Metathesis of alkenes using ruthenium carbene complexes

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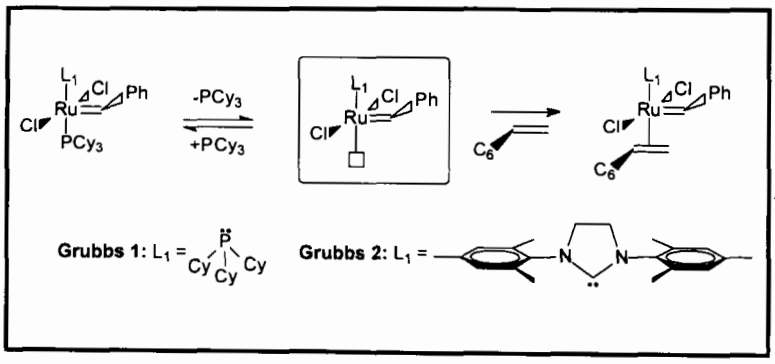

KNG Mtshatsheni

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List of Abbreviations and Structures

Abbreviations

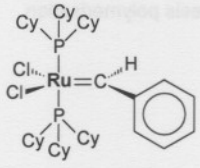
ADMET	Acyclic dienes metathesis polymerisation
BnO	Benzyloxide
BOC	t-Butoxycarbonyl
CM	Cross metathesis
DCDP	Dicyclopentadiene
DME	Dimethoxyethane
EtOH	Ethanol
FG	Functional groups
GC	Gas chromatography
^{1}H-NMR	Proton nuclear magnetic resonance spectroscopy
Hx	Hexyl group
NAr	Nitroaryl
NHC	N-heterocyclic carbene
IP	Isomerisation products
NMR	Nuclear magnetic resonance
OP	Oligomerisation products
PCy_3	Tricyclohexylphosphine
PhCl	Chlorobenzene
PMP	Primary metathesis products
RCM	Ring-closing metathesis
ROMP	Ring-opening metathesis polymerisation
SHOP	Shell Higher Olefin Process
SMP	Secondary metathesis products
SM	Self metathesis
TBDMS	Tert-butyldimethylsilyl
TfOH	Trifluoromethanesulfonic acid
TMS	Trimethylsilane

Structures

Grubbs first generation

Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium

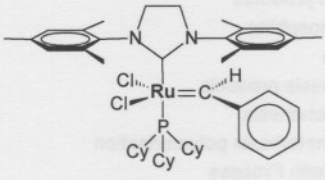
$[Cl_2(PCy_3)_2Ru(=CHPh)]$



Grubbs second generation

[1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium]

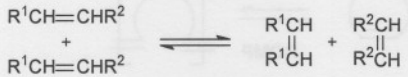
$[Cl_2(PCy_3)(IMes)Ru(=CHPh)]$



1 AIMS AND OBJECTIVES

1.1 Introduction

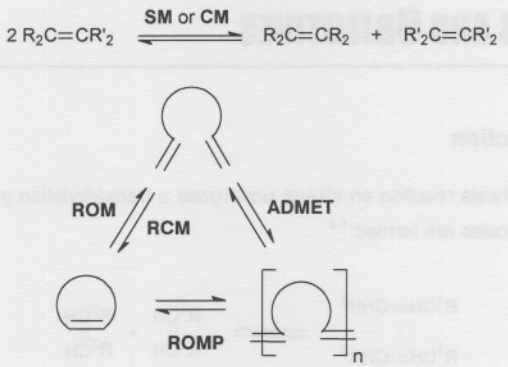
During the metathesis reaction an alkene undergoes a transalkylation process in which new alkene molecules are formed:[1-5]



The process is reversible and the composition of the reaction mixture will reach equilibrium after some time. The statistical distribution of the alkenes at equilibrium may reach a composition of 50 % substrate and 25 % each of the two products.[6-8]

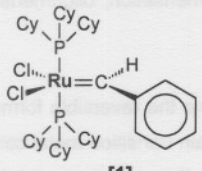
A wide variety of homogeneous and heterogeneous catalytic systems active for the metathesis of alkenes are reported in literature.[7,8] The most active systems are normally based on compounds of the transition metals molybdenum, tungsten, rhenium and ruthenium. Metathesis catalytic systems can be quite selective although it is inhibited in many cases by side reactions such as double bond isomerisation, oligomerisation and the alkylation of the aromatic solvent.[7,8]

The reaction between substrate and catalyst proceeds via the reversible formation of a metallacyclobutane intermediate. In the presence of certain transition metal compounds, including a variety of metal carbenes, alkenes exchange the groups around the double bonds, resulting in several outcomes (**Scheme 1.1**): straight swapping of groups between two acyclic alkenes, i.e. homo- or selfmetathesis (SM) and cross metathesis (CM); closure of large rings, i.e. ring-closing metathesis (RCM); formation of dienes from cyclic and acyclic alkenes, i.e. ring-opening metathesis (ROM); polymerization of cyclic alkenes, ring-opening metathesis polymerization (ROMP) and polymerization of acyclic dienes, i.e. acyclic diene metathesis polymerization (ADMET).[9]

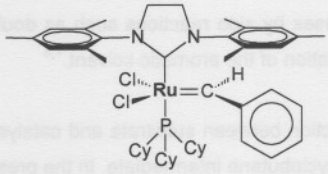


Scheme 1.1 Alkene metathesis reactions

A very important development over the last few years was the discovery and improvement of the so-called Grubbs metal carbenes based on ruthenium, i.e. Grubbs first generation catalyst or Grubbs 1, $[(PCy_3)(Cl_2)Ru{=}CHPh]$ [1] and Grubbs second generation catalyst or Grubbs 2 $[(H_2IMes)(PCy_3)(Cl_2)\ Ru{=}CHPh)$ [2].



[1]



[2]

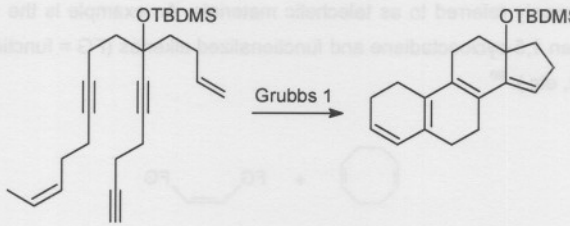
This discovery did not only give a new leash of life for alkene metathesis but also took organic synthesis by storm. Generally, these compounds exhibit a very high activity for alkene metathesis and are also highly tolerant against deactivation by oxygen, water, and other impurities in solvents.

Replacement of one of the phosphine ligands by, for example, a N-heterocyclic ligand, improved the lifetime and reactivity of the metal carbenes.[10,11] The N-heterocyclic carbene coordinated ruthenium benzylidene complex [(H_2IMes)(PCy_3)(Cl_2)Ru=CHPh], [2], is a highly active catalyst for a wide variety of alkene metathesis reactions[12], including those with sterically demanding[13,14] and electron-deficient alkenes.[15]

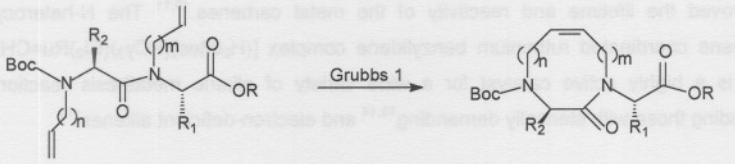
Alkene metathesis reactions are also used in the industry. The largest application of this reaction is found in the Shell Higher Olefin Process (SHOP), which produces more than 10^5 tons of C_{10}-C_{20} alkenes annually.[16]

The first metathesis catalyst that has been widely utilized in organic synthesis was the Grubbs first generation catalyst [1] that effects RCM, CM, and ROMP[12] with high activities and tolerance for functional groups and protic media. The Grubbs 1 catalyst can lead to trisubstituted alkenes via CM,[14] and it ring-closes alkenes with excellent functional group tolerance and selectivity.[13]

The application of ruthenium based alkene metathesis technology to the manufacture of pharmaceutical intermediates is boundless. For example, RCM enables the efficient production of complex ring systems from simple acyclic precursors using Grubbs 1:[17]

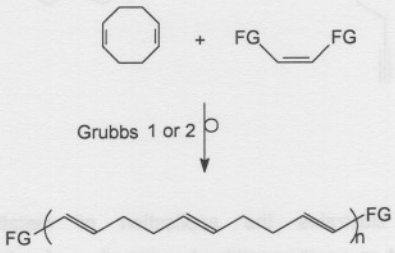


A further example illustrates the application of metathesis reactions to peptidomimetics:[18] RCM on acyclic peptides bearing alkene functionalities results in the formation of cyclic species:



The resulting carbocyclic substructure has a reduced conformational space that often results in an increased affinity for biological receptors, and provides dramatically improved redox stability.[18,19]

In the production of fine chemicals on an industrial scale by RCM and CM reactions, Grubbs metal carbene catalysts have shown remarkable utility.[19] ROMP and ADMET have been used extensively in the field of materials science to produce polymers with unique properties. One such example is the ROMP of dicyclopentadiene (DCDP) to give resins that exhibit remarkable impact and corrosion resistance.[20] DCDP resin is an excellent base resin for a variety of composite products used in the defense/aerospace industry, sports and recreation, marine, ballistics and microelectronics. ROM and CM can be combined to produce a wide variety of terminally functionalized oligomers or polymers, commonly referred to as telechelic materials. An example is the metathesis reaction between 1,5-cyclooctadiene and functionalized alkenes (FG = functional group, i.e. OH, COOH, etc.): [20]



1.2 Aims and Objectives

In the literature, less attention has been paid so far to the metathesis of the linear alkenes catalysed by Grubbs metal carbenes. In this study, the metathesis of longer chain, linear alkenes with the ruthenium carbene complexes, Grubbs first generation [1], and Grubbs second generation [2] catalysts, will be investigated. To reach the aim of the project, the following objectives are stated:

- To optimize the reaction conditions for the metathesis of 1-octene.
- To investigate the reactions of the internal octenes and longer chain alkenes.
- Use NMR to investigate the metathesis of 1-octene.

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2 LITERATURE STUDY

2.1 Introduction

The name "Metathesis" is derived from the Greek words *meta* (change) and *tithemi* (place). Metathesis describes the (apparent) interchange of carbon atoms between a pair of double bonds.[1] Alkene metathesis is a synthetically powerful transformation in which a net exchange of alkene substituents occurs.[2]

Banks and Bailey[3] discovered the catalysed version of the alkene metathesis reaction. The reaction is essentially thermoneutral, involving just the making and breaking of carbon-carbon double bonds. Equilibrium can be reached from either side reaction, and the distribution of products is then statistical. The thermal activation of this entropy-controlled reaction is symmetry forbidden according to the Woodward-Hoffman rules[4], which is consistent with the high temperatures generally necessary for the reaction.[5]

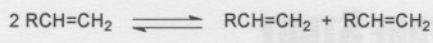
The broad categories of the alkene metathesis reaction have already been described in Chapter 1. The CM reaction involves different alkene substrates which may be either acyclic compounds, the reaction then commonly known as acyclic cross metathesis, or could involve both cyclic and acyclic compounds.[1,6] A simple example of acyclic cross metathesis is the reaction between ethene and 2-butene to form propene.[7] When one of the reactants in a CM reaction is ethene, the reaction is known as ethenolysis:[1,6]

$$R_1CH{=}CHR_2 + CH_2{=}CH_2 \rightleftharpoons R_1CH{=}CH_2 + R_2CH{=}CH_2$$

When the reacting alkenes are the same, the reaction is described as SM.[1,6] SM reactions could either be productive or non-productive (degenerate).[1] Productive SM reactions result in the formation of new products:

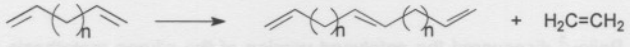
$$2\ RCH{=}CH_2 \rightleftharpoons RCH{=}CHR + CH_2{=}CH_2$$

In non-productive or degenerate SM reactions, no new products are formed:



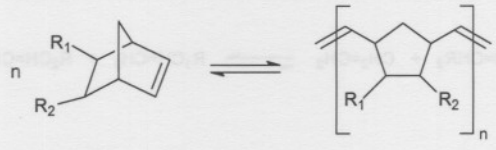
Studies have shown that, with terminal alkenes, non-productive metathesis is generally faster than productive metathesis.[1]

When acyclic CM is applied to dialkenes, the reaction is described as ADMET. [6] Diene compounds can react to form trienes, pentaenes, etc., as shown below:[8]



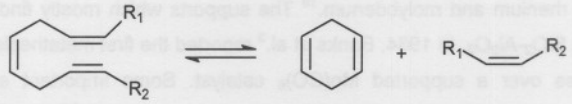
When the appropriate catalyst system is selected, high molecular weight unsaturated polymers can be formed via the ADMET reaction.

ROMP is one of the metathesis reactions which have found application industrially.[1,6] It is a very useful industrial process for producing unsaturated polymers (polyalkenemers) from cycloalkenes. Many polymers can be synthesized from cyclic monoenes, dienes, polyenes, bicyclic and polycyclic alkenes via ROMP. For example, norbonene (bicyclo [2.2.1]hept-2-ene) and its derivatives can undergo metathesis in the presence of a suitable catalyst to produce polymeric materials:[9]



In addition to CM and ROMP, RCM has also received considerable attention in organic synthesis since it offers possibilities for the synthesis of a variety of cyclic alkenes with multiple functionalities. Linear diene or polyene compounds react intramolecularly to

yield closed-ring systems. RCM reactions appear favourable when the end-product is a 5-, 6-, 7-, 8- or higher-membered ring compound:[6]



2.2 Catalytic systems

The number of catalysts that initiate alkene metathesis is very large. The metathesis reaction can be catalyzed by both heterogeneous and homogeneous catalysts.[1] The homogeneous catalysts and their heterogeneous counterparts are strikingly similar. A wide variety of transition metal compounds will catalyze the reaction, the most important ones being based on W, Mo, Re, and Ru (Table 2.1).[1,6,7] These include catalysts containing the transition metal in high as well as low oxidation states.

Table 2.1 Transition metals forming active alkene metathesis precatalysts

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

2.2.1 Heterogeneous Catalysts

Heterogeneous catalysts generally consist of a transition metal oxide or an organometallic precursor deposited on a high-surface area support.[1]

The catalyst and the alkene are present in different phases, usually the catalyst is in the solid phase while the alkene is in a liquid or gas phase. Heterogeneous catalytic systems usually consists of oxides of molybdenum, tungsten or rhenium which is placed

on a support material like silica or alumina.[1]

The most active heterogeneous catalysts for the metathesis of alkenes are based on the oxides of rhenium and molybdenum.[10] The supports which mostly find application are Al_2O_3 and SiO_2-Al_2O_3. In 1964, Banks et al.[3] reported the first metathesis reaction of simple alkenes over a supported $Mo(CO)_6$ catalyst. Some important examples of heterogeneous metathesis catalysts are illustrated in Table 2.2.[1,2] Re_2O_7/Al_2O_3 and Re_2O_7/SiO_2-Al_2O_3 catalysts are very active heterogeneous metathesis catalysts, especially when promoted with a small amount of a tetra-alkyltin compound, e.g., $(CH_3)_4Sn$.[2]

Table 2.2 Examples of W, Mo and Re-based heterogeneous metathesis catalysts[1,2]

Substrate	Catalytic system	T/°C
	Mo-based	
propene	MoO_3/Al_2O_3	207
cis,cis-2,8-decadiene	$MoO_3/CoO/Al_2O_3$	45
cycloalkenes	MoO_3/γ-$Al_2O_3/LiAlH_4$	20
propene	$Mo(CO)_6/\gamma$-Al_2O_3	65
2-pentene	$Mo(CO)_6/\gamma$-Al_2O_3	120
1-hexene	$(\pi$-$C_3H_5)_4Mo/SiO_2$	20
	W-based	
propene	WO_3/SiO_2	400
2-hexene	WO_3/SiO_2	400
propene	$WO_3/Al2O_3$	150
propene	$W(CO)_6/SiO_2$	140
propene	$(\pi$-$C_4H_7)_4W/SiO_2$	250
	Re-based	
pcyclic alkenes	Re_2O_7/Al_2O_3	20-100
cyclic alkenes	Re_2O_7/Al_2O_3	40-140
propene	ReO_3/SiO_2	200
propene	$Re_2O_7/SiO_2.Al_2O_3$	50

2.2.2 Homogeneous catalysts

Homogeneous catalysts mainly consist of a combination of a transition metal compound (usually an (oxo)chloride complex), an organometallic compound as cocatalyst, and sometimes a third compound (promoter), or a well-defined carbene (alkylidine) complex of a transition metal.[1]

The catalyst and the alkene are in the same phase, usually the liquid phase. The first category of homogeneous catalysts has expanded since 1967 to numerous possible combinations of a transition metal salt and a metal alkyl or hydride cocatalyst, which are able to bring about the metathesis of different kinds of alkenes.[11]

Research on homogeneous catalytic systems for the alkene metathesis reaction is stimulated by the idea that homogeneous catalytic systems are more advantageous and effective than the heterogeneous catalytic systems. The following reasons are given:[12]

- With homogeneous catalytic systems, every molecule can act as a catalyst.
- The catalyst gives better repeatable results for alkene metathesis reactions.
- Homogeneous catalysts are more specific for some alkenes as a result of the selectivity of the catalyst.
- Mechanistic clarification of alkene metathesis reactions can be done better in a homogeneous reaction.
- A homogeneous catalytic system has the ability to give high yields of pure metathesis products.

One of the earliest reported homogeneous catalyst systems was the $WCl_6/EtAlCl_2/EtOH$ system of Calderon *et al.*[11] This catalyst combination is already very active at room temperature for the metathesis of 2-pentene to 2-butene and 3-hexene, resulting in a thermodynamic equilibrium within a few minutes at a molar ratio of alkene to tungsten of 10 000:1 with a selectivity of 99.6%. Catalyst systems like WCl_6/Me_4Sn, $WOCl_4/Me_4Sn$, WCl_6/ Ph_2SiH_2, and $WCl_4(OC_6H_3\text{-}Br_2\text{-}2,6)/Bu_4Pb$ bring about the metathesis of acyclic functionalized alkenes.[11] In that case, however, they are several orders of magnitude less active than for normal alkenes. A few examples of homogeneous catalyst systems are given in Table 2.3 (the list is by no means representative or comprehensive but only illustrates typical examples).

