-reactor	36	0.1	1	2	97
1000	ss 50 mL	60	0.1	1	3	96

When investigating the isomerization at 150 °C with different amounts of catalyst for the second reaction step, the following results were obtained.

Table 4.6: Isomerization of 4-octene at 150 °C for 3 hours after metathesis of 1-pentene, different amounts of catalyst for isomerization step

Ratio $C=C_x$/Ru Meta	Ratio $C=C_x$/Ru Iso	Reactor	PMP [%]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
1000	10000	mini-reactor	44	0.5	3	6	90
1000 no solvent	10000	mini-reactor	60	0.7	4	11	84
1000	10000	ss 50 mL	55	0.2	1	3	95

The experiment carried out without solvent in the metathesis step showed a higher PMP yield and more isomerization, indicating that the solvent indeed had an influence in the reaction, possibly diluting the reaction mixture, decreasing the contact possibilities between catalyst and alkene. These results are consistent with the results obtained when the metathesis reaction was investigated (Chapter 2, Table 2.7), where also higher yields were observed in metathesis reactions where no solvent was used.

The higher alkene:Ru ratio in the second step does not seem to have a significant impact on the isomerization, therefore an alkene:Ru ratio of 10,000 was assumed to be sufficient for isomerization. When comparing the results obtained on a slightly larger scale in the stainless steel reactor with the results from the mini-reactor, it can be seen that the isomerization is almost the same, but the metathesis yield in the stainless steel reactor is higher. The metathesis yield for the reaction with solvent in the stainless steel reactor is almost equal to the metathesis yield in the mini-reactor for the experiments without solvent. This indicates that the reaction conditions in the stainless steel reactor were more suitable for metathesis.

When no catalyst was added for the second reaction step, there was slightly less isomerization. Almost no 1-octene was formed, but when the reaction was carried out for 24 hours, more 4-octene was isomerized, but almost no extra PMP was formed. This indicated that indeed with the current reaction conditions (temperature) isomerization was favoured.

In Table 4.8, the isomerization of 4-octene at 150 °C with Grubbs 1 (1st row) was compared to the isomerization that took place after the metathesis in the tandem catalysis (TC) reactions under similar reaction conditions (2nd row).

Table 4.7: Isomerization of 4-octene at 150 °C without extra catalyst after metathesis of 1-pentene

Ratio $C=C_x/Ru$ Meta	Reaction time [h]	Reactor	PMP [%]	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
1000	3	mini	52	0	0.5	1	98.5
1000	3	ss	55	0.1	0.9	3	96
1000	24	mini	60	0	4	17	79

Table 4.8: Comparison of 4-octene isomerization with Grubbs 1 at 150 °C with isomerization after metathesis of 1-pentene [30 °C, 3 hours, 1-pentene:Ru = 1,000]

	Ratio $C=C_x/Ru$ Iso	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
Iso 4-octene	1000	2	11	30	57
TC	10000	0.7	4.6	10.7	84

For this comparison, the best tandem catalysis results were taken, in which no solvent was used. The amount of catalyst in the separate isomerization reaction seems higher, but in the TC experiment it was expected that part of the catalyst from the metathesis step was still active in the second step. Both reactions were performed in the 3 mL mini-reactor and the isomerization was analyzed after 3 hours.

As can be concluded from these results, the isomerization after metathesis in TC was lower than when the isomerization was performed separately. This corresponds with previous TC results, where the yield decreased with every additional reaction step. The reason for this could be that the unreacted components had an influence in the following reaction steps, possibly by diluting the reaction mixture or interfering with the catalyst.

Summary of results of metathesis-isomerization tandem catalysis experiments

The metathesis-isomerization experiments were carried out with Grubbs 1 as a catalyst and with 1-pentene as a starting material for the metathesis. Different reaction times, reaction temperatures and alkene:Ru ratios were used to optimize the reaction. It was found that isomerization was favoured at higher temperatures (150 °C) and that the 1-octene yield was higher when extra Grubbs catalyst was added for the second reaction step.

4.3.3 Comparison of TC metathesis-transalkylation with TC metathesis-isomerization

The main aim of the tandem catalysis reactions was to obtain longer chain 1-alkenes from shorter chain primary alkenes. To achieve this, two different reaction paths were explored, the first being metathesis and transalkylation, the other metathesis combined with isomerization.

