Isomerisation of Alkenes using Metal Carbenes and Related Transition Metal Complexes

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Hons. B.Sc. (UNIN), M.Sc. (PU for CHE)

Thesis submitted in fulfillment of the requirements for the degree
PHILOSOPHIAE DOCTOR
in
CHEMISTRY
of the
Potchefstroomse Universiteit vir Christelike Hoër Onderwys.

Promoter: Prof HCM Vosloo

Potchefstroom
May 2005

Dedicated to Mom, Eric and Tshepang

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LIST OF ABBREVIATIONS

General

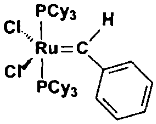
CM	Cross metathesis
GC	Gas chromatography
IR	Infrared spectroscopy
^{1}H NMR	Proton nuclear magnetic resonance
^{13}C NMR	Carbon-13 nuclear magnetic resonance
PMP	Primary metathesis products
RCM	Ring-closing metathesis
ROMP	Ring-opening metathesis products
SMP	Secondary metathesis products

Chemicals and ligands

Ar	Aryl
Bu	Butyl
Cy	Cyclohexyl
Cp	Cyclopentadienyl
COD	Cyclooctadiene
MeO	Methoxy
IMes	Imidazolidinylidene
Ph	Phenyl
PCy_3	Tricyclohexylphenyl
PPh_3	Triphenylphosphine
TCE	Tetrachloroethane

LIST OF CATALYSTS

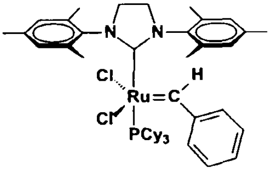
Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium



$RuCl_2(=CHPh)(PCy_3)_2$

1st generation Grubbs catalyst (Grubbs 1)

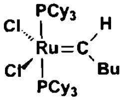
(1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium



$RuCl_2(=CHPh)(PCy_3)(IMes)$

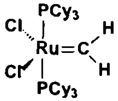
2nd generation Grubbs catalyst (Grubbs 2)

Pentylidene-bis(tricyclohexylphosphine)dichlororuthenium



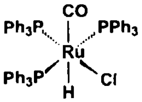
$RuCl_2(=CHBu)(PCy_3)_2$

Methylidene-bis(tricyclohexylphosphine)dichlororuthenium



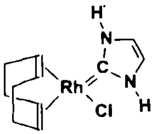
$RuCl_2(=CH_2)(PCy_3)_2$

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II)



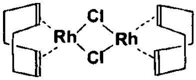
$RuCl(H)(PPh_3)_3(CO)$

Chloro(1,5-cyclooctadiene)(imidazolidene) rhodium carbene



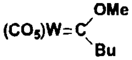
$RhCl(C_3H_5N_2)(COD)$

Chloro(1,5-cyclooctadiene)-rhodium(I)dimer



$[RhCl(COD)]_2$

[Butyl(methoxy)carbene]pentacarbonyl chromium(0)



$(CO_5)W{=}C(OMe)(Bu)$

$W(=C(OMe)Bu)(CO)_5$

Ruthenium trichloride

$RuCl_3$

Rhodium trichloride

$RhCl_3{\cdot}3H_2O$

Bis(cyclopentadienyl)zirconium dichloride

Cp_2ZrCl_2

Bis(cyclopentadienyl)titanium dichloride

Cp_2TiCl_2

1 AIMS AND OBJECTIVES

1.1 Introduction

Double bond isomerisation occurs in many cases as an unwanted side reaction in organometallic catalysed reactions of alkenes, i.e., hydrogenation, metathesis, oligomerisation and hydroformylation.[1,2] It is also found in a number of important industrial processes, such as the SHOP process as an intermediate step.

Alkenes are readily isomerised and the reaction involves either movement of the position of the double bond, or skeletal alteration. The double bond may also include a reorientation of the groups around the double bond to bring about *cis-trans* isomerisation.[3] Alkenes with terminal double bonds are the least stable. They isomerise more rapidly than those in which the double bond carries the maximum number of alkyl groups.[4]

Certain transition metal complexes, such as Fe, Pd, Rh, Pt, Ni, Ir, Ru, and Cr, are known as the catalysts for isomerisation reactions. The extent of isomerisation is a property of the metal itself and its structure, and is little altered by the support in the case of heterogeneous catalysts.[5] A decreasing order of metals for ease of double bond isomerisation is Pd > Ni >> Rh >>Ru ~ Os > Ir > Pt and in the case of the disubstituted catalysts, the following decreasing order in ease of isomerisation is observed: Pd >> Rh, Ru, Pt > Os > Ir. Heterogeneous catalysts are favoured by a low hydrogen concentration at the surface of the metal ("hydrogen poor catalysts").

1.2 Internal Alkene Isomerisation Challenge

The following observations generally apply to alkene isomerisation reactions:[6, 1]

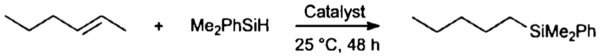
1. *Trans* alkenes are more stable than *cis* alkenes.
2. Internal alkenes are more stable than terminal alkenes.
3. Conjugated di and oligoalkenes are favoured over isolated double bonds.
4. Substituted (internal) alkenes with the highest degree of branching are thermodynamically favoured.
5. Polar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

In summary, the vast majority of isomerisation reactions entails terminal to internal double bond migration and is normally a side reaction of other catalysed alkene reactions. Only a few examples of "contrathermodynamic" or internal to terminal double bond isomerisation are mentioned in literature.

Three broad categories of organometallic systems that seem capable to catalyse the "contra-thermodynamic" isomerisation of internal alkenes can be summarized as follows:

a. Metal hydride and related catalytic systems

The well known Wilkinson catalyst for hydrogenation, $(Ph_3P)_3RhCl$, is reported to give *inter alia* terminal alkenes when an internal alkene is subjected to typical hydrogenation conditions.[9] The Wilkinson catalysts also give only terminal adducts by a series of isomerisations during the hydrosilylation of internal alkenes at moderate reaction conditions, suggesting an internal-to-terminal migration during the reaction:[10]



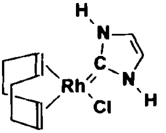
When boranes are added to the metal hydride analogue of the Wilkinson catalyst, $(Ph_3P)_3RhH$, one phosphine ligand is replaced with borane.[11,12] These complexes cause internal alkenes to isomerise under high pressures and even less severe hydrogenation conditions. Platinum hydrides also play a role in the hydrosilylation reaction mentioned above.[13] It was suggested that the mechanism in the hydrosilylation reactions accounts for alkene isomerisation via the reversible formation of the metal alkyl.[14]

b. Metal carbene and related catalytic systems

Double bond migration is also an important side reaction in alkene metathesis reactions. This normally gives rise to a spectrum of products formed due to inter alia cross metathesis between the original alkene and the isomer alkene. A metal carbene and in some cases a metal carbene hydride mechanism was suggested to account for this observation with some evidence that such species may exist.[1,3,15] The features of the metal carbene mechanism are characteristic of the π-allyl mechanism.[1] Double bond migration via a metal carbene may take place via a series of equilibrium transformations and whether these equilibriums do indeed take place need to be investigated.

$Ru(=CHPh)Cl_2(PCy_3)_2$, known as a catalyst for metathesis, is also a catalyst for isomerisation, but the reaction usually affords a mixture of alkene isomers. The Grubbs carbene complex and its second generation counterpart have demonstrated a remarkable efficiency in metathesizing alkenes. Furthermore, the ready availability of these stable ruthenium-based catalysts, coupled with their tolerance toward a wide variety of common functional groups, make the Grubbs catalyst a very convenient synthetic tools. Isomerisation occurred as a side reaction in the metathesis reaction using the Grubbs' metal carbene as the catalyst.

A relatively recent metal carbene system, based on Rh and used in hydroformylation, catalyses the stereospecific isomerisation of 1-alkenes to *cis*-2-alkenes under appropriate conditions (CO atmosphere and high reaction temperatures).[1] These are heterocyclic carbenes derived from imidazole and related N-heterocyclic compounds that form stable metal complexes with a large number of metals, e.g.



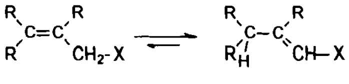
c. Other catalytic systems

In the hydroesterification reaction of internal alkenes Co-complexes are known to rapidly isomerise the double bond to the 1-position to give a linear ester as a major product.[16] The isomerisation of functionalised internal alkenes to terminal alkenes using Cu(I) complexes like (PhCN)CuCl and $R_4N^+CuCl_2$ and Pt chloride complexes as catalyst are well known:[1,2]

$$XCH_2CH{=}CHCH_2X \rightleftharpoons XCH_2\underset{\displaystyle X}{\underset{|}{C}}H{-}CH{=}CH_2$$

X = Cl, OAc

The asymmetric isomerisation of allylic compounds with chiral catalysts can also be of importance to the internal-terminal double bond migration of simple alkenes. Chiral Rh complexes containing a BINAP ligand give terminal alkenes in high yields with allylic compounds:[17]



X = OH, OR, NH_2, NR_2

Finally, with the success of the metallocenes in the polymerization of alkenes and the recent application of these systems to the isomerisation of terminal alkenes, it will be worthwhile to investigate these systems for the isomerisation of internal alkenes. $CpTiCl_2$ combined with a Grignard reagent, Li-organoyls, $LiAlH_4$ or Na-napthalide show high isomerisation activities and selectivities.[18,19]

1.3 Importance of Linear 1-Alkenes

Normal 1-alkenes, featuring highly accessible terminal double bonds, are ideal materials for manufacturing numerous products. Normal 1-alkenes or their derivatives are used extensively as polyethylene comonomers, plasticizers, synthetic motor oils, lubricants, automotive additives, surfactants, paper sizing, and in a wide range of specialty applications. As major petrochemical building blocks, their use in the development of new chemical products is unlimited.

The conversion of a terminal alkene to a near-equilibrium mixture of internal alkenes is carried out on massive scale as one step in the SHOP process. The SHOP process produces linear alkenes which are then converted by other processes (such as hydroformylation) into value added chemicals such as linear detergent alcohols. Linear aldehydes can be prepared from internal alkenes such as 2-decene by using a catalyst that is active for both isomerisation and hydroformylation of alkenes.

1.4 Aims and Objectives

In this study, $Ru(=CHPh)Cl_2(PCy_3)_2$, $Ru(=CHPh)Cl_2(PCy_3)(IMes)$ and other related transition metal carbenes were investigated as catalytic systems for the isomerisation of alkenes. The different factors that could influence the isomerisation reaction and the selectivity of the catalyst were investigated.

To reach the aim of the study the following objectives are stated:

1. To systematically and extensively search the published literature on the "contrathermodynamic" isomerisation of alkenes by organometallic catalysis with special emphasis on metal carbene catalytic systems.
2. To identify and test simple catalytic systems to the "contrathermodynamic" isomerisation of internal alkenes.
3. Optimization of the reaction conditions and kinetic studies of these catalytic systems with regard to the activity and selectivity of the catalytic systems.
4. To investigate other catalytic systems based on the results obtained from literature and the above-mentioned experimental work.

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2 LITERATURE STUDY

2.1 Introduction

It is known that the isomerisation reaction proceeds by acids, bases or by organometallic complexes to produce a thermodynamically stable product. Isomerisation also occurs as a side reaction in hydrogenation, polymerization, hydroformylation and other reactions catalysed by metals, and it has also been recognised as a side reaction in alkene metathesis for some time.[1]

Table 2.1 Formation of the different metathesis products during the metathesis of 1-octene.

Reaction	Substrate*	Products*
Primary metathesis		
Homometathesis	$C_7{=}C$	$C_7{=}C_7 + C{=}C$
Isomerisation	$C_7{=}C$	$C_6{=}C_2$
Secondary metathesis		
Cross metathesis	$C_7{=}C + C_6{=}C_2$	$C_7{=}C_6 + C_2{=}C$
		$C_7{=}C_2 + C_6{=}C$
Homometathesis	$C_6{=}C_2$	$C_6{=}C_6 + C_2{=}C_2$
Isomerisation	$C_6{=}C$	$C_5{=}C_2$
Secondary metathesis		
Cross metathesis	$C_6{=}C + C_5{=}C_2$	$C_2{=}C + C_6{=}C_5$
		$C_5{=}C + C_6{=}C_2$
Homometathesis	$C_6{=}C$	$C_6{=}C_6 + C{=}C$
Homometathesis	$C_5{=}C_2$	$C_5{=}C_5 + C_2{=}C_2$

* Hydrogens omitted for clarity, i.e., $C_7{=}C$ is $(CH_3)_6CH{=}CH_2$.

Double bond isomerisation is highly relevant in metathesis chemistry because it is the primary cause of secondary metathesis products (Table 2.1); this is considered to be a major limitation of alkene metathesis.

2.2 Isomerisation of Alkenes

Industrially, soluble catalysts are used to isomerise alkenes that are involved as intermediates in other homogeneous catalytic processes.[5] Well-defined metathesis catalysts are very selective for alkene metathesis, but there have been reports of isomerisation of substrates with two single component, well defined, metal-alkylidene compounds, the ruthenium alkylidene developed by Grubbs and the molybdenum alkylidene developed in the Schrock laboratories are today the most widely used metathesis initiators.[6]

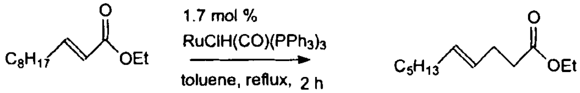
Catalysts of the Grubbs type are of special interest, since they are moderately sensitive to air and moisture and show significant tolerance towards functional groups.[7] For Schrock's molybdenum catalyst, alkene isomerisation was observed in RCM and in the metathesis of simple alkenes. Only trace amounts of isomerisation products were found after long reaction hours.

It is also well known that some Ruthenium complexes promote alkene isomerisation.[8] A number of Ru(II) complexes has been studied through the years (Table 2.2). It was found that in the absence of H_2, solutions of the complexes $RuLH(PPh_3)_3$ (L = Cl or $OCOCF_3$) very slowly isomerise 1-hexene to 2-hexene.[9]

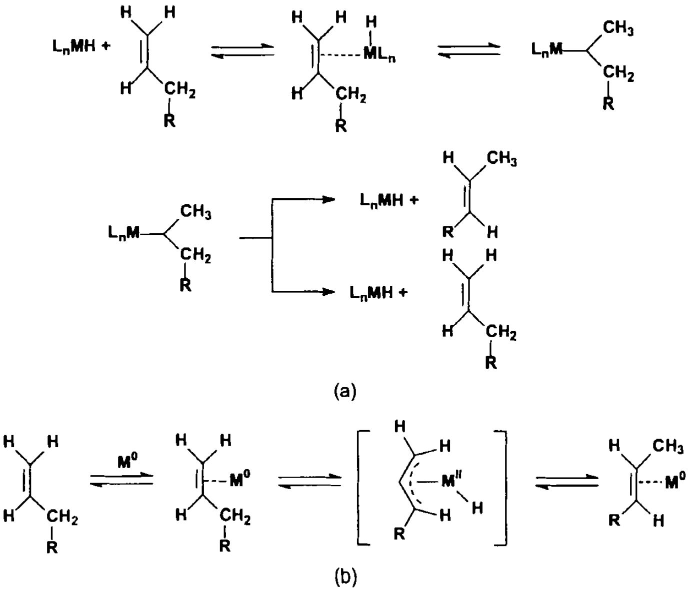
Table 2.2 Isomerisation of alkenes using Ru complexes.

Catalyst precursor	**Substrate**	**Products**
$[RuCl_2(PPh_3)_3]$	Allylbenzene 4-phenylbutene	*Cis*- and *trans*-β-styrene 1-phenylbutenes
$[RuCl_2(PPh_3)_3]$	4-vinylcyclohexene	3- and 4-ethylidenecyclohexenes
$[RuCl_2(PPh_3)_3]$	1,4-diarylbut-2-ene	Mainly 1,4-diarylbut-1-enes
$[RuCl_2(CO)_2(PPh_3)_2]$	*trans*-cyclodecene 1,5-cyclooctadiene	*cis*/*trans*-cyclodecene 1.3- cyclooctadiene
$[RuCl_2(CO)_2(PPh_3)_2]$	1-octene	Mostly 2-octene
$[RuCl_2(\eta\text{-}C_6H_6)]_2$	1-hexene	2-hexene
$[RuCl(CO)_3(\eta\text{-}C_3H_5)$	1-hexene 1-butene N-allylamides	*cis*- and *trans*-2-hexene *cis*- and *trans*-2-butene N-(1-propenyl)amides
$[Ru(PPh_3)_4(\eta\text{-}MeCN)]\cdot MeCN$	allylbenzene	*cis*- and *trans*-β-methylstyrene

Another well-known isomerisation catalyst is $RuClH(CO)(PPh_3)_3$ complex,[10] but the reaction usually affords a mixture of alkene isomers and it has rarely been used as an isomerisation reagent in organic synthesis.[11]



McGrath and Grubbs[10] observed the isomerisation of allylic ethers and alcohols and other alkenes in the presence of $Ru(H_2O)_6(tos)_2$ (tos = p-toluenesulfonate), by a metal hydride mechanism. Two pathways are generally accepted for transition metal catalysed isomerisation of allylic alkenes by pathways other than metal carbenes: the phenomenon can occur either via a π-allyl metal or a hydrometalation-dehydrometalation. (Scheme 2.1)



Scheme 2.1 Common metal-catalysed alkene isomerisation (a) hydrometalation-dehydrometalation and (b) π-allyl mechanism.[12]

There have also been reports of alkene isomerisation of substrates with allylic oxygen or nitrogen functionality with the first generation Grubbs catalyst.[14] Other examples studied so far include papers by Grubbs *et al.* [15] which focuses on cis-2-pentene and terminal alkenes as substrates.

Wagener *et al.*[13] made a detailed study of the double-bond isomerisation activity of the first and the second generation Grubbs catalysts and compared that with the Mo-based Schrock metathesis catalysts. Recently, alkene isomerisation has been reported in metathesis reactions with the second generation Grubbs catalyst. It was found that the N-heterocyclic carbenes, (NHC)-ligated, ruthenium complex promotes extensive isomerisation of both internal and terminal alkenes at temperatures of 50 – 60 °C.[16]

Earlier, Taylor[17,18] had reported on the occurrence of alkene isomerisation during the synthesis of an oxocene by RCM with Ru in dichloromethane, and he attributed it to the residual acidity of the solvent: replacing dichloromethane by diethyl ether prevented isomerisation. While investigating the RCM of substrates requiring high temperatures and extended reaction times, Bourgeois *et al.*[17] noticed significant isomerisation of one of the double bonds in the starting diene, with the recently developed $RuCl_2(=CHPh)(PCy_3)(IMes)]$. He found out that the ruthenium catalyst coordinated to the less sterically crowded alkene.

Double bond isomerisation has also been used in the tandem metathesis-isomerisation reaction for the synthesis of cyclic enol ethers in which the metathesis catalysts were converted by hydrogen after metathesis has ceased, into uncharacterised isomerisation catalysts.[19] The study revealed that treatment of ruthenium alkylidene in CH_2Cl_2 with small amounts of H_2 leads reproducibly to an alkene isomerisation-active catalyst.

To date it is not clear whether alkene isomerisation is promoted by the metathesis catalyst, decomposition products, or by impurities from the catalyst synthesis. Fürstner *et al.*[20] have isolated a ruthenium dihydride complex, $RuCl_2(PCy_3)_2(H)_2$ which they propose may be responsible for alkene isomerisation, presumably through a hydride mechanism. It is clear however that for RCM, isomerisation occurs when the metathesis ring closure event is relatively slow due to large ring size or conformational issues.

Lehman *et al.*[16] suggested from several experimental observations that alkene isomerisation occurs as a side reaction for ADMET with the second generation Grubbs catalyst. In the context of ADMET, isomerisation of a terminal to an internal alkene followed by productive metathesis step with a terminal alkene would liberate an α-alkene such as propene or 1-butene.

In the case of linear internal alkenes, if the metathesis products remain in the reaction mixture, a statistical distribution of reactant and product molecules eventually results. This means that the reaction reach only a 2:1:1 molar composition.

If a catalyst is also active for double bond migration, additional products can be formed by cross-metathesis reactions. This would result in a complex product mixture and in a decrease in the yield of the desired compounds.[21]

2.3 Catalysts for Alkene Isomerisation

It is known that transition-metal compounds are very effective isomerisation catalysts. Various transition metal complexes, such as Fe, Pd, Rh, Pt, Ni, Ir, Ru and Cr have been used as catalysts for isomerisation reaction.[3,4]

2.3.1 Alkene isomerisation with Ni, Pd and Pt complexes

The isomerisation of 1-butene has been reported in the presence of a mixture of $AlEt_3$ and $NiCl_2py_2$, and Cramer[95] has found that a very rapid isomerisation of this alkene occurs in an acidic solution of $Ni[P(OEt)_3]_4$. The initially formed 2-butene has a *cis*-to-*trans* ratio of 2.5:1, although as the time progresses the ratio changes to 1:3 in favour of the *trans*-isomer. The isomerisation with $Ni[P(OEt)_3]_4$ in acid solution has been studied in detail by Tolman.[96] No isomerisation of 1-butene could be found in the absence of added acid, but, in the presence of acids, both 2-butene and butane were formed.

Tolman[96] also studied the reaction of $NiH[P(OMe)_3]_4^+$ 1-penta-4-diene since alkene isomerisation and π-allyl formation can potentially occur in the same system. The results showed that the dimethyl-1.3-π-allylic products were formed along with 1-penta-3-diene, implying that double-bond migration occurred initially, to be followed by formation of allylic complexes.

The isomerisation of 1-pentene was reported with $Ni[bis(diphenylphosphino)butane]_2$ and HCN, and with $Ni[P(OEt)_3]_4$ and CF_3CO_2H.[97] The isomerisation with triethylphosphite was carried over 24 h and the products were 1-pentene (3 %), *cis*-2-pentene (23 %), and *trans*-2-pentene (74 %). One result from this study with 1-pentene which differs from that found with 1-butene is that with 1-pentene the rate of deuterium redistribution is greater than the rate of isomerisation.

The isomerisation of allyl methyl- and allyl phenyl ether occurs readily with $PtH(Cl)(O(PPh_3)_2$, $PtH(NO_3)(PPhMe)_2$, $[PtH(PPh_3)_3(acetone)]BF_4$ and $PtH(SnCl_3)(PPh_3)_2$.[98] A mechanism involving the addition of Pt-H across the terminal C=C bond before double bond migration occurs was also favoured, which led to the catalytic formation of *cis*-propenyl alkyl ethers. A similar mechanism was considered for the reaction of 1-butene, where both Markovnikov and anti-Markovnikov addition occurred.[99]

Isomerisation of 1-pentene to *cis*- and *trans*-2-pentene was catalysed at 50 °C and above by solutions in benzene of $Fe_3(CO)_{12}$ and of $PdCl_2(C_6H_5CN)_2$. In both cases the preferential formation of *trans*-2-pentene occurred. Isomerisation 1-pentene revealed that each reaction proceeded by intramolecular *trans*fer of hydrogen and deuterium atoms. The reaction mechanisms involved the π-allyl mechanism.[100]

2.3.2 Alkene isomerisation with Co carbonyls

Orchin and Roos[108] examined the isomerisation allylbenzene by $HCo(CO)_4$ and $DCo(CO)_4$ at ambient temperature and pressure, and they were both found to catalyse isomerisation to propenyl benzene at the same rate. It has also been observed that rapid isomerisation accompanies the cobalt carbonyl-catalysed hydrosilylation of alkenes. A very effective isomerisation catalyst may be prepared by treatment of a solution of $Co_2(CO)_8$ in alkene with a silicon hydride in sufficient quantity to slightly exceed the cobalt carbonyl concentration. The behaviour of 1-heptene and 1-pentene in the presence of such a catalyst was found to be very similar to that observed with a $RhCl_3 \cdot 3H_2O$ catalyst; migration of the double bond occurs in stepwise fashion. Co-isomerisation of 1-pentene and 1-heptene results in exchange of 0.5 deuterium atoms per molecule of 1-heptene isomerised, the exchanged deuterium being distributed between all the carbon atoms of the allylic system of the 2-pentene.

Since the results obtained with the cobalt carbonyl/silane catalysts parallel so closely to those obtained with the rhodium complex catalysts, and seeing that the latter operate through a metal alkyl intermediate, it seems very likely that such a mechanism is operative with the former catalyst.[101]

2.3.3 Alkene isomerisation by ruthenium carbonyl carboxylates

Salvini *et al.*[102] investigated the isomerisation of 1-hexene in the presence of $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$, $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ and $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$. When using $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ as the catalyst precursor, after 72 h at 80 °C, *trans*-2-hexene, (24.9 %), *cis*-2-hexene (14.9 %), *trans*-3-hexene (1.5 %) and *cis*-3-hexene (0.4 %) were formed. The *cis*-3-hexene, after 6 h, did not exceed 1 %. That behaviour was ascribed to kinetic rather than thermodynamic control of the reaction. The *cis*-isomer initially formed by elimination from the Ru complex is subsequently isomerised to the thermodynamically more stable *trans*-isomer.

The same behaviour was observed with the binuclear complex $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ which was in agreement with the hypothesis that the same catalytic intermediate is formed starting from both the binuclear or tetranuclear precursor. The minor differences in the conversion of isomeric alkenes may be easily ascribed to different ways of formation of the catalytically active intermediate.

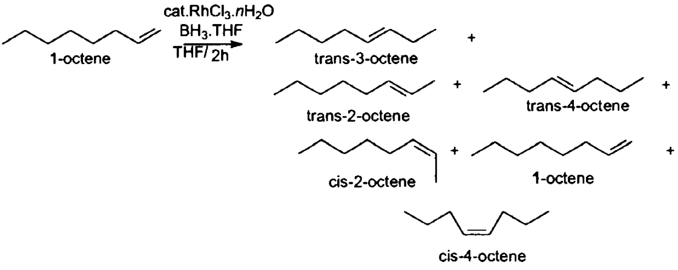
The mononuclear complex $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$ did not isomerise alkenes even after a long reaction time (6 days) at 80 °C. The behaviour of this complex was not investigated at higher temperatures because it transforms into the binuclear $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ which is active for the reaction.

The activity of the ruthenium carbonyl carboxylates in the catalytic isomerisation of 1-hexene provides an indication of the coordinating ability of these complexes toward linear alkenes. When using a terminal alkene, a π-alkene metal complex may be thought as the first reaction step. It is followed by the activation of a hydrogen atom on the carbon atom in α-position with respect to the double bond leading to the formation of a π-allylic system. Addition of the M-H bond to one of the carbon atoms of the allylic systems gives rise either to the initial π-metal complex or to another π-metal complex containing the isomerised alkene. The internal alkene formed is then replaced in the complex by the terminal one to minimize steric hindrance, thus producing a stable complex.[24]

Salvini *et al.*[102] also observed that the Ru(0) complexes $Ru(CO)_3(PnBu_3)_2$, $Ru_3(CO)_9(PnBu_3)_3$, $Ru(CO)_3(PPh_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$ are catalytically active for the isomerisation of 1-hexene to 2-hexene and 3-hexenes whereas the Ru(II) complexes $Ru(CO)_2(OAc)_2(PnBu_3)_2$ and $Ru(CO)_2\,(OAc)_2(PPh_3)_2$ showed little or negligible isomerisation activity.

2.3.4 Isomerisation of alkenes by Rh-based catalysts

It was found that alkenes isomerise rapidly in the presence of catalytic amounts of a hydroborating reagent and rhodium compound. The hydroborating reagent is apparently responsible for the *in situ* generation of a metal hydride species, which has been implicated to account for the stepwise migration of the double bond.[65] To obtain a clear picture of the isomerisation process, Morrill *et al.*[65] carried out the hydroboration/oxidation of 1-octene using less than the stoichiometric amounts of the hydroborating reagents (Scheme 2.2). Analysis of the product mixture revealed the presence of 1-octene (0.6 %) and isomeric internal alkenes (87 %), along with octanes and octanols.



Scheme 2.2 Isomerisation of 1-octene using $RhCl_3 \cdot nH_2O/BH_3 \cdot THF$ in THF.

Typically equilibration favours structures with the double bond farther from the end of the carbon chain. It was also noticed that during the isomerisation of 1-octene, *trans*-4-octene was not the major product, and when 4-octene was subjected to similar experimental conditions, the product ratio resembled that obtained with 1-octene. From this it was deduced that no matter what isomeric alkene one starts with, the final product composition was virtually a thermodynamic mixture of isomeric alkenes.