Table 2.3 Examples of W, Mo, Re and Ru-based homogeneous metathesis catalysts[1]

Substrate	Catalyst system	T/°C
	Mo-based	
2-pentene	$MoCl_5/SnPh_4$	20
2-pentene	$MoCl_3(NO)EtAlCl_2$	20
2-pentene	$MoCl_3(OPPh_3)_2N/EtAlCl_2$	20
	W-based	
2-pentene, 2-butene	$WCl_6/EtAlCl_2/EtOH$	20
2-pentene	$WCl_6/BuLi$	20
2-pentene	$WCl_6/SnMe_4$	20
2-pentene	$W(=CHCMe)Br_2(OCH_2CMe_3)_2/GaBr_3$	-
1-hexene	$WCl_6/SnBu_4$	60
	Re-based	
Norbonene	$ReCl_5/EtAlCl_2$	20
2-pentene	$ReCl_5/SnBu_4$	20
2-pentene	$ReCl(CO)_5/EtAlCl_2$	90
2-pentene	$ReOCl_3(PPh_3)/EtAlCl_2$	20
	Ru-based	
4-nonene	$Ru(=CHPh)Cl_2(PCy_3)_2$	20
4-decene	$Ru(=CHPh)Cl_2(PCy_3)_2$	20
3-heptene	$Ru(=CHPh)Cl_2(PCy_3)_2$	20
methyl oleate	$Ru(=CHPh)Cl_2(PCy_3)_2$	20
methyl elaidate	$Ru(=CHPh)Cl_2(PCy_3)_2$	20

(a) *Molybdenum-based catalysts*

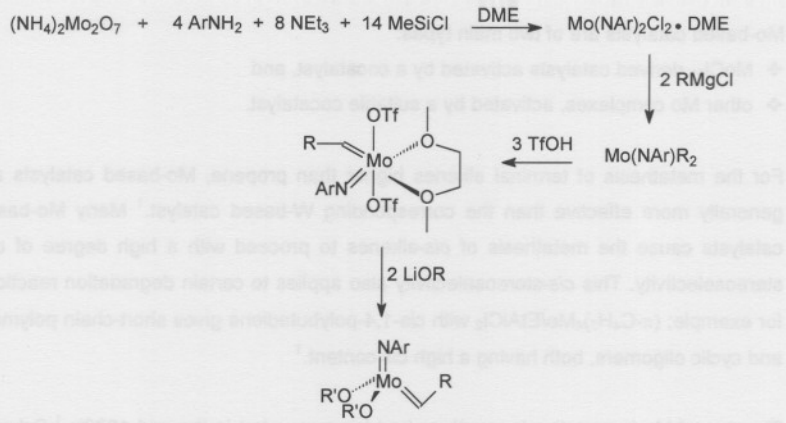
Mo-based catalysts are of two main types:

- $MoCl_5$- derived catalysts activated by a cocatalyst, and
- other Mo complexes, activated by a suitable cocatalyst.

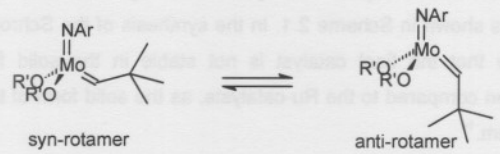
For the metathesis of terminal alkenes higher than propene, Mo-based catalysts are generally more effective than the corresponding W-based catalyst.[1] Many Mo-based catalysts cause the metathesis of *cis*-alkenes to proceed with a high degree of *cis*-stereoselectivity. This *cis*-stereoselectivity also applies to certain degradation reactions for example: $(\pi\text{-}C_4H_7)_4Mo/EtAlCl_2$ with cis-1,4-polybutadiene gives short-chain polymers and cyclic oligomers, both having a high *cis* content.[1]

The use of Mo in metathesis reactions had been reported in the mid 1970's.[1] Schrock published a Mo-catalyst for use in metathesis in 1990 that became known as the Schrock metal carbene or catalyst.[14] The synthesis and general structure of a Schrock carbene catalyst is shown in Scheme 2.1. In the synthesis of the Schrock catalyst, it is important to note that the final catalyst is not stable in the solid form. This is a disadvantage when compared to the Ru-catalysts, as the solid form of the alkylidene is stable for ruthenium.[14]

The instability of the Mo-catalyst is most likely due to the low electron count (12 electrons) around the metal, which makes it very reactive. The geometry of the complex is also tetrahedral. It should be noted that the Mo-catalysts are extremely sensitive to oxygen and moisture, which makes them difficult to handle.[35] RCM also often needs to have some control over the resulting stereo centers. To control this, Schrock has developed Mo-catalysts that contain chiral alkoxide ligands.[35] The *cis/trans* double bond control is the result of an equilibrium between what is called the anti and syn-rotamers[15,16] of the Mo catalyst (Scheme 2.2). Some examples of different Schrock catalysts are given in Table 2.4.

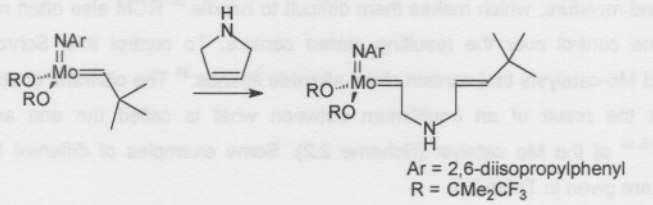


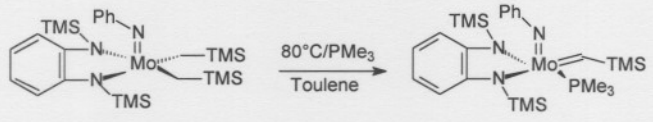
Scheme 2.1 Synthesis and general structure of a typical Schrock carbene catalyst[14]



Scheme 2.2 Equilibrium between syn and anti-rotamers of Schrock's catalyst

Table 2.4 Examples of Schrock carbene catalysts





(b) *Tungsten-based catalysts*

W-based catalysts for alkene metathesis are effective for internal and cyclic alkenes. Studies were done on these catalyst systems in an attempt to elucidate the nature of the active species and its mode of formation.[1] W-based catalysts for the metathesis of terminal alkenes are comparatively few in number. This is partly an illusion because systems such as $WCl_6/EtAlCl_2/EtOH$, although not effective in the sense of yielding ethene and an internal olefin, cause rapid non-productive metathesis in which the products can only be distinguished from the reactants by isotopic labelling.

The stereospecificity, especially for the ROMP of cycloalkenes, can vary widely according to the precise nature of the catalyst system.[1] There is, however, a marked tendency towards retention of *cis* double bonds in certain cases: (i) if the catalyst is $W(=CPh_2)(CO)_5$ or $WF_6/RAlCl_2$; (ii) if the cocatalyst is a metal allyl compound; (iii) if certain additives are present, such as ethyl acrylate,[17] 2-t-butyl-p-cresol[18] and (iv) if the temperature is low. Such effects are associated with increased crowding at the site of reaction and hence greater steric control.

Electrochemical reduction of WCl_6 in methylene chloride under controlled potential at a platinum cathode, with an aluminium anode, gives *in situ* formation of a species that catalyzes alkene metathesis. Good activity and high selectivity is maintained even after several charges of alkene, e.g. 2-pentene, have undergone metathesis.[19,20]

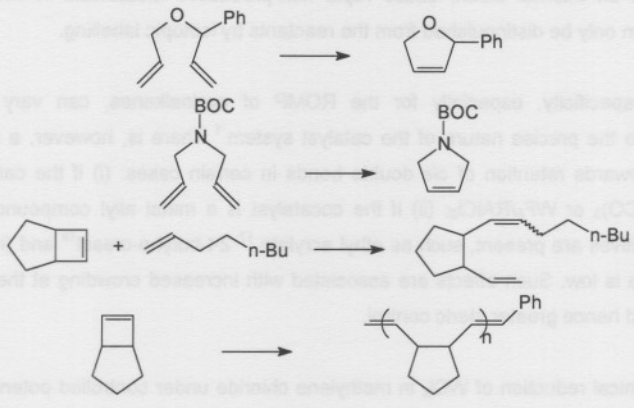
(c) Ruthenium-based catalysts

Ru-based catalysts are excellent metathesis catalysts.[20] Ru-based alkene metathesis catalysts have revolutionized the field of synthetic chemistry by rendering this reaction amenable to a variety of small molecules and polymer applications.[20] The reaction between substrate and catalyst proceeds via the reversible formation of a metalla-cyclobutane intermediate. These catalysts demonstrate many desirable characteristics, including high activity, stability to air and moisture and ease of preparation. The use of Ru in ROMP was first published in 1964 by Natta and co-workers.[21] Natta et al.[21], Michelotti et al.[22] and Lahouste et al.[23] observed that monomers such as cyclobutene, 3-methylcyclobutene, bicyclo[4.2.0]oct-7-ene and norbonene could be polymerized in alcohol as well as aqueous solutions.[21-24] It was obvious that this could be a powerful

reaction since it was compatible with protic solvents.

The Grubbs first generation catalyst [1], was found to be a robust organometallic catalyst that can effect each transformation with high activity and tolerance to functional groups and protic media.[24,25] See Table 2.5 for examples.

Table 2.5 Examples of synthetic organic reactions catalyzed by Grubbs 1 catalysts



A recent advance in the Ruthenium catalysts has been the introduction of N-heterocyclic carbene (NHC) ligands.[26] These ligands are much more basic than the corresponding alkyl phosphine ligands. Grubbs and co-workers[26,27] have published the use of two NHC-ligands on Ruthenium ROMP catalysts. The N-heterocyclic carbene (NHC)-ligated complex[28] is commonly known as the Grubbs second generation catalyst [2].

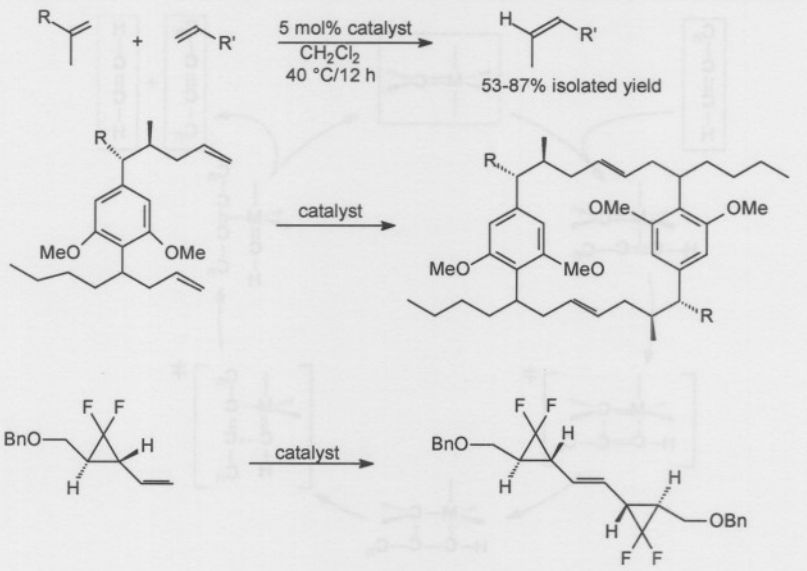
The NHC-ligands are much more basic ligands and thus increase the reactivity of the catalyst by making it easier to push the *trans* PR_3-ligand off the metal (trans effect). The catalysts derived from both the dihydro and unsaturated NHC-ligands have been investigated.[29] The increased reactivity of the Grubbs 2 can do metathesis on tri- and tetrasubstituted double bonds, which used to be done by a Mo-based catalyst. The introduction of the NHC-ligand makes the Ru-catalysts as reactive as the Mo-

catalysts.[29]

Grubbs 2 is a more active analog of the Grubbs 1 catalyst for metathetical transformations[30] and can lead to trisubstituted alkenes via CM,[31] it ring-closes alkenes with excellent functional group tolerance and selectivity. See Table 2.6 for examples.

Alkene isomerization has been reported as a side reaction in RCM reactions with Grubbs 2.[30] The synthetic utility of ruthenium-based catalysts is derived from their ability to orchestrate additional metathetical transformations, including RCM, ROMP, and ADMET.[31] These transformations enable the production of novel compounds and high-performance materials for the pharmaceutical and materials science markets.

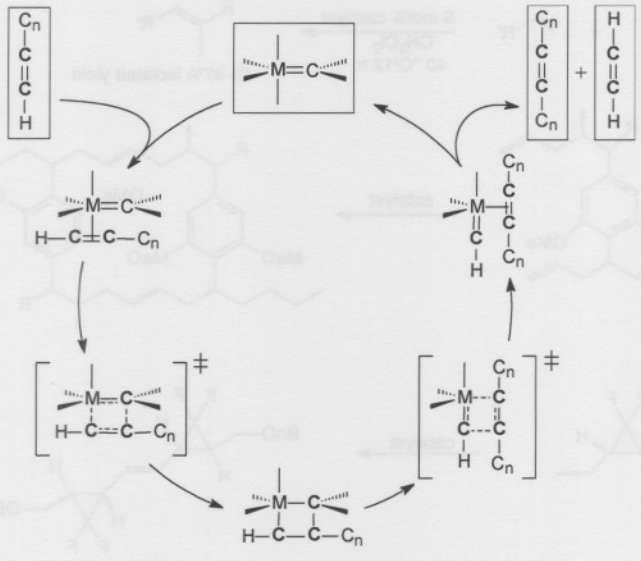
Table 2.6 Examples of synthetic organic reactions catalyzed by Grubbs 2 catalysts



2.3 Mechanism

2.3.1 Introduction

The generally accepted mechanism is the metal carbene mechanism which was proposed by Herisson and Chauvin (Scheme 2.3).[32] The mechanism consists of a series of formal [2+2]-cycloadditions and cycloreversions. Although there is concensus on the general mechanistic features; the detailed course of metathesis reactions depends on the chosen catalyst. According to the mechanism in Scheme 2.3, the propagation reaction involves a transition metal carbene as the catalytic active species with a vacant coordination site at the transition metal. The alkene coordinates at the vacant site, and subsequently a metallacyclobutane intermediate is formed. The metallacyclobutane is unstable and cleaves to form a new metal carbene complex and a new alkene. The cycle then repeats itself.

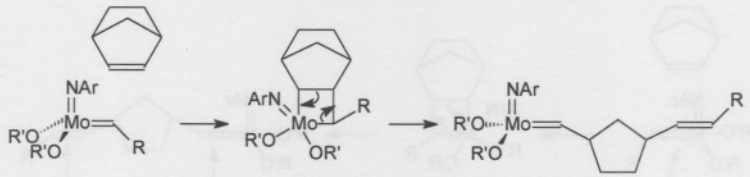


Scheme 2.3 The Herisson–Chauvin metal carbene mechanism for alkene metathesis

Evidence from CM reactions, from the stereochemistry of the metathesis of internal alkenes and from ROMP are all in favour of the metal-carbene mechanism.[1,6] For example, as evidence in favour of the metal carbene mechanism, Kress et al.[36] reported the co-existence of both metallacyclobutanes and metal carbenes under metathesis conditions.

2.3.2 Molybdenum carbene mechanism

The Mo-catalysts have a big advantage over the Ru-based catalysts because they can impart stereochemical control over the formation of *cis* and *trans*-alkenes when used in ROMP and have very high activity, allow synthesis of tri- and tetrasubstituted alkenes. Mo-catalysts catalyses efficient asymmetric RCM reactions.[33] The disadvantage is that they require rigorous exclusion of air and moisture and they have limited functional group tolerance.[33] The mechanism for ROMP using a Schrock catalyst is given in Scheme 2.4.

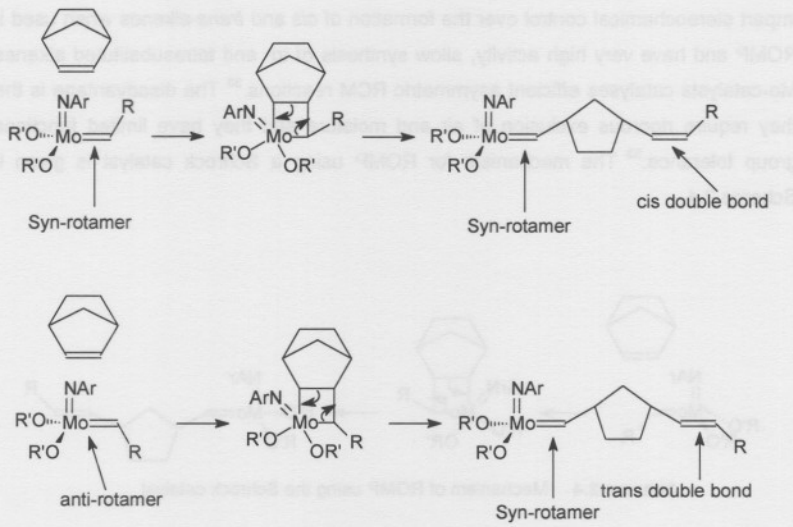


Scheme 2.4 Mechanism of ROMP using the Schrock catalyst

The position of the equilibrium can be adjusted by varying the type of alkoxide ligand. If R' = t-butoxide, the equilibrium favours the anti-rotamer. To access the syn-rotamer, an electron-withdrawing alkoxide ligand, such as hexafluoroisopropoxide, is used. The mechanism for the control of the double bond geometry in the polymer is given in Scheme 2.5.

The interesting part of the mechanism is that the geometry of the double bond is a result of equilibrium between the two rotamers as well as their relative reactivities. In the case of the syn-rotamer, the catalyst reacts with a monomer to give a *cis* double bond and the original syn-rotamer. This will then continue to react with the monomer to give a polymer with *cis*-double bonds in the backbone. When the anti-rotamer reacts with the

monomer it gives the *trans*-double bond, but it forms the syn-rotamer. At this point the next reaction would be predicted to give a *cis*-double bond since the syn-rotamer is now present. However, when R' = t-butoxide, the interconversion between the syn and anti-rotamer is very fast, thus establishing an equilibrium amount of the anti-rotamer. Since the anti-rotamer reacts faster than the syn-rotamer, the polymer formed is very rich in *trans*-double bonds.[33]



Scheme 2.5 Mechanism for *cis* and *trans*-alkene geometry in ROMP

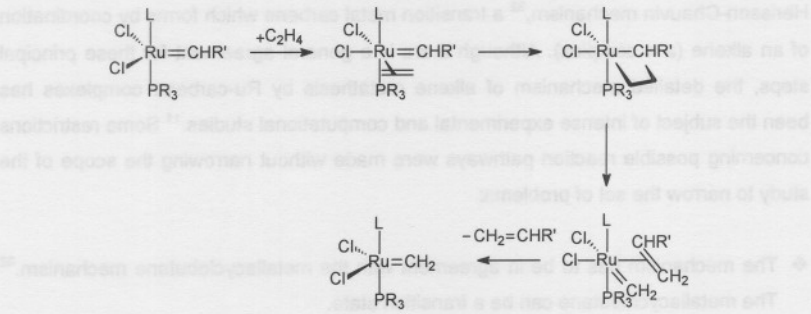
The Mo-catalysts are fairly functional group tolerant. This suggests evidence that the Mo-catalysts can be used in the presence of sulphur, phosphorus and nitriles, but any protic functional group like thiols, alcohol, and carboxylic acids is not compatible.[34] It is rationalized that a mismatch between the hard character of the metal and the soft character of the ligand makes the Mo tolerant to these functional groups.

2.3.3 Ruthenium carbene mechanism

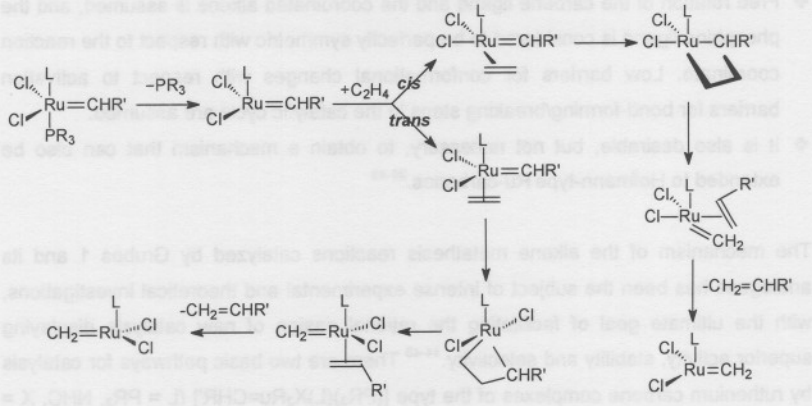
The principal steps of the alkene metathesis mechanism involve, according to the Herisson-Chauvin mechanism,[32] a transition metal carbene which forms by coordination of an alkene (a π complex). Although there is a general agreement for these principal steps, the detailed mechanism of alkene metathesis by Ru-carbene complexes has been the subject of intense experimental and computational studies.[11] Some restrictions concerning possible reaction pathways were made without narrowing the scope of the study to narrow the set of problems:

- The mechanism has to be in agreement with the metallacyclobutane mechanism.[32] The metallacyclobutane can be a transition state.
- The alkene has to be coordinated *cis* to the carbene before formation of the metallacyclobutane. This can be concluded from the fact that RCM works with small- to moderate-sized rings.[37]
- The principle of microscopic reversibility[38] has to be applicable, so the reaction mechanism has to be symmetric for a degenerate reaction.
- Free rotation of the carbene ligand and the coordinated alkene is assumed, and the phosphine ligand is considered to be perfectly symmetric with respect to the reaction coordinate. Low barriers for conformational changes with respect to activation barriers for bond-forming/breaking steps in the catalytic cycle are assumed.
- It is also desirable, but not necessary, to obtain a mechanism that can also be extended to Hofmann-type Ru-carbenes.[39-43]

The mechanism of the alkene metathesis reactions catalyzed by Grubbs 1 and its analogues has been the subject of intense experimental and theoretical investigations, with the ultimate goal of facilitating the rational design of new catalysts displaying superior activity, stability and selectivity.[44-46] There are two basic pathways for catalysis by ruthenium carbene complexes of the type [$(PR_3)(L)X_2Ru{=}CHR'$] (L = PR_3, NHC, X = halide: (i) the associative mechanism (Scheme 2.6), where both phosphine ligands remain on the catalyst, and (ii) the dissociative mechanism (Scheme 2.7), where the phosphine dissociates during catalysis either before or after coordination of the alkene. The dissociative mechanism can be further divided into subgroups, *cis* and *trans*, according to the coordination of the alkene with respect to the phosphine (Scheme 2.7).