Table 4.9: Comparison of octene distribution of tandem catalysis products for metathesis-transalkylation versus metathesis-isomerization

	1-octene [%]	2-octene [%]	3-octene [%]	4-octene [%]
Meta-Transalkylation	95	1	4	0
Meta-Isomerization (mini-reactor)	0.7	4.6	10.7	84
Meta-Isomerization (ss reactor)	0.2	1	3	95

For this comparison, the best results from the TC metathesis-transalkylation were compared to the best results from the TC metathesis-isomerization; the latter was performed in both the mini-reactor and the stainless steel reactor.

When looking at the octene distribution (Table 4.9), it can be concluded that the metathesis-transalkylation method was far more successful. The selectivity towards 1-octene was very high compared to the metathesis-isomerization experiments, where only a small percentage of the octene content was 1-octene.

Table 4.10: Octene yields for metathesis-transalkylation and metathesis-isomerization

	Metathesis yield (4-octene) [%]	Yield second step [%]	Overall 1-octene yield [%]
Meta-Transalkylation	21	41	8.6
Meta-Isomerization (mini-reactor)	40	0.7	0.3
Meta-Isomerization (ss reactor)	37	0.2	0.1

When looking at the average overall yield of the tandem catalysis experiments (Table 4.10) it becomes clear that although the metathesis-transalkylation experiments consist of three reaction steps, the overall 1-octene yield is still higher. The main reason for this is the high selectivity towards 1-octene in the transalkylation.

An advantage of the metathesis-isomerization process is shorter reaction time and the fact that less hazardous chemicals were used. To be able to obtain higher selectivity in the isomerization reaction, more experiments are needed.

Although the tandem catalysis experiments described in literature generally require the addition of an alcohol, a base, hydrogen or a combination of these three, this research shows that by simply increasing the temperature after the metathesis of alkenes with Grubbs 1, an isomerization reaction takes place. This indicates that by increasing the temperature of the reaction a ruthenium hydride species was formed that catalyzed the isomerization.

4.4 CONCLUSIONS

Tandem catalysis experiments were carried out in order to obtain longer chain terminal alkenes. The metathesis reaction was used as the first part of the tandem catalysis sequence, followed by either transalkylation in the presence of a TAA compound or isomerization with Grubbs 1 catalyst. The metathesis and transalkylation reactions were described in Chapter 2 and 3 respectively, and were combined in the tandem reactions, which were subsequently optimized. The results show that 1-octene was identified as reaction product in both types of tandem catalysis reactions. The yield and selectivity of the metathesis-transalkylation reaction was higher than the metathesis-isomerization reaction, which was mainly due to the high selectivity of the transalkylation reaction.

The (homogeneous) tandem catalysis reaction in which metathesis and transalkylation are combined in one single reactor without separation or recirculation steps has not been reported in literature up to date, although patents describing the (heterogeneous) industrial application of a combination of metathesis and transalkylation in a series of reactors have been found.

The octene yield of the transalkylation reaction in the tandem experiment was higher when TIBA was used instead of TEA (41% compared to 22%) and 1-decene as the back-displacing alkene. 1-Decene showed a 41% octene yield, where with ethene and 1-hexene a lower yield was obtained (22 and 11% respectively).

It was also seen that the octene yield decreased with every additional reaction step. For reactions involving TIBA as the alkylaluminum compound and 1-decene as the back-displacing alkene the yield of the transalkylation reactions in the tandem sequence was 41%, compared to 80% when

only the transalkylation was carried out. This indicates that indeed the metathesis reaction has an influence on the transalkylation reaction. This could mean that the Grubbs catalyst interacts with the nickel catalyst that was used in the displacement reaction. It may also be possible that the unreacted pentene that was left after the metathesis reaction also displaces the TIBA, thus decreasing the octene yield after back-displacement.

The overall yield of this tandem sequence was 8.6%, with a 95% selectivity towards 1-octene in the reaction product. The catalysts that were used in the tandem reactions seemed to be compatible, but further studies are needed with different catalyst combinations, preferably including a heterogeneous catalyst system for the metathesis reaction, to improve reaction yields and to facilitate separation of the reaction product.

The conversion of a ruthenium metathesis catalyst to its corresponding hydride species (which catalyzes isomerization and hydrogenation) has been reported in literature. The reported conversion takes place upon addition of reagents (alcohol, base, hydrogen), but there have also been reports on the influence of temperature in combination with the addition of chemicals on this catalyst transformation.