The combination of catalytic amounts of $RhCl_3 \cdot nH_2O$ and $BH_3 \cdot THF$ offered an excellent route for the isomerisation of alkenes. The rapid reversibility of the alkene insertion/β-hydride elimination step in the mechanism is the key to alkene isomerisation.[65]

Isomerisation of 1-hexene to *cis*-2-hexene was observed using the rhodium complex as the catalyst.[2] Although the nature of the active catalytic species has not yet been elucidated in detail, the nucleophilic carbene seems to be retained at the metal throughout the catalytic cycle, thus supporting the specific function of activation and stabilization of this particular class of ligands.[2]

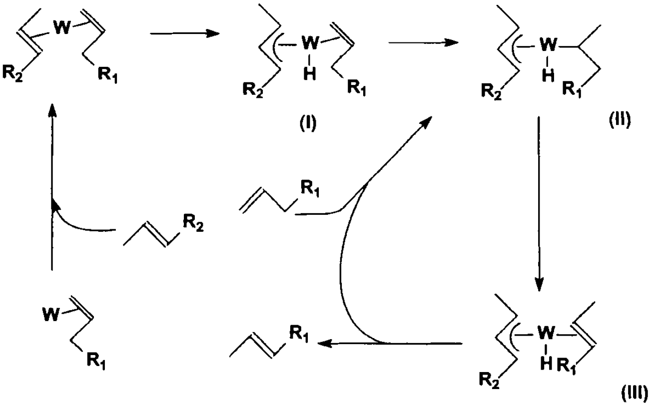
Trzesiak *et al.*[103] studied the isomerisation reaction of 1-hexene, 1,5-hexadiene and 1,7-octadiene catalysed by $HRh(CO)(PPh_3)_3$ and $HRh(PPh_3)_4$ at 40 °C. They found that 1-hexene underwent total conversion to 2-hexene in the presence of both catalysts in 100 min. The reaction products were *cis* and *trans*-2-hexene in comparable amounts. The isomerisation of the dienes was catalysed by the $HRh(CO)(PPh_3)_3$ complex only. The lack of catalytic activity of $HRh(PPh_3)_4$ may be explained by difficulties in 1,5-hexadiene coordination caused by steric hindrance. The catalytic activity of both catalysts may be enhanced by the addition of H_2.

From the results of their calculations as well as experimental studies, Trzesiak *et al.*[103] formulated the following general findings regarding the formation of active rhodium catalysts of alkene isomerisation reaction:

- Electron density on Rh and coordinated hydride ligands depend on donor-acceptor properties of the remaining coordinated ligands.
- Distribution of electron density on the alkene carbon atoms of the coordinated alkene depends on the way it is coordinated to the Rh-atom.
- The branched alkyl Rh-complexes are formed only for some modes of Rh-alkene species and are determined by the electron density distribution.
- Steric factors, i.e. size of coordinated ligands and shape of the carbon chain are decisive for which isomer of the alkene complex will be formed.

2.3.5 Isomerisation of alkenes in the presence of tungsten

In the presence of WCl_6/Et_3Al, the double bond migration of 1-alkenes was enhanced by the addition of 0.1 – 1.0 times the molar amount of internal alkenes including cyclooctene.[109] A mechanism in which a metal hydride formed by the abstraction of hydride from internal alkene was proposed (Scheme 2.3).



Scheme 2.3 Isomerisation of alkenes in the presence of tungsten catalytic system.[109]

The double bond of internal alkenes has higher electron density than the double bond of terminal alkenes, hence they prefer the formation of hydride complex such as (I) which transfers to a σ-alkyl complex (II) to give a thermodynamically more stable internal alkene.

2.3.6 Alkene isomerisation by acid/base catalysts

Double bond isomerisation of butene is described in more detail in relation to the acid-base properties of catalysts. The rate usually increase with either acid strength and acid amount or increasing base strength and base amount. An apparent correlation exists between selectivity and acidity and basicity of catalysts.[68]

a. Catalytic activity of soft acid complexes

The isomerisation of double bonds in alkenes is catalysed by a variety of catalysts. Solid acids like SiO_2-Al_2O_3 and strong protonic acids such as sulfuric acid isomerise alkenes through addition and abstraction of a proton. Isomerisation presumably involving a π-complex intermediate occurs when the catalysts are metal carbonyls. Three possible mechanisms have been discussed: hydride addition and elimination mechanism, π-allyl mechanism and the carbene mechanism.

The isomerisation of n-butenes over Ambelyst 15 in the range 0 – 25 °C was investigated. It was suggested that the *cis*- and *trans*-2-butene were formed via the same intermediate from 1-butene. The investigations of butene isomerisation over polymeric acid catalysts like strong acid macro reticular ion exchange resin showed that a carbonium ion preferentially decomposes into *trans*-2-butene or *cis*-2 butene.[69] During 1-pentene isomerisation, studied over HZSM-5, only double bond isomerisation was observed at low temperature, whereas at higher temperatures the total isomerisation equilibrium was obtained.[70]

It is generally accepted that the acid strength required for these reactions decreases in the order: cracking ≈ oligomerisation > skeletal isomerisation >> double bond isomerisation. However, when the acidity is too low, the activity of the catalyst is only sufficient for double bond isomerisation.

b. Catalytic activity of bases

Materials which possess basic sites stronger than H = 26 are called superbases. They consist of an alkali metal hydroxide and the alkali metal itself supported on γ-alumina, according to the general formula $(MOH)_x/M_y/\gamma\text{-}Al_2O_3$, (M = alkali metal, x = 5 – 15 wt%, y = 3 – 8 wt/%).

Gorzawski *et al.*[71] studied the catalytic activity of superbases in the double bond isomerisation of β-pinene (Table 2.3), the superbases are very efficient for the isomerisation of β-pinene to α-pinene:

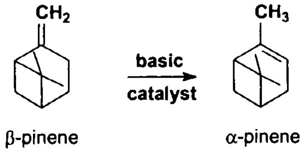


Table 2.3 Isomerisation β-pinene.[71]

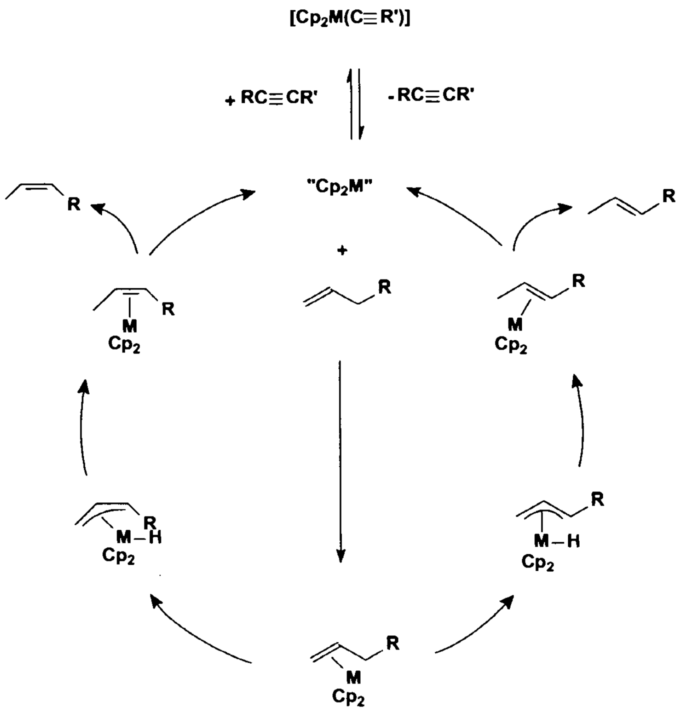
Catalyst	T/°C	Ratio β-pinene/ catalyst (g/g)	Conversion (%)		
			0.5 h	2 h	24 h
$Cs_xO/\gamma\text{-}Al_2O_3$	150	20	97	97	97
$Na/NaOH/\gamma\text{-}Al_2O_3$	150	20	97	97	98
Na/NaOH/MgO	150	20	14	51	97

2.3.7 Isomerisation of alkenes by metallocene complexes

Ohff *et al.*[27] achieved efficient isomerisation of aliphatic and cyclic alkenes by using well-defined metallocene alkyne complexes as catalysts (Scheme 2.4). Zirconocene complexes were found to be mainly inactive in isomerisation reactions of aliphatic alkenes whereas titanocene complexes (Table 2.4) isomerised 1-alkenes to internal alkenes under mild conditions.

The activity of the titanocene complexes is dependent on the nature of the alkyne ligand. A decreasing catalytic activity of the alkyne complexes is in the order: $[Cp_2Ti(Me_3SiC{\equiv}CSiMe_3]$ > $[Cp_2Ti(Me_3SiC{\equiv}CtBu]$ > $[Cp_2Ti(Me_3SiC{\equiv}CPh]$. These isomerisations were exclusive transformations of 1-alkenes to 2-alkenes producing preferentially the E-isomers, which is in accordance with the factors influencing the thermodynamic stability of alkenes.[107]

Special organotitanium catalysts effect regio- and stereoselective isomerisations. Nakamura *et al.*[72] discovered outstanding activities and selectivities for the permethylated titanocene. Titanocene dichloride with various activating reagents (e.g., Grignard compounds, lithium organyls, lithium aluminium hydride) has been employed to convert 1-alkenes into 2-alkenes with preferred *trans* geometry using the immobilized catalytic system and t-butylmagnesium bromide.



Scheme 2.4 Proposed π-allyl mechanism for the isomerisation of aliphatic alkenes by metallocene alkyne complexes.[27]

Table 2.4 Isomerisation of alkenes catalysed by (η^5-$C_5Me_5)_2TiCl_2$/Na naphthalide at 20 °C in 60 – 120 min (alkene/catalyst ratio 100:1).[72, 73]

Starting alkene	**Product**	**Yield [%]**	***Trans* isomer [%]**
1-Butene	2-Butene	> 99	99
3-Phenyl-1-propene	1-Phenyl-1-propene	> 99	99
4-methyl-1-pentene	4-Methyl-2-pentene	25	99
1,4-pentadiene	1,3-Pentadiene	99	> 99

The larger atomic radius of Zr which, in contrast to Ti, allows coupling reactions, could explain the difference in the activity between titanocene and zirconocene.

2.3.8 *In situ* generated ruthenium hydride species

Grubbs *et al.*[74] discovered that ruthenium carbene complexes, after mediating an alkene metathesis reaction, catalyse the hydrogenation of the C-C double bond formed in the metathesis step if the reaction vessel is pressurised with hydrogen. The reactivity of the ruthenium carbene in the hydrogenation reactions originates from a hydrogenolysis of the carbene complex to a ruthenium hydride species. A process that has been investigated mechanistically[75,76] described the conversion of allyl ethers to cyclic enol ethers using an alkene metathesis/double bond migration sequence. Ruthenium carbene complexes were activated to catalyze the double bond migration step by addition of hydride sources, such as NaH or $NaBH_4$. It has previously been noted that alkene isomerisation reactions may interfere with alkene metathesis reactions, normally as an undesired side reaction.[77,78]

Snapper *et al.*[19] published a paper that describes an alkene metathesis–double bond migration sequence that proceeds via ruthenium hydride intermediates. The metathesis catalyst was activated to promote the isomerisation step by treatment with molecular hydrogen diluted with nitrogen.

Fürstner[20] suggested that hydrides such as $Ru(PCy_3)_2Cl(CO)H$ might be responsible, at least in part, for the carbon-carbon double bond isomerisation sometimes seen as byproducts of metathesis reactions. Mol *et al.*[64] determined the efficiency of $Ru(PCy_3)_2Cl(CO)H$ in the double–bond isomerisation of 1-octene at various temperatures. The catalyst showed a high degree of selectivity toward the formation of 2-octene, even when high conversions were attained. A reaction of 88 000 mol equivalent of 1-octene with $Ru(PCy_3)_2Cl(CO)H$ at 100 °C gave 97 % conversion with 92 % selectivity for 2-octene after 3h.

At 120 °C, selectivity was compromised, decreasing to 56 % after 3h. The *cis:trans* ratio of the 2-octene formed was found to be independent of the reaction temperature. At higher temperatures more isomerisation was observed. The 3-octene formed was relatively high which imply that 2-octene does not easily decompose the catalyst. The decrease in selectivity over time is largely attributable to the decomposition of the active catalyst.[64]

When the 2nd generation Grubbs catalyst was treated with methanol in the presence of triethylamine, the initially dark-brown solution turned dark-orange.[79] The 2nd generation system was more active than the 1st generation system, and the reaction proceeded readily at lower temperatures than for the 1st generation. However ^{31}P and ^{1}H NMR spectroscopy revealed a complex reaction in which three different hydrides were produced. The major product, showing a doublet at -27.8 ppm in the ^{1}H NMR spectrum, was assigned as the expected mixed ligand hydride species $Ru(PCy_3)(H_2IMes)Cl(CO)H$. A second hydride showed δ = -24.2 ppm as a triplet, and was determined to be $Ru(PCy_3)_2Cl(CO)H$ by comparison with the authentic sample.[79]

The formation of $Ru(PCy_3)_2Cl(CO)H$ from 2nd generation Grubbs catalyst is noteworthy since it could only have originated from an unexpected H_2IMes ligand exchange with PCy_3. NHC ligands in ruthenium systems generally show stronger covalent bonds than phosphanes, and so tend to dissociate.[7]

$HRu(CO)Cl(PCy_3)(IMes)$ was characterised by both ^{1}H and ^{31}P NMR spectroscopy.[80] The ^{31}P NMR spectrum showed a singlet at δ 47.5, indicating the presence of the PCy_3 ligand. In the ^{1}H NMR spectrum, the methyl signals of the IMes ligand were observed at δ 2.17, 2.37, and 2.48, respectively, and the signal of the imidazolyl ring protons was observed at δ 6.23. The metal-hydride signal was observed at δ -24.83 as a doublet. The upfield chemical shift suggested a *cis* disposition of the hydride and CO.

2.3.9 Isomerisation by hydrido-ruthenium complexes

Ewing *et al.*[104] found that solutions of $[RuHCl(PPh_3)_3]$ in benzene catalyse the double bond migration in 1-pentene at 50 °C to give *cis*-2-pentene (60%) and *trans*-2-pentene (40 %):

The probable reaction path for this reaction is the dissociation of phosphine to give coordinative unsaturated species, which reacts with 1-pentene to form an alkene complex and then formation of a pentyl intermediate:

$$\text{1-pentene} + \text{H-Ru} \rightleftharpoons \text{Ru-(pentyl)} \rightleftharpoons \text{2-pentene} + \text{Ru-H}$$

Higher catalyst concentrations favoured the formation of the *cis*-alkene; as the catalyst concentration was lowered, more of the *trans*-isomer was formed. This change in selectivity, which is not accompanied by a change in mechanism, is attributed to a progressive decongestion of the catalytic site brought about by a gradual increase in the degree of dissociation of the catalyst by loss of PPh_3 ligands.[100]

The isomerisation of 1-pentene is also catalysed at 25 °C by toluene solutions of [$RuH_4(PPh_3)_3$] and [$RuH_2(N_2)(PPh_3)_3$].[105] The reaction occurs in two stages: it proceeds very rapidly initially, and then the rate quickly declines. The reaction rates both initially and in the second stage is inhibited by nitrogen, and this is attributed to the ability of N_2 to compete with the alkene coordination to the ruthenium.

The carboxylato complex [$RuH(O_2CCF_3)(PPh_3)_3$] is also a catalyst, although a poor one, for the isomerisation of 1-hexene.

2.3.10 Alkene Isomerisation by metal chlorides

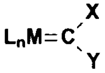
Simple $RuCl_3$ hydrate was reported in the 1960s to be an effective catalyst for ring opening metathesis of highly strained cyclic alkenes such as norbonene, but it does not catalyse metathesis of acyclic alkenes.[1] $RuCl_3$ is one of the starting materials in the synthesis of the Grubbs catalysts, and those reported by Hermann and Fürstner *et al.*[38]

Nubel and Hunt[81] carried the metathesis reactions of 1-alkenes by combining the alkene with $RuCl_3$ $3H_2O/RuBr_3$ dissolved in alcohol, phosphine and an alkyne at temperatures ranging from 60 – 90 °C. The only side reaction observed in the self-metathesis of 1-octene was a small amount of isomerisation of 1-octene to internal octenes, GC analysis indicated that less than 5 % of 1-octene isomerised after 2h. The dominant reaction obtained with little or no alkyne present was isomerisation of 1-octene to internal octenes, not metathesis. In the presence of an alkyne, isomerisation tended to increase relative to metathesis with increasing reaction time and with increasing reaction temperature.

A solution of $RuCl_3$ in ethanol catalyses the isomerisation of 1-hexene, an induction period of 1 h was observed due to reduction of Ru(III) to Ru(II) to provide active species for alkene isomerisation.[106]

2.4 Metal carbenes in Alkene Isomerisation

The term metal carbene complexes refers to the compounds of the general type[28]

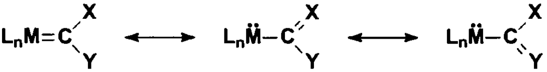


$$L_nM=C\begin{matrix}X\\Y\end{matrix}$$

in which a carbene, =CXY, is coordinated to a transition metal atom, M, and L_n represents various other coordinated ligands. The carbene ligand is usually bound terminally, but is also found as a bridging moiety. Complexes are usually neutral, but cationic species are also known and anionic ones have been postulated as reaction intermediates. The carbene may be considered as a "soft" ligand, being normally found in complexes in which the metal is in a low oxidation state. Although the carbene complexes were evidently prepared in 1915, they were not recognized until the synthesis of $(OC)_5W{=}C(OMe)Ph$, the first carbene complex to be formulated.[28]

Two types of isomerisations are known for carbene complexes, those which involve rearrangement of the ligands in the coordination sphere of the metal, and those in which two rotamers are interconverted by rearrangement within the aminocarbene ligand.[28] For the square planar Pd(II) and Pt(II) carbene complexes, it has been shown that the *cis* isomers are thermodynamically the more stable. Another method of isomerisation involves heating in refluxing alcohol, the reactivity sequences with respect to ease of isomerisations of such *trans* complexes are Pd > Pt. The *trans* complexes owe their preparation to kinetic rather than thermodynamic factors.[28]

Carbene complexes contain transition metal-stabilized carbenes which can be divided into two classes, i.e., the Fischer type and the Schrock type named after their discoverers.[29] Fischer type compounds contain a metal from Groups VI to VIII. It is present in a low oxidation state, which is stabilized by a series of other ligands with pronounced acceptor properties. The carbene carbon in this compound is considered to be sp^2-hybridised; the bonding is therefore described by the three resonance structures:

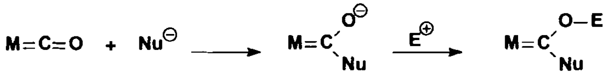


Complexes of the Schrock type are characterised by an early transition metal carbene complex.

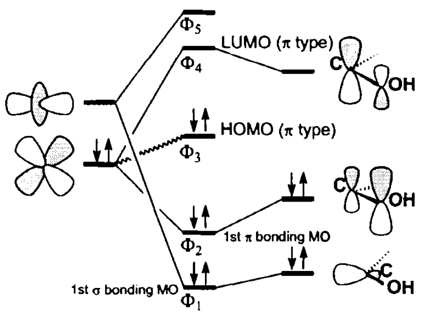
2.4.1 Fischer carbenes

Electrophilic carbenes are called Fischer carbenes in honour of E.O. Fischer, who reported the first example in 1964 and later won a Nobel Prize for his pioneering work on ferrocene with Wilkinson.[30] The discovery of the carbene complexes was a major breakthrough in organometallic chemistry. These carbene complexes are implicated in many crucial processes, such as alkene metathesis and polymerization.

Fischer carbenes are typically found on electron-rich, low oxidation state metal complexes (mid to late transition metals) containing π-acceptor ligands. The presence of the heteroatom on the α carbon allows us to draw a resonance structure that is not possible for an unsubstituted (Schrock type) alkylidene:



If we look at this from a molecular/atomic orbital perspective (Scheme 2.5), one lone pair is donated from the singlet carbene to an empty d-orbital on the metal, and a lone pair is back donated from a filled metal orbital into a vacant p_z-orbital on carbon. There is competition for this vacant orbital by the lone pair(s) on the heteroatom, consistent with our second resonance structure. Overall, the bonding closely resembles that of carbon monoxide. Therefore, carbene ligands are usually thought of as neutral species, unlike dianionic Schrock alkylidenes (which usually lack electrons for back-donation).[30]



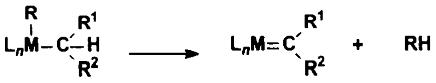
Scheme 2.5 Molecular orbital diagram which shows the metal orbitals which are involved in bonding to carbene.[30]

As above, the σ-type MO's give a pattern typical of a classical single bond. However, the π-system is comprised of three MO's in an allyl-like arrangement: one bonding (Φ_2), one non-bonding (Φ_3), and one antibonding (Φ_4). The antibonding LUMO of the carbonic system is localized on the carbon, whilst the HOMO resides mainly on the metal.

Common synthetic methods of Fischer carbenes include nucleophilic attack of metal carbonyls, alkylation of an acyl complex, tautomerization of terminal alkyne complexes to acetylides followed by the transfer of the hydride to the β-carbon and from activated alkenes.

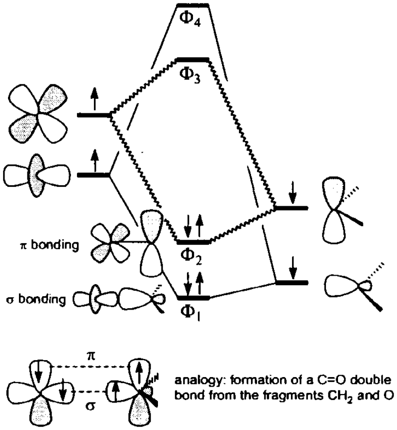
2.4.2 Schrock carbenes

The Schrock complexes were discovered 10 years after the Fischer carbenes. They have carbon substituents which confer nucleophilic properties. Complexes of the Schrock-type are characterised by an early *trans*ition metal:



$$L_nM(R)-CHR^1R^2 \longrightarrow L_nM{=}CR^1R^2 + RH$$

Their bonding may be interpreted as the interaction of a triplet carbene and a triplet ML_n fragment, as for the case of ethylene.[30]



Scheme 2.6 Molecular orbital diagram which shows the metal orbitals which are involved in bonding to carbene.[30]

From Scheme 2.6 it can be concluded that two MO's are formed, of which the highest, the HOMO, is localized mainly upon the carbon; consequently the LUMO is localized on the metal, which is precisely the reverse of the situation in Fischer carbenes. During investigations of intermolecular metathesis polymer degradation using a stable molybdenum Schrock carbene complex, $Mo(=CHMe_2Ph)(=NAr^iPr_2)[OCMe(CF_3)_2]_2$, alkene isomerisation was found as a side reaction.[31]

2.4.3 Ruthenium carbenes

The Grubbs metathesis catalysts $RuCl_2(=CHPh)(PCy_3)_2$ and $[RuCl_2(=CHPh)(H_2IMes)(PCy_3)]$ has become an increasingly useful tool for organic transformation.[36] Single–component tandem catalysis in the presence of the above catalysts has so far included metathesis followed by hydrogenation, dehydrogenation, and most recently isomerisation.[19] Little effort has been made to identify the active species responsible for the secondary reactions although various hydride species are thought to be involved.

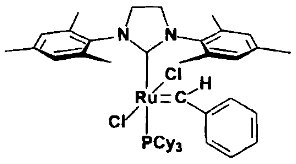
Natta *et al.*[1] first published the use of ruthenium in ROMP in 1964. Since these first published reports, many different catalysts were developed. However, it was not until 1992 that the Grubbs group published the synthesis of a well-defined Ruthenium catalyst. These complexes contain a late transition metal in a low oxidation state.[15] Unlike the early metathesis catalytic systems these catalysts do not require Lewis acid cocatalysts or promoters.[37]

The Ruthenium carbene complex, $RuCl_2(=CHPh)(PCy_3)_2$, developed by Grubbs *et al.*[38] is moderately sensitive to air and moisture and show significant tolerance to functional groups. The well balanced electronic and coordinative unsaturation of their Ru(II) center account for the high performance and the excellent tolerance of these complexes toward an array of functional groups,[39] unlike the early systems (i.e. $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$) which were only effective in the ROMP of highly strained alkenes and displayed rather limited thermal stability.[40] The incorporation of more bulky and electron-donating phosphines, i.e. $RuCl_2(=CHPh)(PCy_3)_2$, afforded catalysts that are active in wide variety of RCM, CM, and ROMP applications.[15] However they are limited to alkene substrates that are not sterically hindered.

The influence of the ligands on the catalytic activity of 5-coordinate, 16-electron ruthenium complexes has been studied. The effect of the Cl electron-withdrawing group, is counter-balanced by electron-donating 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.[45] The nature of the carbene moiety has been shown to influence not only the initiation but also the propagation of the catalytic reaction.[38] 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.[35]

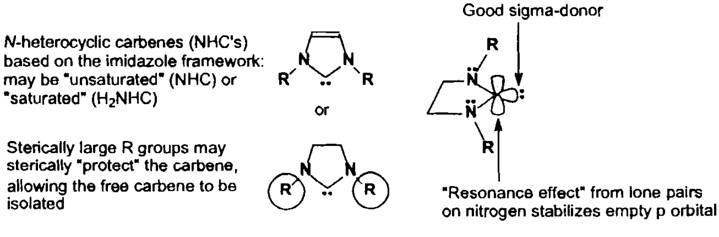
A recent advance in the Ruthenium catalysts has been the introduction of N-heterocyclic carbene (NHC) ligands:



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 by making it easier to push the *trans*-PR_3 ligand off the metal. This correlates well with a dissociative mechanism.

It was found in 1994 that heterocyclic carbenes derived from imidazole and related N-heterocyclic compounds are similar to electron rich phosphines in many respects. They form stable metal complexes with metals across the periodic table and they form efficient catalysts for C-C bond forming reactions.[2,46]

NHC's are σ-donating ligands and are more comparable to P-, N- or O-donating ligands rather than to classical Fischer or Schrock carbenes (Scheme 2.7). In contrast to the "conventional" carbene ligands, the metal-carbon bond is much longer and is chemically and thermally more inert towards cleavage. In striking contrast to many other heteroatom donating ligands, NHC's show very high dissociation energy.[47] They are also very poor π-acceptor ligands that show little tendency to dissociate from the metal center. Since they can be easily endowed with sterically demanding substituents on their N-atoms, they are able to stabilize the catalytically relevant intermediates by electronic and steric means against uni- as well as bimolecular decomposition pathways.[20]



Scheme 2.7 N-heterocyclic Grubbs metal carbenes.

This ruthenium catalyst, efficiently mediates the isomerisation of β,γ-unsaturated ethers and amines to the corresponding vinyl ethers and enamines.[48] This complex is the most efficient ruthenium metathesis catalyst to date, displaying substantial enhancements in both activity and versatility when compared to its predecessors.[36,41,49-51] It exhibits the ability to metathesize alkenes that are essentially unreactive when using either Grubbs' 1st generation or Schrock's molybdenum catalysts.[17,38]

The initial problem facing the development of NHC-coordinated catalysts is the known air and water sensitivity of free NHC's.[52] The isomerisation may occur analogously to that of related 16e$^-$ Ru complexes, by hydrometallation followed by β-elimination. The active catalyst is probably the corresponding hydrido derivatives formed *in situ* under the reaction conditions.

Nucleophilic carbene ligands imidazol-2-ylidenes are neutral, two electron donor ligands with negligible π-back-bonding tendency. Recently, Grubbs and co-workers[53] have presented an extensive *in situ* NMR study in which it was concluded that the origin of the greatly increased activity in the second-generation catalysts derived from a more favorable branching ratio for the competition in which the active carbene complex, $RuCl_2(=CHR)(PCy_3)L$ ($L = PCy_3$ or NHC), partitions between entry into the catalytic cycle and rebinding of a phosphine.[54-56]

2.4.4 Isomerisation of alkenes with Grubbs metal carbenes

Lehmann *et al.*[16] found that exposure of a mixture of 1-octene to second generation Grubbs catalyst resulted in a mixture of products. Similar mixtures were obtained whether the catalyst had been purified by column chromatography or not, which suggested that alkene isomerisation is promoted by the catalyst itself or a species formed *in situ* during a metathesis reaction. Simultaneous alkene isomerisation and metathesis easily describe the formation of such a product mixture of 1-octene.

The ^1H and ^{13}C NMR spectra of the product mixtures were also consistent with a mixture of straight chain alkenes. Both terminal and internal alkenes are present in a ratio of 5.6:100. The levels of isomerisation products were tracked as a function of time. Alkene isomerisation occurred rapidly at 60 °C in a time similar to alkene metathesis. The amount of the expected C_{14} products was high in the initial stages of the reaction relative to the C_{12} and C_{13} alkenes, but the relative amounts of these isomerised products increased at longer reaction times. Only small amounts of alkenes greater than 14 carbons were produced, which indicated that alkene substituents consisting of more than six carbons were relatively non-abundant in the reaction mixture. This is consistent with the alkene isomerisation occurring concurrently with metathesis rather than metathesis occurring before isomerisation. By actively removing the gaseous byproducts during the reaction, the amount of isomerisation products relative to C_{14} alkene is modestly reduced. This may be that the rapid elimination of ethylene reduces the occurrence of the reverse metathesis reaction of product alkene and ethylene to produce the starting alkene.