Scheme 2.6 Associative mechanism of alkene metathesis with a Grubbs carbene[49]



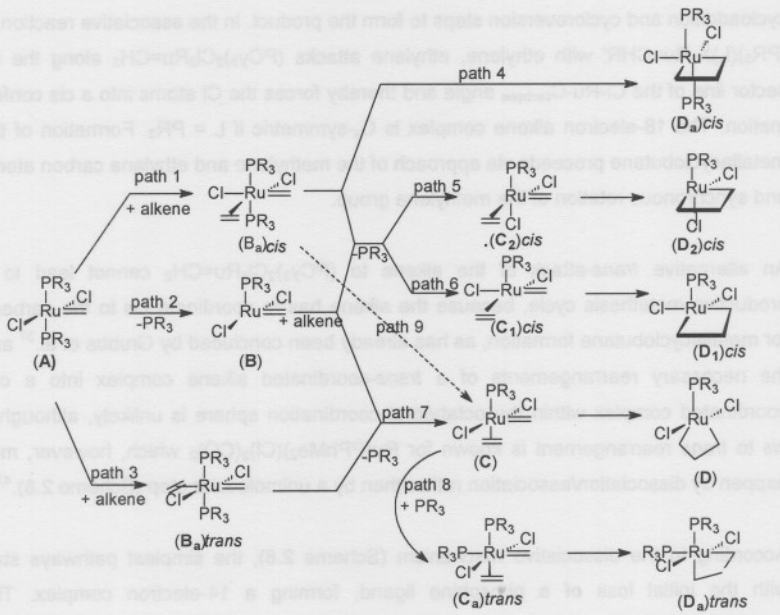
Scheme 2.7 Dissociative mechanism of alkene metathesis with a Grubbs carbene[49]

The associative pathway (Scheme 2.6) assumes that the alkene simply coordinates to the catalyst, forming an 18-electron alkene π complex, followed by the actual [2+2] cycloaddition and cycloreversion steps to form the product. In the associative reaction of $(PR_3)(L)X_2Ru{=}CHR'$ with ethylene, ethylene attacks $(PCy_3)_2Cl_2Ru{=}CH_2$ along the bi-sector line of the Cl-Ru-$C_{carbene}$ angle and thereby forces the Cl atoms into a cis conformation. The 18-electron alkene complex is C_s-symmetric if L = PR_3. Formation of the metallacyclobutane proceeds via approach of the methylene and ethylene carbon atoms and synchronous rotation of the methylene group.

An alternative *trans*-attack of the alkene to $(PCy_3)_2Cl_2Ru{=}CH_2$ cannot lead to a productive metathesis cycle, because the alkene has to coordinate *cis* to the carbene for metallacyclobutane formation, as has already been concluded by Grubbs et al.[37] and the necessary rearrangements of a *trans*-coordinated alkene complex into a *cis*-coordinated complex within the octahedral coordination sphere is unlikely, although a *cis* to *trans* rearrangement is known for $Ru(PPhMe_2)(Cl)_2(CO)_2$ which, however, may happen by dissociation/association rather than by a unimolecular step (Scheme 2.8).[47]

According to the dissociative mechanism (Scheme 2.8), the simplest pathways start with the initial loss of a phosphine ligand, forming a 14-electron complex. The endothermic dissociation of PCy_3 proceeds without any enthalpic barrier beyond that due to ΔH of the reaction itself, although there may be an additional contribution due to entropic effects. The alkene in the five-coordinate Ru-alkene complex may be either in a *cis* or in a *trans*-position with respect to the phosphine. The attack of the alkene on the 14-electron complex may occur either *cis*, along the bisector line of the Cl-Ru-$C_{carbene}$ angle, or *trans* to the phosphine ligand. Upon the *cis* attack, the Cl may be pushed either *trans* to the phosphine ligand or *trans* to the carbene. Metallacyclobutane formation is straightforward.

A variant, where the phosphine again coordinates to the alkene complex, has recently been suggested.[51,52] Configurational fluxionality and isomerization processes at certain intermediate stages such as the isomerization of the *cis*-dichloro-metallacyclobutane into the *trans*-dichloro-isomer have been thoroughly investigated, and the activation barriers found are too high to play a significant role in the overall mechanism.[53]



Scheme 2.8 Postulated dissociative mechanism for alkene metathesis with Grubbs carbenes[52]

2.4 Factors influencing the ruthenium carbene catalyzed metathesis reactions

2.4.1 Ligands

The influence of the ligands on the catalytic activity of 5-coordinate, 16-electron ruthenium complexes has been studied. The use of ligands with different steric and electronic effects optimizes the activity and selectivity of a catalyst,[54] thus ligands form an integral part of the active metathesis catalyst. The effect of the Cl electron-withdrawing group, is counterbalanced by electron phosphines with large cone angles, such as PCy_3.

The catalytic activity of the complex originates from the liberation of one phosphine followed by coordination of the alkene substrate.[37] The nature of the carbene moeity has been shown to influence not only the initiation but also the propagation of the catalytic reaction.[25] Sterically demanding and highly donating phosphine ligand (PCy_3) stabilize the intermediate catalytic species. Despite its versatility, this catalyst displays a low thermal stability as a result of easily accessible bimolecular decomposition pathways.[13]

A recent advance in the Ruthenium catalysts has been the introduction of N-heterocyclic carbene (NHC) ligands [2]. These ligands are much more basic than the corresponding alkyl phosphine ligands. The fact that the NHC ligands are much more basic increases the reactivity of the catalyst. This correlates well with a dissociative mechanism.

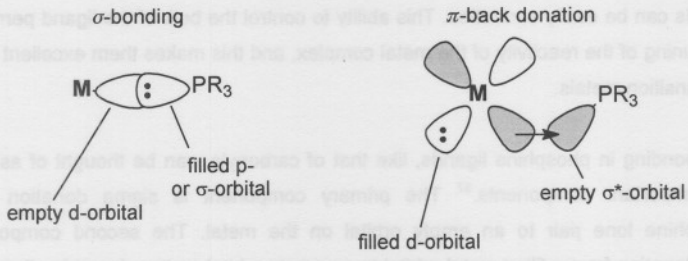
The steric bulk of the ligands may also contribute to phosphine dissociation by destabilizing the crowded bis(phosphine) alkene complex. Phosphines that are more basic or bulkier (Table 2.7) than PCy_3 result in unstable complexes[30] The phosphine ligands can be easily controlled. This ability to control the bulk of the ligand permits the fine-tuning of the reactivity of the metal complex, and this makes them excellent ligands for transition metals.

The bonding in phosphine ligands, like that of carbonyls, can be thought of as having two important components.[57] The primary component is sigma donation of the phosphine lone pair to an empty orbital on the metal. The second component is backdonation from a filled metal orbital to an empty orbital on the phosphine ligand. The empty phosphorus orbital or an antibonding sigma orbital is more appropriate given the relatively high energy of a phosphorous d-orbital (Scheme 2.9).[57]

Changing the phosphine ligand (L) in the $IMesH_2$-coordinated catalysts has a dramatic effect on both catalyst initiation and catalyst activity. For example, replacing the PCy_3 with PPh_3 leads to an increase in k_1 of over 2 orders of magnitude. This effect may be related to the lower basicity of the PPh_3 ligand relative to PCy_3 (the pKa's of the conjugate acids are 2.73 and 9.7 respectively) since a less electron donating phosphine is generally expected to be more labile.[58]

Table 2.7 Cone angles for some common phosphine ligands[56]

Phosphine ligands	Cone angle (°)
PH_3	87
PF_3	104
$P(OMe)_3$	107
PMe_3	118
PMe_2Ph	122
PEt_3	132
PPh_3	145
PCy_3	170
$P(t\text{-}Bu)_3$	182
$P(Mes)_3$	212



Scheme 2.9 The d-orbital and p-orbital of the σ-bonding and π-back donation The empty phosphine ligand can be considered as a d-orbital or as an anti-bonding σ -orbital

2.4.2 Solvents

Solvents generally have a great influence on the metathesis reaction. Benzene and chlorobenzene are the used solvents most often in the metathesis reactions. Toluene and diluted hydrocarbons like pentane and hexane have also been used. There are more examples that can be mentioned, e.g. the ROMP of strained, cyclic alkenes in

aqueous solution initiated by the ruthenium complexes [e.g. $RuCl_3.xH_2O$ or $Ru(H_2O)_6(tos)_2$, tos = p-toluenesulfonate] which is well known.[59] While these "classical" initiators are completely soluble in water, the lack of preformed alkylidene moieties in these pre-catalysts limits their practical usefulness. For example, initiation efficiency is poor and these initiators cannot be used to initiate living ROMP.

Furthermore, complexes such as $RuCl_3.xH_2O$ and $Ru(H_2O)_6(tos)_2$ do not initiate the metathesis of acyclic alkenes, and thus cannot be applied to CM or RCM reactions in protic solvents.[60]

2.4.3 Oxygenates

It has been found out that oxygen influences the alkene metathesis reactions drastically.[62] Oxygen-containing compounds have great influence on the alkene metathesis reactions because most metathesis reactions are poisoned by polar groups.[63-65]

One of the ways that the poisoning of the alkene metathesis can take place is the competing complexation of the alkene metathesis. Some oxygen containing groups can compete with the alkene to complexate the metathesis catalyst:[63]

$$L_nM + RCH{=}CH_2 \rightleftharpoons L_nM(RCH{=}CH_2) \rightleftharpoons \text{METATHESIS}$$

$$L_xM + R{-}X: \rightleftharpoons L_xM(X{-}R)$$

(X = oxygen containing group)

The competition based on the coordination position will delay the rate of the metathesis reaction, but the reaction will not be prevented as a result of its reversibility.

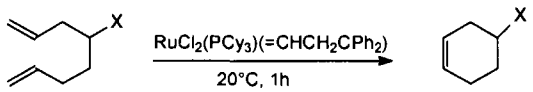
The remarkable functional group tolerance of Grubbs 1 for alkene metathesis, has been widely hailed and extensively utilized in recent times, so much so that RCM and CM readily invaded even carbohydrate and peptide chemistry. [66] The precise nature of activation or deactivation of metathesis by neighbouring oxygen bearing functions (hydroxy or alkoxy groups) are yet to be rationalized in terms of a consistent pattern. It

is usually believed that an allylic alcohol adversely affects metathesis involving the adjacent double bond, presumably by strong coordination with the catalyst, thereby arresting the cycle. There are several reported instances of such difficulty.[67,68] Even when the allylic OH group is protected as an ether, there could be interference by such groups to the detriment of catalytic efficiency. A remotely placed hydroxyl function or a tertiary alcohol usually does not affect the course of the reaction. On the other hand, several recent reports describe not only efficient metathesis despite the presence of an allylic alcohol, some results suggest that this function could even assist the process.[69]

In a water medium, both $RuCl_2(PCy_3)(=CHCH=Ph_2)$- and $RuCl_2(PCy_3)(=CHPh)$-catalysts are active for ROMP of different norbornenes with different functional groups as well as 7-oxanorbornene.[70] The polymers formed in an anhydrous organic solvent have lower molecular masses than those formed in a water medium.

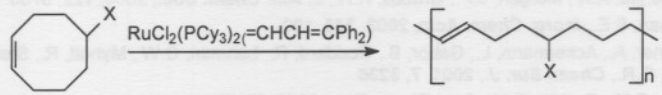
Ruthenium complexes like $RuCl_2(PCy_3)(=CHCH=Ph_2)$ show a high resistance towards acids, aldehydes[71] as well as acetic acid and diethylether solutions of HCl.[72] Protic solvents and coordinative solvents show no influence on the metathesis activity of cis-2-pentene.[72] This catalyst can also be used to metathesize substrates with functional groups, for example allylether, allylalcohol, 3-buteen-1-ol and methyloleate.

Fu et al.[71] have made use of RCM in their studies to prepare oxygen containing heterocyclic products:



X = CO_2H, CH_2OH, CHO

Hilmeyer et al.[73] showed in their studies that the $RuCl_2(PCy_3)_2(=CHCH=Ph_2)$- catalytic system can be used for the ROMP of cyclo-octene with different functional groups:



X = OH, Br, $OCOCH_3$, RCOR'

This catalyst is reactive towards functionalised alkenes which have polar functional groups like alcohols, aldehydes, ketones, esters, and ammonium salts.

2.5 References

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3 EXPERIMENTAL SECTION

3.1 Experimental

3.1.1 Reagents and solvents

The ruthenium complexes, $[Cl_2(PCy_3)_2Ru(=CHPh)]$ and $[Cl_2(PCy_3)(IMes)(Ru=CHPh)]$ (Aldrich), were used as they were obtained. The substrates 1-octene ($C=C_7$), 2-octene ($C_2=C_6$), 3-octene ($C_3=C_5$) (Fluka), and 1-tetradecene (Aldrich), were thoroughly bubbled with nitrogen and thereafter stored under a nitrogen atmosphere. 1-Octene was passed through a column with basic alumina to remove peroxides and thereafter stored under a nitrogen atmosphere. The solvents, chlorobenzene (PhCl), toluene (PhMe), chloroform ($CHCl_3$), cyclohexane ($c\text{-}C_6H_{12}$) and ethanol (EtOH) (Merck), were dried according to standard methods and stored under nitrogen.

3.1.2 Apparatus

All glass apparatus was thoroughly washed and thereafter dried in an oven at 100 °C before use. The metathesis reactions were conducted in glass mini reactors (Supelco) equipped with Mininert® valves (Supelco) under a dry nitrogen atmosphere. A heating block was used to heat the reactors. Calibrated Hamilton 1000 series GASTIGHT® syringes were used to transfer all liquids stored under nitrogen into the reactor. A Hamilton 7000 series GC syringe (1µl) was used to withdraw samples from the reaction mixture and inject the sample into the GC.

3.1.3 Reaction procedure

The metathesis procedures are illustrated in **Figure 3.1**. The mini reactor containing a stirring bar (❶) was first flushed with nitrogen (❷). Thereafter, the catalysts with different molar ratios (100, 1000 and 10000 respectively) were weighed into the mini-reactor (❸). The solvent (1 mL), followed by the octene substrate (2 mL), was transferred with a GASTIGHT® syringe to the reactor (❹ and ❺). The reaction mixture

was stirred continuously at the desired reaction temperature (❻) while monitored by gas chromatography (GC) at regular intervals. A gradual colour change from purple/pink to black was generally observed.

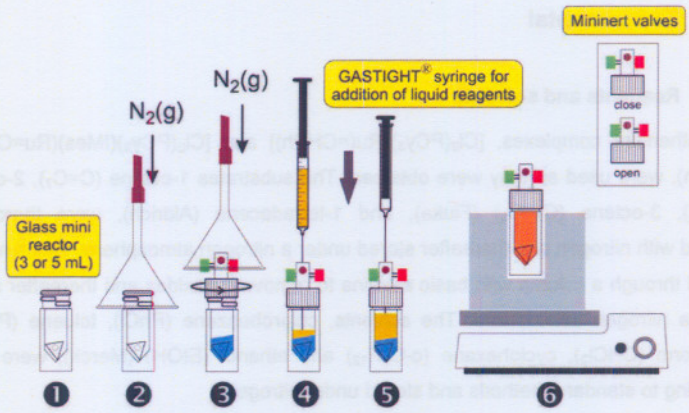


Figure 3.1 Illustration of the catalytic reaction procedure

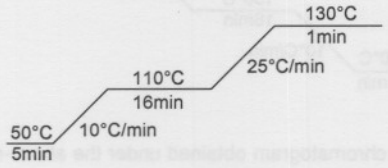
3.2 Analysis

3.2.1 Gas chromatography (GC)

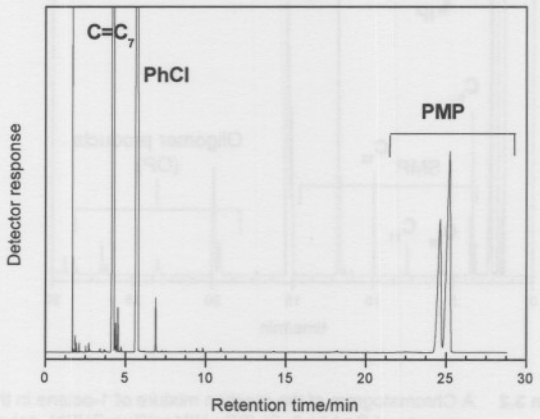
Gas chromatograms were obtained with an Agilent Technologies 6890 GC with a 7683 Series Injector auto sampler. An HP5 5% phenyl methyl siloxane capillary column (30m x 320μm x 0.25μm nominal) was used. The general GC settings were as follows:

Injection temperature	:	280 °C
FID temperature	:	300 °C
Column temperature	:	250 °C
N_2 carrier gas flow	:	2 mL min^{-1} at 20 °C
H_2 gas flow rate	:	25 mL min^{-1} at 20 °C
Air flow rate	:	350 mL min^{-1} at 20 °C
Injection volume	:	0.2 μl
Split ratio	:	45.7:1

Different oven temperature programmes were used to obtain the best separation for each of the reaction mixtures. The oven temperature programme for the Grubbs 1 reaction mixtures was as follows:

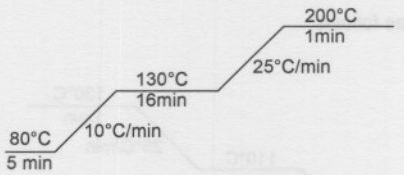


A typical example of the chromatogram obtained under the above-mentioned conditions is illustrated in **Chromatogram 3.1**.