In this study, isomerization of 4-octene was observed when the reaction temperature was increased after metathesis without the addition of chemicals to induce the catalyst transformation. Although the overall 1-octene yield was relatively low in the tandem reactions (<1%), it was found that isomerization was considerably higher when 4-octene was reacted with Grubbs 1 catalyst at 150 °C in a one-step experiment (43% isomerization, 2% of which was 1-octene). This indicates that the Grubbs 1 catalyst favours isomerization at higher temperatures, even without additional reagents, but that the yield decreases when the number of reaction steps is increased.

Further studies, involving other catalyst systems for the tandem reactions in an attempt to increase the 1-octene yields are needed, which would also improve understanding of the reaction mechanism.

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CHAPTER 5

Conclusions

5.1 Metathesis

The metathesis reaction was studied and optimized with different alkenes and under different reaction conditions with Grubbs 1 as a catalyst. It was not the scope of this study to perform an in dept investigation into the metathesis reaction and mechanism, since this has already been done by numerous researchers. The aim of this study was merely to find the best reaction conditions for the metathesis reaction so that it could be used as the first step in the tandem experiments.

When the metathesis reaction was carried out at 30°C with an alkene:Ru ratio of 1,000, a high selectivity towards the PMP was observed and no significant SMP or isomerization was detected. Reproducible PMP yields were obtained from different alkenes, ranging from 45% after 5 hours for 1-octene to around 60% when 1-pentene was used, when the reaction was performed without solvent (with 1-octene) or when the equilibrium of metathesis of 1-octene was shifted to the right.

The metathesis reaction proved to be a suitable way to produce longer chain (internal) alkenes, with high yields and relatively short reaction times, making it possible to incorporate this reaction in the tandem catalysis reactions.

5.2 Transalkylation

It proved to be a challenge to develop a quantitative analysis method for the transalkylation reaction. Despite the fact that the most suitable analysis technique, NMR analysis, was not available in this project (the only accessible NMR apparatus could not detect any of the aluminum compounds and therefore could not be used), a successful analysis method was found. Although not as accurate as NMR analysis, this method, that involved the boiling off of excess alkenes after the first part of the transalkylation in combination with GC analysis, proved to be a suitable tool to quantitatively investigate the transalkylation reaction and test different reaction conditions.

Simultaneous with the development of this analysis method, a suitable reactor setup was built, reflecting the special precautions that were needed to work with the alkylaluminum compounds. The reactor setup was modified and improved as the experimental method was developed.

With the analysis and reactor in place, the transalkylation reaction could be thoroughly investigated under different reaction conditions and with different aluminum compounds and alkenes. The reaction yield at optimized reaction conditions using 4-octene was reproducible and sufficient for the tandem catalysis experiments. The highest octene yield (82%) was obtained when the displacement reaction was carried out at 100°C for 3 hours with 1 mol% $Ni(acac)_2$ as a catalyst, followed by back-displacement of the TOA with 1-decene at 25°C for 2 hours. No additional catalyst was needed for the back-displacement reaction and COD was used to prevent isomerization.

This research proved that the transalkylation reaction was a suitable way to obtain terminal alkenes from internal ones, and could potentially be incorporated as the second step in the tandem catalysis experiments.

5.3 Tandem catalysis

Since the reactor setup was already developed and the metathesis and transalkylation reactions were studied and optimized, the first type of tandem reactions could be carried out relatively easy. The yields for the metathesis-transalkylation tandem reactions were reproducible, and a high selectivity towards 1-octene was observed. When starting with 1-pentene the final product of the tandem reactions contained mostly 1-octene, as was confirmed with GC analysis. When looking at the aim, which was producing longer chain terminal alkenes, this tandem catalysis setup certainly proved to be a suitable way to achieve this.

The overall yield of the tandem experiments was 8.6% (21% yield in the metathesis and 41% from the transalkylation) with 95% selectivity towards 1-octene. It can be concluded that the yield of the separate parts of the tandem reactions decreased with every additional reaction step. Since no separation steps were included in the reaction sequence, there must have been an interaction between the reaction components of the different reactions.

For the metathesis-isomerization tandem experiments, only the reaction conditions suitable for the isomerization part had to be determined. Although reports about the *in situ* transformation of a metathesis catalyst into an isomerization catalyst in literature almost invariably include the addition of certain chemicals that induce this change, this research proves that an increase in temperature also increases isomerization. It may be true that the yield and efficiency of the isomerization was relatively low (<1% overall yield), but it is certainly interesting to see that it is possible. Naturally, more research is needed to optimize this method and to fully understand the reaction mechanism.