2-Octene reacts in an analogous manner to 1-octene, producing a complex mixture of isomerisation and metathesis products, although the rate of isomerisation for 2-octene is slower than for 1-octene. This suggests that the methylidene complex is not solely responsible for the isomerisation side reaction. However, just one alkene isomerisation event in the reaction of second generation Grubbs catalyst with 2-octene could provide 1-octene, which could then form a methylidene complex by metathesis.

To clarify this issue, the reaction of 7-tetradecene, the expected product of self-metathesis of 1-octene, was explored. The double bond of this alkene is far from the terminal position, so many isomerisation events would have to occur to obtain the terminal alkene. Reaction of 7-tetradecene with the 2nd generation Grubbs catalyst results in symmetrical distribution of GC-peaks corresponding to C_9 – C_{21} alkenes, arising from isomerisation occurring concurrently with metathesis. Analysis of the mixture indicated that no terminal or branched alkenes were formed. Only the *cis-* and *trans-*carbon signals were present in a ratio of 3:20 based on integration.[16]

Significant isomerisation occurs for some intermolecular metathesis reaction with 2nd generation Grubbs at temperatures of 50 – 60 °C in neat alkene. The extent of isomerisation is greatly reduced but not totally suppressed at room temperature to 30° C, both internal and external alkenes undergo isomerisation, which excludes the possibility that the methylidene complex is solely responsible for the observed alkene isomerisation.[16]

Huang *et al.*[62] monitored toluene solutions of catalysts of the Grubbs type (benzylidene and vinyl-alkylidene) using NMR. When subjected to elevated temperatures, signs of decomposition afforded a straightforward gauge of the thermal stability of the carbene complexes. The initial step of thermal decomposition is presumably the elimination of one phosphine ligand from the metal center. Since the IMes-ligand is the stronger binder to the metal center and provides better steric protection than the phosphine ligands, the lifetime of the resulting 14-electron intermediate and therefore the thermal stability of the mixed phosphine/ carbene compounds of 2nd generation Grubbs catalyst should be enhanced compared to that of the 1st generation. Ruthenium alkylidenes of the type $RuCl_2(=CHR)(PCy_3)L$ display characteristic chemical shifts in their NMR spectra that provide valuable information for elucidating solution state geometries of the complexes (Table 2.5).[63]

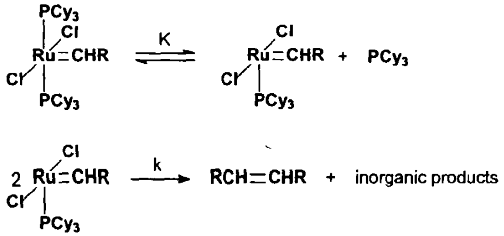
Table 2.5 Selected ^{1}H, ^{13}C, and ^{31}P NMR δ values of $RuCl_2(=CHR)(PCy_3)L$.

Complex	^{1}H NMR Ru=CH	^{13}C NMR Ru=C	^{31}P NMR
$RuCl_2(=CHPh)(PCy_3)_2$	20.02	294.72	36.6
$RuCl_2(=CHEt)(PCy_3)_2$	19.12	322.59	36.4
$RuCl_2(=CHOEt)(PCy_3)_2$	14.49	276.86	37.4
$RuCl_2(=CHSEt)(PCy_3)_2$	17.67	281.60	32.9
$RuCl_2(=CHPh)(PCy_3)(IMes)$	19.91	295.26	34.9
$RuCl_2(=CHOEt)(PCy_3)(IMes)$	13.81	277.50	35.0
$RuCl_2(=CHPh)(PCy_3)(H_2IMes)$	19.16	294.24	31.4

Thermolytic decomposition pathways were studied for several ruthenium carbene-based alkene metathesis catalysts.[35] Although the benzylidene complex $RuCl_2(=CHPh)(PCy_3)_2$ is used to initiate most metathesis reactions, the propagating species in RCM,[36] is usually either an alkylidene, $RuCl_2(=CHR)(PCy_3)_2$ with R from the alkene substrate, or the methylidene, $RuCl_2(=CH_2)(PCy_3)_2$, since the phenyl of the starting carbene is lost in the first turnover. To gain understanding of the decomposition pathway the NMR spectra of these reaction mixtures were studied.

^{1}H NMR spectrum of the decomposition of propylidene showed the initial quantitative formation of *trans*-3-hexene while there was still a large amount of intact carbene present. Over time, additional alkene peaks appeared in the spectrum. These were accompanied by the formation of a new quartet carbene signal (δ 19.66 ppm) next to the propylidene triplet at δ 19.60 ppm. The presence of minute signals at δ -7 ppm suggested that some of the decomposition products were ruthenium hydrides. These provide a possible explanation for the formation of new alkenes and the new carbene. The hydrides could isomerise the dimerised carbene fragments, 3-hexene to 2-hexene and possibly other alkenes. Metathesis of 2-hexenes could form ethylidene, which accounts for the quartet signal.[35]

The ^{31}P NMR spectrum of the propylidene decomposition reaction mixture showed that the predominant product was free PCy_3, but a number of other small unidentifiable phosphine signals also grew in over the course of the decomposition.[35] The above observations are consistent with a decomposition mechanism involving dissociation of a phosphine followed by coupling of the two monophosphine species (Scheme 2.8). The build-up of generated free phosphine as the decomposition progresses is expected to inhibit the formation of the monophosphine species and retard the rate of decomposition.



Scheme 2.8 Proposed pathway for alkylidene decomposition.

Assuming a pre-equilibrium in the first step and the formation of n moles of free phosphine for every mole of decomposed $RuCl_2(=CHR)(PCy_3)_2$, the following rate equation was deduced for alkylidene decomposition:

$$\frac{d[\mathrm{conc}]_t}{dt} = \frac{Kk}{n^2}\frac{[\mathrm{conc}]_t^2}{\left([\mathrm{conc}]_0 - [\mathrm{conc}]_t\right)^2}$$

$$\begin{aligned} f(\mathrm{conc}) &= 2([\mathrm{conc}]_0)\mathrm{Ln}\frac{[\mathrm{conc}]_n}{[\mathrm{conc}]_t} + \frac{\left([\mathrm{conc}]_t - [\mathrm{conc}]_0\right)\left([\mathrm{conc}]_t + [\mathrm{conc}]_0\right)}{[\mathrm{conc}]_t} \\ &= \left(\frac{Kk}{n^2}\right)t \end{aligned}$$

Where $[\mathrm{conc}]_t$ is the concentration of the alkylidene at time t, $[\mathrm{conc}]_0$ is the initial alkylidene concentration, K is the equilibrium constant for the first step and k is the rate constant for the second step (Scheme 2.8). Intergration of the first equation produced the second equation.

When the catalyst $RuCl_2(=CHPh)(PCy_3)_2$ was reacted with an excess of methanol in toluene at 70 °C for 2 days, the initially purple red solution gradually became clear dark orange. The progress of the reaction was monitored by ^{31}P NMR which showed the slow disappearance of the signal at δ 37.3 ppm from $RuCl_2(=CHR)(PCy_3)_2$ concomitant with the emergence of a new peak at δ 47.4 ppm. Similarly, in the ^1H NMR, the benzylidene resonance from $RuCl_2(=CHR)$ $(PCy_3)_2$ at δ 20.6 ppm was gradually replaced with hydride signal at δ -24.3 ppm. Whereas ethanol and propanol were found to readily generate the hydride, 2-propanol and water were found to be ineffective.[64]

2.5 Factors influencing the isomerisation behaviour

2.5.1 Catalytic activity and selectivity of $RuX_2(=CHPh)L_2$

The activity of $RuX_2(=CHPh)L_2$ is highly dependent on the identity of X- and L-type ligands. Whereas catalyst activity increases with larger and more electron-donating phosphines, it decreases with larger and more electron-donating halides. One of the contributions of the phosphine ligand is σ-donation to the metal center, which promotes formation of the mono phosphine alkene complex by facilitating phosphine dissociation and stabilizing the vacant *trans* site in the $16e^-$ intermediate. σ-Donation also helps to stabilize the $14e^-$ metallacyclobutane intermediate.[22]

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 2.6) than PCy_3 result in unstable complexes.[22]

2.5.2 Steric effects in phosphine ligands

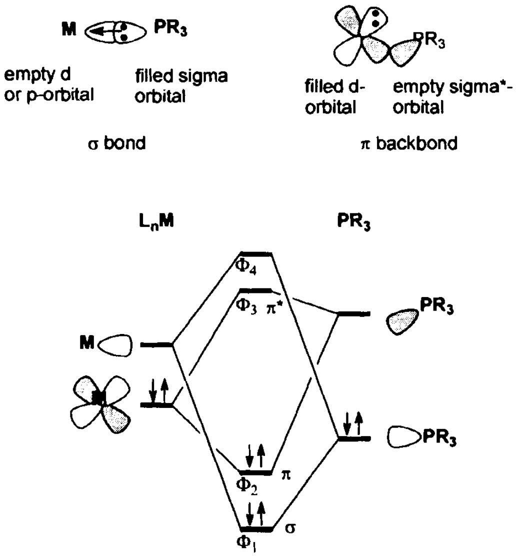
The phosphine ligands can be easily controlled. This ability to control the bulk of the ligand (Table 2.6) permits the fine-tuning of the reactivity of the metal complex, and this makes them excellent ligands for transition metals.

Table 2.6 Cone angles for some common phosphine ligands.[23]

Phosphine Ligand	Cone Angle
PH_3	87°
PF_3	104°
$PF(OMe)_3$	107°
PMe_3	118°
PMePh	122°
PEt_3	132°
PPh_3	145°
PCy_3	170°
$P(t\text{-}Bu)_3$	182°
$P(mesityl)_3$	212°

2.5.3 Electronic Effects

The bonding in phosphine ligands can be subdivided into two components. The primary component is σ donation of the phosphine lone pair to an empty orbital on the metal. The second component is back-donation from a filled metal orbital to an empty orbital on the phosphine ligand (Scheme 2.9). This empty phosphorus orbital has been described as being either a d-orbital or an antibonding σ-orbital.[23]



Scheme 2.9 Molecular orbital diagram showing the bonding and antibonding tendency between the metal and the phosphine ligand.

As electronegative groups are placed on the phosphorus atom, the σ-donating capacity of the phosphine ligand tends to decrease. At the same time, the energy of the π-acceptor on phosphorus is lowered in energy, providing an increase in backbonding ability. Therefore, phosphine ligands can exhibit a range of σ-donor and π-acceptor capabilities, and the electronic properties of a metal center can be tuned by the substitution of electronically but different isoteric phosphines.[23]

In contrast to the trend of the phosphines, the halide ligands correlate with the decreasing activity as they become larger and more strongly electron-donating, in the order Cl, Br >> I. Since the incoming alkene may initially bind *trans* to a halide, a more electron-donating halide should weaken the ruthenium-alkene bond and disfavour alkene coordination. These small changes in the steric and electronic character of the X- and L-type ligands combine to influence alkene binding, phosphine dissociation, and the stability of the intermediates, which results in large variations of catalyst activity.[22]

Systematic investigations on the factors governing the catalytic activity of ruthenium carbenes have been carried out. From these studies it can be deduced that that the electron-donating phosphines with large cone angles lead to particularly active catalysts [PPh_3 << $P(^iPr)_2Ph$ < PCy_2Ph < $P(^iPr)_3$ < PCy_3]. In contrast, the following order of increasing activity was determined for the anionic ligand I < Br < Cl, i.e. the smaller and more electron-withdrawing chloride leads to the most active species.[39,57]

The overall activity also depends on catalyst initiation and thus on the nature of the alkylidene moiety. In general, alkyl-substituted alkylidenes display more efficient initiation than the methylidene complex. The benzylidene seems to be the intermediate case, the phenyl group is somewhat electron withdrawing, but its size may assist phosphine dissociation.[22]

The catalyst lifetime is another important factor in its overall activity. The kinetics of the thermal decomposition pathways of various catalysts reveal that substituted alkylidene complexes decompose by a different mechanism than the methylidene complex, which is the only propagating species observed during RCM. For substituted alkylidenes, observations are consistent with a bimolecular decomposition mechanism involving phosphine dissociation followed by coupling monophosphine species. In contrast, the methylidene complex decomposes through a unimolecular pathway that is independent of concentration. In this way, the relative stabilities of the initiating and propagating species directly influence catalyst activity.[22]

Optimum conditions for the metathesis of internal alkenes in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ were found in dichloromethane and dichloroethane solutions at temperatures of 20 – 70 °C. The reaction proceeded with high selectivity to primary metathesis products, which were formed as *trans/cis*-mixtures. The final *trans/cis*-ratios corresponds to the thermodynamic equilibrium values, regardless of the configuration of the substrate.[21]

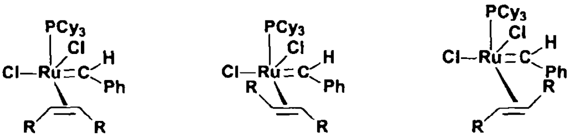
2.5.4 Relative reaction rates

Ulman and Grubbs[58] studied the metathesis of terminal alkenes having different steric bulk and different geometries as well as electronically different *para*-substituted styrenes with the ruthenium based initiator $RuCl_2(=CHR)(PCy_3)_2$. They found that bulkier alkenes were found to react slower, and that *trans*-internal alkenes were slower than their *cis* counterparts. The kinetic product of all reactions was found to be the alkylidene rather than the methylidene. These effects were then used to explain the mechanism of ring-opening cross metathesis.

2.5.5 Relative steric effects

The observed relative activity of the carbenes was rationalized as a function of their electronic and steric properties. The most active carbenes are the alkylidenes. Their electron-donating properties and their relative size help to dissociate the phosphine and speed up metathesis. The least active carbene is the methylidene, which lacks both the size and the electron-donating ability of the alkylidenes. The benzylidene is an intermediate case where the resonance of the phenyl ring is somewhat electron-withdrawing while the size of the ring helps to dissociate a phosphine.[58]

When the relative rates of *cis*- and *trans*-alkenes were examined, the benzylidene reacted approximately twice as fast with *cis*-3-hexene as with *trans*-3-hexene. This can be explained by considering the binding of the alkene to the complex (Scheme 2.10). When the *cis*-alkene binds to the metal, the substituents can point away from the bulky phosphine. The *trans* alkene can bind either **2** or as **3**; in either case there is an adverse steric interaction with the phosphine, which results in a slower rate of initial alkene binding.[58]



1 **2** **3**

Scheme 2.10 Alkene complex formation affecting the rates of metathesis of *cis*- and *trans*-alkenes.

2.6 Mechanisms of alkene isomerisation

Alkene isomerisation catalysed by transition metal complexes has been interpreted in many ways. Different mechanisms are reported for the isomerisation process connected with the use of different catalytic systems or reaction conditions. The most favoured hypothesis involves the reaction of metal hydride with an alkene, giving an π-alkene metal complex, which by subsequent addition/elimination steps makes the alkene isomerisation possible. This mechanism involves the formation and decomposition of an alkyl metal complex.[24]

A key step in the isomerisation of alkenes under hydride free conditions is believed to be the oxidative addition of a *trans*ition metal complex to an allylic carbon-hydrogen bond of alkene substrate and formation of a π-allyl hydride intermediate. Reductive elimination of the alkene from this intermediate can then result in isomerisation if the hydrogen moves to C_1 instead of returning to C_3 (in the case of terminal alkene).[25-27] A different mechanism may be suggested when the starting catalyst is not a metal hydride or when a hydride cannot be formed in a preliminary step of the reaction. The formation of a π-alkene metal complex is suggested, followed by the formation of a π-allyl system coordinated to a metal hydride complex.

The distinction between these two major mechanisms is usually made on the basis of deuterium-labelling studies. Other mechanisms such as radical abstraction of hydrogen from allylic sites may be significant but are less well characterised.

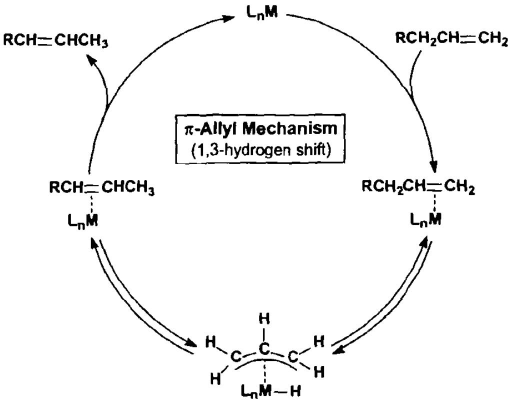
2.6.1 The π-allyl mechanism

In the less common π-allyl metal mechanism, 1,3-hydrogen shift (Scheme 2.11), a free alkene coordinates to the metal, followed by oxidative addition of the activated allylic C-H bond, yielding a hydride. Mechanistic studies have shown that ruthenium-assisted isomerisations proceed through an intermolecular 1,3-migration of the allylic-C-H, analogous to a π-allyl metal-type mechanism. Transition metals favoring π-allyl complex formation are normally very active in alkene isomerisation. Good examples are Fe, Ni, Rh and Pd.[2]

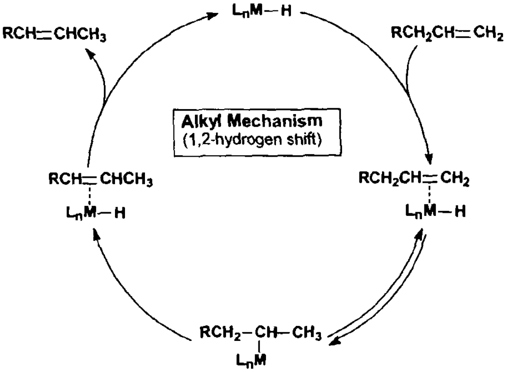
The key feature of the allyl mechanism is the aliphatic β-C-H activation, a step which includes the three-carbon arrangement in π-bonding to the metal. The metal-attached hydride has thus two positions to which it may be *trans*ferred (α and γ), until the thermodynamic equilibrium is established.

2.6.2 The alkyl mechanism

The alkyl mechanism, 1,2-hydrogen shift, is favoured when the catalytic species are capable of metal hydride formation (Scheme 2.12). Depending on the metal and the nature of the ligand (especially steric bulk), the hydride migration or insertion step may follow a Markovnikov or an anti-Markovnikov pathway.[2] Typical catalysts are nickel hydrides and rhodium hydrides such as $HRhCl[P(C_6H_5)_3]_3$ and $[HNi\{P(C_6H_5)_3\}_3]^+$



Scheme 2.11 The π–allyl mechanism.



Scheme 2.12 The alkyl mechanism.

2.7 Alkene Metathesis

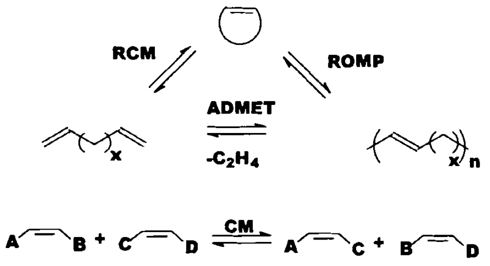
Since alkene isomerisation occurs as a side reaction in many metathesis reactions, a few things about the metathesis of alkenes related to isomerisation will be mentioned.

Catalysed alkene metathesis reactions represent one of the most important synthetic processes discovered in the past four decades. It is regarded as a catalytic reaction in which alkenes are converted into new products via the rupture and reformation of carbon-carbon double bonds:

$$2CH_3HC{=}CH_2 \rightleftharpoons H_2C{=}CH_2 + CH_3HC{=}CHCH_3$$

If one of the product alkenes is volatile (such as ethylene), or easily removed, then the reaction shown above can be driven completely to the right. Likewise, using a high pressure of ethylene, internal alkenes can be converted to terminal alkenes.[23] In the early years the majority of alkene metathesis reactions were carried out with ill-defined multi-component systems containing an early transition metal oxide and a main group metal cocatalyst.[1]

Both terminal and internal alkenes can undergo metathesis and 1-alkenes yields ethylene and a symmetrical internal alkene. The reverse reaction, cross-metathesis with ethylene, makes it possible to prepare linear 1-alkenes from internal alkenes. Synthetically useful reactions (Scheme 2.13) includes ring-opening metathesis polymerisation (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis polymerisation (ADMET), ring-opening metathesis (ROM) and cross-metathesis (CM) have been catalysed by early transition alkylidenes which were usually generated via a α-hydrogen abstraction routes, alkylidene transfer from phosphoranes or the ring-opening of cyclopropenes.[38]



Scheme 2.13 A variety of alkene metathesis reactions.

The catalytic systems used for alkene metathesis involve almost invariably transition metal compounds. First generation catalytic systems often require the presence of a cocatalyst, and sometimes a third compound (promoter) must be added to the reaction mixture. The most common systems are based on Mo, W, Re, Os and Ir. $EtAlCl_2$, R_3Al, and R_4Sn are typical cocatalysts, while compounds containing oxygen can be used as promoters.

The first generation of metathesis catalysts exhibits the characteristics of mixed Ziegler catalysts. They show high activity at the expense of a poor compatibility with polar functional groups, due to a strongly Lewis acidic and alkylating character. The catalyst employed in alkene metathesis can also catalyse other types of reaction, including isomerisation, oligomerisation, etc. The discovery of metal alkylidene complexes has led to the development of a new generation of high performance, stable and very tolerant catalysts.

The renewed interest in alkene metathesis can be largely attributed to the introduction of the well-defined, functional-group tolerant homogeneous catalyst $RuCl_2(=CHPh)(PCy_3)_2$ developed by Grubbs and coworkers[30] together with the molybdenum-based catalysts developed by Schrock.[82-85] The ruthenium carbene complexes $RuCl_2(=CHR')PR_3$ were used to carry out metathesis of a number of different alkenes such as strained and low strain cyclic alkenes, exocyclic alkenes, and straight chain alkenes.[86]

Table 2.7 Functional group tolerance of early and late transition metal catalysts.

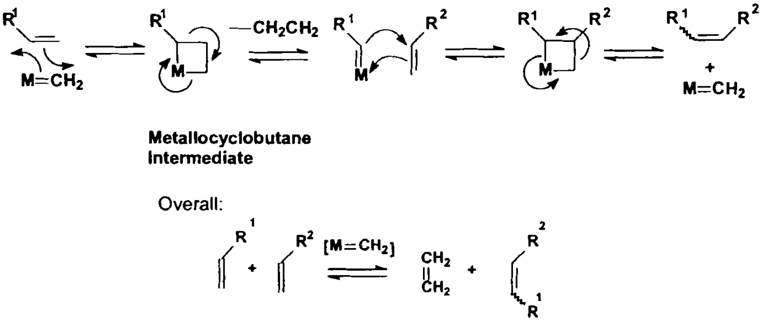
Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	Alkenes
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	Alkenes	Aldehydes
Esters, Amides	Alkenes	Ketones	Ketones
Alkenes	Esters, Amides	Esters, Amides	Esters, Amides

In any catalyst system, functional groups in the substrate or solvent can interfere with catalytic activity in several ways. They may bind competitively to the active center and deactivate the catalyst, or they may react directly with the metal center and destroy the active species. The advent of single-component catalysts allowed the relationships between structure and reactivity to be more clearly defined. These catalysts were observed to react more selectively with alkenes as the metal centers were varied from left to right and bottom to top on the periodic table. This trend is illustrated in Table 2.7

Although the early transition metals showed high activity, they react readily with polar functional groups such as carbonyls.[77] Conversely, the late transition metals showed higher reactivity toward alkenes, but the overall catalyst activity was severely depressed relative to the titanium and molybdenum systems.

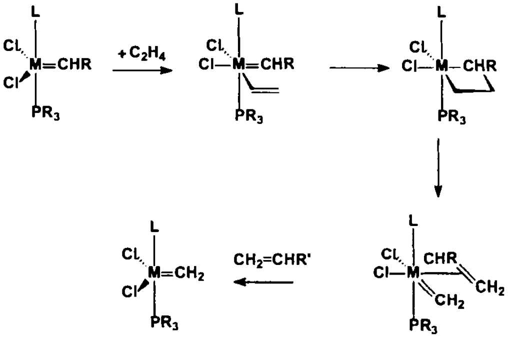
2.7.1 Reaction mechanisms

It is universally accepted that alkene metathesis reaction proceeds via the metal carbene chain mechanism, first proposed by Herisson and Chauvin in 1971 (Scheme 2.14).[89] The generally accepted Chauvin mechanism of metathesis reactions consists of a series of formal [2+2] cycloadditions and cycloreversions. The propagation reaction involves a transition metal carbene as the active species with a vacant coordination site at the transition metal. The alkene coordinates at this vacant site, and subsequently a metallacyclobutane intermediate is formed. The metallacycle is unstable and cleaves to form a new metal carbene complex and a new alkene.

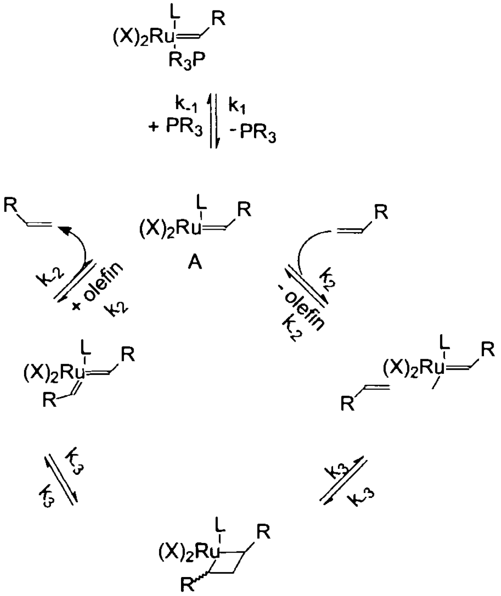


Scheme 2.14 The general reaction pathway for alkene metathesis: the Chauvin mechanism.

Since all individual steps of the catalytic cycle are reversible, an equilibrium mixture of alkenes is obtained.[44] The mechanism of the Grubbs catalyst has been under discussion and was not fully understood. However, in a recent publication by Grubbs *et al.*,[90] attempts were made in elucidating the mechanism of the first generation catalysts. Since the Grubbs catalyst is a 16e$^-$ complex, two different mechanisms were proposed: an associative mechanism (Scheme 2.15) and a dissociative mechanism (Scheme 2.16).



Scheme 2.15 The associative mechanism.



Scheme 2.16 The dissociative mechanism.

The associative mechanism was believed to be the actual mechanism due to the fact that after the alkene coordinates to the metal a stable 18e$^-$ complex is formed. In the dissociative mechanism the loss of the trialkylphosphine ligand give the very unstable 14e$^-$ species. The dissociative mechanism also describes the increased reactivity of the Grubbs second generation very well. Using density functional calculations the associative and dissociative pathways for alkene metathesis reactions involving ethene and model ruthenium-based catalysts were identified.[44]

Subsequent kinetic and mechanistic studies showed that the dissociative mechanism was the operative mechanism.[53] A complex enters the catalytic cycle (i.e. initiates) by loss of phosphine with a first order rate constant k_1 (Scheme 2.16). The resultant 14e$^-$ intermediate **A** can either rebind phosphine (with a rate constant k_{-1}) or bind alkene (with a rate constant k_2). Rebinding of phosphine removes the complex from the catalytic cycle, whereas reaction of A with alkene (propagation) continues the catalytic cycle. Intermediate **A** is thus the propagating species. Although neither k_{-1} nor k_2 could be measured directly in solution,[91] the ratios of k_{-1}/k_2 were determined.[53]

This ratio of rate constants is the measure of the extent to which a catalyst prefers to remain in the catalytic cycle. Application of the steady state approximation to the concentration of **A** gives the rate equation:

$$\text{rate}=\frac{k_1k_2[\text{Ru}][\text{alkene}]}{k_{-1}[\text{PR}_3]+k_2[\text{alkene}]}$$

Whereas the initiation of the 1st generation Grubbs is twice as fast than that of the 2nd generation Grubbs catalyst, the k_{-1}/k_2 ratio of the 1st generation is four times greater than that of the 2nd generation, indicating that the rate of metathesis catalysed by the 2nd generation can be up to twice that of the 1st generation.[92] A recent report noted that in acyclic diene metathesis the 2nd generation Grubbs catalyst exhibits higher activity than the 1st generation, yet requires higher reaction temperatures due to its lower initiation efficiency.[93]

The mechanism of ruthenium alkylidene catalysed alkene metathesis has recently been the subject of intense studies.[44, 53] These results clearly indicate that the key step in the catalytic cycle of the metathesis reaction is initial phosphine substitution by an alkene substrate. The substitution may proceed via an associative or dissociative pathway.

Fomine *et al.*[94] studied the three possible reaction pathways for the $\text{RuCl}_2(=\text{CH}_2)(\text{PMe}_3)_2$ and

$RuCl_2(=CH_2)(PCy_3)_2$ mediated metathesis reaction of propylene by quantum-mechanical DFT calculations. They found that in all cases the metathesis reaction proceeds via dissociative substitution of a phosphine ligand with propylene, giving a monophosphine complex.