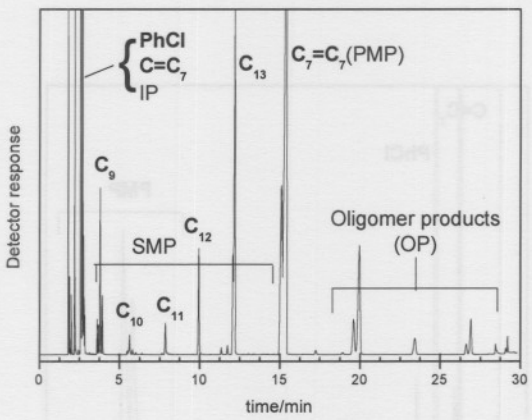


Chromatogram 3.1 Chromatogram of the reaction mixture of 1-octene in the presence of Grubbs 1, $Cl_2(PCy_3)_2Ru(=CHPh)$, solvent = chlorobenzene, 1-octene/Ru = 100, 25 °C

The oven temperature programme for the Grubbs 2 reaction mixtures was as follows:



A typical example of the chromatogram obtained under the above-mentioned conditions is illustrated in **Chromatogram 3.2**



Chromatogram 3.2 A Chromatogram of the reaction mixture of 1-octene in the presence of Grubbs 2, $Cl_2(PCy_3)(IMes)Ru(=CHPh)$, solvent = chlorobenzene, 1-octene/Ru = 100, 25 °C

The internal standard method (with chlorobenzene as internal standard) was used to calculate the mole percentage of the products (IP, SMP and PMP). Mixtures of different mole fractions 1-octene and PhCl was prepared to determine the response factor (f). The variation of the concentration of alkene was done so that the amount of area used in the metathesis reaction was included. The internal standard in the mixture was kept constant throughout. All calculations was performed in Micrsoft Excel.

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

$$f = \frac{V_{Cn} \times A_{PhCl}}{V_{PhCl} \times A_{Cn}}$$

Cn = alkene
V_{Cn} = volume of alkene used
V_{PhCl} = volume of chlorobenzene used
f = response factor
A_{Cn} = area of alkene peak from GC chromatogram
A_{PhCl} = area of chlorobenzene peak from GC chromatogram

The mole percentage alkene was calculated using the following formula:

$$n\%Cn = 100 \times f \times \frac{V_{PhCl}}{V_{Cn}} \times \frac{A_{Cn}}{A_{PhCl}}$$

To use different reaction products through the f-value and the GC-intergration values, the mole percentage of the reaction products was determined with respect to the number of moles of alkene present initially. These values were used to draw the graphs.

The percentage **selectivity** (%S) towards PMP was calculated using the following formula:

$$\%S = \frac{\%PMP}{\%PMP + \%SMP} \times 100$$

Turnover number (TON)

TON is defined as the mole amount of product formed for each mole amount of pre-catalyst. For simplicity and uniformity, the calculation was based on the mole amount of Ru used in each reaction.

mole product = % product from GC analysis / 100 x
initial mass of reaction mixture / molar mass.

mole Ru = mass catalyst / molar mass catalyst

TON = (mole product) / (mole pre-catalyst)

3.2.2 Nuclear magnetic resonance spectrometry (NMR)

^{1}H-NMR spectra (at 300 MHz) of the reactions of 1-octene in the presence of Grubbs 1 and Grubbs 2 were obtained by using a Varian Gemini 300 spectrometer. NMR samples were prepared by dissolving the sample mixture (100 mg) in $CDCl_3$.

Grubbs 1 and Grubbs 2 were weighed into a NMR tube under argon; the solvent, $CDCl_3$, and the substrate, 1-octene, were transferred with a GASTIGHT® syringe into the NMR tube. The reaction mixture was then analysed by NMR.

3.3 References

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4 RESULTS AND DISCUSSION

4.1 Introduction

In this study, the metathesis of 1-octene, in the presence of Grubbs first and second generation catalysts was investigated. Influence of temperature, reaction time, molar ratio and solvent on the catalytic activity of the Grubbs metal carbenes was tested for the metathesis of 1-octene in order to determine the optimum conditions. In each test, the conversion of 1-octene and the composition of the reaction products were determined. Optimum reaction conditions determined for the metathesis of 1-octene were used to study the metathesis of 2-octene, 3-octene and 1-tetradecene.

Possible alkene products that can be formed from a typical metathesis reaction of 1-octene are shown in Table 4.1.

Table 4.1 Possible reactions of 1-octene in the presence of metathesis catalysts[1]

Reaction	Substrate[a]	Products[a]	
Primary metathesis *Homometathesis*[b]	$C{=}C_7$	$C{=}C + C_7{=}C_7$	(PMP)[c]
Isomerisation	$C{=}C_7$	$C_2{=}C_8 + C_3{=}C_5 + C_4{=}C_4$	(IP)[d]
Secondary metathesis *Cross metathesis*[e]	$C{=}C_7 + C_2{=}C_6$	$C_2{=}C_7 + C{=}C_6 + C{=}C_2 + C_6{=}C_7$	(SMP)[f]
Homometathesis[b]	$C_2{=}C_6$	$C_2{=}C_2 + C_6{=}C_6$	(SMP)[f]
Oligomerisation	$C{=}C_7$	C_{16}, C_{24}, etc.	(OP)[g]

a Hydrogens are omitted for simplicity.

b Homometathesis refers to the metathesis reaction between the same alkenes.

c Primary metathesis products (PMP) refers to the homometathesis products of 1-octene i.e. $C_7{=}C_7$ and $C{=}C$.

d Isomerisation is the double bond reaction of terminal alkenes to internal alkenes.

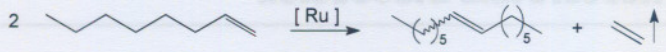
e Cross metathesis refers to the metathesis reaction between different alkenes.

f Secondary metathesis products (SMP) refers to the metathesis products of the isomerisation products of 1-octene.

g Oligomerisation refers to repeated reactions of the substrate with itself.

The primary metathesis reaction is the homometathesis of 1-octene to form ethene and

7-tetradecene, the primary metathesis products (PMP):



Double bond isomerisation to 2-octene can take place with alkene metathesis and thus give rise to the formation of secondary metathesis products (SMP), i.e. from the cross metathesis of 1- and 2-octene, and the homometathesis of 2-octene. One of the SMP's formed is 1-heptene which in turn can undergo primary metathesis, isomerisation and secondary metathesis. This process is repeated with each 1-alkene forming, giving rise to a product range from C_2 to C_{14} alkenes. Oligomerisation reactions, i.e. dimerisation, trimerisation, etc., are also possible.[1] The following reaction schemes illustrate all the possible reactions that can occur:

Primary self-metathesis 1 : $2\ C{=}C_7 \rightleftharpoons C{=}C + C_7{=}C_7$

Isomerisation 1 : $C{=}C_7 \longrightarrow C_2{=}C_6 \longrightarrow C_3{=}C_5 \longrightarrow C_4{=}C_4$

Secondary self-metathesis 1 : $2\ C_2{=}C_6 \rightleftharpoons C_2{=}C_2 + C_6{=}C_6$

$2\ C_3{=}C_5 \rightleftharpoons C_3{=}C_3 + C_5{=}C_5$

Secondary cross-metathesis 1 : $C{=}C_7 + C_2{=}C_6 \rightleftharpoons C{=}C_2 + C{=}C_6 + C_2{=}C_7 + C_6{=}C_7$

$C{=}C_7 + C_3{=}C_5 \rightleftharpoons C{=}C_3 + C{=}C_5 + C_3{=}C_7 + C_5{=}C_7$

$C{=}C_7 + C_4{=}C_4 \rightleftharpoons C{=}C_4 + C_4{=}C_7$

$C_2{=}C_6 + C_3{=}C_5 \rightleftharpoons C_2{=}C_3 + C_2{=}C_5 + C_3{=}C_6 + C_5{=}C_6$

$C_2{=}C_6 + C_4{=}C_4 \rightleftharpoons C_2{=}C_4 + C_4{=}C_6$

$C_3{=}C_5 + C_4{=}C_4 \rightleftharpoons C_3{=}C_4 + C_4{=}C_5$

Dimerisation 1 : $2\ C{=}C_7 \longrightarrow C_{16}$

Primary self-metathesis 2 :

$$\left[\begin{array}{l} 2\ C{=}C_4 \rightleftharpoons C{=}C + C_4{=}C_4 \\ 2\ C{=}C_5 \rightleftharpoons C{=}C + C_5{=}C_5 \end{array}\right]$$

$$2\ C{=}C_6 \rightleftharpoons C{=}C + C_6{=}C_6$$

Isomerisation 2 : $C{=}C_6 \longrightarrow C_2{=}C_5 \longrightarrow C_3{=}C_4$

Secondary cross-metathesis 2:

$$C{=}C_6 + C_2{=}C_5 \rightleftharpoons C{=}C_2 + C{=}C_5 + C_2{=}C_6 + C_5{=}C_6$$

$$C{=}C_6 + C_3{=}C_4 \rightleftharpoons C{=}C_3 + C{=}C_4 + C_3{=}C_6 + C_4{=}C_6$$

$$C_2{=}C_5 + C_3{=}C_4 \rightleftharpoons C_2{=}C_3 + C_2{=}C_4 + C_3{=}C_5 + C_4{=}C_5$$

Secondary self-metathesis 2 :

$$2\ C_2{=}C_5 \rightleftharpoons C_2{=}C_2 + C_5{=}C_5$$

$$2\ C_3{=}C_4 \rightleftharpoons C_3{=}C_3 + C_4{=}C_4$$

Dimerisation 2 : $2\ C{=}C_6 \rightleftharpoons C_{14}$

Primary self-metathesis 3 :

$$\left[2\ C{=}C_4 \rightleftharpoons C{=}C + C_4{=}C_4\right]$$

$$2\ C{=}C_5 \rightleftharpoons C{=}C + C_5{=}C_5$$

Isomerisation 3 : $C{=}C_5 \longrightarrow C_2{=}C_4 \longrightarrow C_3{=}C_3$

Secondary self-metathesis 3 : $2\ C_2{=}C_3 \rightleftharpoons C_2{=}C_2 + C_3{=}C_3$

Secondary cross-metathesis 3 :

$$C{=}C_5 + C_2{=}C_4 \rightleftharpoons C{=}C_2 + C{=}C_4 + C_2{=}C_5 + C_4{=}C_5$$

$$C{=}C_5 + C_3{=}C_3 \rightleftharpoons C{=}C_3 + C_3{=}C_5$$

$$C_2{=}C_4 + C_3{=}C_3 \rightleftharpoons C_2{=}C_3 + C_3{=}C_4$$

Dimerisation 3 : $2\ C{=}C_5 \longrightarrow C_{12}$

Trimerisation 3 : $3\ C{=}C_5 \longrightarrow C_{18}$

Primary self-metathesis 4 : $2\ C{=}C_4 \rightleftharpoons C{=}C + C_4{=}C_4$

Isomerisation 4 : $C{=}C_4 \longrightarrow C_2{=}C_3$

Secondary self-metathesis 4 : $2\ C_2{=}C_3 \rightleftharpoons C_2{=}C_2 + C_3{=}C_3$

Secondary cross-metathesis 4 : $C{=}C_4 + C_2{=}C_3 \rightleftharpoons C{=}C_2 + C{=}C_3 + C_2{=}C_4 + C_3{=}C_4$

Dimerisation 4 : $2\ C{=}C_4 \longrightarrow C_{10}$

Trimerisation 4 : $3\ C{=}C_4 \longrightarrow C_{15}$

Primary self-metathesis 5 : $2\ C{=}C_3 \rightleftharpoons C{=}C + C_3{=}C_3$

Isomerisation 5 : $C{=}C_3 \longrightarrow C_2{=}C_2$

Secondary self-metathesis 5 : —

Secondary cross-metathesis 5 : $C{=}C_3 + C_2{=}C_2 \rightleftharpoons C{=}C_2 + C_2{=}C_3$

Dimerisation 5 : $2\ C{=}C_3 \longrightarrow C_8$

Trimerisation 5 : $3\ C{=}C_3 \longrightarrow C_{12}$

Tetramerisation 5 : $4\ C{=}C_3 \longrightarrow C_{16}$

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

Isomerisation 6 : —

Secondary self-metathesis 6 : —

Secondary cross-metathesis 6 : —

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

Oligomerisation 6 : $3\ C{=}C_2 \longrightarrow C_9$

$4\ C{=}C_2 \longrightarrow C_{12}$

$5\ C{=}C_2 \longrightarrow C_{15}$

$6\ C{=}C_2 \longrightarrow C_{18}$

4.2 Reactions of 1-octene

The reactions of 1-octene in the presence of Grubbs 1 and 2 were investigated at 25 °C. The results are illustrated in Chromatogram 4.1, 4.2 and 4.3, and Figure 4.1 and 4.2.

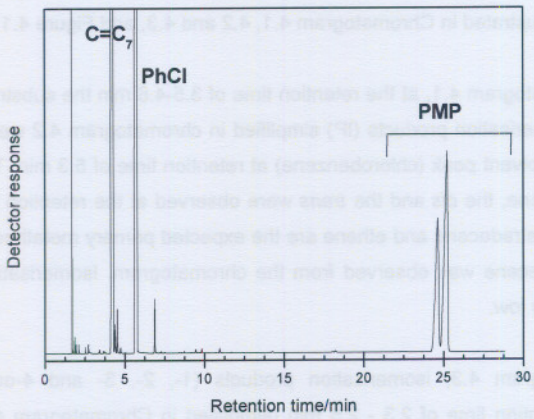
From the Chromatogram 4.1, at the retention time of 3.5-4.8 min the substrate peak (1-octene) and isomerisation products (IP) simplified in chromatogram 4.2 were observed followed by the solvent peak (chlorobenzene) at retention time of 5.3 min. Two isomers of the 7-tetradecene, the *cis* and the *trans* were observed at the retention time of 24.9 min. Although 7-tetradecene and ethene are the expected primary metathesis products, only the 7-tetradecene was observed from the chromatogram. Isomerisation products are gradually very low.

From Chromatogram 4.3, isomerisation products (1-, 2-, 3- and 4-octene) were observed at retention time of 2.3 - 2.5 min (simplified in Chromatogram 4.4). Chloro-benzene peak was observed at retention time of 2.8 min. Secondary metathesis products (C_9, C_{10}, C_{11}, C_{12} and C_{13}) were observed at retention time of 4.0-12.2 min, 7-tetradecene (PMP) was observed at 15 min and oligomerisation products (C_{16}, C_{24}, etc.) were observed from retention times of 18 – 28 min. All the compounds were confirmed by GC/MS and injections of authentic samples.

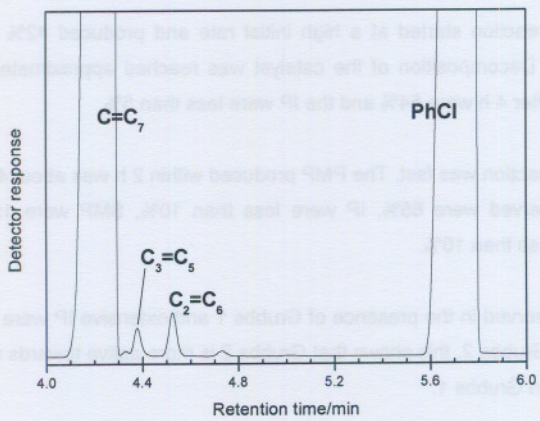
Figure 4.1, the reaction started at a high initial rate and produced 42% of the PMP within an hour. Decomposition of the catalyst was reached approximately after 2 h. PMP observed after 4 h were 54% and the IP were less than 5%.

Figure 4.2, the reaction was fast. The PMP produced within 2 h was about 45 %. After 5 h, the PMP observed were 65%, IP were less than 10%, SMP were 15% and OP observed were less than 10%.

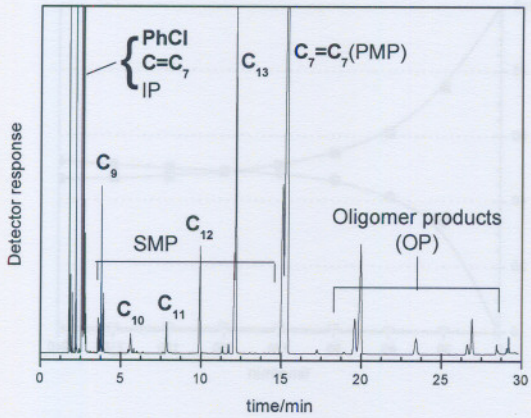
Little IP were observed in the presence of Grubbs 1 and extensive IP were observed in the presence of Grubbs 2, this shows that Grubbs 2 is more active towards double bond isomerisation than Grubbs 1.



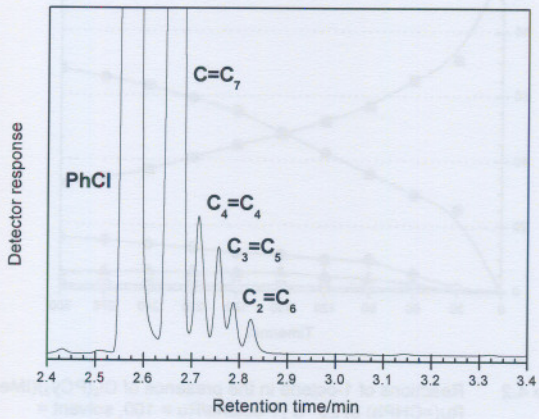
Chromatogram 4.1 Chromatogram of the reaction mixture of 1-octene in the presence of Grubbs 1, $Cl_2(PCy_3)_2Ru(=CHPh)$, solvent = chlorobenzene, 1-octene/Ru = 100, 25 °C



Chromatogram 4.2 Enlarged view of the octene region of Chromatogram 4.1



Chromatogram 4.3 A Chromatogram of the reaction mixture of 1-octene in the presence of Grubbs 2, $Cl_2(PCy_3)(IMes)Ru(=CHPh)$, solvent = chlorobenzene, 1-octene/Ru = 100, 25 °C



Chromatogram 4.4 Enlarged view of the octene region of Chromatogram 4.3

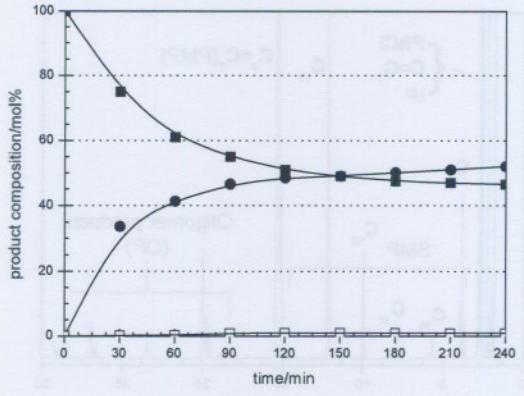


Figure 4.1 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]
(■ 1-octene, ● PMP, □ IP)

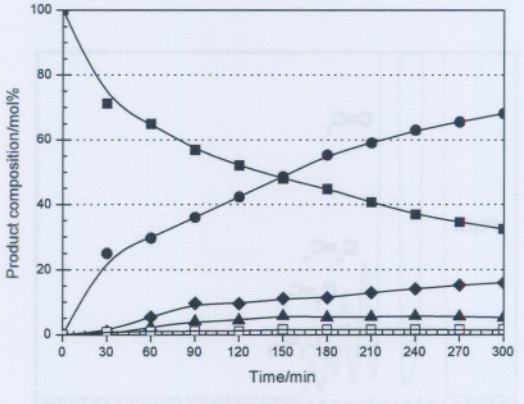


Figure 4.2 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]
(■ 1-octene, ● PMP, ◆ SMP, ▲ $>C_{14}$, □ IP)

4.3 Influence of reaction temperature

4.3.1 Grubbs first generation catalyst (Grubbs 1)

The influence of reaction temperature on the metathesis of 1-octene using Grubbs 1, $Cl_2(PCy_3)_2Ru(=CHPh)$, is illustrated in Figures 4.3 - 4.4 and Table 4.2.

At 50 °C (Figure 4.3), the reaction was fast. Metathesis occured faster than isomerisation even though isomerisation products increased as the temperature was increased to 50°C. The catalyst showed to be active as 35% of the PMP was formed within 2 h. 40% of the PMP and 30% of the IP was formed after 5 h. The activity of the catalyst increased as 60% of the PMP was formed within 1h when the temperature was increased to 100 °C (Figure 4.4). 62% of the PMP and 22% of the IP was formed after 4 h. No SMP was formed with Grubbs 1 catalyst. Table 4.2 summarizes the catalytic activity of Grubbs 1and the selectivity at different temperatures. At 50 °C selectivity drops from 95% to 57% but isomerisation of 1-octene to 2-, 3- and 4-octene increases from 4% to 30%. Selectivity at 100 °C is 74%.