Needless to say that in the comparison of the two tandem catalysis variations mentioned above, the highest overall 1-octene yields were obtained with the metathesis-transalkylation reaction. Although the yield decreased with every additional reaction step, this method certainly can be a valuable tool to obtain longer chain terminal alkenes. However, when this reaction is applied in industry on a large scale, this tandem setup might not be the best choice. When the overall yield of the tandem metathesis-transalkylation reactions (8.6%) is compared to the yields of the separate metathesis (45%) and transalkylation reactions (82%), the 1-octene yield could theoretically be as high as 37%. This would include separation and purification steps, leading to longer reaction times and possible yield losses due to purification steps.

A multiple reactor system would probably be more appropriate when looking at a continuous flow and the possibility of recycle streams in the process. And even though Grubbs 1 is a very suitable metathesis catalyst, when dealing with larger scale experiments and industrial applications, a heterogeneous catalyst would probably be a better alternative when looking at separation and cost perspective.

5.4 Overview and recommendations

The aim of this study was to make longer chain terminal alkenes by using metathesis and transalkylation or metathesis and isomerization in tandem catalysis. The results presented in this thesis prove that this was achieved and a new tandem catalysis method was developed. The tandem catalysis reactor setup was suitable for laboratory scale experiments and improved the knowledge of transalkylation reactions.

When looking at industrial scale applications, a number of other factors that determine the feasibility of a certain method have to be taken into account, possibly resulting in a totally different outcome. Some of these factors that play a role are: catalyst choice (price, separation possibilities, selectivity and required reaction conditions), reaction setup (batch scale in tandem catalysis or continuous flow in multiple reactors) and many others.

Using the transalkylation reaction in combination with metathesis to obtain longer chain terminal alkenes provides certain advantages with respect to the well-known Ziegler "growth" reaction. Although this growth reaction also results in longer chain terminal alkenes, this reaction can only produce even numbered alkenes, since ethene is used by inserting it into the aluminum-alkyl bond.

Apart from the application of a wider variety of short chain terminal alkenes as starting materials, the transalkylation reaction also has the advantage that the carbon number of the product is known beforehand, whereas with the growth reaction the chain growth has to be stopped at the desired chain length, which generally produces a mixture of alkenes with different chain lengths.

Before it would be possible to determine the actual feasibility of this specific tandem catalysis technique and apply it in commercial processes, more research in combination with more accurate analysis methods is definitely necessary.

Summary

Metathesis and transalkylation in tandem catalysis

Longer chain terminal alkenes, which are in high demand in industry, can be obtained from widely available shorter chain terminal alkenes in a tandem catalysis reaction. Tandem catalysis involves the combination of multiple catalytic reactions in a single reactor without separation steps in between. In this study, longer chain terminal alkenes were obtained by combining metathesis and transalkylation in a tandem experiment and the results were compared to a different type of tandem experiment, involving metathesis and isomerization.

The metathesis reaction was investigated in **Chapter 2**, where a short chain terminal alkene is used as the starting material, producing a longer chain internal alkene as primary metathesis product. In these reactions, Grubbs 1 catalyst was used and the experiments were carried out in a mini-reactor with different alkenes (1-pentene, 1-octene and 1-decene) under different reaction conditions. The PMP yield decreased with increasing alkene:Ru ratio and the alkene chain length influence was not very clear. Reproducible yields were obtained with all three of the alkenes and the yield increased when the reaction was carried out without solvent or when the gas formed during the reaction was allowed to escape (equilibrium shift). The average PMP yield for 1-octene was 45% after 5 hours at 30 °C with an alkene:Ru ratio of 1,000 and above 60% for 1-pentene or when 1-octene was used in reactions without solvent or when the equilibrium was shifted to the right.

In **Chapter 3** the transalkylation reaction was carried out. This transalkylation reaction is based on the Ziegler "Aufbau" (growth) reaction and transforms an internal alkene into a terminal alkene. In this project the main focus was to obtain terminal octenes, therefore the starting alkene for the transalkylation reaction was an internal octene. The first part of the transalkylation reaction, the displacement, involves the displacement of the alkyl groups of a trialkylaluminum compound by octene. This internal octene is isomerized to 1-octene before displacing the alkyl group, in the presence of an isomerization catalyst. The second part of the reaction is the back-displacement, where the newly formed octyl groups of the trioctylaluminum compound are replaced again with another (terminal) alkene, setting free a terminal octene.