2.8 Factors influencing metathesis

2.8.1 Maximum turnover number

The metathesis of 1-octene is fully reversible, but if the product ethene is allowed to escape, the reaction is rendered essentially irreversible. Metathesis catalysts also bring about the non-productive metathesis of 7-tetradecene. The total turnover number for a given catalyst for the metathesis of 1-octene cannot be calculated with any degree of certainty because the metathesis events cannot be followed. Also, the active metathesis catalyst is the phosphine dissociated species,[90] 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.

The only figure that can be calculated with any degree of certainty is the effective TON, this being the total number of 1-octene molecules converted to metathesis products per molecule of the catalyst precursor. To ensure the highest possible TON, an excess of the substrate should be added.[84]

2.8.2 Effect of the temperature

The 1st generation Grubbs catalyst showed a steady increase in TON at elevated temperatures. Above 80 °C, a sharp drop-off in activity was noted; this presumably represents the decomposition temperature of the catalyst. The Grubbs 2nd generation catalyst does not succumb appreciably to thermally induced degradation until over 100 °C. From this point on a slight, but steady, decrease in TON was observed at 122 °C. This catalyst also displays a very sudden increase in TON between 50 and 52 °C.

2.8.3 Selectivity

Selectivity is dependent on reaction time, temperature and concentration. For example, in the case of $RuCl_2(=CHPh)(PCy_3)_2$, when all metathesis activity had ceased, the remaining unreacted 1-octene was slowly isomerised giving almost equal parts of 1-, 2-, and 3-octene. This finding suggests that the decomposed metathesis initiator becomes a quite efficient double bond isomerisation catalyst.

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3 EXPERIMENTAL

3.1 Experimental

3.1.1 Reagents, solvents and substrates

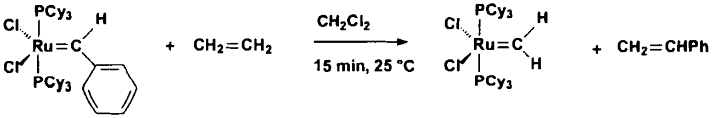
The complexes $RuCl_2(=CHPh)(PCy_3)L$ [L = PCy_3 or IMes], $RuCl(H)(PPh_3)_3(CO)$, $[RhCl(COD)]_2$, $RuCl_3$, $RhCl_3{\cdot}3H_2O$, Cp_2ZrCl_2, Cp_2TiCl_2 and $W(CO)_6$ were purchased from Aldrich and used as they were. The following complexes were synthesized and used without further purification: $RuCl_2(=CHR)(PCy_3)_2$ [R = H or Bu] from $Ru(=CHPh)(PCy_3)_2Cl_2$, $RhCl(C_3H_5N_2)(COD)$ from $[RhCl(COD)]_2$ and $W(=C(OMe)Bu)(CO)_5$ from $W(CO)_6$. The octenes (Aldrich) were passed through a column packed with basic alumina oxide to remove peroxides and distilled over 4A molecular sieves. Chlorobenzene (Aldrich) was refluxed with CaH_2 and distilled over 4A molecular sieves. Diethyl ether (Merck) was dried with sodium wire. Pentane, hexane, 1-hexene, EtOH, CH_2Cl_2, Na, butyllithium, imidazole, trimethyloxonium tetrafluoroborate, Celite, anhydrous magnesium sulphate, D_5-chlorobenzene, D_8-toluene and TCE were purchased from Aldrich and used as they were. All the gasses used in this study were supplied by Afrox and used as they were.

3.1.2 Apparatus

All the glassware used was washed, rinsed with acetone and dried in the oven at 120 °C over-night.

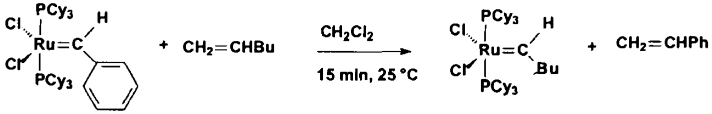
3.2 Catalyst preparation and experimental procedure

3.2.1 Synthesis of the $RuCl_2(=CH_2)(PCy_3)_2$ complex



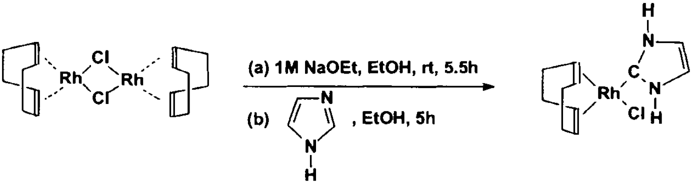
A solution of 467 mg of $RuCl_2(=CHPh)(PCy_3)_2$ in CH_2Cl_2 (15 mL) was stirred under an atmosphere of ethylene for 15 min at room temperature. The solvent was removed under vacuum and the residue was repeatedly washed with pentane (5 mL) and dried under vacuum for several hours. IR spectrum given in Appendix A.1 (Spectrum A.1.2). The IR spectrum shows the disappearance of the aromatic C-H bands at 3000 – 3100 cm^{-1} and the aromatic C=C bands at 1640 – 1680 cm^{-1} observed for Grubbs 1 (Spectrum A.1.1).

3.2.2 Synthesis of the $RuCl_2(=CHBu)(PCy_3)_2$ complex



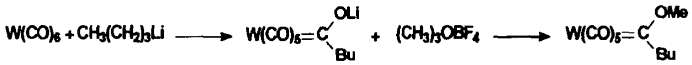
To a solution of 0.1641 g of $RuCl_2(=CHPh)(PCy_3)_2$ in 15 mL of CH_2Cl_2, 1-hexene (0.25 mL) was added and the reaction mixture was stirred at room temperatrure for 15 min. The solvent was removed under vacuum and the residue was repeatedly washed with pentane (5 mL) and dried under vacuum for several hours. IR spectrum given in Appendix A.1 (Spectrum A.1.3). The IR spectrum shows the disappearance of the aromatic C-H bands at 3000 – 3100 cm^{-1} and the aromatic C=C bands at 1640 – 1680 cm^{-1} observed for Grubbs 1 (Spectrum A.1.1).

3.2.3 Synthesis of the $RhCl(C_3H_5N_2)(COD)$ complex



A 1 mol L^{-1} sodium ethoxide (NaOEt) solution was prepared by adding Na metal (0.12 g, 5.217 mmol) in small pieces to EtOH (5.29 mL) at 0 °C in a 10 mL round-bottomed flask. It was stirred until the metal had been completely consumed. In an oven-dried 25 mL round-bottomed flask $[RhCl(COD)]_2$ (556.5 mg, 1.126 mmol) was suspended in ethanol (14.8 mL), followed by addition of the freshly prepared NaOEt solution (4.50 mL). The colour of the mixture changed from orange to yellow after stirring for 5.5 h. The imidazole (153.5 mg, 2.254 mmol) was added and the reaction stirred at room temperature for another 5 h. The crude was concentrated under high vacuum and the residue was redissolved in CH_2Cl_2 and then filtered through Celite to obtain a dark orange solution. Evaporation of the solvent under high vacuum and purification by crystallization from a solution 1:3 CH_2Cl_2/hexane yielded a dark orange solid. IR spectrum given in Appendix A.1 (Spectrum A.1.5). The IR spectrum shows a broad N-H stretch at 3300 – 3500 cm^{-1}.

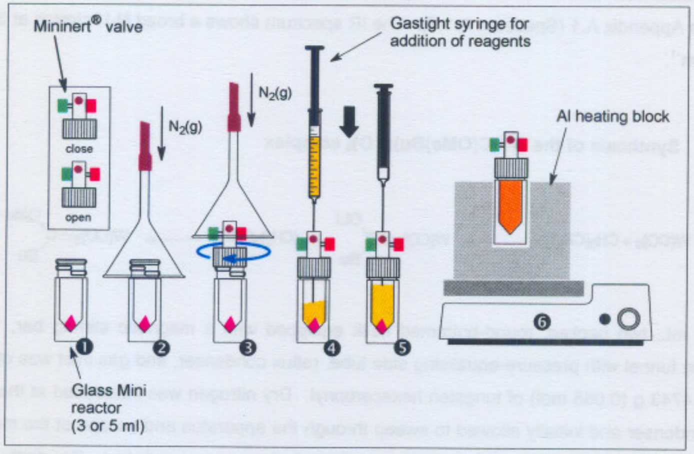
3.2.4 Synthesis of the W(=C(OMe)Bu)(CO)$_5$ complex



A 250 mL, two necked, round-bottomed flask equipped with a magnetic stirring bar, 100mL addition funnel with pressure-equalising side tube, reflux condenser, and gas inlet was charged with 7.4743 g (0.085 mol) of tungsten hexacarbonyl. Dry nitrogen was introduced at the top of the condenser and initially allowed to sweep through the apparatus and escape at the mouth of the dropping funnel. After a few minutes the flow of nitrogen was reduced. Dry diethyl ether (125 mL) was transferred into the flask and stirring was commenced. The addition funnel was charged with 17 mL (1.6 mol L^{-1} in hexane, 0.085 mol) of butyllithium and rapid drop-wise addition was begun. The butyllithium was added over a 10 min period, during which time the solution turned from bright yellow to dark brown. The solution was heated under reflux for approximately 1.5 h. After the solution was cooled, the solvent was removed by rotary evaporation. The dark- brown residual was taken up in 40 mL of water (in air), and 3.14 g of trimethyloxonium tetrafluoroborate was added over a 20 min period with stirring. The mixture was extracted several times with 50 mL portions of cold pentane. The combined pentane layers were dried over anhydrous magnesium sulfate and filtered through a bed of Celite. The solution was concentrated by rotary evaporation to approximately 20 mL and was cooled to -20 °C under N_2. After 1 h the resulting bright-yellow crystals were collected and dried at 25 °C under reduced pressure for 10 min. NMR spectra given in Appendix A.2 (Spectrum A.2.2 and A.2.3).

3.2.5 Experimental procedure for catalytic reactions

The catalyst (4.01×10^{-3} mmol) was weighed in a mini reactor. The reactor was thoroughly flushed several times with nitrogen and the Mininert® valve placed on the reactor. The alkene (3.82×10^{-3} mol) and the solvent, C_6H_5Cl (0.3 cm^3), were then added with Hamilton GASTIGHT® syringes to the reactor. Following the addition the reactor was placed in the heating block at the desired temperature, and the consumption of the alkene determined by GC analysis at regular intervals. All the reactions were repeated at least twice. The experimental procedure is illustrated in the following scheme:

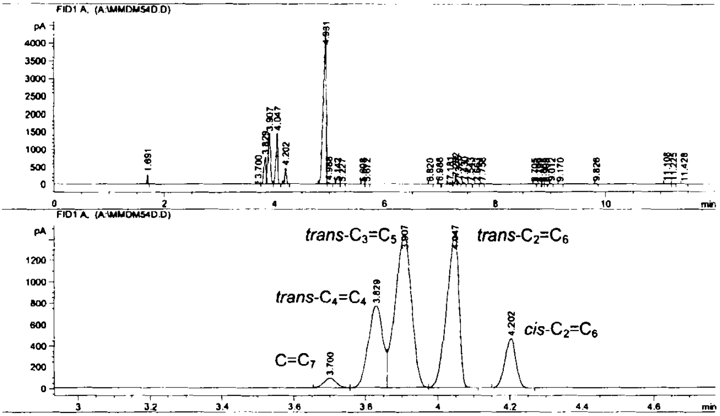


3.3 Analytical methods

3.3.1 GC analyses of isomerisation reactions

Gas chromatograms (an example shown in Chromatogram 3.1) were obtained with an Agilent Technologies 6890N gas chromatograph. A HP-5 5% phenyl methyl siloxane capillary column (30 m x 320 μm x 0.25 μm nominal) was used. The analysis conditions were:

Inlet temperature : 280 °C
N_2 carrier gas flow rate : 2 mL min^{-1} at 20 °C
Injection volume : 0.02 μl (manual injection)
Split ratio : 50:1
Oven programming : 50 °C for 4 min
50 to 255 °C at 20 °C min^{-1}
255 °C for 2 min
Detector : FID at 300 °C
H_2 flow rate : 25 mL min^{-1} at 20 °C
Air flow rate : 350 mL min^{-1} at 20 °C



Chromatogram 3.1 A typical gas chromatogram and an enlargement of the octene region of the product mixture obtained during the isomerisation of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 150 °C.

The octenes were identified by analysis of authentic samples of each octene by GC under the same conditions. Only *trans*-octenes (or alkenes) were used and mainly *trans*-octenes (or alkenes) formed. For simplicity the *trans* were omitted in the rest of the thesis and only the *cis*-alkenes specifically indicated.

The intemal standard method was used to determine the percentage composition of octene, with C_6H_5Cl used as the internal standard. The following formula was used to determine the response factor (f):

$$\frac{V_{C8}}{V_{PhCl}} = f\,\frac{A_{C8}}{A_{PhCl}}$$

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

V_{C8} = volume of octene/cm^3

V_{PhCl} = volume of internal standard (C_6H_5Cl)/cm^3

A_{C8} = area of initial octene peak obtained from the GC

A_{PhCl} = area of the internal standard peak (C_6H_5Cl) obtained from the GC

f = response factor

The mole percentage (% octene) conversion was calculated using the following formula:

$$\%\text{composition} = \frac{n_r}{n_i} \times 100$$

n_i = number of moles of octene before reaction

n_r = number of moles of octene during reaction

These values were used to plot graphs of % composition against the reaction time in min.

3.3.2 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR (at 300 mHz), ^{13}C-NMR (at 75 mHz) and ^{31}P-NMR spectra were obtained by using a Varian Gemini 300 spectrometer and the Bruker Avance Spectrometer with QNP Probe. NMR samples were prepared by dissolving the catalyst (26 mg) in a suitable deuterated solvent.

3.3.3 Infrared spectroscopy (IR)

IR-spectra were obtained by using a Nicolet FTIR 550 spectrophotometer. The pellets were prepared by thoroughly mixing the sample (0.005 g) with dry KBr (0.28 g) and pressed into a disc. The spectra were taken at a resolution of 4 cm^{-1} over a wave number range of 400 - 4000 cm^{-1} and number of scans = 32.

3.4 Kinetics

The experimental procedure to determine the kinetics and calculate the activation energy of the deactivation of the Grubbs 1 catalyst was performed as follows: In a 1 ml NMR tube, 26 mg of $RuCl_2(=CHPh)(PCy_3)_2$ was weighed out. Then 0.7 ml of the deuterated solvent was added. The tube was closed and shaken to dissolve the solids. The disappearance of the carbene ^{1}H-NMR signal was monitored at different temperatures against time. The Ru=CH peak integration values obtained were converted to concentration using the initial concentration of the complex.

The data was fitted to a mathematical model method of least-squares in an attempt to determine the order of the reaction and estimate the rate constants. All the alculations, including standard deviation calculations, were done in MicroSoft Excel 2002 using *inter alia* the Solver analysis tool as described in literature.[1] The method of least-squares yields the parameters which minimize the sum of the residuals (the deviation of each measurement of the dependent variable from its calculated value) such that

$$([\text{model}]-[\text{observed}])^2 = \text{minimum}$$

Using the Arrhenius plot ln k = ln A - E/RT, the activation energy (E) was calculated.[2]

3.5 References

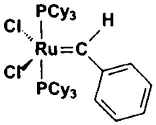
1. BE Joseph, ***Excel for chemists: A comprehensive guide***, Wiley-VCH, New York, 1997, p271-300
2. PW Atkins, ***Physical Chemistry***, Fifth Edition, Oxford University Press, Oxford, 1994, p877

4 RESULTS AND DISCUSSION

4.1 Introduction

It is known that the Grubbs 1 catalyst, $RuCl_2(=CHPh)(PCy_3)_2$, is very active for the metathesis of 1-octene at 25 °C.[1] It was also shown that it catalyses the double bond isomerisation of 1-octene to 2-, 3-, and 4-octene at temperatures ranging from 60 - 80 °C.[2] In this study the influence of temperature, reaction time, catalyst concentration, substrate, and solvent on the catalytic activity of the Grubbs metal carbenes (and other related complexes) was tested for the isomerisation of internal and terminal alkenes in order to determine the optimum conditions. In each test, the conversion of the octenes and the composition of the reaction products were determined. These variables were evaluated by changing one parameter at a time while the other conditions were kept constant. The total products in most of the graphs do not add up to 100 %; the products unaccounted for may be longer chain oligomers not observed under GC analysis conditions and/or it may be due to the loss of high volatile products under the high temperature conditions before injection into the GC.

4.2 The $RuCl_2(=CHPh)(PCy_3)_2$/PhCl catalytic system



4.2.1 Reactions of 4-octene

a. *Influence of the reaction temperature*

Figures 4.1 – 4.4 display the influence of the reaction temperature on the isomerisation of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$/PhCl catalytic system. The catalyst was found to be inactive at room temperature as no isomerisation took place. Exposure of 4-octene to the catalytic system at different temperatures resulted in a mixture of isomers. At 80 °C (Figure 4.1) the reaction is very slow and the catalyst is selective for the formation of 3-octene, 8 % of 3-octene was formed after 6 h.

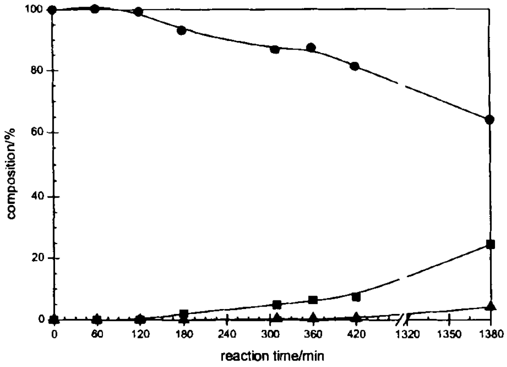


Figure 4.1 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 80 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).

[● 4-octene, ■ 3-octene, ▲ 2-octene]

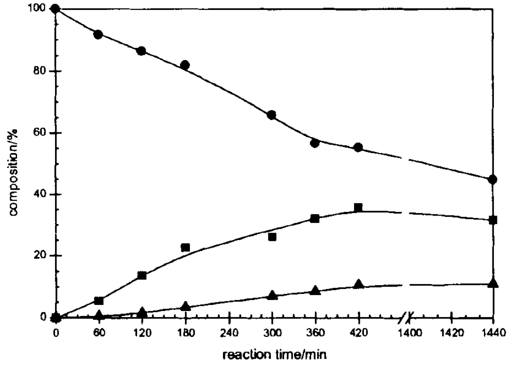


Figure 4.2 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 100 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).

[●4-octene, ■3-octene, ▲ 2-octene]

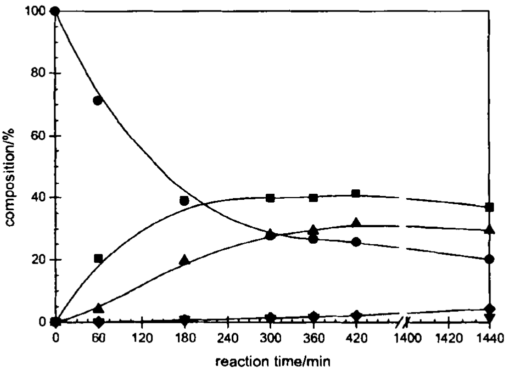


Figure 4.3 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 120 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).

[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

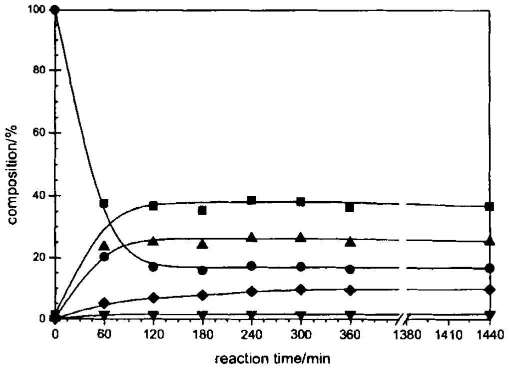


Figure 4.4 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 150 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).

[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

Increasing the temperature to 100 °C caused a decrease in the selectivity of the catalyst (Figure 4.2), 10 % of 2-octene was formed in 6 h. The activity of the catalyst increased as 35 % of 3-octene was formed.

At 120 – 150 °C, the reaction was getting faster at the initial stages (Figure 4.3 and 4.4). From figure 4.4 it can be seen that a mixture of isomers were already formed within 60 min. The reaction reached equilibrium after 2 h and 40, 28, 10 % of 3-octene, 2-octene, and *cis*-2-octene were formed respectively. Only trace amounts of 1-octene were formed, but it also increased with increasing temperature.

At low temperatures there are slow initial rates, but the isomerisation rate was increased with an increase in temperature. The highest temperature, i.e. 150 °C, also gives the highest conversion.

b. Influence of the alkene/catalyst molar ratio

4-Octene was isomerised in the presence of $RuCl_2(=CHPh)(PCy_3)_2/PhCl$ catalytic system at different alkene/Ru molar ratios.

(Figure 4.5 – 4.7) display the effect of the alkene/catalyst molar ratio on the activity of the catalyst. At the molar ratio of 100 (Figure 4.5), the only isomer formed after 5 h was 3-octene with % composition of 37. Increasing the molar ratio to 500 (Figure 4.6), led to the formation of more isomers, 35 % of 3-octene; 25 % of 2-octene and 5 % of cis-2-octene. The reaction is also very fast at the initial stages; all the isomers were already formed in 60 min. There catalytic system is highly reactive at the molar ratio of 1000. In all the molar ratios, 1-octene is less than 2 %.

When comparing Figure 4.5 and 4.6, it is clear in both cases that an increase in alkene/ catalyst molar ratio resulted in an increase in percentage conversion as well as the activity of the catalytic system.

c. Influence of the solvent

The influence of solvents on the isomerisation 4-octene using the $RuCl_2(=CHPh)(PCy_3)_2$/ 150 °C catalytic system was investigated. The results are displayed in Table 4.1.

The following solvents were tested in consideration to their polarity (Table 4.2): carbon tetrachloride, dichloromethane and chlorobenzene. The nature of the solvent affects the isomerisation rate of 4-octene. Little or no conversion to internal octenes was obtained

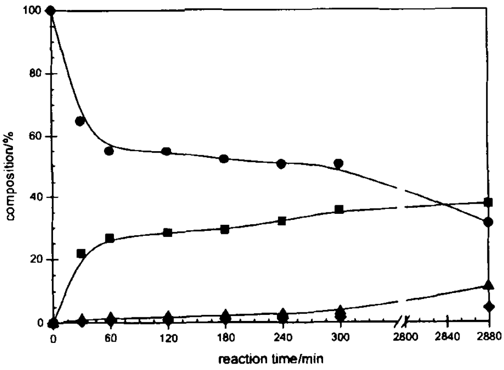


Figure 4.5 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ with an alkene/Ru molar ratio = 100 (T = 150°C; solvent = PhCl)
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene]

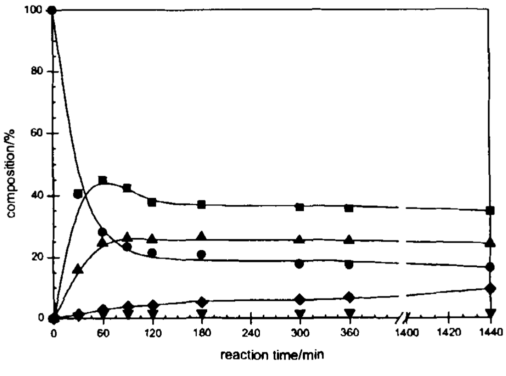


Figure 4.6 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ with an alkene/Ru molar ratio = 500 (T = 150 °C; solvent = PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

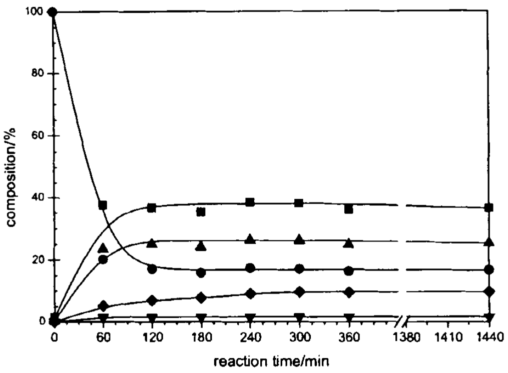


Figure 4.7 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ with an alkene/Ru molar ratio = 1000 (T = 150 °C; solvent = PhCl).

[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

Table 4.1 Influence of the solvent on the isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$/150 °C after 24 h.

Solvent	**Octenes (%)**				
	$C_4=C_4$	**$C_3=C_5$**	**$C_2=C_6$**	**$C=C_7$**	***cis*-$C_2=C_6$**
CCl_4	63	9	2	0	0
CH_2Cl_2	15	33	27	1.5	9
PhCl	17	37	25	2	10
None	45	31	21	0.8	1.7

Table 4.2 Solvent polarities according to Reichardt's E_T-scale.[3]

Solvent	Polarity (E_T values)
CCl_4	0.052
PhCl	0.188
1,2-$C_6H_4Cl_2$	0.225
CH_2Cl_2	0.309
Propanol	0.617
Methanol	0.762

when CCl_4 was used as the solvent, only 9 % conversion to 3-octene was obtained, whereas 35 % conversion to 3-octene was obtained with a haloarene such as 1,2-dichlorobenzene. When the solvent was not used, the reaction was finished after 2 h, but 38 % conversion to 3-octene and 18 % conversion to 2-octene were obtained.

d. Influence of alcohols

Figure 4.8 and 4.9 display the isomerisation of 4-octene at 150 °C using $RuCl_2(=CHPh)(PCy_3)_2$ with alcohols as the solvent. The nature of the solvent greatly affects the isomerisation rate of 4-octene, this is evident from the % composition of the resultant isomers. 60 % 3-octene; 32 % 2-octene; 10 % *cis*-2 octene were formed when methanol was used as the solvent after 5 h (Figure 4.8). When propanol was used as the solvent (Figure 4.9), the reaction was faster at the initial stages than when methanol was used. 40 % of 3-octene was formed in just 30 min. After 1 h, the reaction slowed down and 60 % 3-octene; 40 % 2-octene; 15 % *cis*-2-octene were formed in 5h. 1-octene was only formed in trace amounts.

e. Kinetics

Table 4.3 displays the influence of the reaction time on the activity and selectivity of the catalyst. The data collected between 100 °C and 150 °C show the 3-octene/2-octene ratio increases with temperature, and at higher temperatures the thermodynamic equilibrium is obtained rapidly. At 100 °C, the conversion increases from 18 to 55 % when the reaction time increases from 3 to 24 h.

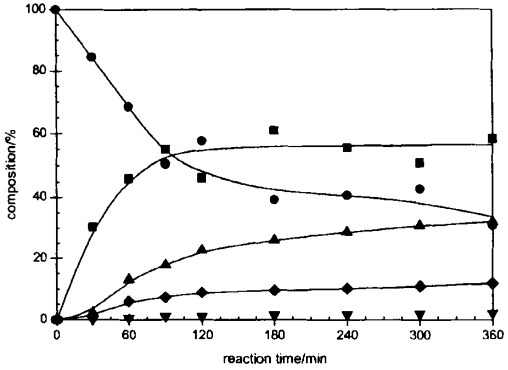


Figure 4.8 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ in methanol (T = 150 °C; alkene/Ru molar ratio = 1000).

[● 4-octene, ■ 3 -octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

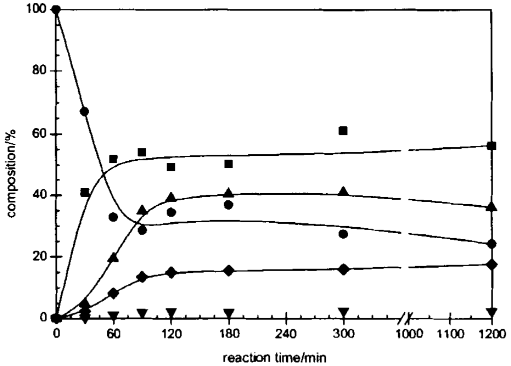


Figure 4.9 Isomerisation reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ in propanol (T = 150 °C; alkene/Ru molar ratio = 1000).

[● 4-octene, ■ 3-octene, ▲ 2-octene,▼ 1-octene, ◆ *cis*-2-octene]

Table 4.3 Isomerisation of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at different reaction temperatures.

Reaction time (h)	T (°C)	Conversion (%)	Octenes (%)			
			$C_4=C_4$	$C_3=C_5$	$C_2=C_6$	$C=C_7$
1	100	8	92	5.4	0.5	0
3		18	82	23	3	0
6		43	57	32	9	0.2
24		55	45	32	11	0.4
1	120	29	71	20	4	0.1
3		61	39	39	20	0.9
6		63	27	40	29	1.6
24		80	20	37	30	1.6
1	150	80	20	38	25	1.5
3		84	16	35	24	1.5
6		84	16	36	25	1.6
24		83	17	37	25	1.6

Catalyst: 2.62 mg (3.18 μmol); 4-octene: 0.5 ml (3.18 mmol); substrate/catalyst molar ratio 1000; PhCl: 0.3 ml; reaction time: 3h

A kinetic study was done for the run at 120 °C to check the order of the reaction. The first order rate law for the consumption of a reactant A was used in the calculation:

$$\frac{d[A]}{dt} = -k[A]$$

$$\ln\frac{[A]}{[Ao]} = -kt$$

To confirm that the reaction is first order, a plot of ln([A]/[Ao]) against time should give a straight line. If a straight line is obtained, then its slope can be identified with -k. Only the initial concentrations were used in the calculation where A is the final concentration of 4-octene and Ao is the initial concentration of 4-octene in terms of % conversion.