Table 4.2 The influence of reaction temperature on the reactions of 1-octene in the presence of $Cl_2(PCy_3)_2Ru(=CHPh)$ at 4 h (1-octene/Ru = 100, solvent = PhCl)

T/°C	PMP/%	IP/%	%S[a]
25	54	< 10	95
50	40	30	57
100	62	22	74

a. Selectivity towards the PMP's

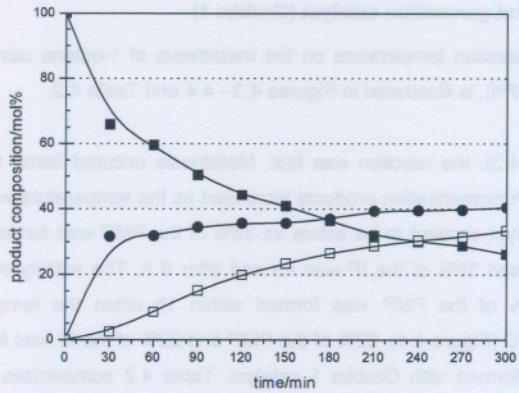


Figure 4.3 Reaction of 1-octene in the presence of $Cl_2(PCy_3)_2Ru(=CHPh)$ at 50 °C [1-octene/Ru = 100, solvent = chlorobenzene]
(■ 1-octene, ● PMP, □ IP)

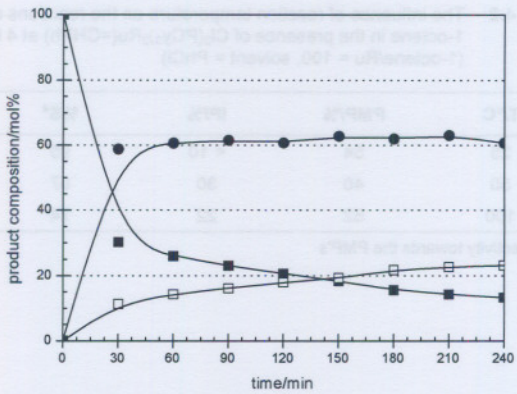


Figure 4.4 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 100 °C [1-octene/Ru = 100, solvent = chlorobenzene]
(■ 1-octene, ● PMP, □ IP)

4.3.2 Grubbs second generation catalyst (Grubbs 2)

Exposure of 1-octene to Grubbs 2 resulted in a complex mixture of products. The influence of reaction temperature on the metathesis of 1-octene with Grubbs 2 is illustrated in Figures 4.5 - 4.6 and Table 4.3.

At a temperature of 50 °C (Figure 4.5), the catalyst was active. The PMP formed after 2 h was 35%. After 5 h, 47% of the PMP, 18% SMP, 10% IP and 4% OP was formed. Increasing the temperature to 100 °C (figure 4.6) produced an increase in the SMP than the PMP, only 7% of the PMP was formed after 5 h. 47% SMP, 8% IP and 5% OP was also formed after 5 h.

Table 4.3 summarizes the products observed in the presence of Grubbs 2 and the selectivity at different temperatures selected. The selectivity decreased as the temperature was increased to 100 °C.The SMP increased from 15% to 47% at 100 °C.

Table 4.3 The influence of reaction temperature on the reactions of 1-octene in the presence of Grubbs 2 after 4 h, (1-octene/Ru = 100, solvent = PhCl)

T/°C	PMP/%	IP/%	SMP/%	OP/%	%S[a]
25	65	< 10	15	< 10	81
50	47	10	18	< 10	72
100	< 10	10	47	< 10	18

a. Selectivity towards PMP

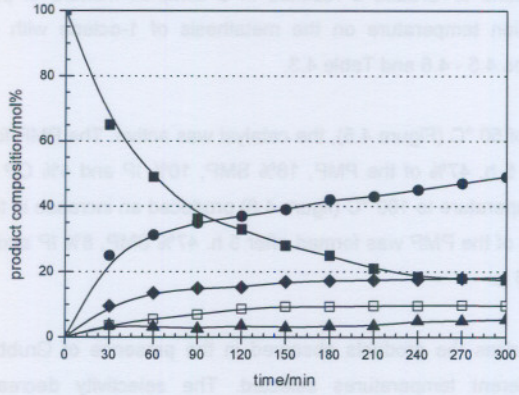


Figure 4.5 Reaction of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 50 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■1-octene, ●PMP, ◆SMP, ▲ OP, □ IP)

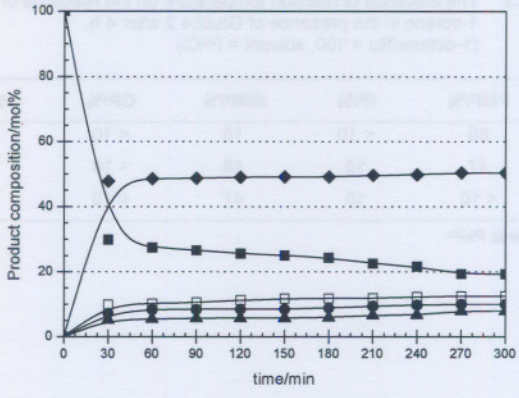


Figure 4.6 Reaction of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 100 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■1-octene, ●PMP, ◆SMP, ▲ OP, □ IP)

4.4 Influence of molar ratio

4.4.1 Grubbs 1 and Grubbs 2

The influence of the alkene/Ru molar ratio on the metathesis of 1-octene using Grubbs 1 is illustrated in Figure 4.7 – 4.9 and using Grubbs 2 in in Figure 4.10 – 4.12.

Table 4.4 summarizes the dependence of activity of Grubbs 1 and 2 catalysts on the alkene/Ru molar ratio. The reactions were run at 25 °C because at room temperature more metathesis is observed. The PMP for the metathesis activity of both Grubbs 1 and Grubbs 2 were observed at time = 4 h. It is apparent that the catalytic systems are more active for metathesis at the alkene/Ru molar ratio of 100. As the alkene/Ru molar ratio increases, the metathesis decreases and selectivity decreases.

Table 4.4 The influence of the 1-octene/Ru molar ratio on the reactions of 1-octene in the presence of Grubbs 1 and 2 after 4 h, (temperature = 25 °C, solvent = PhCl)

Ru/1-octene molar ratio				
	PMP/%	%S[a]	PMP/%	%S[a]
100	54	84	62	81
1000	22	81	38	72
10000	< 10	50	< 10	67

a. Selectivity towards PMP

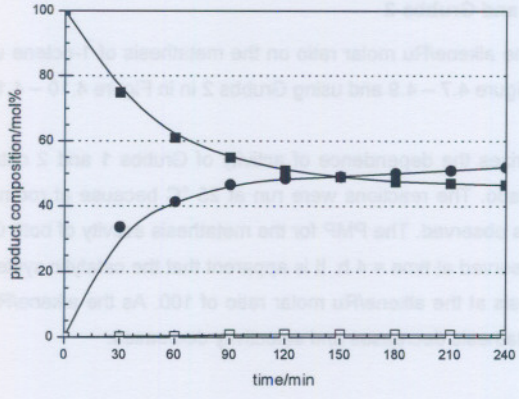


Figure 4.7 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■1-octene, ●PMP, □ IP)

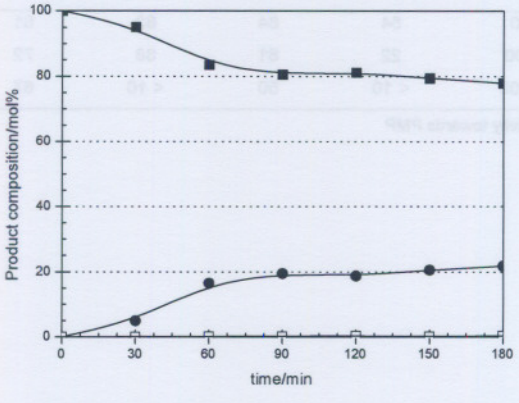


Figure 4.8 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 1000, solvent = chlorobenzene]

(■1-octene, ●PMP, □ IP)

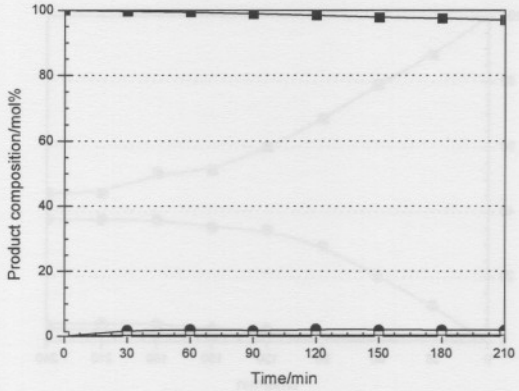


Figure 4.9 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 10 000, solvent = chlorobenzene]

(■1-octene, ●PMP, □ IP)

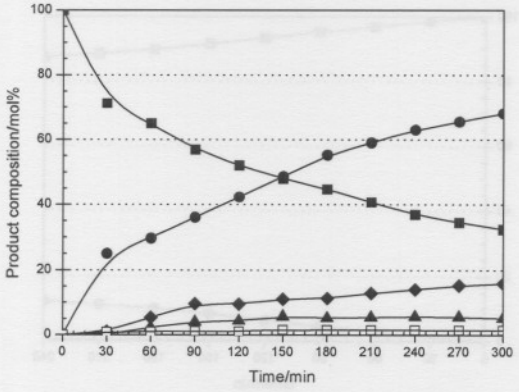


Figure 4.10 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■1-octene, ●PMP, ◆SMP, ▲ OP, □ IP)

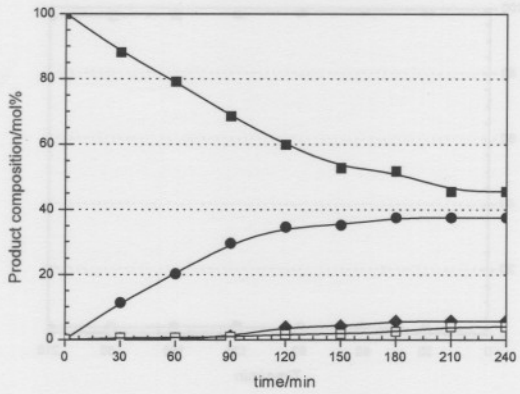


Figure 4.11 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 1000, solvent = chlorobenzene]

(■ 1-octene, ● PMP, ◆ SMP, □ IP)

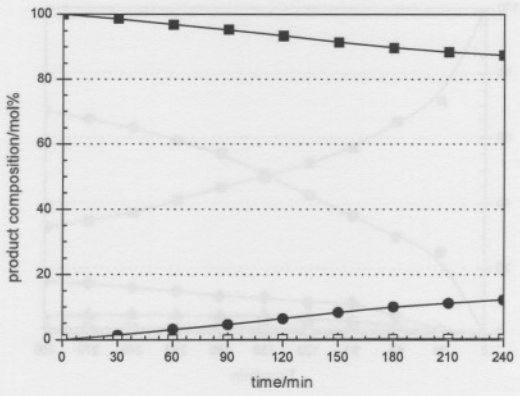


Figure 4.12 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 10 000, solvent = chlorobenzene]

(■ 1-octene, ● PMP, □ IP)

4.4.2 Turnover numbers (TON)

Effective turnover numbers (TON) have been obtained for the metathesis of various substrates in the presence of ruthenium-based catalysts.[3] Dinger and Mol[3] found that the TON of 1-octene could not be calculated with any degree of certainty because the metathesis events could not be followed. Moreover, because the active metathesis catalyst is the phosphine dissociated species, whose concentration at any given time cannot be accurately determined, the actual number of substrate molecules that have undergone metathesis by a particular ruthenium center also cannot be determined. So the best way was to use the effective TON, which the total number of 1-octene molecules converted to metathesis products per molecule of the catalyst precursor.

The TON's of the metathesis experiments at different molar ratios of 100 to 10000 were calculated for the Grubbs 1 and 2 catalysts (Figure 4.13 and 4.14). Grubbs 2 catalyst generally perfomed better than Grubbs 1 displaying higher TON's after 4 h; faster initiation rates should give rise to higher TON's. At a molar ratio of 10000 the TON's were comparable.

TON's have been calculated for the metathesis of 1-octene at the different molar ratios. Both Grubbs 1 and 2 gave TON's averaging from approximately 50 to below 1000 at the different molar ratios (100 to 10 000) investigated while maintaining a high degree of selectivity for the formation of the PMP product, 7-tetradecene. Generally Grubbs 2 performed better than Grubbs 1 displaying higher TON's. When measuring the rate profiles of the reactions, the values at any given time represent a TON averaged over all of the ruthenium species present in the solution.

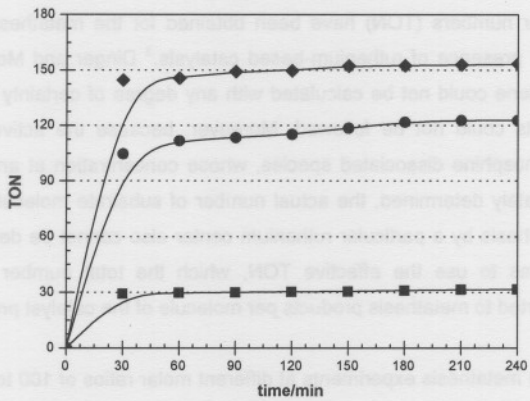


Figure 4.13 The influence of molar ratio on the turnover number of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [solvent = chlorobenzene]

(■ 100 ● 1000 ◆ 10 000)

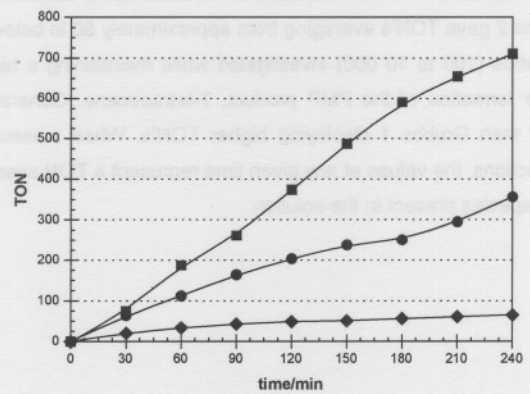


Figure 4.14 The influence of molar ratio on the turnover number of 1-octene in the presence of $Cl_2(PCy_3)$(IMes) Ru(=CHPh) at 25 °C [solvent = chlorobenzene]

(■ 100, ● 1000, ◆ 10 000)

4.5 Influence of solvents

4.5.1 Grubbs 1

In order to find the most suitable conditions for the metathesis reactions with ruthenium catalysts, I examined the effect of some solvents. The solvents that were used for investigation were chlorobenzene, ethanol, toluene, cyclohexane and chloroform. These solvents were tested with consideration of their polarity (Table 4.5).

The influence of solvents on the reactions of 1-octene in the presence of Grubbs 1 is illustrated in Figures 4.15 - 4.18 and Table 4.5.

Large differences in activities of the catalysts were found in selected solvents. From all the solvents used, the best perfomance was observed in chlorobenzene, chloroform and cyclohexane. These solvents produced the highest product composition, from 55% - 68%. Low IP yields were observed, less than 5% for all three of them. Toluene produced 42% of the PMP and less than 5% IP were observed. Bad perfomance was observed in ethanol, only 25% of the PMP was formed after 3h.IP formed was less than 10% after 3h.

Table 4.5 displays the catalytic activity of Grubbs 1 with the 1-octene reactions in different solvents observed after time = 120 min. Selectivity ranges from 83%-99%. Best perfomance was observed in chloroform and bad perfomance was found in ethanol. Ethanol produced the lowest % yield of the PMP.

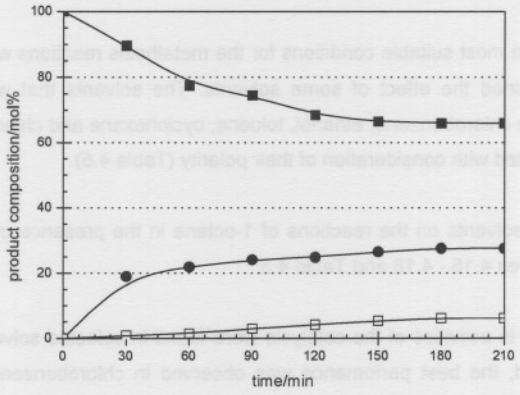


Figure 4.15 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = ethanol]
(■ 1-octene, ● PMP, □ IP)

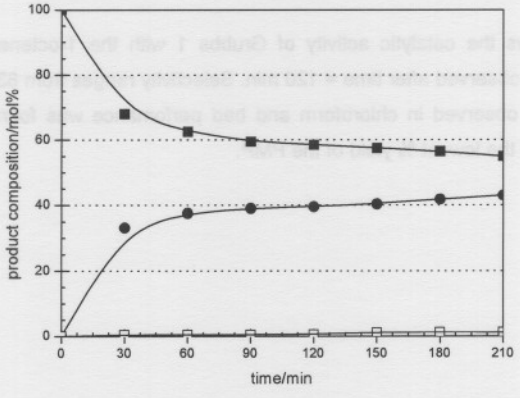


Figure 4.16 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = toluene]
(■ 1-octene, ● PMP, □ IP)

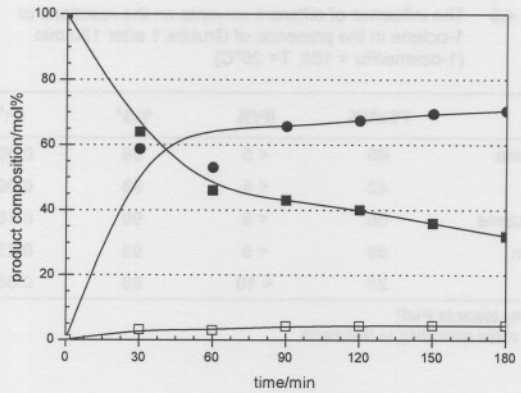


Figure 4.17 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chloroform]

(■ 1-octene, ● PMP, □ IP)

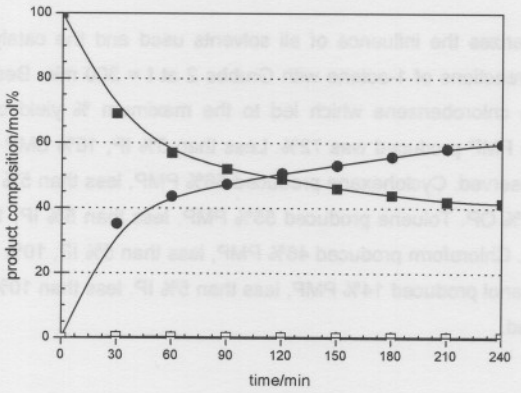


Figure 4.18 Reactions of 1-octene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = cyclohexane]

(■ 1-octene, ● PMP, □ IP)

Table 4.5 The influence of different solvents on the reactions of 1-octene in the presence of Grubbs 1 after 120 min (1-octene/Ru = 100, T= 25°C)

Solvents	PMP/%	IP/%	%S[a]	E_T[b]
cyclohexane	60	< 5	99	0.006
toluene	42	< 5	98	0.099
chlorobenzene	55	< 5	99	0.188
chloroform	68	< 5	93	0.259
ethanol	25	< 10	83	0.654

a. Selectivity towards PMP
b. Polarity scale according to Reichardt

4.5.2 Grubbs 2

The influence of solvents on the reactions of 1-octene in the presence of Grubbs 2 is illustrated in Figures 4.19- 4.22 and Table 4.6.`

Table 4.6 summarizes the influence of all solvents used and the catalytic selectivity obtained for the reactions of 1-octene with Grubbs 2 at t = 300 min. Best perfomance was observed in chlorobenzene which led to the maximum % yield of the product composition. The PMP produced was 72%. Less than 5% IP, 16% SMP and less than 10% OP were observed. Cyclohexane produced 56% PMP, less than 5% IP, 20% SMP and less than 10% OP. Toluene produced 55% PMP, less than 5% IP, 10% SMP and less than 5% OP. Chloroform produced 46% PMP, less than 5% IP, 10% SMP and less than 5% OP. Ethanol produced 14% PMP, less than 5% IP, less than 10% SMP and no OP were observed.