A reactor setup was built that was suitable for these experiments and could also be used in the tandem catalysis experiments. After the development of a quantitative analysis method, which

consisted of boiling off the excess octene after displacement in combination with GC analysis, the transalkylation reaction was investigated and optimized.

The best results were obtained when TIBA was used in combination with 1-decene as a back-displacing alkene. The optimal yields were obtained when the displacement reaction was carried out at 100 °C for 3 hours with 1 mol% $Ni(acac)_2$ catalyst, followed by the back-displacement at 25 °C for 2 hours, both reactions with an alkene:Al ratio of 5:1. When starting with 4-octene, an 82% yield was obtained. 1,5-Cyclooctadiene was used to stop isomerization after back-displacement, which proved to be a very successful isomerization-inhibiting agent.

The optimized metathesis and transalkylation reactions were combined in tandem experiments in **Chapter 4.** An overall yield of 8.6% was obtained after metathesis of 1-pentene with Grubbs 1 as a catalyst, followed by transalkylation where TIBA was used as the aluminum compound and 1-decene as the back-displacing alkene, in the presence of the $Ni(acac)_2$ catalyst. The octene product consisted mostly of 1-octene (95%), but some isomerization had taken place.

The metathesis-isomerization experiments showed a very low 1-octene yield in the isomerization step, and therefore the overall yield of these experiments was lower than that of the metathesis-transalkylation experiments.

An overview of the conclusions of the different chapters was given in **Chapter 5**, where the potential of the project on a larger scale was discussed. The tandem catalysis experiments in which metathesis and transalkylation were combined proved to be successful in obtaining longer chain terminal alkenes, as was set as the main aim of this study. Although this method was suitable for laboratory scale experiments, more aspects have to be taken into account to determine the feasibility on a larger industrial scale.

Samenvatting

Metathese en transalkylering in tandem katalyse

Terminale alkenen met langere ketens, waarvoor vanuit de industrie een grote aanvraag is, kunnen verkregen worden uit makkelijk beschikbare kortere terminale alkenen door middel van een tandem katalyse reaktie. Tandem katalyse behelst de kombinatie van meerdere katalytische reakties in een enkele reaktor zonder scheidingsstappen tussenin. In deze studie werden langere terminale alkenen verkregen uit een kombinatie van metathese en transalkylering in een tandem reaktie, waarna de resultaten vergeleken werden met een ander type tandem experiment, waarbij metathese gekombineerd werd met een isomerisatie stap.

De metathese reaktie werd onderzocht in **Hoofdstuk 2**, waarbij een korte terminale alkeen werd gebruikt als uitgangsmateriaal wat een langere terminale alkeen oplevert als primaire metathese produkt. Grubbs 1 werd in deze reakties gebruikt als katalysator, welke uitgevoerd werden in een mini-reaktor met verschillende alkenen (1-penteen, 1-okteen en 1-dekeen) en onder verschillende reaktie-omstandigheden. De PMP opbrengst nam af met toenemende alkeen:Ru verhouding en de invloed van de alkeen ketenlengte was niet kwantitatief aantoonbaar. Reproduceerbare opbrengsten werden verkregen met alle drie de alkenen en de opbrengst was hoger wanneer de reaktie uitgevoerd werd zonder oplosmiddel en wanneer het gas wat vormde tijdens de reaktie kon ontsnappen (verschuiving van het evenwicht). De gemiddelde PMP opbrengst voor 1-okteen was 45% na 5 uur bij 30 °C met een alkeen:Ru verhouding van 1,000 en boven 60% voor reakties met 1-penteen of voor de reakties waarin 1-okteen gebruikt werd zonder oplosmiddel en wanneer het evenwicht naar rechts werd geschoven door het gas te laten ontsnappen.