Plotting ln([A]/[Ao]) as a function of t gave a straight line which means that the reaction is first order with the slope $k = 1.4663 \times 10^{-5} s^{-1}$ (Figure 4.10).

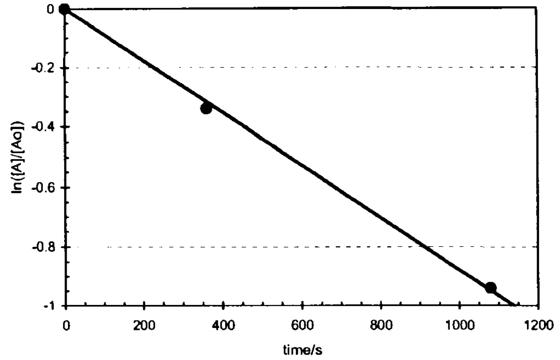


Figure 4.10 Application of the first-order rate law to the isomerisation reaction of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 120 °C.

4.2.2 Reactions of 3- and 2-octene

The catalytic activity of the $RuCl_2(=CHPh)(PCy_3)_2$ in the isomerisation of different alkene substrates has been tested using the other internal isomers of octene. In each test, the conversion of the octenes and the composition of the reaction products were determined.

The results obtained to ascertain the isomerisation activity of the $RuCl_2(=CHPh)(PCy_3)_2$ catalyst are illustrated in Figures 4.11 and 4.12. It is evident that the steric hindrance around the double bond of an internal alkene plays a fundamental role; 1-octene may be easily coordinated to the catalyst to form a π-alkene ruthenium complex and isomerised. The isomers having a low steric hindrance are much too crowded and less efficiently coordinated to the catalyst, thereby giving a π-complex in lower concentrations. The formation of 3-octene takes place through several reaction steps that do not involve the displacement of the intermediate 2-octene from the catalyst.

4.2.3 Reactions of 1-octene

a. Influence of the reaction temperature

The influence of temperature on the catalytic activity of the 1st generation Grubbs catalyst was tested on the isomerisation of 1-octene (Figure 4.13 – 4.17).

In Figure 4.13, at room temperature, only primary metathesis (PMP) was observed. In Figure 4.14, at 80 °C, 3 reactions were observed, i.e. primary metathesis and isomerisation to 2-octene and 3-octene. Metathesis occurs faster than the isomerisation to 2-octene for the first 90 min, thereafter more isomerisation than metathesis occurs.

When the temperature was increased to 100 °C (Figure 4.15), there was more isomerisation of 1-octene to 2-, 3- and 4-octene with the composition of 2- and 3-octene in the end product of about 30 %.

Increasing the temperature to 120 °C (Figure 4.16) caused an increase in the conversion of 3-octene to that of 2-octene after 5 h, but for the first 120 min, there was more isomerisation to 2-octene. At 150 °C (Figure 4.17), no isomerisation to 4-octene occurred, the conversion of 3-octene also decreased. More self-metathesis to C_{14} occurs than isomerisation.

b. Influence of the alkene/catalyst molar ratio

Table 4.4 displays the dependence of activity of the catalyst on the alkene/Ru molar ratio. The reactions were run at 100 °C because at high temperatures more metathesis than isomerisation occurs. It is apparent that the catalytic system is more active for isomerisation at the alkene/Ru molar ratio of 1000. As the alkene/Ru molar ratio increases, the metathesis decreases and the isomerisation increases.

c. Influence of the solvent

In order to find the most suitable conditions for the isomerisation with the ruthenium catalysts, we examined the effect of the solvent (Table 4.5). The following solvents were tested with consideration of their polarity (Table 4.2): carbon tetrachloride, 1,2-dichlorobenzene, chlorobenzene and dichloromethane.

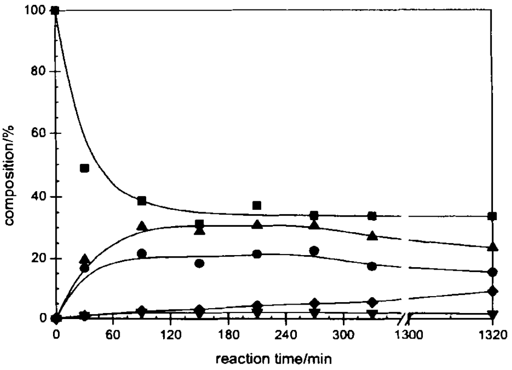


Figure 4.11 Isomerisation reactions of 3-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; solvent = PhCl).

[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

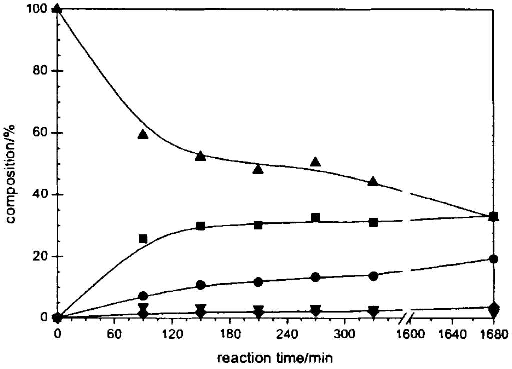


Figure 4.12 Isomerisation reactions of 2-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; solvent = PhCl)

[● 4-octene, ■ 3-octene, ▲ 2-octene,▼ 1-octene, ◆ *cis*-2-octene]

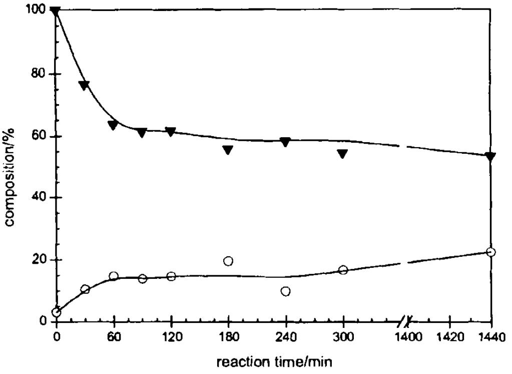


Figure 4.13 Reaction of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 25 °C (alkene/Ru molar ratio = 1000; solvent = PhCl). [▼ 1-octene, ○ PMP]

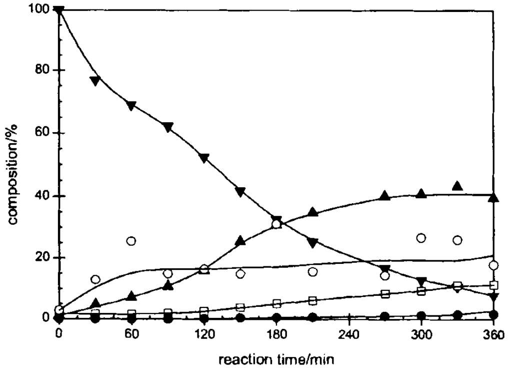


Figure 4.14 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 80 °C (alkene/Ru molar ratio = 1000; solvent = PhCl) [● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ○ PMP, □ SMP]

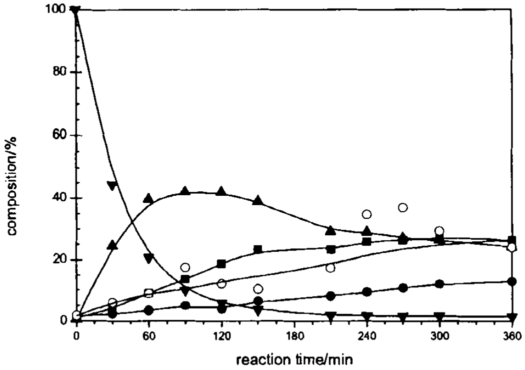


Figure 4.15 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 100 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ○ PMP]

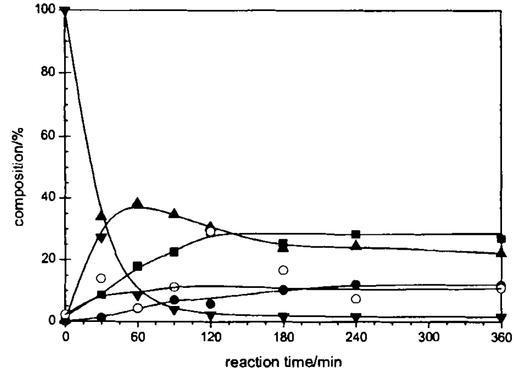


Figure 4.16 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 120 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene,▼1-octene, ○ PMP]

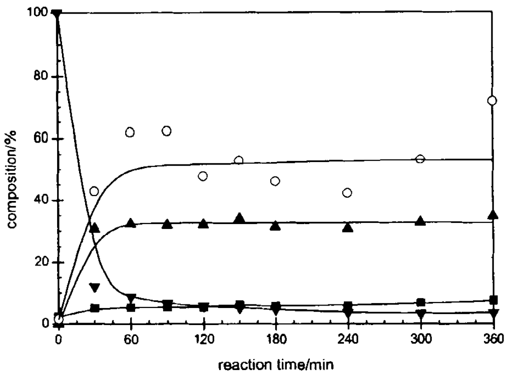


Figure 4.17 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 150 °C (alkene/Ru molar ratio = 1000; solvent = PhCl).
[■ 3-octene, ▲ 2-octene, ▼ 1-octene, ○ PMP]

Large differences in activities of the catalyst were found in the selected solvents. CCl_4 was found to be selective for the self-metathesis of 1-octene to C_{14}. When dichloromethane was used as the solvent, more metathesis products than isomerisation products were formed.

The best performance was observed in haloarenes such as PhCl and 1,2-$C_6H_4Cl_2$, which led to more isomerisation products than metathesis. All of the 1-octene was consumed after 6 h and isomerised to 30 % 2-octene, 25 % 3-octene, and 5 % 4-octene, the rest was metathised to C_{14}. Isomerisation also occurred even when the solvent was not used.

The amount of the solvent (0, 0.3, 1, 1.5 mL) did not have any effect on the isomerisation of 1-octene in the presence of the $RuCl_2(=CHPh)(PCy_3)_2$/PhCl/150 °C catalytic system. The results showed a very small difference in the product compositions.

Table 4.4 Influence of the alkene/Ru molar ratio on the reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ after 6 h (T = 100 °C; PhCl).

Alkene/Ru molar ratio	Reaction products composition (%)				
	$C=C_7$	$C_2=C_6$	$C_3=C_5$	$C_4=C_4$	PMP
100	10	25	5	5	45
500	0	20	10	0	70
1000	0	30	25	15	30

Table 4.5 Influence of the solvent on the reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ after 6 h (T = 150 °C; alkene/Ru molar ratio = 1000).

Solvent	Reaction products composition (%)				
	$C=C_7$	$C_2=C_6$	$C_3=C_5$	$C_4=C_4$	PMP
CCl_4	78	0	0	0	22
CH_2Cl_2	5	20	5	0	65
1,2-$C_6H_4Cl_2$	5	40	20	5	10
PhCl	0	30	25	15	30
None	5	40	30	5	20

d. Kinetics

Table 4.6 displays the effect of the reaction time on the activity of the $RuCl_2(=CHPh)(PCy_3)_2$/PhCl/1-octene at various temperatures. At 80 °C, the conversion increases from 31 to 81 % when the reaction time increases from 1 to 5 h. The amount of 2-octene increases from 7 after 1 h to 41 % after 5 h; similarly, 3-octene increases from 1.6 to 9.4 %, and 4-octene increases from 0 to 1.2 %. At 100 and 120 °C, the opposite happens, the amount of 2-octene decreases from 40 % after 1 h to 26 % after 5 h at 100 °C and decreases from 38 % to 23 % at 120 °C.

Table 4.6 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at different reaction temperatures (alkene/Ru molar ratio = 1000; PhCl).

Reaction time (h)	T /°C	Conversion (%)	Reaction products composition (%)				
			$C=C_7$	$C_2=C_6$	$C_3=C_5$	$C_4=C_4$	PMP
1	−25	36	64	0.28	1.5	0	14.6
2		37	63	0.25	1.4	0	14.7
3		44	56	0.45	1.4	0	15.3
5		45	55	0.76	1.5	0	16.8
1	80	31	69	7.1	1.6	0	25
2		47	53	16	2.4	0.18	16
3		67	33	31	5.0	0.54	31
5		87	13	41	9.4	1.2	27
1	100	97.9	2.1	40	9.0	3.4	8.9
2		94.2	5.8	42	19	3.9	12
3		97	30.	35	23	7.2	13
5		98.3	1.7	26	27	12	29
1	120	91.4	8.6	38	18	4.2	43
2		97.6	2.4	30	30	5.6	29
3		98.3	1.7	24	25	10	15
5		98.4	1.6	23	27	12	9
1	150	91.3	8.7	32	5.2	0	62
2		94.3	5.7	32	5.5	0.12	48
3		95.3	4.7	31	5.7	0.15	46
5		96.7	3.3	33	7.0	0.13	53

A kinetic study was done for the 1-octene run at 120 °C to check the order of the reaction. The first-order rate law for the consumption of a reactant A was used in the calculation:

$$\frac{d[A]}{dt} = -k[A]$$

$$\ln\frac{[A]}{[Ao]} = -kt$$

Only the initial concentrations were used in the calculation where A is the final concentration of

1-octene and Ao is the initial concentration of 1-octene in terms of % conversion. Plotting ln([A]/[Ao]) as a function of time did not give a straight line which means that the reaction is not first-order (Figure 4.18). A second order rate law was used:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[Ao]} = kt$$

$$\frac{1}{[Ao]} = -kt + \frac{1}{[A]}$$

The solution shows that to test for a second-order reaction a plot of 1/[Ao] against time should give a straight line with the slope k. Plotting 1/[Ao] as a function of time gave a straight line which means that the reaction is second-order with the slope k = 5.65×10^{-4} s^{-1}(Figure 4.19).

4.2.4 Reactions of longer chain alkenes

4-Nonene and 4-decene were isomerised under identical reaction conditions as the 4-octene using the $RuCl_2(=CHPh)(PCy_3)_2/PhCl$ catalytic system. The results are illustrated in Figure 4.20 and 4.21. The monomer consumption decreases with an increase in the chain length. For 4-octene 72 % was isomerised after 5 h (Figure 4.4), whereas for 4-nonene and 5-decene, 55 % and 40 % were isomerised respectively. From the results obtained it can be seen that $RuCl_2(=CHPh)(PCy_3)_2$ is highly active in the presence of 4-octene followed by 4-nonene and the 4-decene. For the 4-decene reaction, there was no isomerisation to 1-decene after 24 h.

4.2.5 Catalyst addition

The influence of the catalyst addition was tested for the isomerisation of 4-octene using the $RuCl_2(=CHPh)(PCy_3)_2/PhCl/150$ °C catalytic system. The catalyst was added in solid and in solution form. From the obtained results, it was clear that adding more catalyst when the reaction is running does not have any impact on the isomerisation of 4-octene

4.2.6 Influence of acids

Acids such as catpoly (a solid acid catalyst obtained from Sasol), H_2SO_4, HCl were used as catalysts alone and were also added to the $RuCl_2(=CHPh)(PCy_3)_2$ catalyst at 150 °C to check if they will have any effect on the isomerisation of 4-octene. The acid suppressed the isomerisation reaction.

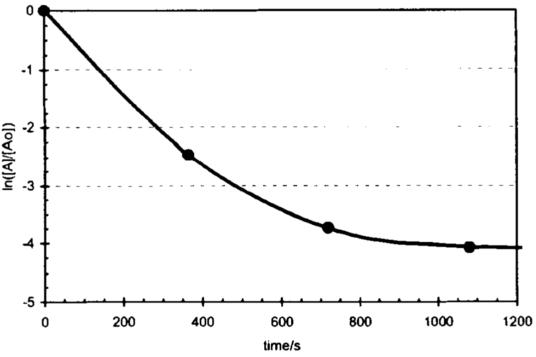


Figure 4.18 Application of the first-order rate law to the isomerisation reaction of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 120 °C.

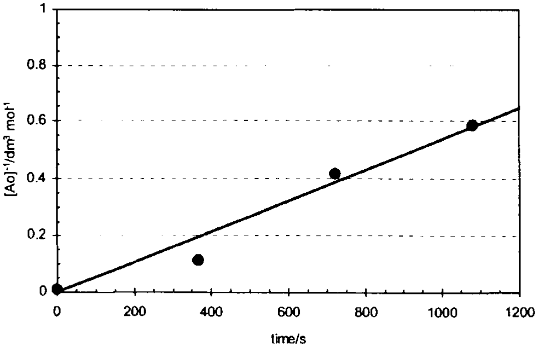


Figure 4.19 Application of the second-order rate law to the isomerisation reaction of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ at 120 °C.

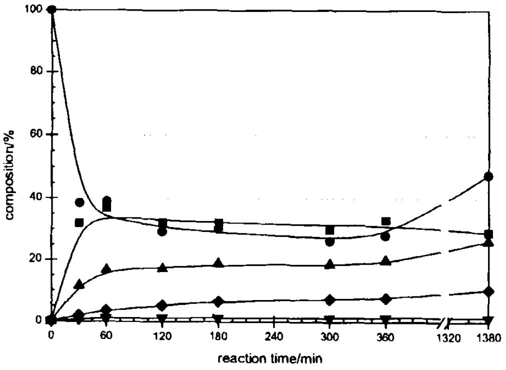


Figure 4.20 Reactions of 4-nonene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-nonene, ■ 3-nonene, ▲ 2-nonene, ▼ 1-nonene, ◆ *cis*-2-nonene]

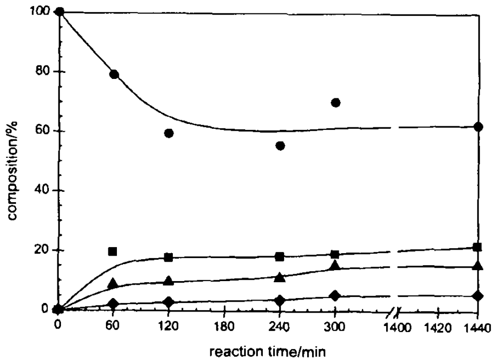
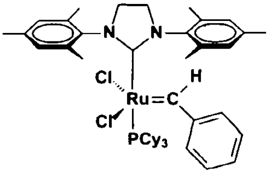


Figure 4.21 Reactions of 4-decene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-decene, ■ 3-decene, ▲ 2-decene, ◆ *cis*-2-decene]

4.3 The $RuCl_2(=CHPh)(PCy_3)(IMes)/PhCl$ catalytic system



4.3.1 Reactions of 4-octene

a. Influence of the reaction temperature

Isomerisation experiments ranging from ambient conditions up to 150 °C were carried out to determine the effect of temperature on the activity of the second generation Grubbs catalyst. The results are illustrated in Figure 4.22 – 4.26.

At room temperature, the catalyst was selective for the formation of 3-octene (Figure 4.22), 15 % of 3-octene was formed after 5 h. As the temperature was increased to 60 and 100 °C (Figure 4.23 and 4.24), the amount of 3-octene formed also increased.

At higher temperatures (≥ 120 ° C) more isomers began forming and there was a decrease in the selectivity as metathesis products were also formed (Figure 4.25 and 4.26). Secondary metathesis products detected were nonene, decene, dodecene and tridecene with the latter in trace amounts. The composition of total metathesis products were less than 10 %. No isomerisation to 1-octene took place.

At 150 °C, the metathesis reaction is suppressed and more isomerisation occurs (Figure 4.26). 4-octene is isomerised to 42 % of 3-octene; 15 % of 2-octene and 10 % of cis-2-octene. The metathesis product, C_9, formed was 10 %. No isomerisation to 1-octene was observed.

b. Influence of the alkene/Ru molar ratio

Figure 4.27 – 4.29 displays the dependence of the activity of the catalyst on the alkene/Ru molar ratio. At low alkene/Ru molar ratios of 100 – 500, only isomerisation products were observed, but increasing the molar ratio to 1000 (Figure 4.29) lead to the formation of C_9. It is clear that decreasing the [Ru] leads to the formation of both isomerisation and metathesis products.

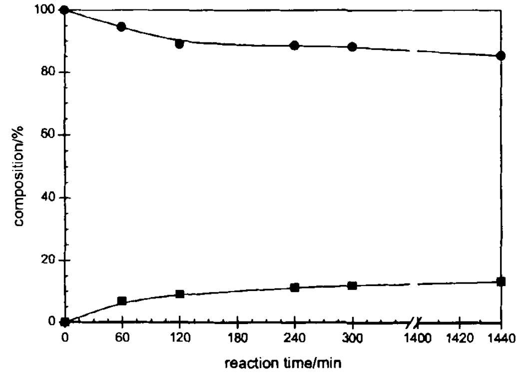


Figure 4.22 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) at *ca.* 25 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene]

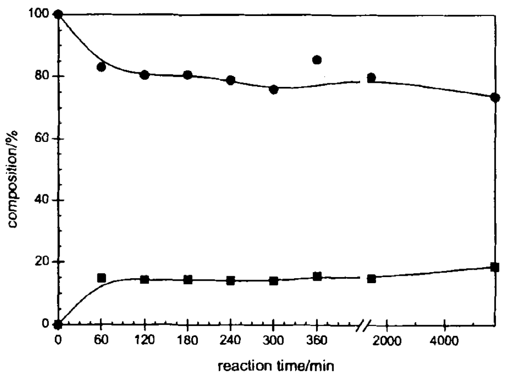


Figure 4.23 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) at 80°C (alkene/Ru molar ratio = 1000; Ph*Cl*).
[● 4-octene, ■ 3-octene]

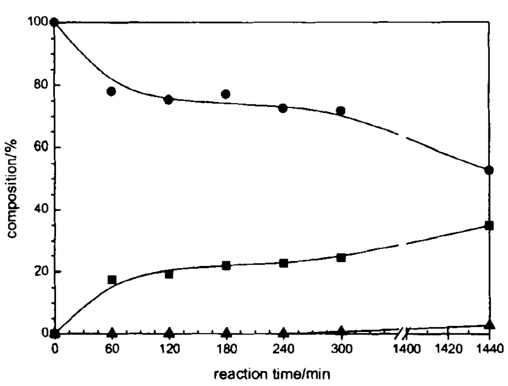


Figure 4.24 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) at 100 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene]

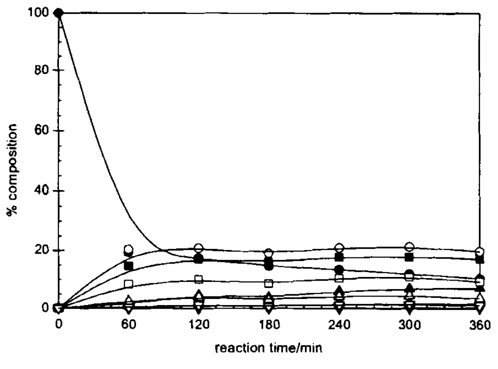


Figure 4.25 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) at 120 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene, ○ C_9, □ C_{10}, △ C_{11}, ▽ C_{12}]

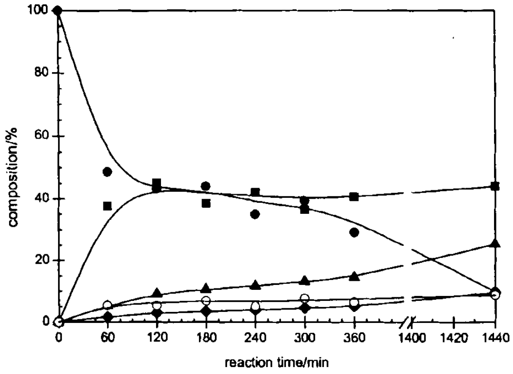


Figure 4.26 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) at 150 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene, ○ C_9]

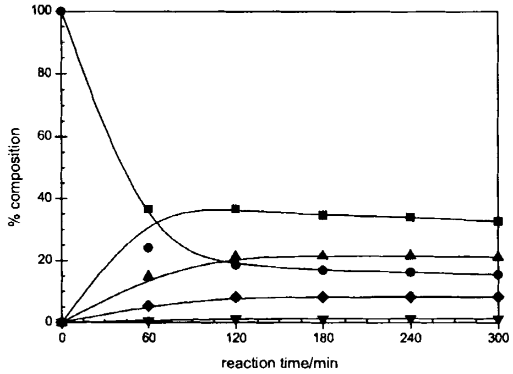


Figure 4.27 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) with an alkene/Ru molar ratio = 100 (T = 150 °C; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene, ▼ 1-octene]

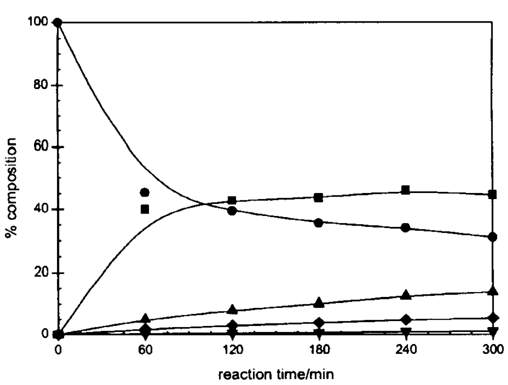


Figure 4.28 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) with an alkene/Ru molar ratio = 500 (T = 150 °C; PhCl). [● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene, ▼ 1-octene]

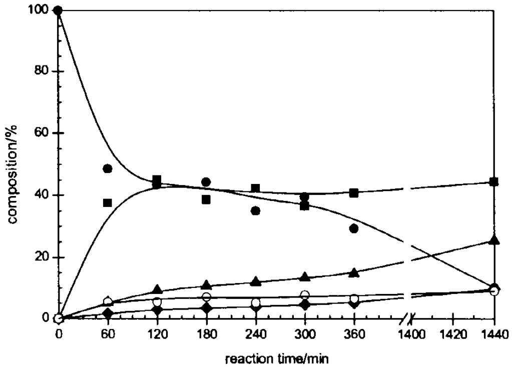


Figure 4.29 Reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) with an alkene/Ru molar ratio = 1000 (T = 150 °C; PhCl). [● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene, ○ C_9]

4.3.2 Reactions of 3- and 2-octene

The catalytic activity of the second generation Grubbs catalyst in the isomerisation of different alkene substrates has been tested using all linear isomers of 4-octene. The results obtained to ascertain the isomerisation activity of the $RuCl_2(=CHPh)(PCy_3)(IMes)$ catalyst are illustrated in Figure 4.30 and 4.31. In Figure 4.30, for 3-octene, 3 reactions were observed, i.e. primary metathesis and isomerisation to 4-octene and 2-octene. Metathesis occurs faster than the isomerisation to 2-octene for the first 2 h, after 120 min more isomerisation than metathesis occurs. Only trace amounts of 1-octene were formed. 3-octene was isomerised to 18 % 2-octene and 17 % 4-octene after 2 h.

For the 2-octene reaction, (Figure 4.31), the catalyst afforded a mixture of the metathesis and isomerisation products, with the isomerisation preceeding the metathesis. 2-octene was isomerised to 19 % 3-octene, 19 % 4-octene, 1-octene was formed in trace amounts. The amount of PMP decreased to 10 % compared to the 20 % observed for the 3-octene reaction.

4.3.3 Reactions of 1-octene

Isomerisation experiments ranging from ambient conditions to up to 150 °C were carried out to determine the effect of temperature on the activity of the second generation Grubbs catalyst using 1-octene, the results are displayed in Figure 4.32 – 4.34. At 25 °C, there was no reaction. The catalyst is selective for the metathesis to C_{14} at 60 °C (Figure 4.32), the reaction is very slow at the initial stages and starts increasing after 2 h. 38 % of 1-octene is metathesised to C_{14} after 6 h.

As the temperature is increased to 100 °C, isomerisation products are formed but they are less than 10 % (Figure 4.33). The amount of C_{14} formed also increased to 50 %. At 150 °C, the composition of C_{14} reached 60 % after 6 h (Figure 4.34).

4.3.4 Reactions of longer chain alkenes

Figure 4.35 and 4.36 show the reactions of 4-nonene and 4-decene using the $RuCl_2(=CHPh)(PCy_3)(IMes)/PhCl$ catalytic system at 150 °C. The system was found to be more active for the metathesis of higher alkenes than the isomerisation, which is the opposite of what we obtained for 4-octene (Figure 4.29). The number and the composition of the isomers formed decrease with an increase in the carbon chain length. There was no isomerisation to terminal alkenes observed after 5 h.