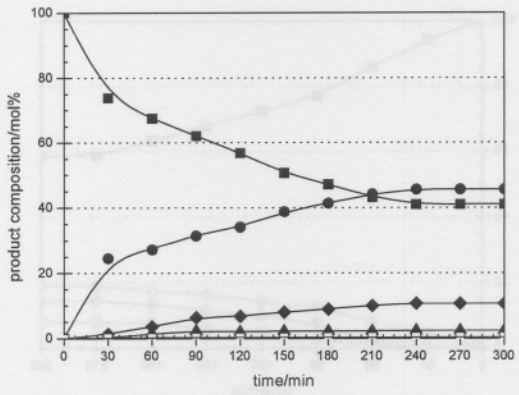


Figure 4.19 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = chloroform]

(■ 1-octene, ● PMP, ◆ SMP, ▲ OP, □ IP)

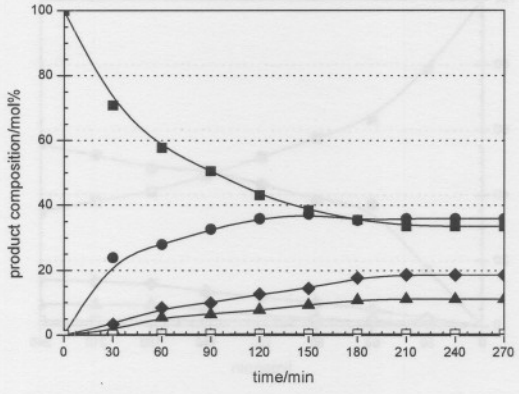


Figure 4.20 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = cyclohexane]

(■ 1-octene, ● PMP, ◆ SMP, ▲ OP, □ IP)

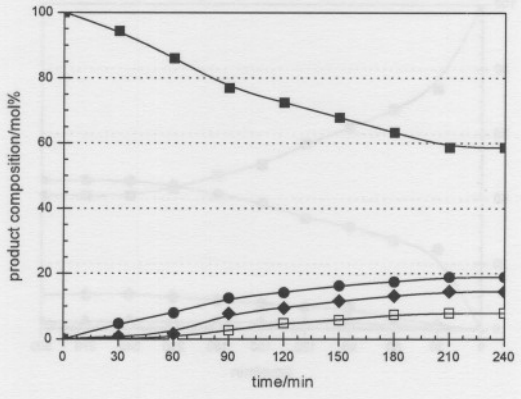


Figure 4.21 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = ethanol]
(■ 1-octene, ● PMP, ◆ SMP, □ IP)

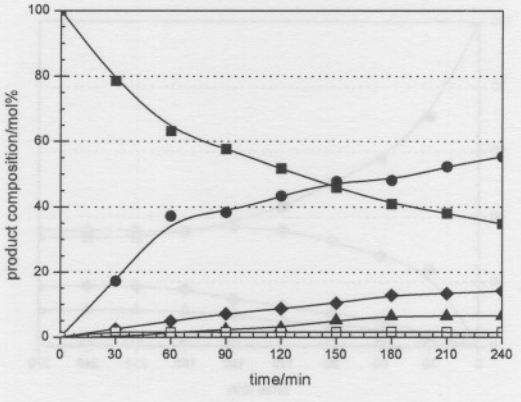


Figure 4.22 Reactions of 1-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = toluene]
(■ 1-octene, ● PMP, ◆ SMP, ▲ OP, □ IP)

Table 4.6 The influence of different solvents on the reactions of 1-octene in the presence of Grubbs 2 after 300 min (1-octene/Ru = 100, T= 25°C)

Solvents	PMP/%	IP/%	SMP/%	OP/%	%S[a]	E_T[b]
cyclohexane	56	< 5	20	<10	62	0.006
toluene	55	< 5	15	< 5	76	0.099
chlorobenzene	72	< 5	16	< 10	70	0.188
chloroform	46	< 5	10	< 5	80	0.259
ethanol	20	< 5	15	0	61	0.654

a. Selectivity towards PMP
b. polarity scale according to Reichardt

4.6 Reactions of 2- and 3-octene

The catalytic activity of Grubbs 1and 2 catalysts in the metathesis of different alkene substrates has been tested using 2- and 3-octene linear isomers of 1-octene.
The results obtained to ascertain the metathesis activity of Grubbs 1 catalyst is illustrated in Figure 4.23 and Figure 4.24 respectively.

For the reaction of 2-octene (Figure 4.23), the catalyst afforded a mixture of the metathesis and isomerisation products. 6-Dodecene was formed as the PMP. After 3h 70% of the PMP and 16% IP were formed. SMP formed was less than 5%.
For the reaction of 3-octene (Figure 4.24), the catalyst afforded only the metathesis products. 1-Decene formed as the PMP. 10% of the PMP was formed after 4h. No SMP or IP observed.

The results obtained to ascertain the metathesis activity of Grubbs 2 catalyst is illustrated in Figure 4.25 and Figure 4.26 respectively.

For the reaction of 2-octene (Figure 4.25), the catalyst afforded a mixture of the metathesis and isomerisation products. Metathesis occurs faster than isomerisation. 43% of the PMP, 15% SMP (C_9 and C_{11}), 11% IP and < 10% products greater than C_{12} (C_{13} and C_{15}) were formed after 4h.

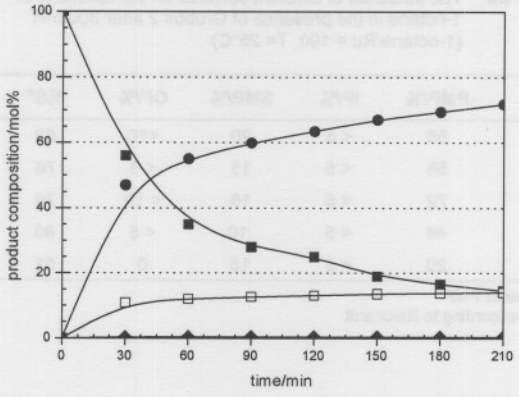


Figure 4.23 Reactions of 2-octene in the presence of $Cl_2(PCy_3)_2Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 2-octene, ● PMP, ◆ SMP, □ $C=C_7 + C_3=C_3$)

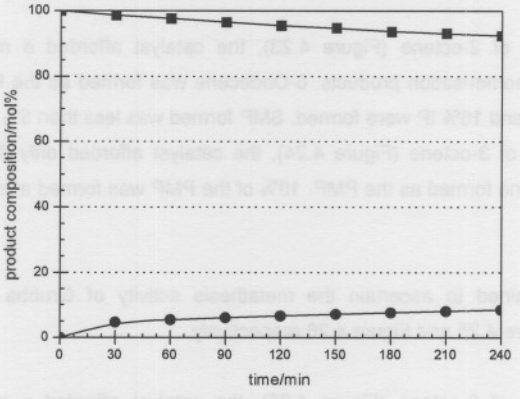


Figure 4.24 Reactions of 3-octene in the presence of $Cl_2(PCy_3)_2Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 3-octene, ● PMP)

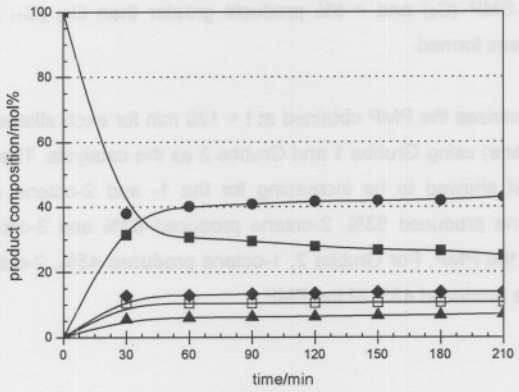


Figure 4.25 Reactions of 2-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 2-octene, ● PMP, ◆ SMP, ▲ > C_{12}, □ IP)

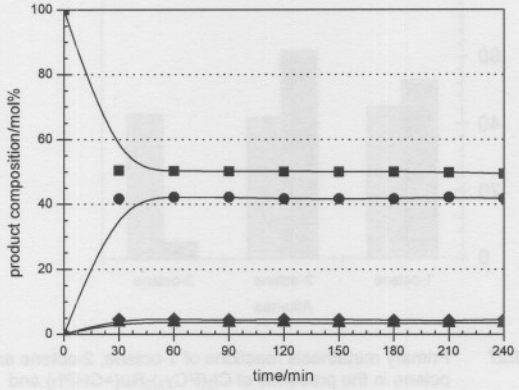


Figure 4.26 Reactions of 3-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ at 25°C, [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 3-octene, ● PMP, ◆ SMP, ▲ > C_{10})

For the reaction of 3-octene (Figure 4.26), the catalyst afforded only the metathesis products. Decomposition of the catalyst was observed. 45% of the PMP was formed after 4h. < 10% SMP (C_9) and < 5% products greater than C_{10} (C_{11} and C_{13}) was observed. No IP was formed.

Figure 4.27 summarizes the PMP obtained at t = 120 min for each alkene (1-octene, 2-octene and 3-octene) using Grubbs 1 and Grubbs 2 as the catalysts. The activity of the Grubbs 1 catalyst showed to be increasing for the 1- and 2-octene reactions. For Grubbs 1, 1-octene produced 53%, 2-octene produced 62% and 3-octene produced less than 10% of the PMP. For Grubbs 2, 1-octene produced 45%, 2-octene produced 42% and 3-octene produced 43% of the PMP.

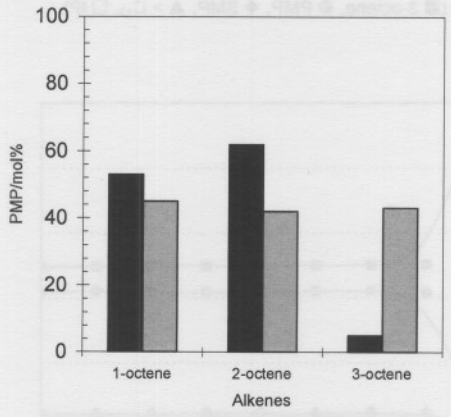


Figure 4.27 Primary metathesis reactions of 1-octene, 2-octene and 3-octene in the presence of $Cl_2(PCy_3)_2Ru(=CHPh)$ and $Cl_2(PCy_3)(IMes)$ Ru(=CHPh) at t = 120 min [T = 25 °C, alkene/Ru = 100, solvent = chlorobenzene]
[■ Grubbs 1, ■ Grubbs 2]

4.7 Reactions of a mixture of 1- and 2-octene

The influence of the reaction mixture of 1- and 2-octene in the presence of Grubbs 1 and 2 is illustrated in Figures 4.28 and 4.29. The reaction of 1- and 2-octene in the presence of Grubbs 1 and 2 was done with an equimolar mixture i.e 50:50 ratio. The reaction appears to be a fast reaction as the equilibrium was reached within 30 min.

Grubbs 1 and 2 catalysed the homometathesis of 1-octene and 2-octene. 6-dodecene and 7- tetradecene were produced as the PMP and C_9, C_{11} and C_{13} as the CM products from the reaction mixture. For Grubbs 1 the yield for the C_{12} and C_{14} obtained was 20% after 4 h, C_9 and C_{13} formed was 15%and less than 10% for C_9. For Grubbs 2 the % yield for the C_{12} and C_{14} was less than 20% and the C_9, C_{11} and C_{13} is less than 10%. When 1-octene undergoes metathesis ethene, and 1-tetradecene is expected but from the gas chromatograph only 7-tetradecene appeared. From isomerisation of 1-octene to 2-octene, C_2=C_2 and C_{12} was expected but only C_{12} was observed. Cross metathesis of 1- and 2-octene should produce C=C_2, C=C_6, C_2=C_7 and C_6=C_7 but only C_2=C_7, C_5=C_6 and C_6=C_7 were observed.

4.8 Reactions of 1-tetradecene

The reactions of 1-tetradecene in the presence of Grubbs 1 and 2 are illustrated in Figure 4.30 and 4.31 respectively.

Both the catalysts showed to be active for the reaction of 1-tetradecene. The reactions for 1-tetradecene in the presence of Grubbs 1 are very slow. The conversion of 1-tetradecene within 30 min was 15% and the PMP (C_{26}) observed was 12% within the first 30 min. 1-tetradecene isomer was less than 5% within that 30 min. After 3 h the PMP formed was 20% and 1-tetradecene isomer was 15%. Exposure of 1-tetradecene to Grubbs 2 resulted in a complex mixture of products. The reaction commenced at a very fast rate. Within 30 min the conversion of 1-tetradecene was 45% and the PMP observed were 30%, 1-tetradecene isomer were 15% and the SMP were about 10%. After 3 h, the PMP observed were 38%, 1-tetradecene isomer formed was 20% and the SMP formed was 15%.

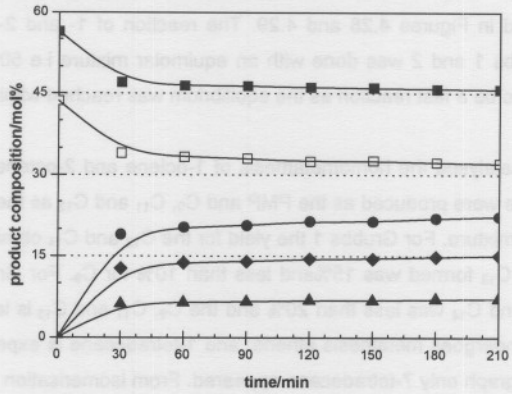


Figure 4.28 Reactions of an equimolar mixture of 1- and 2-octene in the presence of $Cl_2(PCy_3)Ru(=CHPh)$ at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 1-octene, □ 2-octene, ● $C_{12} + C_{14}$, ◆ $C_9 + C_{13}$, ▲ C_9)

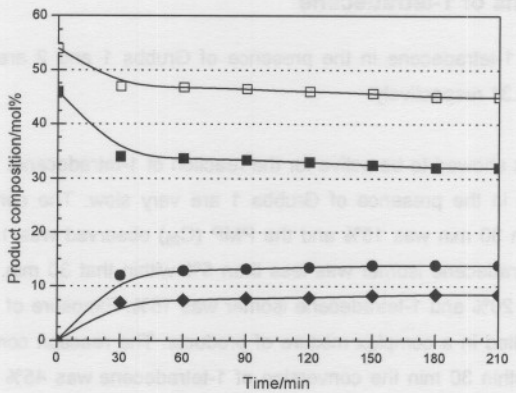


Figure 4.29 Reactions of an equimolar mixture of 1- and 2-octene in the presence of $Cl_2(PCy_3)(IMes)Ru(=CHPh)$at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ 1-octene, □ 2-octene, ● $C_{12} + C_{14}$, ◆ $C_9 + C_{11} + C_{13}$)

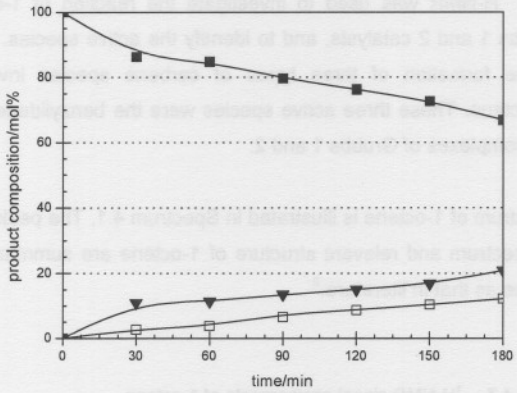


Figure 4.30 Reactions of 1-tetradecene in the presence of $Cl_2(PCy_3)_2$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ $C{=}C_{13}$, □ $C{=}C_{13}$ isomer, ▼ PMP (C_{26})

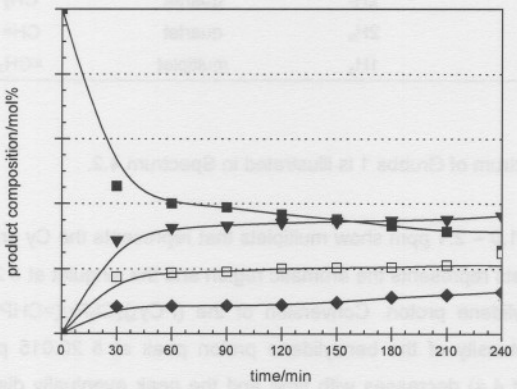


Figure 4.31 Reactions of 1-tetradecene in the presence of $Cl_2(PCy_3)(IMes)$ Ru(=CHPh) at 25 °C [1-octene/Ru = 100, solvent = chlorobenzene]

(■ $C{=}C_{13}$, □ $C{=}C_{13}$ isomer, ▼ PMP (C_{26}), ◆ SMP)

4.9 NMR studies of the ruthenium complexes

In this study, the ^{1}H-NMR was used to investigate the reaction of 1-octene in the presence of Grubbs 1 and 2 catalysts, and to identify the active species. The ^{1}H-NMR study showed the formation of three types of carbene species involved in the metathesis of 1-octene. These three active species were the benzylidene, heptylidene and methylidene complexes of Grubbs 1 and 2.