Hoofdstuk 3 beschrijft de transalkyleringsreaktie. In deze reaktie, die is gebaseerd op de "Aufbau" (groei) reaktie van Ziegler, wordt een interne alkeen omgezet in een terminale alkeen. Het doel van dit onderzoek was om terminale oktenen te verkrijgen, daarom was het uitgangsprodukt van de transalkyleringsreaktie een interne okteen. In het eerste deel van de transalkyleringsreaktie, de verplaatsingsreaktie, wordt de alkyl groep van de trialkylaluminium vervangen door okteen. De interne okteen wordt geïsomeriseerd naar 1-okteen voordat het de alkyl group vervangt in de aanwezigheid van een isomerisatie katalysator. Het tweede deel van de reaktie is de terug-verplaatsing, waarin de nieuw gevormde oktyl-groepen van de aluminium opnieuw worden vervangen met een andere (terminale) alkeen, en waarbij dan 1-okteen wordt vrijgesteld.

Een geschikte reaktor opstelling werd ontworpen en gebouwd voor de transalkyleringsreakties, die eveneens gebruikt kon worden in de tandem experimenten. Na de ontwikkeling van een kwantitatieve analyse methode, die bestond uit het afdampen van de overmaat okteen na de verplaatsingsreaktie in kombinatie met GC analyse, werd de transalkyleringsreaktie onderzocht en geoptimaliseerd.

De beste resultaten werden verkregen wanneer TIBA werd gebruikt samen met 1-dekeen als de terug-verplaatsende alkeen. De grootste opbrengst werd behaald wanneer de verplaatsingsreaktie werd uitgevoerd bij 100 °C gedurende 3 uur met 1 mol% $Ni(acac)_2$ katalysator, gevolgd door de terug-verplaatsingsreaktie bij 25 °C gedurende 2 uur, beide met een alkeen:Al verhouding van 5:1. Wanneer 4-okteen werd gebruikt als uitgangsstof voor de reaktie werd een opbrengst van 82% behaald. 1,5-cyclo-oktadieen bleek succesvol om de isomerisatie na de terug-verplaatsingsreaktie te stoppen.

De geoptimaliseerde metathese en transalkyleringsreakties werden gekombineerd in tandem experimenten in **Hoofdstuk 4**. Een totale opbrengst van 8.6% werd verkregen na de metathese van 1-penteen met Grubbs 1 als katalysator, gevolgd door de transalkyleringsreaktie waarbij TIBA werd gebruikt als de aluminium komponent en 1-dekeen als de terug-verplaatsende alkeen in de aanwezigheid van de $Ni(acac)_2$ katalysator. Het okteen produkt bestond voor het grootste deel uit 1-okteen (95%) maar een geringe mate van isomerisatie had plaatsgevonden.

De 1-okteen opbrengst in de isomerisatie stap van de metathese-isomerisatie experimenten was erg laag, waardoor de totale opbrengst van deze experimenten veel lager was dan die van de metathese-transalkyleringsexperimenten.

In **Hoofdstuk 5** wordt een overzicht gegeven van de conclusies van de verschillende hoofdstukken, waarbij de mogelijkheden van dit projekt op grotere schaal worden besproken. De tandem katalyse experimenten waarbij metatese en transalkylering werden gekombineerd bleken succesvol in het verkijgen van langere terminale alkenen, wat het doel was van dit onderzoek. Hoewel deze methode geschikt was op laboratoriumschaal moet er met meer aspekten rekening gehouden worden om te kunnen beoordelen wat de haalbaarheid van deze methode is op grotere industriële schaal.

Acknowledgements

When I got the opportunity to do my PhD at the North-West University I didn't expect how much my life would change. Not only did it involve moving to South Africa, it also included working in a totally different field, which was almost completely new to me. Looking back, it was a wonderful and interesting experience. Therefore I would like to thank a number of people who helped me during the last 4 years and made it possible to present this booklet to you today:

- Prof. Manie Vosloo, for giving me the opportunity to do my PhD in his group, always being creative in finding funds for my research and for the interesting discussions during our biweekly meetings.
- Dr Comie van Sittert, for always being there with advice when I knocked on her door.
- The catalysis and synthesis group, a very nice and supporting group to be part of. Johan (and Rita), thanks for the original ideas and feedback!
- Anriëtte Pretorius, and the other library staff, for their help and support.
- Sasol and the C*Change centre of excellence (NRF) for their funding.
- Dr. Thys Botha and Dr. Charl van Schalkwyk for the interesting discussions and useful ideas.
- My friends and family, for their support during the sometimes difficult times, for their patience, post packets (dropjes!!), emails and phone calls.
- My father, for his support, especially in the last few months, taking as much work around the house off my shoulders as possible.
- Last but not least, Wimpie, for always being at my side, for your love, trust and support, I couldn't have done it without you!