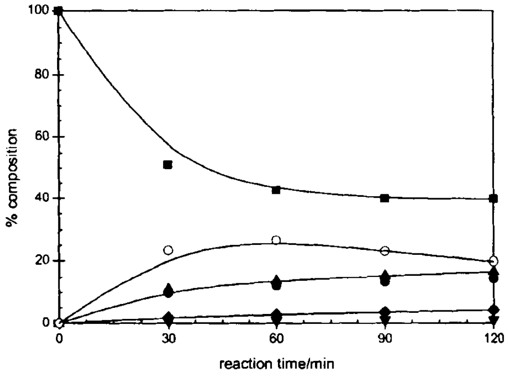


Figure 4.30 Reactions of 3-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, O PMP]

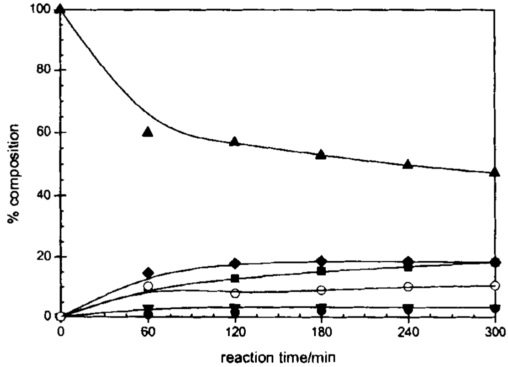


Figure 4.31 Reactions of 2-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 1-octene, ■ 4-octene, ▲ 2-octene, ◆3-octene ,
▼ *cis*-2-octene, O PMP]

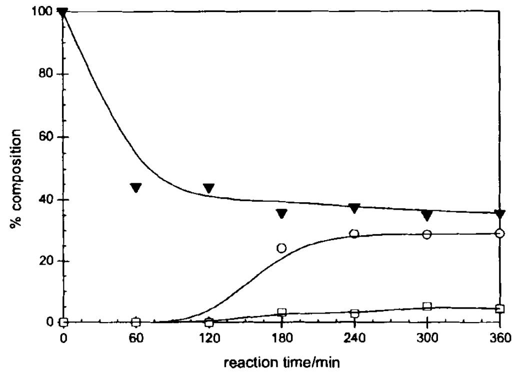


Figure 4.32 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) at 60 °C (alkene/Ru molar ratio = 1000; PhCl). [▲ 1-octene, ○ PMP, □ SMP]

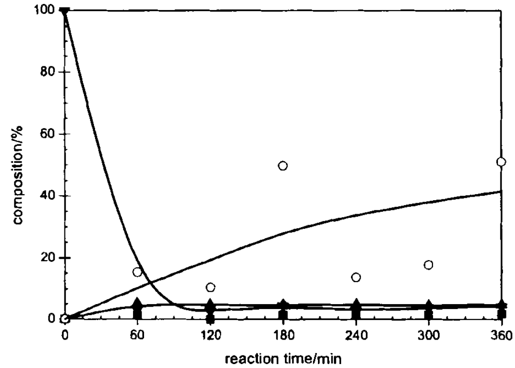


Figure 4.33 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$(IMes) at 100°C (alkene/Ru molar ratio = 100; PhCl). [▲ 2-octene, ▼ 1-octene, ○ PMP]

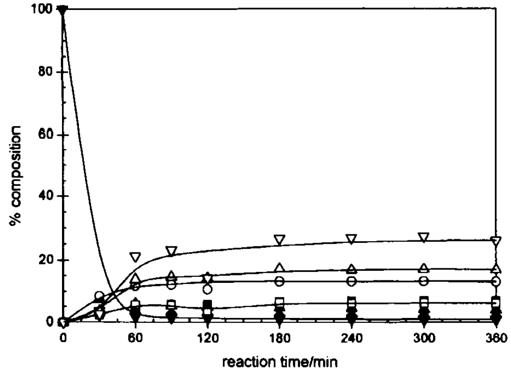


Figure 4.34 Reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) at 150°C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ○ C_9, □ C_{10}, △ C_{11}, ▽ C_{12}]

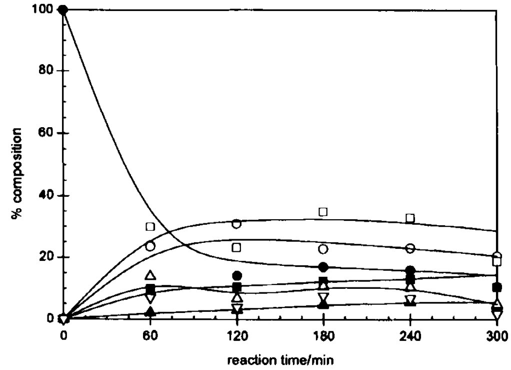


Figure 4.35 Reactions of 4-nonene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-nonene, ■ 3-nonene, ▲ 2-nonene, ○ C_8, □ C_{10}, △ C_{11}, ▽ C_{12}]

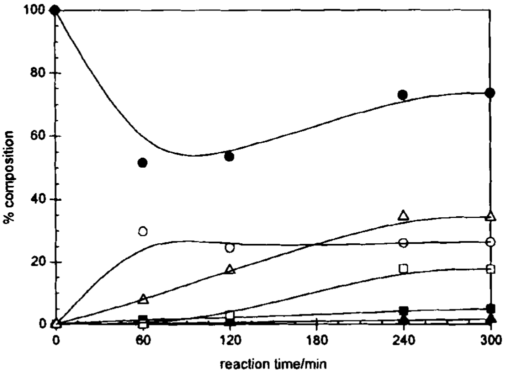
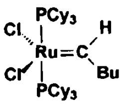


Figure 4.36 Reactions of 4-decene in the presence of $RuCl_2(=CHPh)(PCy_3)$ (IMes) (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-decene, ■ 3-decene, ▲ 2-decene,○ C_8, □ C_9, △ C_{12}]

4.4 The $RuCl_2(=CHBu)(PCy_3)_2$/PhCl catalytic system



4.4.1 Reactions of 4-octene

The ruthenium alkylidene $[RuCl_2(=CH\text{-}n\text{-}Bu)(PCy_3)_2]$ catalytic system was tested for the isomerisation of 4-octene at various temperatures. (Figure 4.37 and 4.38) At 25 °C, there was no reaction. At 120 °C, the reaction was slow at the initial stages and speeds up after 2 h (Figure 4.37). After 5 h, 4-octene isomerised to 30 % 3-octene and 25% 2-octene; 1-octene was formed in trace amounts.

At 150 °C, the reaction was getting faster at the initial stages. From Figure 4.38 it can be seen that a mixture of isomers were already formed within 60 min. The reaction reached equilibrium after 2 h and 40, 25, 10 % of 3-octene, 2-octene, and *cis*-2-octene were formed respectively.

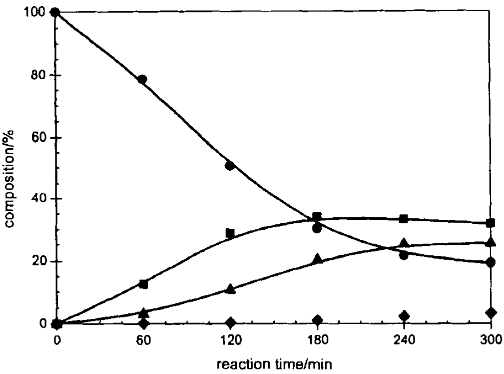


Figure 4.37 Reactions of 4-octene in the presence of $RuCl_2(=CHBu)(PCy_3)_2$ at 120 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene]

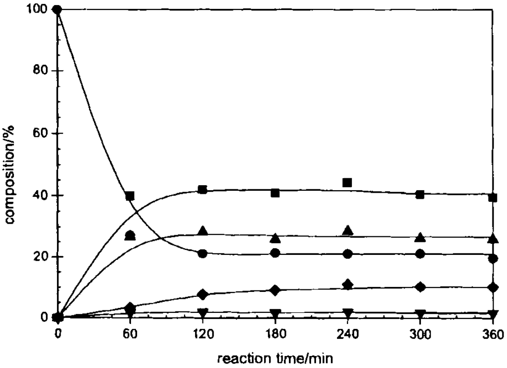


Figure 4.38 Reactions of 4-octene in the presence of $RuCl_2(=CHBu)(PCy_3)_2$ at 150 °C (alkene/Ru molar ratio = 1000; PhCl).
[●4-octene, ■ 3-octene, ▲ 2-octene,▼ 1-octene, ◆ *cis*-2-octene]

Only trace amounts of 1-octene were formed, but it also increased with increasing temperature.

4.4.2 Reactions of 1-octene

Figure 4.39 display the isomerisation of 1-octene using the ruthenium alkylidene as a catalyst at 150 °C. The catalyst affords a mixture of the metathesis and isomerisation products, with the isomerisation preceeding the metathesis. When $RuCl_2(=CHBu)(PCy_3)_2$ was used as the catalyst, 1-octene was isomerised to 39 % 3-octene, 29 % 2-octene and 18 % 4-octene. PMP and SMP were also formed in less than 10 %. The reaction was fast at the initial stages but slowed down after 60 min.

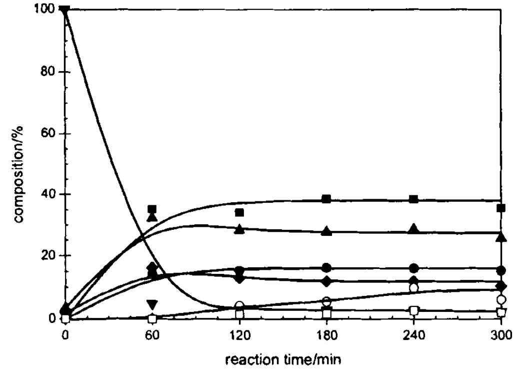


Figure 4.39 Reactions of 1-octene in the presence of $RuCl_2(=CHBu)(PCy_3)_2$ at 150°C (alkene/Ru molar ratio = 1000; solvent = PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, O PMP, □ SMP]

4.4.3 Reactions of longer chain alkenes

Figure 4.40 and 4.41 display the influence of the alkene chain length on the activity of the $[RuCl_2(=CHBu)(PCy_3)_2]$ catalytic system. From the results it is clear that $RuCl_2(=CHBu)(PCy_3)_2$ is highly active in the presence of 4-octene followed by 4-nonene and the 4-decene. The % composition of the isomers formed decreases with an increase in the chain length. With 4-decene, there was no isomerisation to 1-decene.

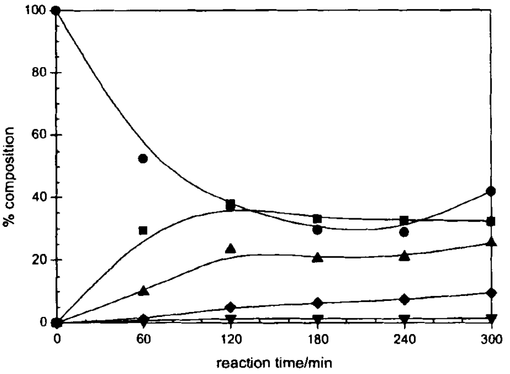


Figure 4.40 Reactions of 4-nonene in the presence of $RuCl_2(=CHBu)(PCy_3)_2$ (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-nonene, ■ 3-nonene, ▲ 2-nonene, ▼ 1-nonene, ◆ *cis*-2-nonene]

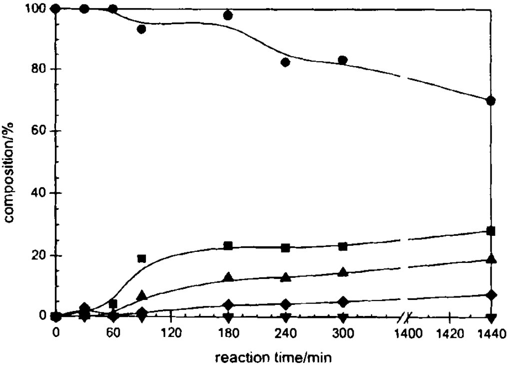
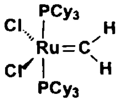


Figure 4.41 Reactions of 4-decene in the presence of $RuCl_2(=CHBu)(PCy_3)_2$ (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-decene, ■ 3-decene, ▲ 2-decene, ▼ 1-decene ◆ *cis*-2-decene]

4.5 The $RuCl_2(=CH_2)(PCy_3)_2/PhCl$ catalytic system



4.5.1 Reactions of 4-octene

The ruthenium methylidene catalytic system $RuCl_2(=CH_2)(PCy_3)_2$ was tested for the isomerisation of 4-octene at various temperatures (Figure 4.42 and 4.43). At 25 °C, there was no reaction and at 120 °C the reaction was slow at the initial stages and started increasing after 2 h (Figure 4.42). After 6h, 4-octene isomerised to 40 % 3-octene and 35% 2-octene; 1-octene was formed in trace amounts, and there was no metathesis.

From Figure 4.43 it can be seen that the reaction was faster at 150 °C.

4.5.2 Reactions of 1-octene

Figure 4.44 shows that using $RuCl_2(=CH_2)(PCy_3)_2$ as the catalyst also affords a mixture of isomerisation and metathesis products. More metathesis than isomerisation products were formed for this reaction. The % composition of the isomers formed are less than those formed when $RuCl_2(=CHBu)(PCy_3)_2$ was used (Figure 4.41), but the opposite happened with the metathesis products; 55 % of PMP and 10 % of SMP was formed.

4.5.3 Reactions of longer chain alkenes

Figure 4.45 and 4.46 display the influence of the chain length on the activity of the $RuCl_2(=CH_2)(PCy_3)_2$ catalytic system. From the results it is clear that $RuCl_2(=CH_2)(PCy_3)_2$ is highly active in the presence of 4-octene followed by 4-nonene and the 4-decene. After 2h, for the 3 reactions, 80% of 4-octene, 55 % of 4-nonene and 20 % of 4-decene were consumed. The % composition of the isomers formed decreases with an increase in the chain length. With 4-decene, there was no isomerisation to 1-decene.

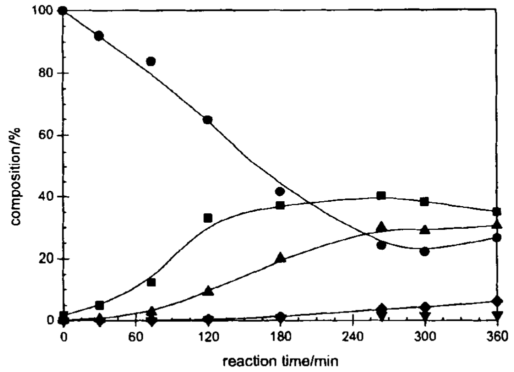


Figure 4.42 Reactions of 4-octene in the presence of $RuCl_2(=CH_2)(PCy_3)_2$ (T = 120 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

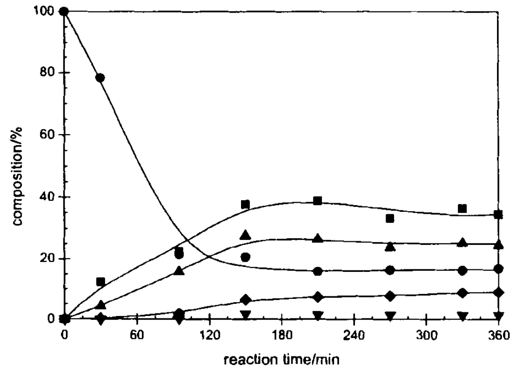


Figure 4.43 Reactions of 4-octene in the presence of $RuCl_2(=CH_2)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

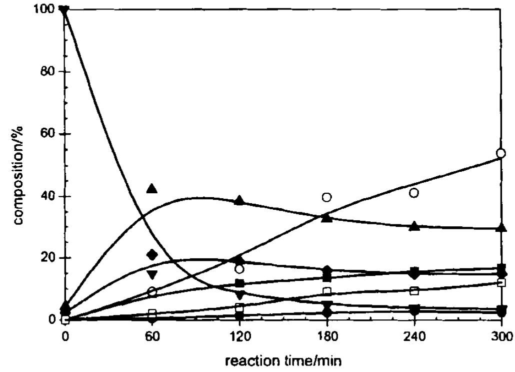


Figure 4.44 Reactions of 1-octene in the presence of $RuCl_2(=CH_2)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ○ PMP, □ SMP]

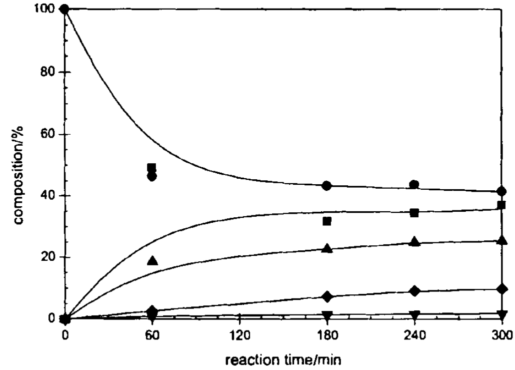


Figure 4.45 Reactions of 4-nonene in the presence of $Ru(=CH_2)(PCy_3)_2Cl_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-nonene, ■ 3-nonene, ▲ 2-nonene, ▼ 1-nonene, ◆*cis*-2-nonene]

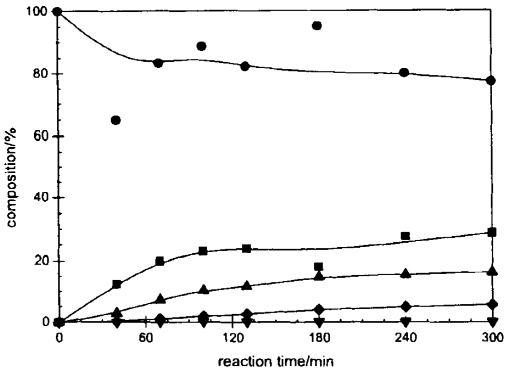


Figure 4.46 Reaction of 4-decene in the presence of $RuCl_2(=CH_2)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-decene, ■ 3-decene, ▲ 2-decene, ▼ 1-decene, ◆ *cis*-2-decene]

4.6 The $RuCl(H)(PPh_3)_3(CO)$ catalytic system

4.6.1 Reactions of 4-octene

The $RuCl(H)(PPh_3)_3(CO)$ catalytic system was tested for the isomerisation of 4-octene at temperatures ranging from 25 – 150 °C. The catalytic system was found to be inactive at 25, 80 and 120 °C as no isomerisation was observed.

At 150 °C (Figure 4.47), the catalyst is selective to the formation of 3-octene after 6 h. After 24h traces of 2- and *cis*-2-octene were observed whereas the composition of 3-octene was 35 %

4.6.2 Reactions of 1-octene

Figure 4.48 and 4.49 illustrate the influence of the reaction temperature on the catalytic activity of $RuCl(H)(PPh_3)_3(CO)$ catalytic system in the isomerisation of 1-octene.

At 25 °C (Figure 4.48), the reaction is very slow and only 10 % of 2- and *cis*-2-octene were formed after 4 h. After 24 h, trace amounts of 3-octene were formed. Increasing the temperature to 150 °C (Figure 4.49) led to an increase in the reaction rate. All isomers were formed within 30 min and reached equilibrium in 1h. 1-Octene was isomerised to 42, 35, 20 and 10 % of 2, 3, 4 and *cis*-2-octene respectively.

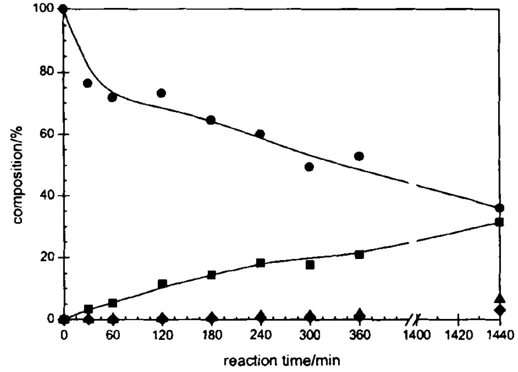


Figure 4.47 Reactions of 4-octene in the presence of $RuCl(H)(PPh_3)_3(CO)$ complex (temp = 150°C; alkene/Ru molar ratio = 1000; PhCl) [● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene]

4.6.3 Reactions of longer chain alkenes

Figure 4.50 and 4.51 illustrated the influence of the chain length towards the activity of $RuCl(H)(PPh_3)_3(CO)$ catalytic system. The catalyst seems to be active towards the isomerisation of 4-nonene followed by 4-octene and then 4-decene. 4-Nonene (Figure 4.50) isomerised to 40 %, 30 % and 12 % of 3, 2 and *cis*-2-octene respectively. 1-Nonene formed was less than 2 %. The reaction is also very fast at the initial stages as most of the isomers were already formed in 30 min. From Figure 4.51 it can be seen that the reaction is very slow, no reaction occurred for the first 4 h. After 24 h only 15 % of 3-octene was formed, 2-octene formed was in trace amounts.

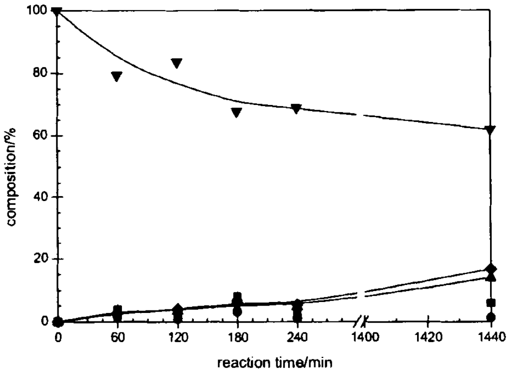


Figure 4.48 Reactions of 1-octene in the presence of RuCl(H)(PPh_3)$_3$(CO) at *ca.* 25 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

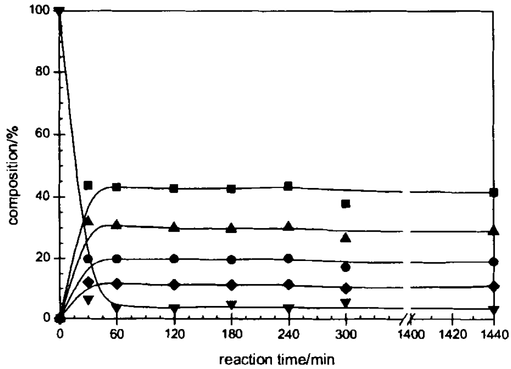


Figure 4.49 Reactions of 1-octene in the presence of RuCl(H)(PPh_3)$_3$(CO) at 150 °C (alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

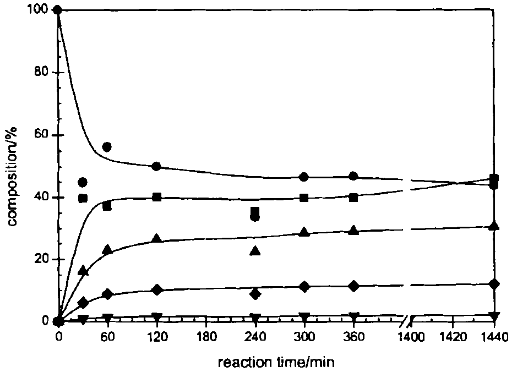


Figure 4.50 Reactions of 4-nonene in the presence of $RuCl(H)(PPh_3)_3(CO)$ (T = 150°C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-nonene, ■ 3-nonene, ▲ 2-nonene, ▼ 1-nonene, ◆ *cis*-2-nonene]

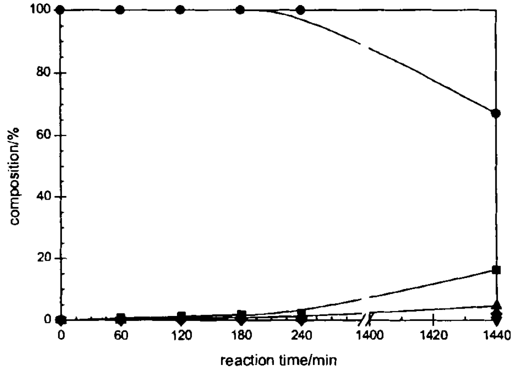
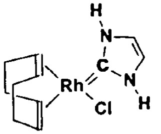
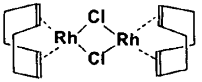


Figure 4.51 Reactions of 4-decene in the presence of $RuCl(H)(PPh_3)_3(CO)$ (T = 150 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-decene, ■ 3-decene, ▲ 2-decene, ◆ *cis*-2-decene]

4.7 Rhodium complexes as catalysts



$RhCl(C_3H_5N_2)(COD)$



$[RhCl(COD)]_2$

4.7.1 Reactions of 4-octene

The heterocyclic rhodium carbene $RhCl(C_3H_5N_2)(COD)$ is selective for the isomerisation of 4-octene at 120 and 150 °C. No metathesis products were formed at these temperatures. At room temperature there was no reaction. Figure 4.52 shows the isomerisation of 4-octene to 25 % 3-octene and 6 % 2-octene after 24 h, there was no isomerisation to 1-octene. Isomerisation to 3-and 2-octene increases with an increase in the reaction temperature and a decrease in the octene/Ru molar ratio. The solvent was also observed (results not shown) to have an effect on the amount of the products formed. When the solvent was not used, only 15 % of the monomer was consumed after 24h.

The rhodium dimer $[RhCl(COD)]_2$, from which the carbene was prepared, also catalyses the isomerisation of 4-octene to 3- and 2-octene (Figure 4.53), no metathesis was observed in any of the reactions. 1-octene formed after using the two Rhodium catalysts was less than 1 %. The rhodium dimer is more active than the carbene for the isomerisation of 4-octene.

4.7.2 Reactions of 1-octene

Figure 4.54 displays the effect of using $RhCl(C_3H_5N_2)(COD)$ for the isomerisation of 1-octene. The catalyst was found to be active for isomerisation only; no metathesis products formed. 1-Octene was isomerised to 35 % 2-octene, 13 % *cis*-2-octene and 10 % 3-octene after 4 h. 4-Octene was formed in trace amounts.

The $[RhCl(COD)]_2$ was also tested for the isomerisation of 1-octene at 150 °C (Figure 4.55). This catalyst was found to be active for isomerisation only; no metathesis products were formed. This catalyst is more active than the carbene, 35 % 2-octene; 15 % *cis*-2-octene; 10 % 3-octene were formed after 4 h. 4-Octene was only formed in trace amounts.

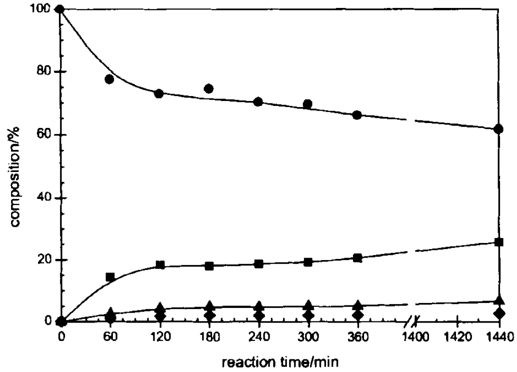


Figure 4.52 Reaction of 4-octene in the presence of the $RhCl(C_3H_5N_2)(COD)$ (T = 120 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene]

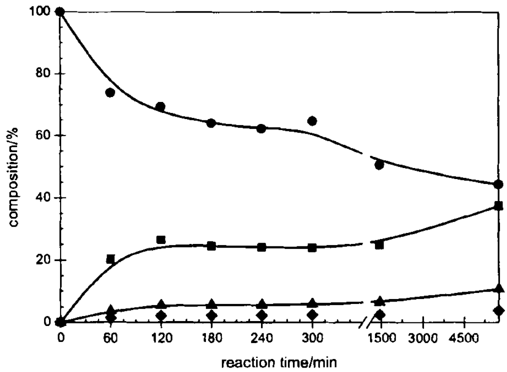


Figure 4.53 Reactions of 4-octene in the presence of $[RhCl(COD)]_2$ (T = 120 °C; alkene/Ru molar ratio = 1000; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ◆ *cis*-2-octene]

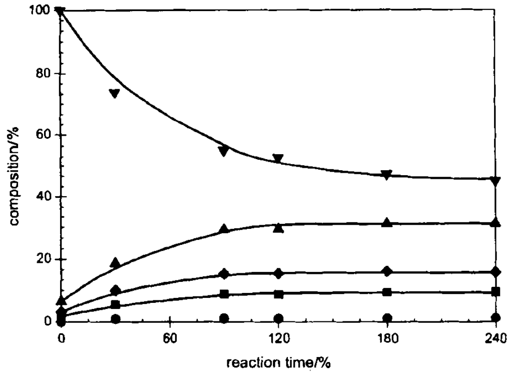


Figure 4.54 Reactions of 1-octene in the presence of $RhCl(C_3H_5N_2)(COD)$ (T = 150 °C; alkene/Ru molar ratio = 100; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

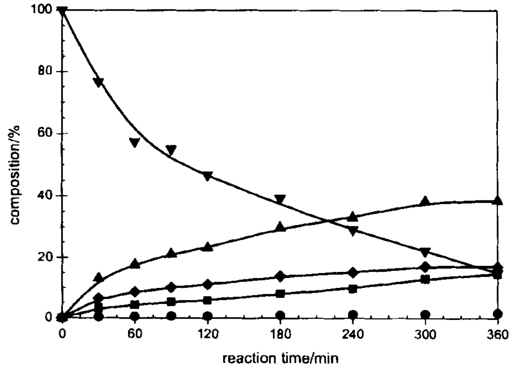


Figure 4.55 Reactions of 1-octene in the presence of $[RhCl(COD)]_2$ (T = 150 °C; alkene/Ru molar ratio = 100; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ 1-octene, ◆ *cis*-2-octene]

4.8 The W(=C(OMe)Bu)(CO)$_5$/PhCl catalytic system

When W(CO)$_5$C(OMe)Bu/PhCl was used as the catalyst for the isomerisation of 4-octene, isomerisaton did not occur at temperatures ranging from 25 – 150 °C after 24 h.