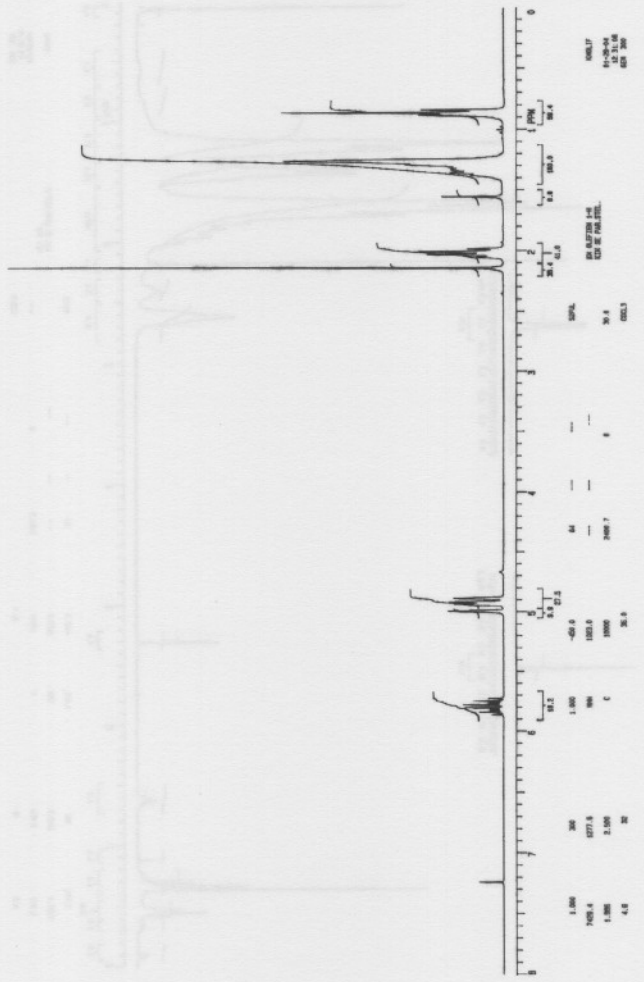
The ^{1}H-NMR spectrum of 1-octene is illustrated in Spectrum 4.1. The peak assignments of the ^{1}H-NMR spectrum and relevant structure of 1-octene are summarised in Table 4.7 and is the same as that in literature.[2]

Table 4.7 ^{1}H-NMR signal assignments of 1-octene

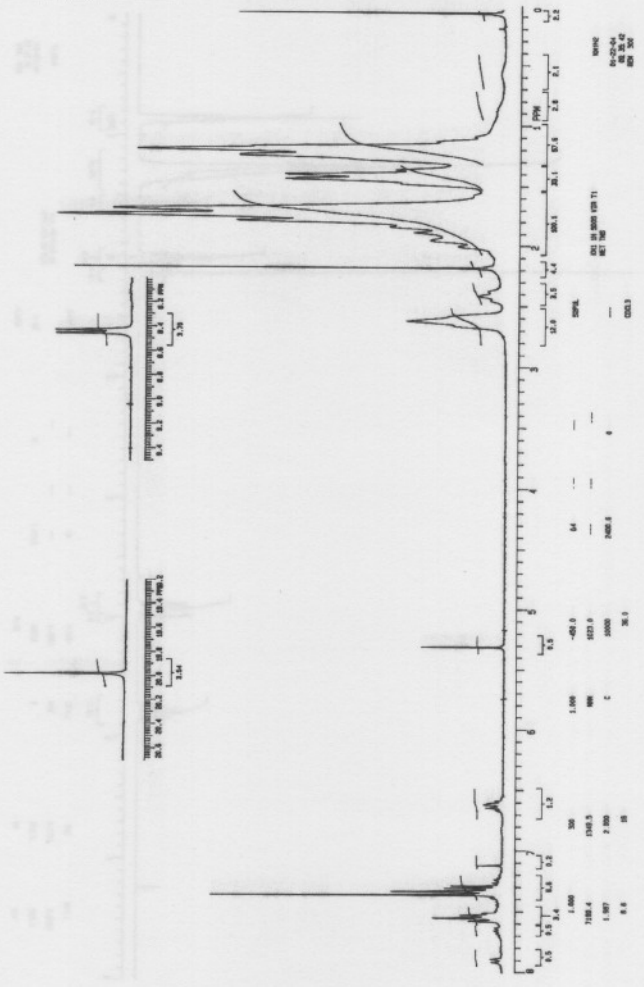
$CH_3{}^aCH_2{}^bCH_2{}^cCH_2{}^cCH_2{}^dCH_2{}^eCH_2{}^fCH^g{=}CH_2{}^h$			
δ(ppm)	**Intergration**	**Split pattern**	**Assignment**
0.90	$3H_a$	triplet	CH_3
1.35	$8H_{b\text{-}e}$	singlet	4 x CH_2
2.15	$2H_f$	quartet	CH_2
4.95	$2H_h$	quartet	CH=
5.85	$1H_g$	multiplet	$=CH_2$

The ^{1}H-NMR spectrum of Grubbs 1 is illustrated in Spectrum 4.2.

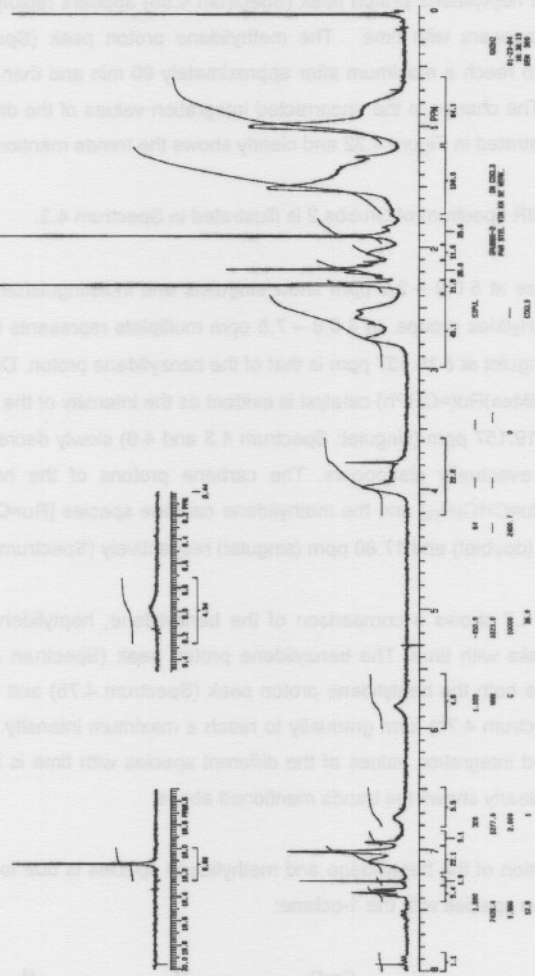
Resonances at δ 1.0 – 2.1 ppm show multiplets that represents the Cy groups, at δ 6.5 – 7.9 ppm multiplets represents the aromatic region and the singulet at δ 20.015 ppm is that of the benzylidene proton. Conversion of the $(PCy_3)_2Cl_2Ru(=CHPh)$ catalyst is evident as the intensity of the benzylidene proton peak at δ 20.015 ppm (singulet; Spectrum 4.2 and 4.4) decreases with time and the peak eventually disappears. The carbene protons of the heptylidene carbene species [$Ru{=}CHC_6H_{13}$] and the methylidene carbene species [$Ru{=}CH_2$] were observed at δ 19.310 (triplet) and 18.954 (singulet) ppm respectively (Spectrum 4.4).



Spectrum 4.1 ^{1}H-NMR spectra of 1-octene in $CDCl_3$



Spectrum 4.2 ^{1}H-NMR spectra of Grubbs 1 in $CDCl_3$



Spectrum 4.3 ^{1}H-NMR spectra of Grubbs 2 in $CDCl_3$

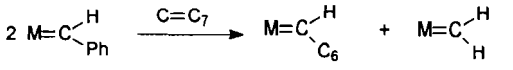
Spectrum 4.5 shows a comparison of the benzylidene, heptylidene and methylidene proton peaks with time. The benzylidene proton peak (Spectrum 4.5a) slowly disappears. The heptylidene proton peak (Spectrum 4.5b) appears rapidly within 14 min and slowly disappears with time. The methylidene proton peak (Spectrum 4.5c) forms gradually to reach a maximum after approximately 90 min and then slowly decrease in intensity. The change in the uncorrected integration values of the different species with time is illustrated in Figure 4.32 and clearly shows the trends mentioned above.

The ^{1}H-NMR spectrum of Grubbs 2 is illustrated in Spectrum 4.3.

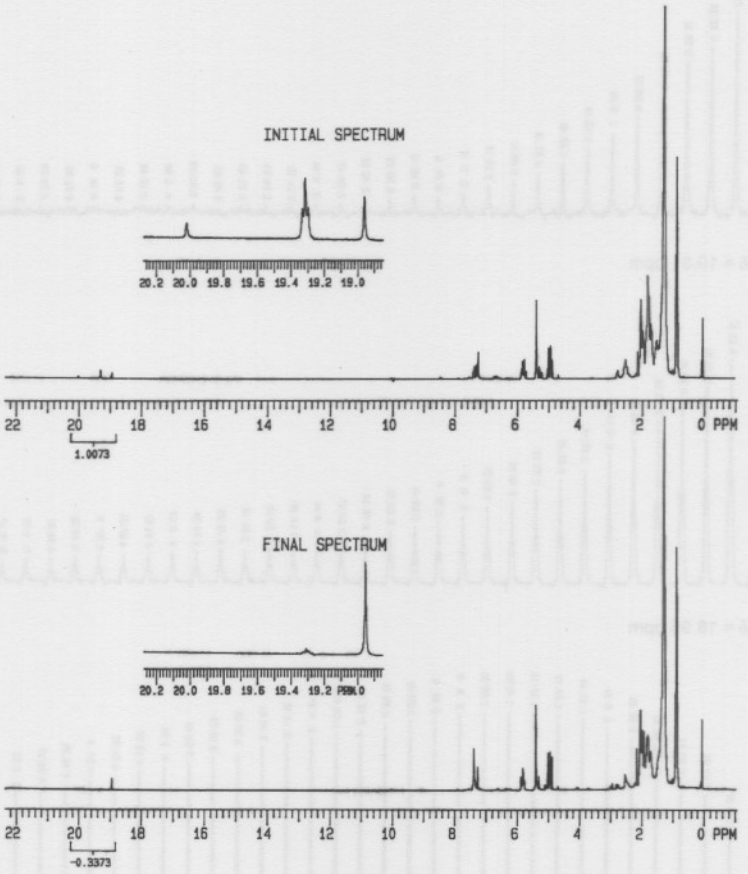
Resonances at δ 0.9 – 2.9 ppm show singulets and indistinguishable multiplets of the PCy_3 and H_2IMes groups, at δ 6.8 – 7.5 ppm multiplets represents the aromatic region and the singulet at δ 19.157 ppm is that of the benzylidene proton. Decomposition of the $Cl_2(PCy_3)(IMes)Ru(=CHPh)$ catalyst is evident as the intensity of the benzylidene proton peak at δ 19.157 ppm (singulet; Spectrum 4.3 and 4.6) slowly decreases with time and the peak eventually disappears. The carbene protons of the heptylidene carbene species [$Ru=CHC_6H_{13}$] and the methylidene carbene species [$Ru=CH_2$] were observed at δ 18.64 (doublet) and 17.80 ppm (singulet) respectively (Spectrum 4.6).

Spectrum 4.7 shows a comparison of the benzylidene, heptylidene and methylidene proton peaks with time. The benzylidene proton peak (Spectrum 4.7a) slowly disappears while both the heptylidene proton peak (Spectrum 4.7b) and methylidene proton peak (Spectrum 4.7c) form gradually to reach a maximum intensity. The change in the uncorrected integration values of the different species with time is illustrated in Figure 4.33 and clearly shows the trends mentioned above.

The formation of the heptylidene and methylidene species is due to the reaction of the benzylidene species with the 1-octene:

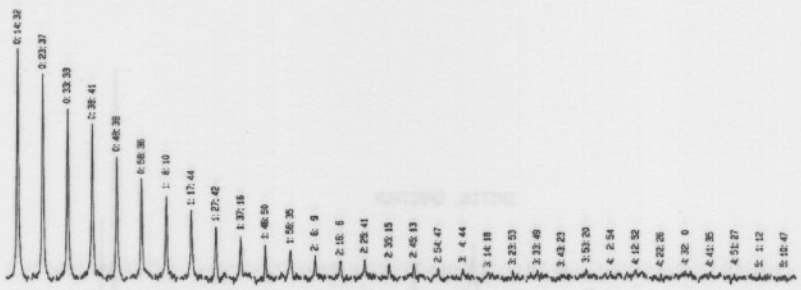


benzylidene heptylidene methylidene

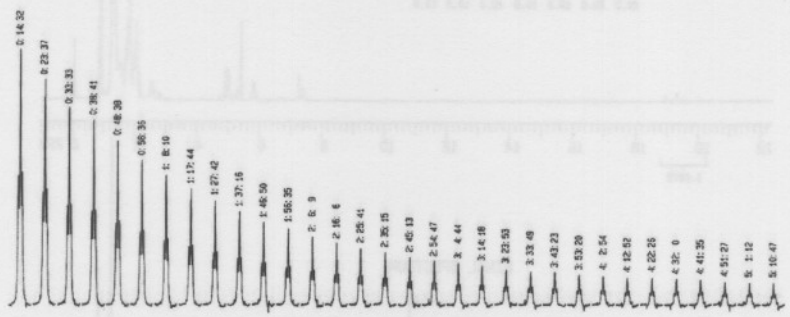


Spectrum 4.4 Initial (reaction time = 20 min) and final (reaction time = 316 min) ^{1}H-NMR spectra of an 1-octene/Grubbs 1 reaction mixture in $CDCl_3$ at 25 °C

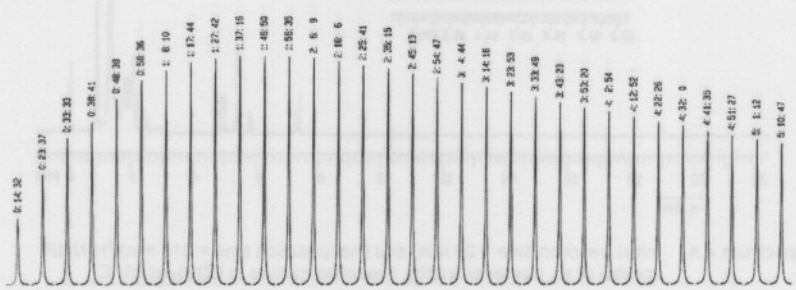
(a) δ = 20.015 ppm



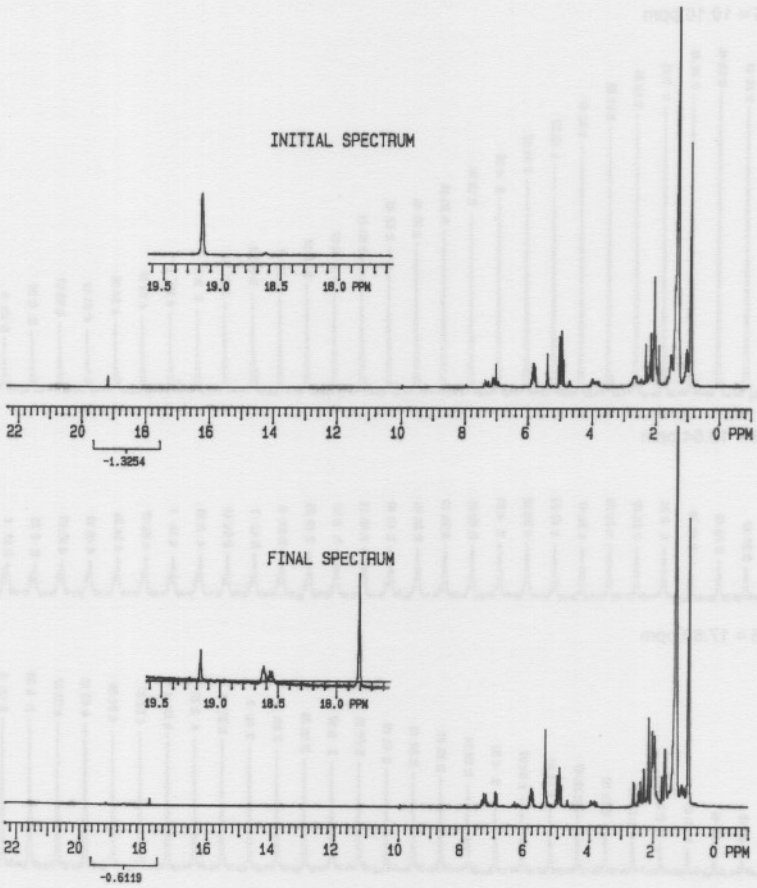
(b) δ = 19.31 ppm



(c) δ = 18.95 ppm

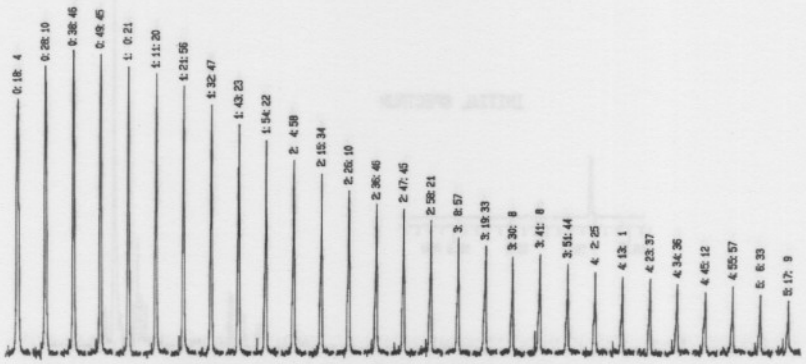


Spectrum 4.5 Change in integration of ^{1}H-NMR α-H carbene peaks in an 1-octene/Grubbs 1 reaction mixture in $CDCl_3$ at 25 °C [(a) Ru=C**H**Ph, (b) Ru=C**H**Hx, (c) Ru=CH_2]

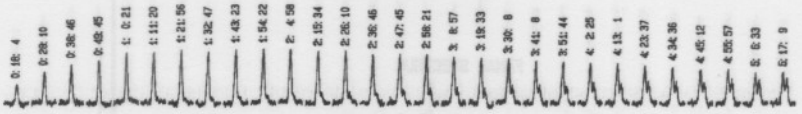


Spectrum 4.6 Initial (reaction time = 23 min) and final (reaction time = 322 min) ^{1}H-NMR spectra of an 1-octene/Grubbs 2 reaction mixture in $CDCl_3$ at 25 °C

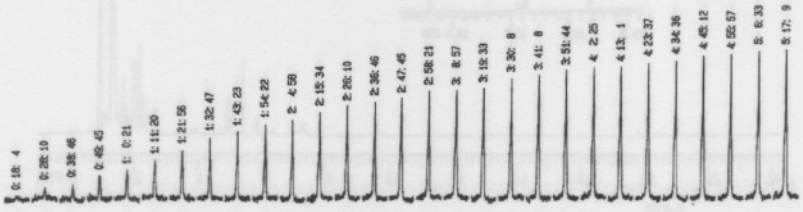
(a) δ = 19.16 ppm



(b) δ = 18.64 ppm



(c) δ = 17.80 ppm



Spectrum 4.7 Change in integration of ^{1}H-NMR α-H carbene peaks in an 1-octene/Grubbs 2 reaction mixture in $CDCl_3$ at 25 °C [(a) Ru=CHPh, (b) Ru=CHHx, (c) Ru=CH_2]

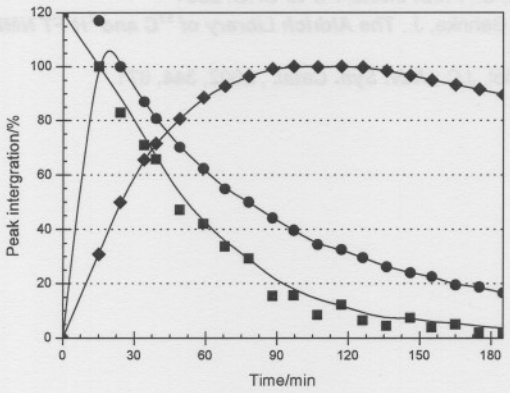


Figure 4.32 The ^{1}H-NMR Peak integration values (uncorrected) of the carbenes involved in the metathesis reaction of 1-octene in the presence of Grubbs 1

(■ δ 20.015 ppm, ● δ 19.31 ppm, ◆ δ 18.95 ppm)

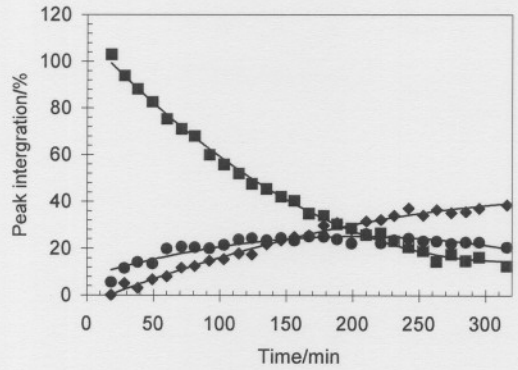


Figure 4.33 The ^{1}H-NMR Peak integration values (uncorrected) of the carbenes involved in the metathesis reaction of 1-octene in the presence of Grubbs 2

(■ δ 19.16 ppm, ● δ 18.641 ppm, ◆ δ 17.80 ppm)

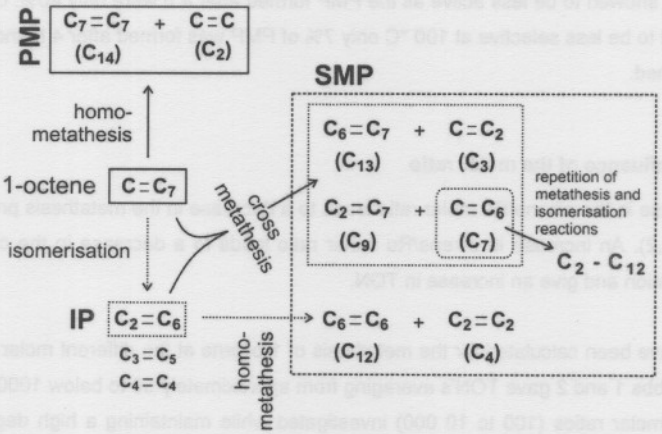
4.10 References

1. Van Schalkwyk, C., *Ph.D. thesis*, PU vir CHO, 2001
2. Pouchert, C.J., Behnke, J., ***The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra***, Volume 1, p 18
3. Dinger, M.B., Mol, J.C., ***Adv. Syn. Catal.*** , 2002, **344**, 671

5 Conclusions

5.1 Introduction

In this study, the metathesis of linear terminal and internal alkenes with the ruthenium carbene complexes, Grubbs 1 and 2, was studied. In the metathesis reaction of 1-octene, two reactions namely isomerisation and metathesis (homo- and cross metathesis) formed a range of products depending on the catalyst and can be illustrated as follows:



Note: Hydrogen atoms omitted for simplicity.