4.9 The Metallocenes catalytic systems

Metallocene mixtures such as Cp$_2$TiCl$_2$/PhCl, Cp$_2$ZrCl$_2$/PhCl, Cp$_2$ZrCl$_2$/LiAlH$_4$/PhCl at alkene/ catalyst molar ratios = 100 and a reaction temperature 120 °C were tested for the isomerisation of 4-octene. The 4-octene did not isomerise.

4.10 The MCl$_3$/PhCl catalytic systems

The isomerisation of 4-octene using the MCl$_3$/PhCl (M = Rh or Ru) catalytic systems at 150 °C is only effective after long reaction hours (Figure 4.56 and 4.57). For RhCl$_3$·H$_2$O (Figure 4.56), only 10 % of 3-octene was formed after 5 days. Figure 4.57 shows that for RuCl$_3$, 40 % 3-octene and 18 % 2-octene were formed after 5 days. No 1-octene was formed in either reaction and there was no metathesis.

4.11 NMR study of RuCl$_2$(=CHPh)(PCy$_3$)$_2$

4.11.1 Kinetics of RuCl$_2$(=CHPh)(PCy$_3$)$_2$ decomposition

NMR studies on several ruthenium carbene complexes were done, monitoring their rates of decomposition and their ability to carry out isomerisation. ^{1}H NMR and ^{13}C NMR shifts were reported relative to internal TMS. Grubbs 1 catalyst RuCl$_2$(=CHPh)(PCy$_3$)$_2$ was chosen for this study, as it were highly active for the isomerisation of alkenes amongst the other catalysts.

To draw further conclusions on the stability of Grubbs 1 its ^{1}H NMR spectra was obtained in a sealed tube in C$_6$D$_5$Cl or TCE. Decomposition of RuCl$_2$(=CHPh)(PCy$_3$)$_2$ is evident as the intensity of the carbene peak at 20.0 ppm slowly declines. Formation of other carbenes is excluded since new resonances in the range 22 – 19 ppm are not observed.

Figure 4.58 shows a comparison of the ^{1}H NMR concentration (calculated from peak intergration) accompanying a thermal reaction of RuCl$_2$(=CHPh)(PCy$_3$)$_2$. The ^{1}H NMR of RuCl$_2$ (=CHPh)(PCy$_3$)$_2$ in C$_6$D$_5$Cl shows that the rate of carbene decomposition increases at temperatures $\geq$ 60 °C.

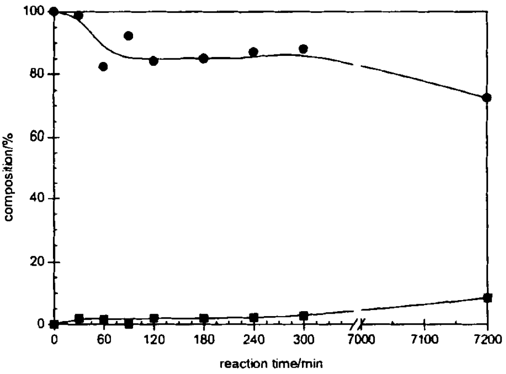


Figure 4.56 Reactions of 4-octene in the presence of $RhCl_3 \cdot H_2O$ (T = 150 °C; alkene/Ru molar ratio = 100; PhCl).
[● 4-octene, ■ 3-octene]

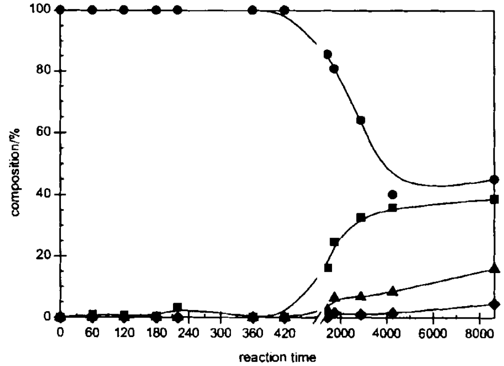


Figure 4.57 Reactions of 4-octene in the presence of $RuCl_3$ (T = 150 °C; alkene/Ru molar ratio = 100; PhCl).
[● 4-octene, ■ 3-octene, ▲ 2-octene, ▼ *cis*-2-octene]

From Figure 4.58 it is clear that the rate of the catalyst decomposition increases as the temperature is raised, and the larger the value of k, the more rapid the decomposition (Table 4.7). The reaction has rate constants that follow the Arrhenius equation $\ln k = \ln A - E_a/RT$, that is the plot of ln k against 1/T gives a straight line. The factor A is called the pre-exponential factor and E_a is called the activation energy, collectively they are called the Arrhenius parameters and they are purely empirical quantities that will enable us to discuss the variation of rate constants with temperature. The activation energy is the minimum energy that reactants must have in order to form products.[4]

In Figure 4.59, the least-squares fit on the lines is with the slope -5.1274 for the forward reaction and -2.2791 for the reverse reaction. This means that the minimum enegy reqiured to form products is 51.274 kJ.mol^{-1}. From Table 4.8 it is can be seen from the correlation that k_f (rate of the forward reaction) is better defined than k_r (rate of the reverse reaction).

Another ^{1}H NMR study was done on $RuCl_2(=CHPh)(PCy_3)_2$, this time using TCE as the solvent (**Spectrum 4.1**). At 30 °C, a carbene resonance appeared at 20 ppm, as the temperature was increased to 90 °C, the benzylidene resonance at 20 ppm was gradually replaced by a broad hydride signal at –18 ppm. The reaction was followed with time at 90 °C and the carbene disappeared completely after 50 min.

Table 4.7 Table of calculated reaction rates and standard deviations of the decomposition of $RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl.

Temp/K	$(RT)^{-1}$/ J mol^{-1}	k_f/s^{-1}	StdDev k_f/s^{-1}	k_r/s^{-1}	StdDev k_r/s^{-1}	ln k_f	StdDev ln k_f	ln k_r	StdDev ln k_r
393	3.06×10^{-4}	1.10×10^{-3}	3.30×10^{-5}	1.55×10^{-4}	1.59×10^{-5}	-6.82	0.030	-8.77	0.098
373	3.22×10^{-4}	4.22×10^{-4}	1.74×10^{-5}	3.63×10^{-5}	1.03×10^{-5}	-7.77	0.041	-10.20	0.250
353	3.41×10^{-4}	2.02×10^{-4}	1.50×10^{-6}	7.66×10^{-5}	1.40×10^{-6}	-8.51	0.007	-9.48	0.018
333	3.61×10^{-4}	6.53×10^{-5}	7.99×10^{-7}	4.39×10^{-5}	2.27×10^{-6}	-9.64	0.012	-10.00	0.050
313	3.84×10^{-4}	1.86×10^{-5}	8.68×10^{-7}	4.63×10^{-6}	9.33×10^{-6}	-10.90	0.046	-12.30	1.100
293	4.10×10^{-4}	5.13×10^{-6}	1.49×10^{-6}	2.00×10^{-5}	6.25×10^{-5}	-12.20	0.255	-10.8	1.420

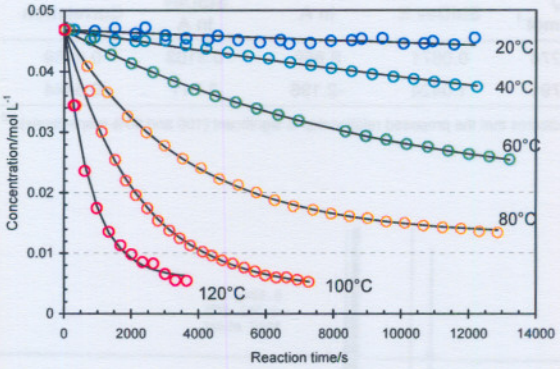


Figure 4.58 The decomposition of the carbene at different temperatures ($RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl)

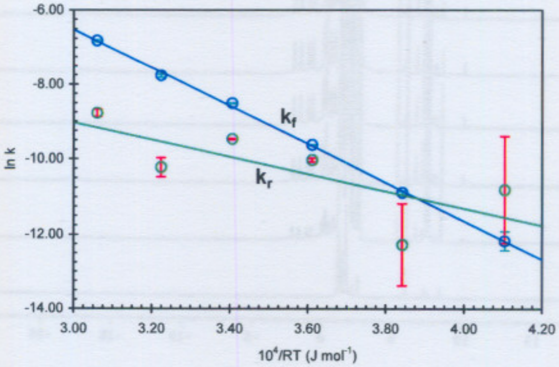
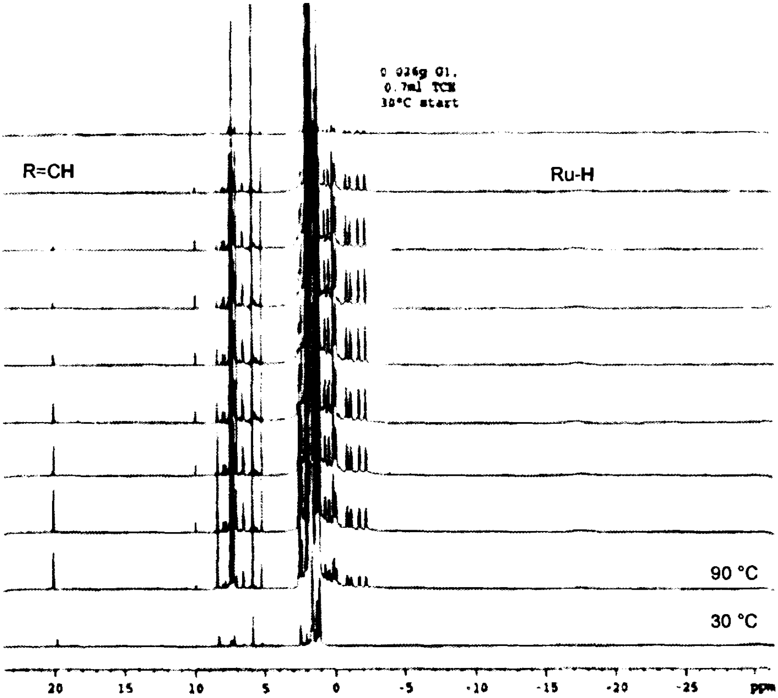


Figure 4.59 Arrhenius plot for the decomposition of ($RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl.

Table 4.8 Table of the Arrhenius parameters, standard deviations and other statistic values of the decomposition of $RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl.

	E_a/ 10^4 J mol^{-1}	StdDev E	ln A	StdDev ln A	Correlation	F_{obs}(1)
k_f	-5.1274	0.0871	8.859	0.3103	0.9989	3460
k_r	-2.2791	1.0424	-2.196	3.711	0.5444	4.8

(1) F-statistic indicates that the proposed relationship is significant (100 and 88% respectively).[5,6]



Spectrum 4.1 The disappearance of the carbene hydrogen peak (Ru=CH) and the appearance of a metal hydride peak (Ru-H) with time. The 1st spectrum was taken at 30 °C and then the temperature was raised to 90 °C [$RuCl_2(=CHPh)(PCy_3)_2$/deuterated TCE] (see Appendix for individual spectra).

4.11.2 Isomerisation reactions with $RuCl_2(=CHPh)(PCy_3)_2$

The product mixtures of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene and $RuCl_2(=CHPh)(PCy_3)_2$/1-octene were characterized by both ^1H and ^{13}C NMR NMR spectroscopy. The results are displayed in Spectrum 4.2 – 4.5.

Spectrum 4.6 shows the ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$ /1-octene in deuterated TCE at 30 °C. The disappearance of the benzylidene at -20 ppm was observed along with the initial formation the alkylidene. On heating the deuterated TCE solution of $RuCl_2(=CHPh)(PCy_3)_2$ to 90 °C, the alkylidene resonance disappeared and a broad hydride resonance appeared at -18 ppm (Spectrum 4.7).

The most characteristic feature in the NMR spectra of thermolysis products of $RuCl_2(=CHPh)(PCy_3)_2$ are signals of the π–allyl ligands which appear in the range 4.5 – 3.3 ppm. These resonances do not overlap the resonances of $RuCl_2(=CHPh)(PCy_3)_2$ and of the free octenes.

In ^{31}P NMR, the benzylidene shows a singlet at 36.23 ppm. The mixture containing 1-octene showed the disappearance of the benzylidene peak at 36.23 ppm and the appearance of the alkylidene at 35.45 ppm. Upon heating the mixture, ^{31}P NMR showed the slow disappearance of the signal at 35.45 ppm from $RuCl_2(=CHPh)(PCy_3)_2$ concomitant with the emergence of a new peak at 43.04 ppm among others, which may be due to formation of the hydride (Spectrum 4.8 – 4.10)

Spectrum 4.11 shows the ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$ /4-octene in deuterated toluene at 90 °C. After approximately 10 min, the benzylidene at 19.6 ppm had disappeared and there was no new peak formed (Spectrum 4.12).

^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene in TCE showed a resonance at δ = 19.6 ppm (Spectrum 4.13). On heating the deuterated TCE solution of $RuCl_2(=CHPh)(PCy_3)_2$ at 90 °C, the bezylidene peak disappeared completely after approximately 6 min and a new, broad hydride peak appeared at -17 ppm (NMR spectrum 4.14).

After 2 h of heating at 90 °C, the mixture was cooled down to 30 °C, the broad resonance at δ = -17 ppm disappeared (Spectrum 4.15). After heating the sample back to 90 °C, the signal at δ = -17 ppm reappeared. The temperature was increased to 110 °C, and this led to a sharper hydride peak (See Appendix).

The sample was left overnight at 90 °C, a new signal was observed at 12.5 ppm (Spectrum 4.16). The temperature was gradually decreased and the intensity of the hydride peak at -17 ppm slowly declined while that of the new peak at 12.5 ppm was enhanced.

At 40 °C the hydride peak disappeared completely and after cooling the sample to 0 and -30 °C, the broad signal at 12.5 ppm gives two sharp resonances at 15.5 ppm and 13.5 ppm (Spectrum 4.17 – 4.19). After leaving it overnight at 90 °C in the NMR, the temperature was decreased to 80, 70, 60 and 40 °C (See Appendix, Spectrum B2.17 - B2.21).

4.12 References

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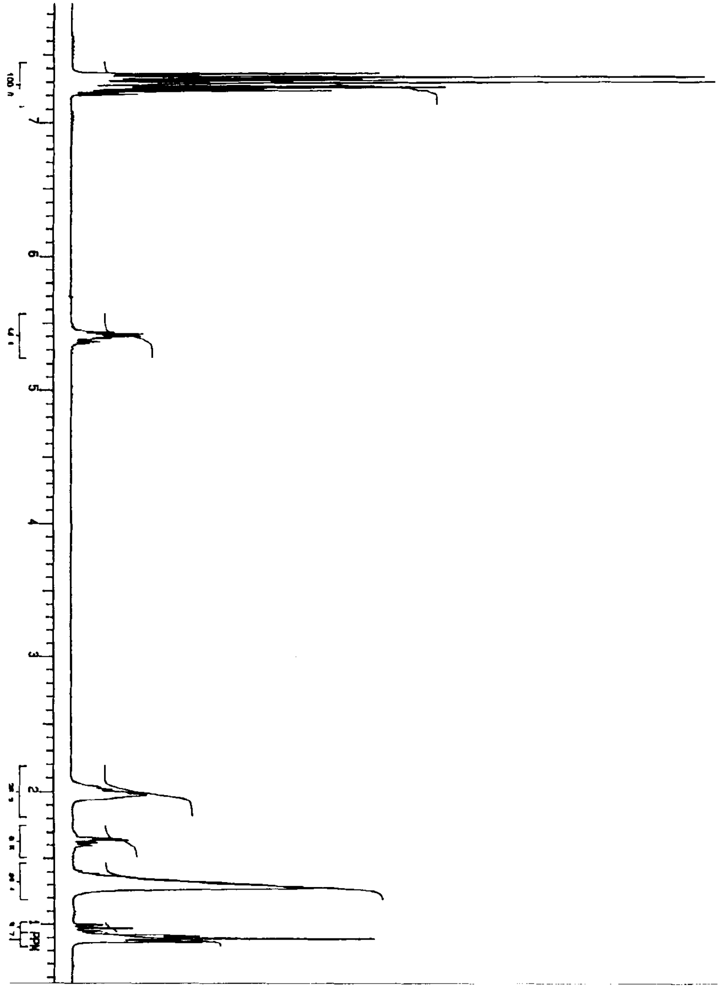
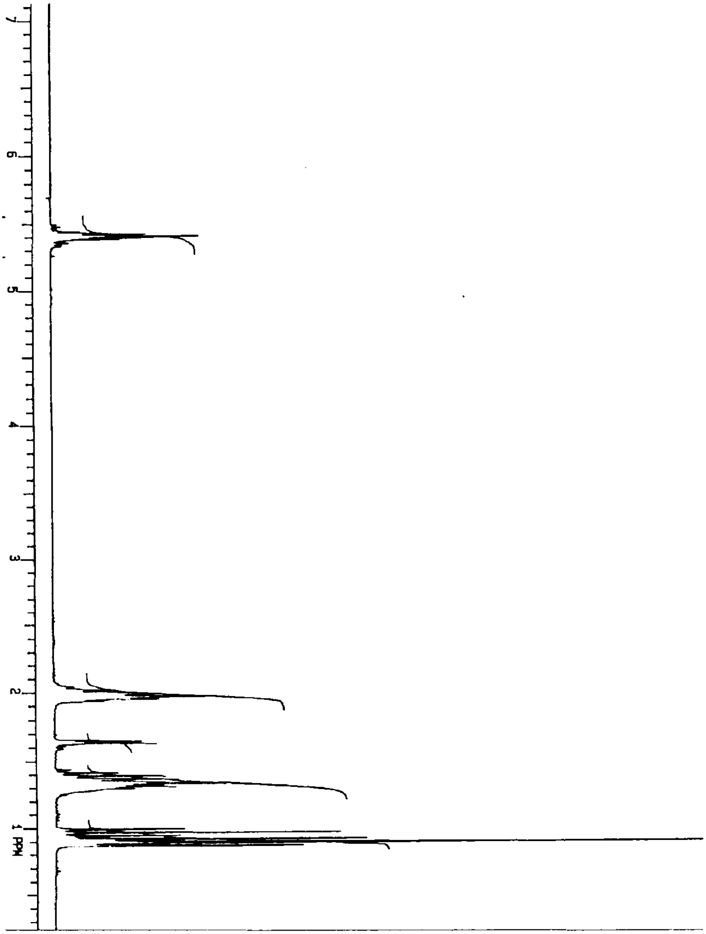
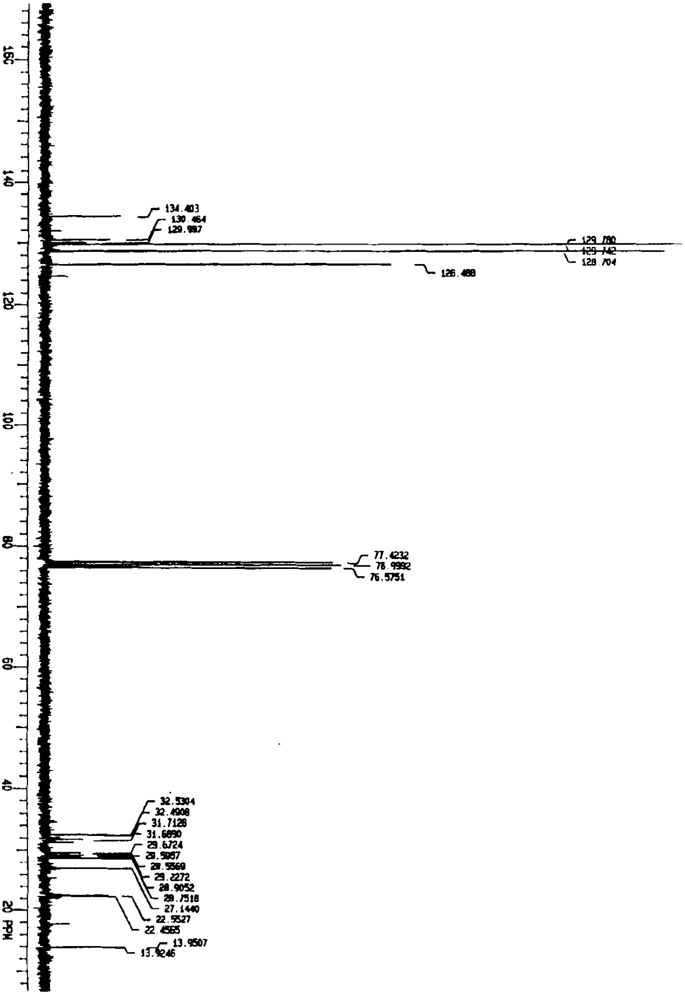


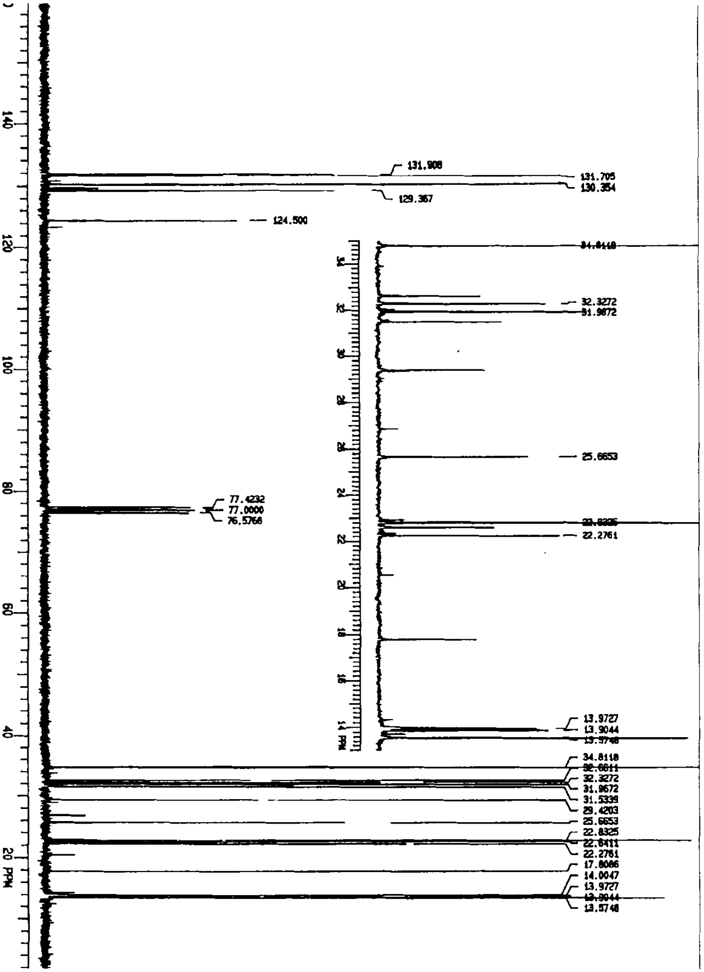
Spectrum 4.2 ^{1}H NMR spectrum of 1-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl at 120 °C after 24 h.



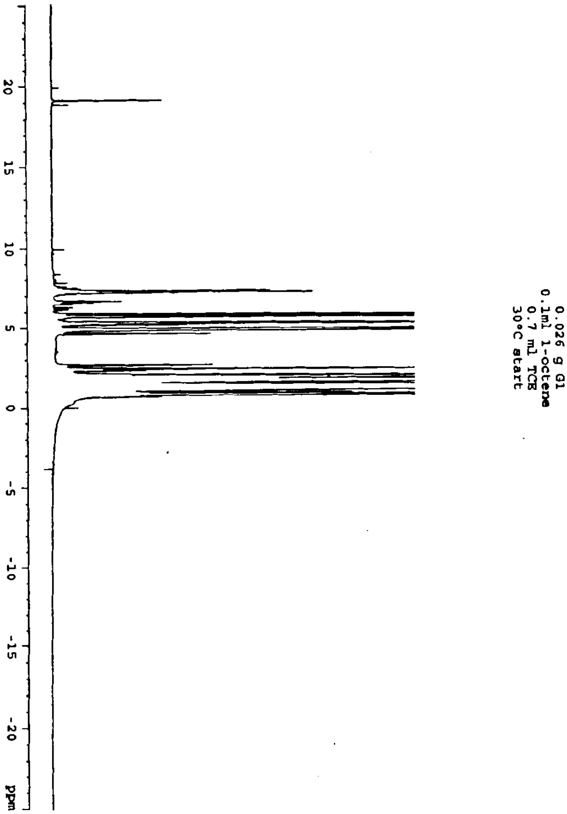
Spectrum 4.3 ^{1}H NMR spectrum of 4-octene/RuCl$_2$(=CHPh)(PCy$_3$)$_2$ in C_6D_5Cl at 120 °C after 24 h.



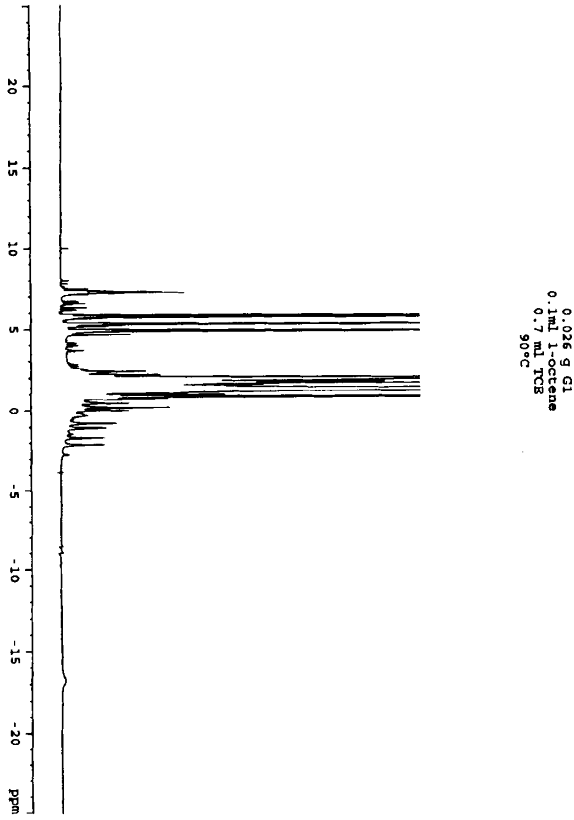
Spectrum 4.4 ^{13}C NMR spectrum of 1-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl at 120 °C after 24 h.



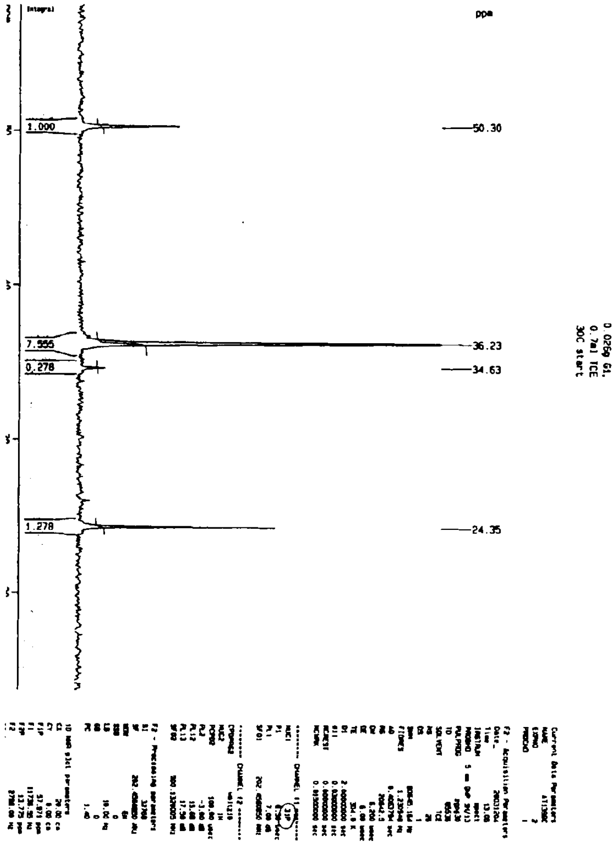
Spectrum 4.5 ^{13}C NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl at 120 °C after 24 h.