Firstly 1-octene undergoes a homometathesis leading to 7-tetradecene (C_{14}) and ethene (C_2) as the PMP's and isomerisation to form 2-, 3- and 4-octene. 2-Octene undergoes homometathesis to 6-dodecene (C_{12}) and 2-butene (C_4). A mixture of 1- and 2-octene can undergo cross metathesis to yield propene (C_3), 1-heptene (C_7), 2-nonene (C_9) and 6-tridecene (C_{13}). These reactions can be repeated with 1-hexene to give rise to alkenes ranging from C_2 to C_{12}. The homo- and cross metathesis products of 2-octene, and the cascade of products from 1-heptene form the SMP's.

5.2 Factors influencing the metathesis of 1-octene with Grubbs 1

5.2.1 Influence of the reaction temperature

It is clear that temperature plays an important role in the metathesis reaction of 1-octene. Grubbs 1 and 2 catalysts showed to be active for the metathesis reaction of 1-octene at all temperatures selected (Figure 4.1 - 4.6). Isomerisation products were detected in these reactions especially at higher temperatures. The activity of the catalysts in the catalytic isomerisation of alkenes is an indication of the coordinating ability of these complexes towards linear alkenes. It is evident that an increase in temperature results in an increase in isomerisation and optimum reaction temperature for an active metathesis catalytic system is $\leq$ 25 °C. Figure 5.1 summarizes the influence of temperature on the metathesis activity for both Grubbs 1 and 2. At 50 °C Grubbs 1 showed to be less active as the PMP formed after 4 h were only 40%. Grubbs 2 showed to be less selective at 100 °C only 7% of PMP was formed after 4 h and more SMP formed.

5.2.2 Influence of the molar ratio

An increase in the alkene/Ru molar ratio leads to a decrease in the metathesis products (Figure 5.2). An increase in alkene/Ru molar ratio leads to a decrease in the catalyst concentration and give an increase in TON.

TON's have been calculated for the metathesis of 1-octene at the different molar ratios. Both Grubbs 1 and 2 gave TON's averaging from approximately 50 to below 1000 at the different molar ratios (100 to 10 000) investigated while maintaining a high degree of selectivity for the formation of the PMP product, 7-tetradecene. Generally Grubbs 2 performed better than Grubbs 1 displaying higher TON's. When measuring the rate profiles of the reactions, the values at any given time represent a TON averaged over all of the ruthenium species present in the solution.

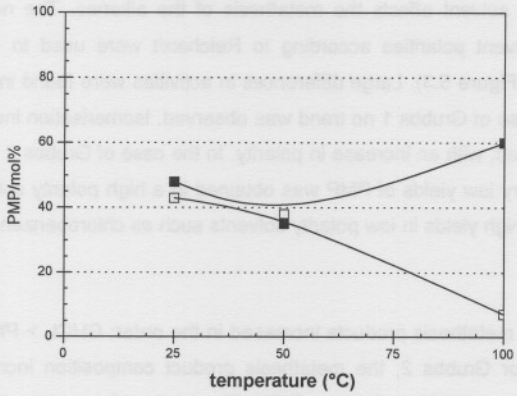


Figure 5.1 The influence of reaction temperature on the metathesis activity of the Grubbs 1 and 2 complexes with 1-octene [solvent = chlorobenzene, alkene/Ru molar ratio = 100]

■ Grubbs 1, □ Grubbs 2

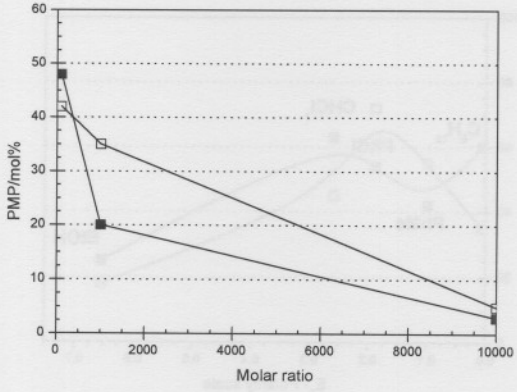


Figure 5.2 Influence of the molar ratio in the reaction of 1-octene in the presence of Grubbs 1 and 2 at 25 °C, solvent = chlorobenzene

(■ Grubbs 1, □ Grubbs 2)

5.2.3 Influence of solvents

The nature of the solvent affects the metathesis of the alkenes. The normalised E_T values for the solvent polarities according to Reichardt were used to compare the different solvents (Figure 5.3). Large differences in activities were found in the selected solvents. In the case of Grubbs 1 no trend was observed. Isomerisation increased, thus selectivity decreased, with an increase in polarity. In the case of Grubbs 2 no trend was also observed. Very low yields of PMP was obtained in a high polarity solvent such as ethanol, whereas high yields in low polarity solvents such as chlorobenzene, chloroform and cyclohexane.

For Grubbs 1, the metathesis products increased in the order: $CHCl_3$ > PhCl > C_6H_{12} > PhMe > EtOH. For Grubbs 2, the metathesis product composition increased in the order: PhCl > C_6H_{12} > $CHCl_3$ > PhMe > EtOH. The best perfomance was observed in PhCl for all internal alkenes used. The catalysts performed badly in EtOH.

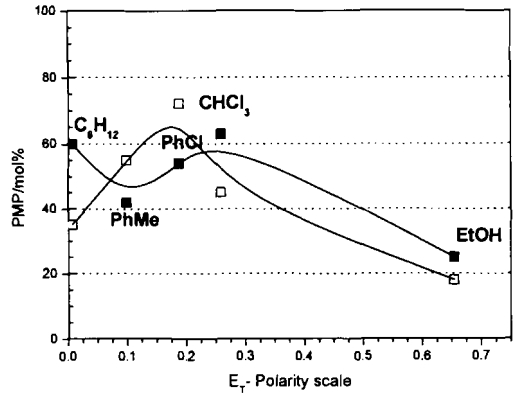


Figure 5.3 The influence of different solvents on the metathesis activity of Grubbs 1 and Grubbs 2 complexes with 1-octene, [Temperature = 25 °C, alkene/Ru = 100]

■ Grubbs 1, □ Grubbs 2

5.2.4 Reactions of 2-octene and 3-octene

Grubbs 1 and Grubbs 2 showed to be catalytically active for the metathesis reaction of 2-octene and 3-octene. Grubbs 1 catalyst perfomed significantly better than Grubbs 2 for the metathesis reaction of 2-octene giving 70% yield. For the metathesis reaction of 3-octene, decomposition of both Grubbs 1 and Grubbs 2 was observed.

5.2.5 Reactions of a mixture of 1- and 2-octene

When an equimolar mixture of 1-octene and 2-octene were exposed to Grubbs 1 and 2 catalysts, homometathesis and cross metathesis were observed: 6-dodecene (C_{12}) and 7-tetradecene (C_{14}) were formed as the primary homometathesis products and C_9, C_{11} and C_{13} were formed as the cross metathesis products.

5.2.6 Reaction of 1-tetradecene

The Grubbs 1 and 2 catalysts showed to be active towards the metathesis of 1-tetradecene with Grubbs 2 being more effective (Figure 4.32 and 4.33).

5.3 NMR studies

Previous studies showed that when the benzylidene initiator, $RuCl_2(=CHPh)(PCy_3)_2$, reacted with terminal acyclic alkenes, the observed organometallic products are other alkylidenes.[4] In this study ^1H NMR spectroscopy showed complete conversion of the starting benzylidene to two new alkylidenes, i.e. the heptylidene and methylidene species. Conversion of both the catalysts is clearly visible as the benzylidene proton peak at δ 20.015 for Grubbs 1 and δ 19.157 ppm for Grubbs 2 respectively disappears slowly with time. The rate of disappearance of the benzylidene peak is equal to the rate of activation of the catalyst. After 190 min, all of Grubbs 1 and 2 were converted to the catalytically active methylidene and heptylidene species. $RuCl_2(=CHPh)(PCy_3)(IMes)$ possesses a greater thermal stability than the parent complex and exhibits activity comparable to that of the most active early transition metal systems while retaining the functional group tolerance of $RuCl_2(=CHPh)(PCy_3)_2$.

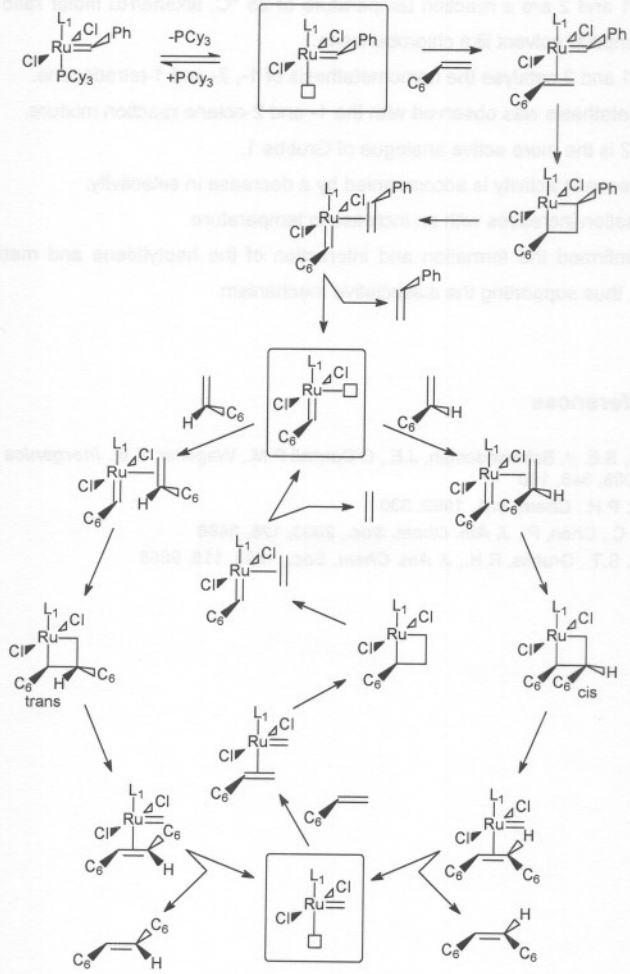
5.4 Reaction Mechanism

A number of reaction mechanisms have been proposed for the metathesis of alkenes. Mechanistic studies have shown that metathesis of ruthenium complexes proceed through either an associative and dissociative mechanism of which the dissociative mechanism is the accepted mechanism.[3] The dissosiative mechanism[3] illustrated in Scheme 5.1 is adapted to explain the occurrence of the 1-octene metathesis reaction.

In the first step, the activation of the Grubbs catalyst takes place by the formation of the catalytically active 14 electron benzylidene species due to the dissociation of one of the phosphine ligands (PCy_3). The benzylidene species then reacts with the alkene with the loss of the styrene (detected by GC/MS) which lead to the formation of an active 14-electron heptylidene species via a metallacyclobutane intermediate. The alkene coordinates to the heptylidene species either *cis* or *trans* and rearranges to form the different metallacyclobutane intermediates. The metallacycles are unstable and cleaves to form a methylidene species. The methylidene then reacts with an alkene to form the heptylidene species again via a metallacyclobutane intermediate. The heptylidene-methylidene interconversion was clearly observed and confirmed by NMR.

5.5 Summary and concluding remarks

Reactions of 1-, 2-, 3-octene, 1-tetradecene and the mixture of 1- and 2-octene can be metathesized in the presence of Grubbs 1 and 2. Grubbs 2 show a higher activity than Grubbs 1.The activity and selectivity of both Grubbs 1 and 2 can be improved by optimizing a number of parameters, e.g. 1-alkene/Ru molar ratio, reaction time, reaction temperature, solvents, etc. In this study, the reaction temperature, the 1-alkene/Ru molar ratio and solvents used showed a great influence on the reaction of 1-octene in the presence of Grubbs 1 and 2. NMR results obtained was evident as it showed the decomposition of both Grubbs 1 and 2 catalysts, a complete conversion of benzylidene and formation of the methylidene and the heptylidene.



Scheme 5.1 Dissociative mechanism adapted for 1-octene metathesis.[3]

In conclusion the results presented can be summarized as follows:

- Optimum reaction conditions for the metathesis of 1-octene in the presence of Grubbs 1 and 2 are a reaction temperature of 25 °C, alkene/Ru molar ratio < 1000 and a nonpolar solvent like chlorobenzene.
- Grubbs 1 and 2 catalyse the homometathesis of 1-, 2- and 1-tetradecene.
- Cross metathesis was observed with the 1- and 2-octene reaction mixture.
- Grubbs 2 is the more active analogue of Grubbs 1.
- The increase in activity is accompanied by a decrease in selectivity.
- Isomerisation increases with an increase in temperature.
- NMR confirmed the formation and interaction of the heptylidene and methylidene species, thus supporting the dissociative mechanism.

5.6 References

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SUMMARY

Metathesis of alkenes using ruthenium carbene complexes

In this study different ruthenium carbene complexes, Grubbs 1 and 2 were investigated for the reactions of 1-, 2-, 3-octene and 1-tetradecene. All reactions were conducted in glass mini reactors equipped with Mininert® valves under a dry nitrogen atmosphere. A heating block was used to heat the reactors. Gas chromatography was used to determine the product composition of reaction mixtures.

The influence of reaction temperature, solvents and catalyst concentration on the reactions of 1-octene were investigated. The optimum reaction conditions for activity and selectivity with Grubbs 1 and 2 were determined. Increased temperature for Grubbs 2 results in decrease in activity in the homometathesis reaction of 1-octene while the product yield increased as a result of isomerisation. Grubbs 2 catalyst displayed a higher metathesis product yield (65%) at lower temperatures (25 °C) with 1-octene and lower metathesis products (less than 10%) at higher temperatures (100 °C). Grubbs 1 displayed higher metathesis products (55-64%) at both lower (25 °C) and higher temperatures (100 °C). Secondary metathesis products due to isomerisation were less than 20% with Grubbs 2 the more active isomerization catalyst.

Grubbs 1 and 2 were active for the metathesis of both 2- and 3-octene. With 2-octene high yields of secondary metathesis products were observed. The optimum reaction conditions for the metathesis of 1-octene were used for the reaction of 2-, 3-octene and 1-tetradecene. A higher metathesis yield (70%) was obtained with 2-octene. Secondary metathesis products (C_9 - C_{13}) and oligomers (C_{16} and longer) were obtained in the presence of Grubbs 2. Grubbs 1 and 2 also catalyzed the metathesis of 1-tetradecene. The reaction is very slow in the presence of Grubbs 1 and little metathesis products are observed (less than 20%). In the presence of Grubbs 2 40% primary and less than 10% secondary metathesis products were observed. The reaction mixture of 1- and 2-octene in the presence of Grubbs 1 and 2 produced metathesis products less than 20%. Cross metathesis was observed from the mixture, C_9 and C_{13} were produced.

Both Grubbs 1and 2 showed a high activity and selectivity towards the metathesis reaction of 1-octene. These catalysts showed that they are still active at high alkene/Ru molar ratios and in different solvents that were used. Relatively high turnover numbers (TON) were obtained for both Grubbs 1 and 2. NMR studies confirmed the existence of the original benzylidene complex and the formation of the active heptylidene and methylidene complexes.

OPSOMMING

Metatese van alkene met behulp van ruteniumkarbeenkomplekse

In hierdie studie is verskillende karbeenkomplekse, Grubbs 1 en 2, vir die reaksies van 1-, 2-, 3-okteen en 1-tetradeseen ondersoek. Al die reaksies is in glas minireaktore, toegerus met 'n Mininert®-klep onder 'n droë stikstofatmosfeer uitgevoer. 'n Verhittingsblok is gebruik om die reaktore te verhit. Gaschromatografie is gebruik om die produksamestelling van die reaksiemengsels te bepaal.

Die invloed van reaksietemperatuur, oplosmiddels en katalisatorkonsentrasie op die reaksies van 1-okteen is ondersoek. Die optimum reaksietoestande ten opsigte van aktiwiteit en selektiwiteit met Grubbs 1 en 2 is bepaal. Verhoogde temperature vir Grubbs 2 het tot 'n afname in aktiwiteit vir die homometatesereaksie van 1-okteen gelei terwyl die produkopbrengs as gevolg van isomerisasie toegeneem het. Grubbs 2 het 'n hoër metateseprodukopbrengs (65%) by laer temperature (25 °C) met 1-okteen vertoon en laer metateseprodukte (minder as 10%) by hoër temperature (100 °C). Grubbs 1 het hoër metateseopbrengste (55-64%) by beide laer (25 °C) en hoër (100 °C) temperature vertoon. Sekondêre metateseprodukte as gevolg van isomerisasie was minder as 20% met Grubbs 2 die meer aktiewe isomerisasiekatalisator.

Grubbs 1 and 2 was aktief vir die metatese van beide 2- en 3-okteen. Met 2-okteen is hoë opbrengste sekondêre metateseprodukte waargeneem. Die optimum reaksiekondisies vir die metatese van 1-okteen is vir die reaksies van 2-, 3-okteen en 1-tetradeseen gebruik. 'n Hoër metateseopbrengs (70%) met 2-okteen as met 3-okteen (45%) is vir 2-okteen verkry. Sekondêre metateseprodukte (C_9 – C_{13}) en oligomere (C_{16} en langer) is in die teenwoordigheid van Grubbs 2 verkry. Grubbs 1 en 2 het ook die metatese van 1-tetradeseen gekataliseer. In die teenwoordigheid is 40% primêre en minder as 10% sekondêre metatesprodukte waargeneem. 'n Reaksiemengsel van 1- en 2-okteen het minder as 20% metateseprodukte in die teenwoordigheid van Grubbs 1 en 2 opgelewer. Kruismetatese was vanaf die mengsel waargeneem, C_9 en C_{13} is gevorm.

Beide Grubbs 1 en 2 het 'n hoë aktiwiteit en selektiwiteit ten opsigte van die metatesereaksie van 1-okteen vertoon. Hierdie katalisatore is ook aktief by hoë alkeen/Ru-molverhoudings en in verskillende oplosmiddels. Relatiewe hoë omsettingsgetalle is vir beide Grubbs 1 en 2 verkry. KMR-studies het die bestaan van die oorspronklike bensilideenkompleks en die vorming van die aktiewe heptilideen- en metilideen-komplekse bevestig.

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