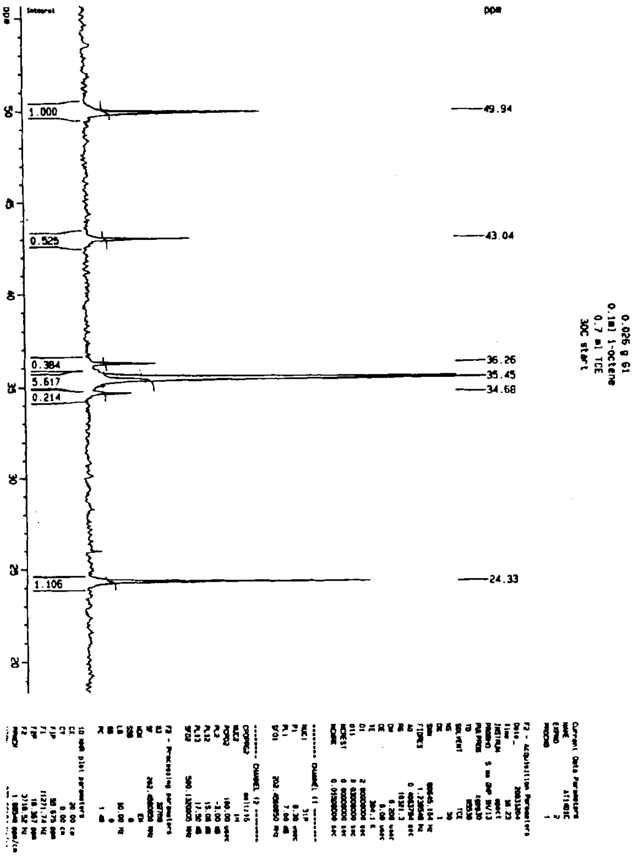
Spectrum 4.6 ^{1}H NMR spectrum of 1-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 30 °C.



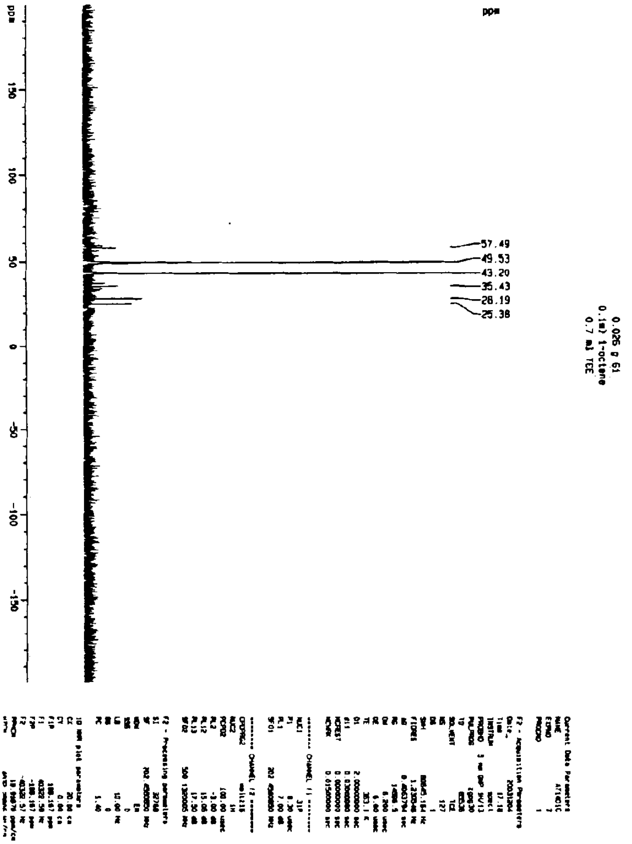
Spectrum 4.7 ^1H NMR spectrum of 1-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 90 °C.



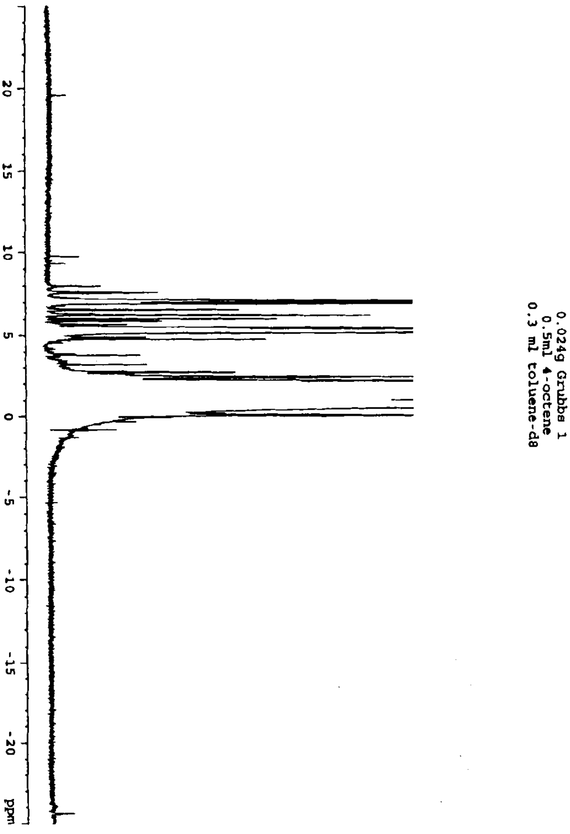
Spectrum 4.8 ^{31}P NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 30 °C.



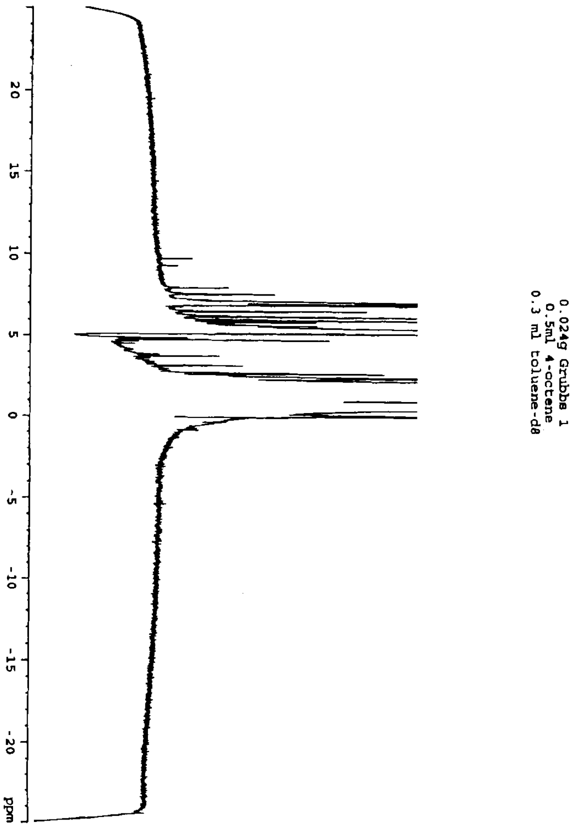
Spectrum 4.9 ^{31}P NMR spectrum of 1-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 30 °C



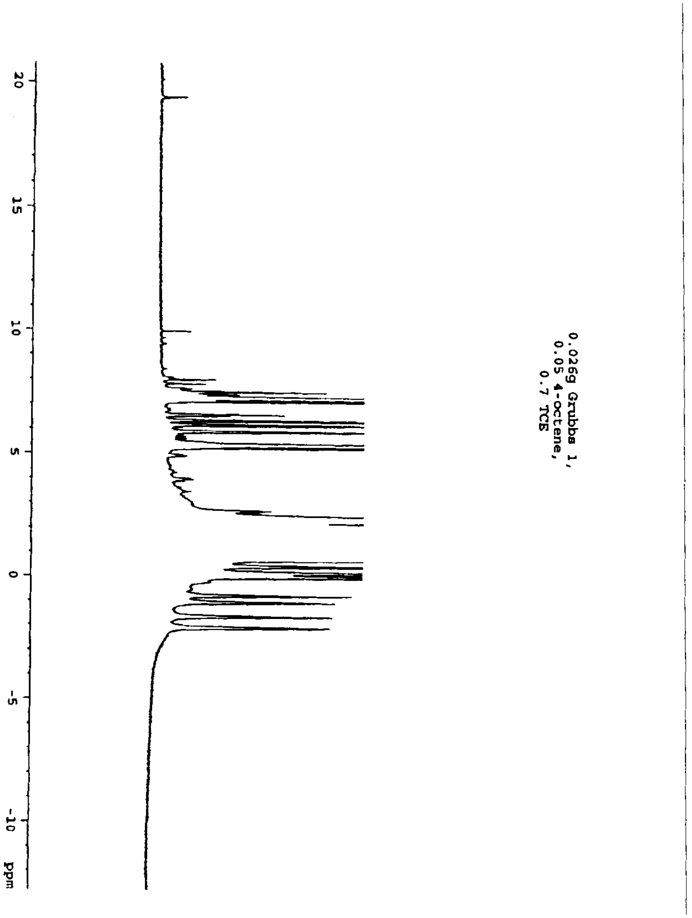
Spectrum 4.10 ^{31}P NMR spectrum of 1-octene/RuCl$_2$(=CHPh)(PCy$_3$)$_2$ in TCE at 90 °C.



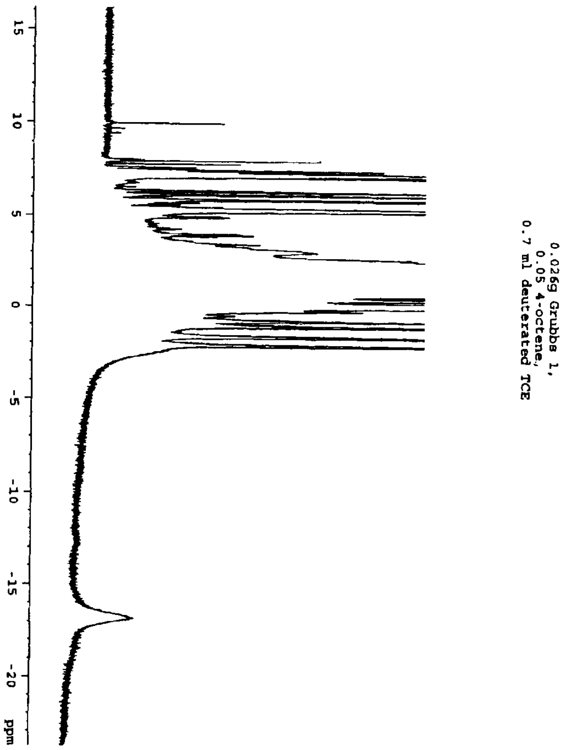
Spectrum 4.11 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in $C_6D_5CD_3$ at 90 °C.



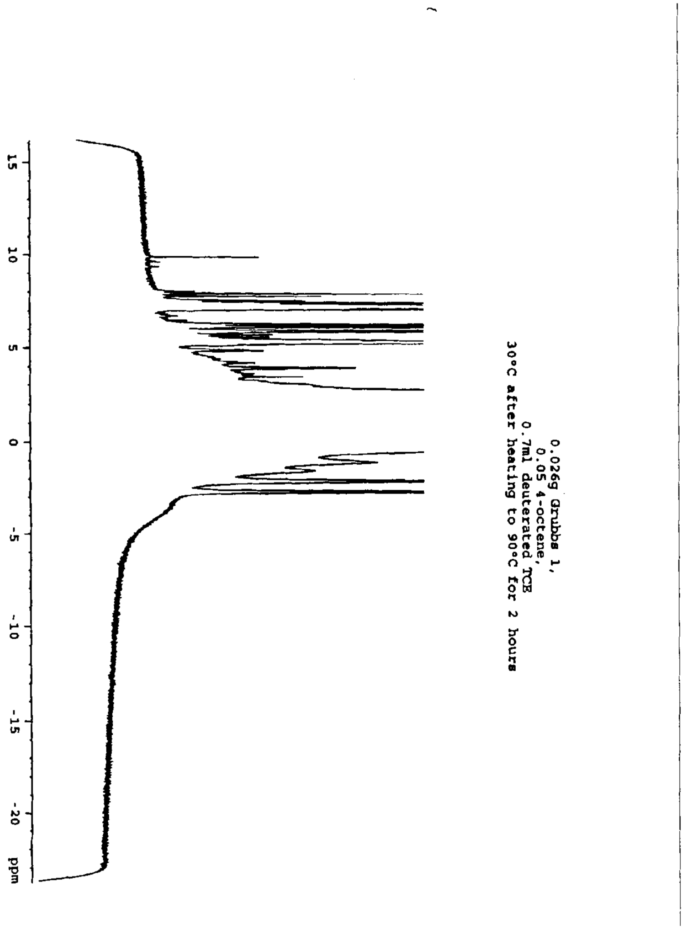
Spectra 4.12 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in $C_6D_5CD_3$ at 90 °C after12 min.



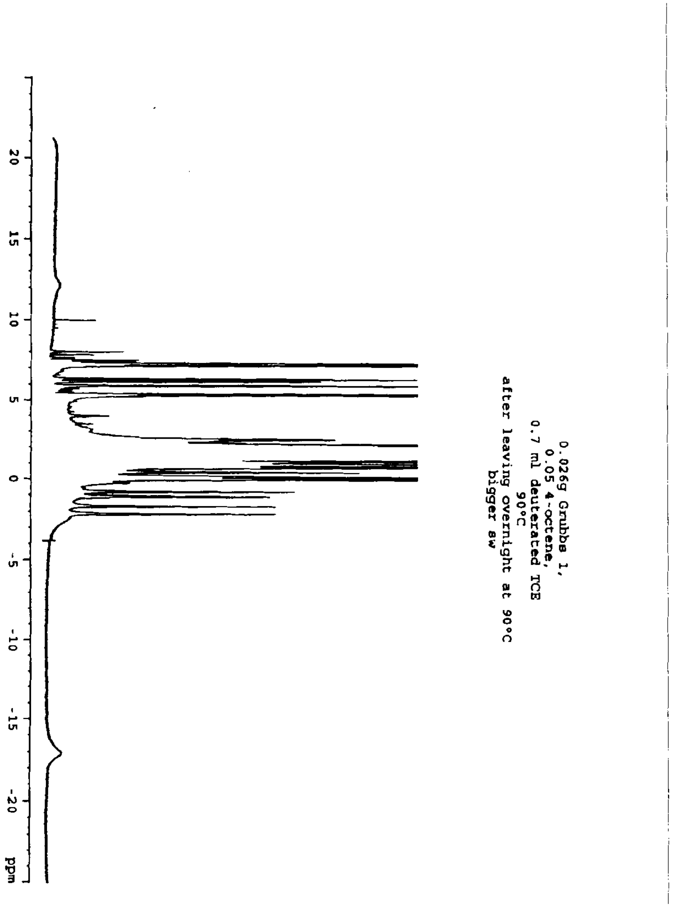
Spectrum 4.13 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 90 °C.



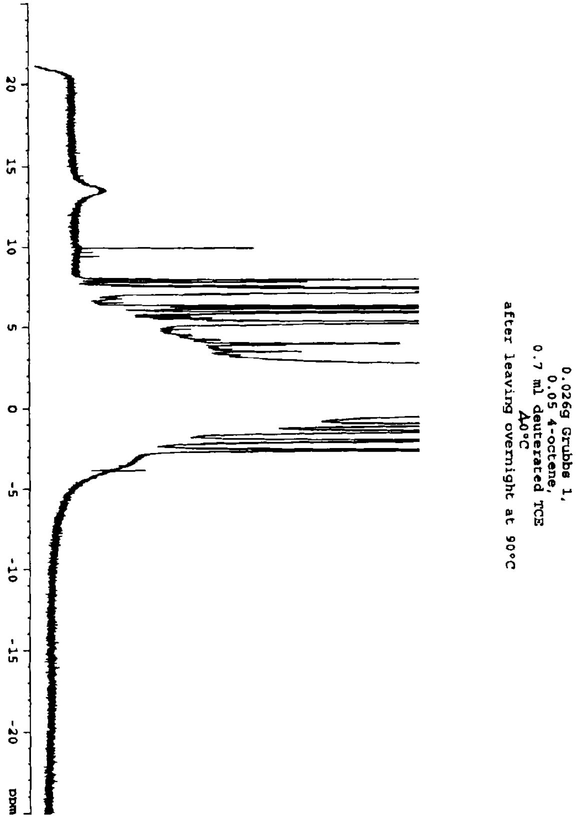
Spectrum 4.14 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 90 °C after 6 min.



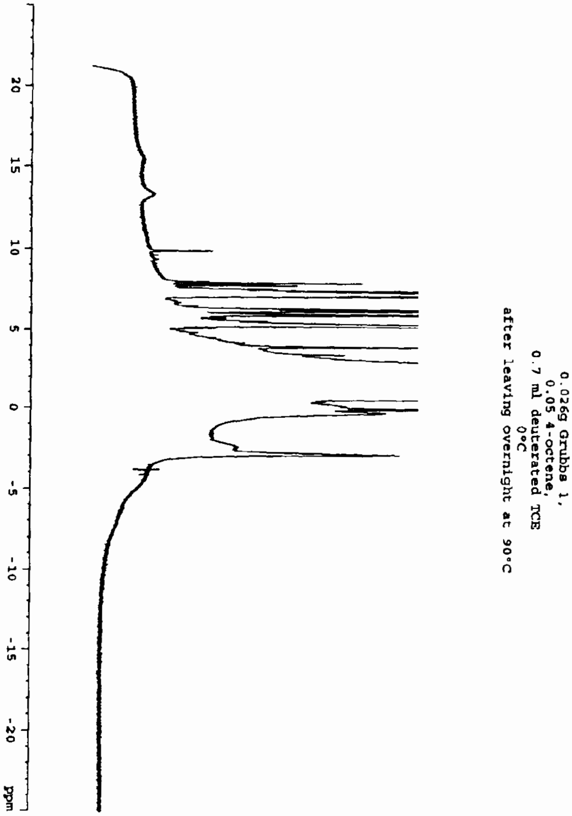
Spectrum 4.15 ^{1}H NMR spectrum of 4-octene/RuCl$_2$(=CHPh)(PCy$_3$)$_2$ in TCE, after heating at 90 °C for 2 h and cooling to 30 °C



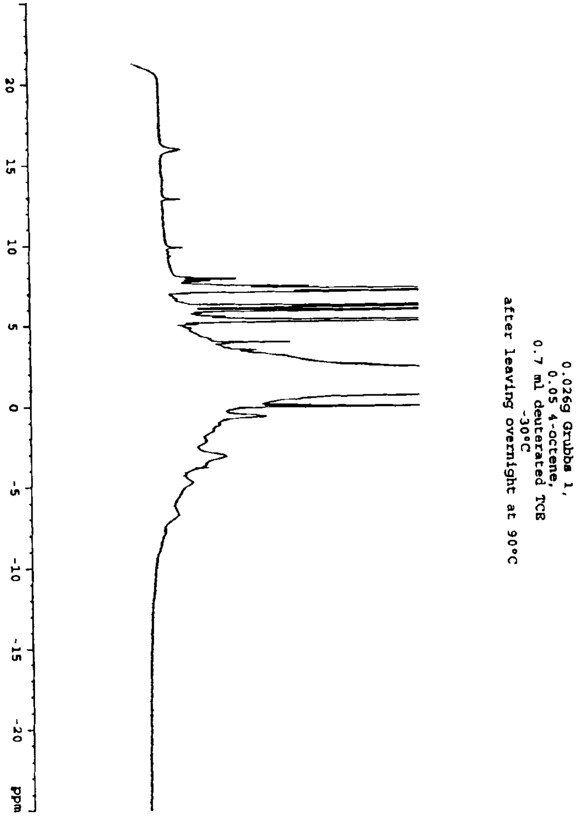
Spectrum 4.16 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE at 90 °C after 24 h.



Spectrum 4.17 ^{1}H NMR spectrum of 4-octene/RuCl$_2$(=CHPh)(PCy$_3$)$_2$ in TCE, left overnight at 90 °C and then cooled from 90 °C to 40 °C.



Spectrum 4.18 ^{1}H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE, left overnight at 90 °C and then cooled after from 40 °C to 0 °C.



Spectrum 4.19 ^1H NMR spectrum of 4-octene/$RuCl_2(=CHPh)(PCy_3)_2$ in TCE, left overnight at 90 °C and then cooled from 0 °C to -30 °C.

5 CONCLUSIONS

5.1 Discussion of the results

A number of ruthenium complexes, particularly hydrides, have been found to exhibit catalytic double bond isomerisation toward alkenes.[1] In this study the ruthenium carbenes were found to be more catalytically active towards alkene isomerisation than metathesis at high temperatures. A clear understanding of the role, activity and the selectivity of the catalysts has been formed.

5.1.1 $RuCl_2(=CHPh)(PCy_3)_2/PhCl$ catalytic system

a. *Effect of temperature*

It is clear that $RuCl_2(=CHPh)(PCy_3)_2$ is a capable double bond isomerisation catalyst for internal alkenes (Figure 4.1 – 4.8). No metathesis products were detected in any of the reactions using it. The activity of this catalyst in the catalytic isomerisation of alkenes is an indication of the coordinating ability of this complex towards linear alkenes. It is evident that an increase in temperature results in an increase in initial reaction rate as expected. The end of run conversions show that, at higher temperatures, significant catalyst decomposition is occurring. At temperatures > 120 °C, at 120 min, there is no further catalyst activity (Figure 4.3). In contrast, the run at 80 °C show no real indication of catalyst deactivation (Figure 4.1).

A temperature of 80 °C is necessary to obtain a detectable conversion of the substrate. The conversion increases from 15 % at 80 °C to 85 % at 150 °C for the internal alkene and from 55 % to 95 % for the terminal alkene (Figure 4.14 and 4.17) after 2 h. The number of linear isomers of 4-octene increases almost ten times when the temperature is raised from 80 to 150 °C. Catalyst performance could be significantly improved by using a higher temperature.

When it comes to terminal alkenes, the complex is catalytically active for isomerisation and metathesis. At room temperature the catalyst showed high selectivity towards metathesis, but low conversion (Figure 4.14). An increase in temperature results in an increase in initial reaction rate for isomerisation, although slower compared to the internal alkenes (Figure 4.15 – 4.17).

b. *Effect of ruthenium concentration*

An increase in the catalyst concentration affects the rate of the isomerisation reaction differently for internal and terminal alkenes. The conversion decreases from 75 % to 45 % for internal alkenes when the catalyst concentration increases (Figure 4.5 – 4.7). With the terminal alkenes the difference is not significant (Table 4.4). This may indicate that bimolecular decomposition is a predominant pathway for the decomposition of Grubbs 1. As the catalyst concentration increases, the chances of two ruthenium centers interacting is increased. While absolute ruthenium concentration increases, the effective ruthenium concentration decreases with increasing [Ru], and reaction rates are slower than expected.

c. *Effect of solvents*

The nature of the solvent also affects the isomerisation rate of both terminal and internal alkenes. Very low or no conversion was obtained in a low polarity solvent such as CCl_4, whereas high conversions were obtained in a hydrogen donor solvent such as propanol (Table 4.1, Table 4.5 and Figure 4.8 – 4.9). The higher value obtained in propanol may be attributed to a transformation of the catalytic precursor in the reaction conditions adopted, and consequently the mechanism changes[2]. Large differences in activities were found in the selected solvents. The best performance was observed in dichloromethane for terminal alkenes and for internal alkenes in chlorobenzene (Figure 5.1 and 5.2).

d. *Effect of chain length*

The chain length of the alkene has a significant influence on the isomerisation activity and selectivity of Grubbs 1. Upon increasing the chain length from 4-octene to 4-nonene to 5-decene, isomerisation activity increased in the following order: 4-octene > 4-nonene > 4-decene (Figure 4.20 and Figure 4.21). It is clear that short chain alkenes achieve high isomerisation activity (Figure 5.3).

Alkenes with longer chain alkyl groups on the π-bond carbons are more stable due to the inductive effect of alkyl groups which release electron density toward the sp^2 carbons.[3,4] The order of stability is 4-octene > 3-octene > *trans*-2-octene > *cis*-2-octene > 1-octene (Figure 5.4). The greater potential energy of *cis*-isomers can be attributed to strain caused by the crowding of two alkyl groups on the same side of the double bond. Isomerisation favours the formation of more stable internal alkenes. For 1-octene, more metathesis than isomerisation products were formed.

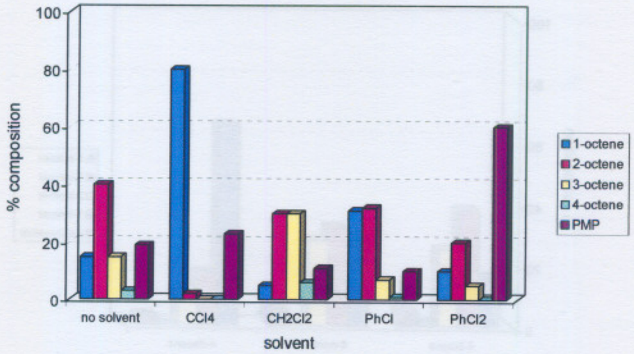


Figure 5.1 The influence of the solvent on the reactions of 1-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min).

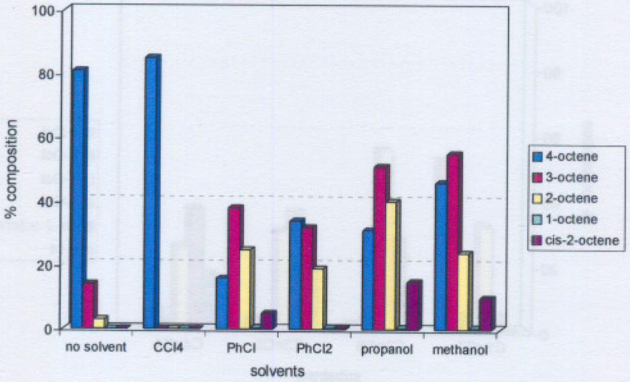


Figure 5.2 The influence of the solvent on the reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min).

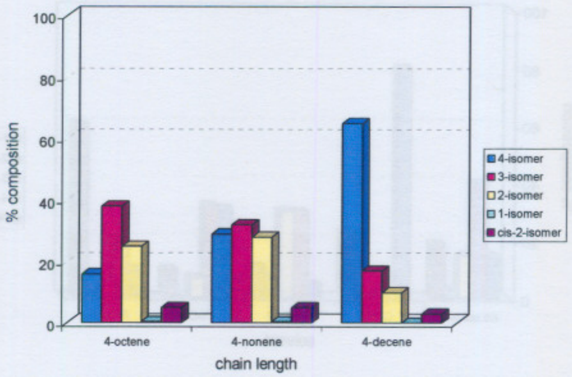


Figure 5.3 The influence of the chain length on the reactions of internal alkenes in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

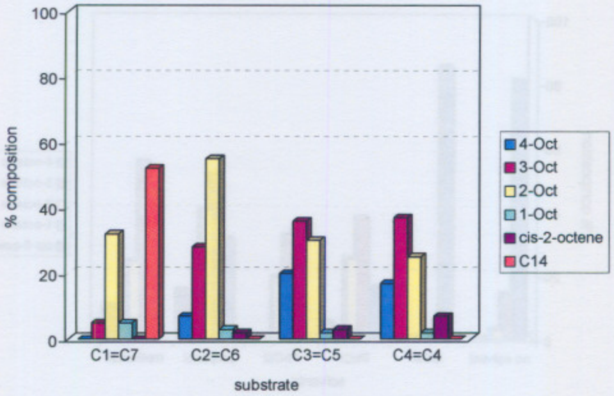


Figure 5.4 The influence of the double bond position on the reactions of octene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

5.1.2 RuCl$_2$(=CHPh)(IMes)(PCy$_3$)/PhCl catalytic system

a. *Effect of temperature*

It is evident that at temperatures ≥ 100 °C, the catalyst is highly selective towards the isomerisation to 3-octene (±100 %) but with low end conversion of about 30 % (Figure 4.22 – 4.24). At higher temperatures the selectivity decreases as more isomers and metathesis products are formed. Another factor is that catalyst decomposition is occurring because after 60 min at 120 °C, there is no further catalyst activity (Figure 4.25). At 150 °C, the metathesis reaction is suppressed (Figure 4.26).

When it comes to terminal alkenes, the catalyst is selective toward the metathesis reaction. At temperatures ≤ 100 °C, primary metathesis products are formed, but as the temperature is increased more secondary metathesis products are formed Figure (4.32 – 4.34).

b. *Effect of ruthenium concentration*

Doubling of catalyst concentration did not lead to a significant change in the reaction rate, in fact, for the first hour of the reaction, they looked almost similar. At the end of the runs it was the high ruthenium concentration that had the highest conversion. The selectivity also increases with increasing ruthenium concentration (Figure 4.27 – 4.29).

A decrease in the catalyst concentration leads to the formation of metathesis products and slows down the isomerisation product formation (Figure 5.5). Different results were obtained for 1-octene where high catalyst concentrations led to more metathesis products ($C_9 - C_{20}$).

c. *Effect of chain length*

The catalyst is selective towards the metathesis reaction over isomerisation. With the isomerisation of higher alkenes, activity decreased with an increase in the chain length and more metathesis products were formed (Figure 4.35, 4.36 and Figure 5.6).

The more stable alkenes give more isomerisation products than metathesis products. The rate of the reaction decreases with the increasing stability of the substrate (Figure 5.7).

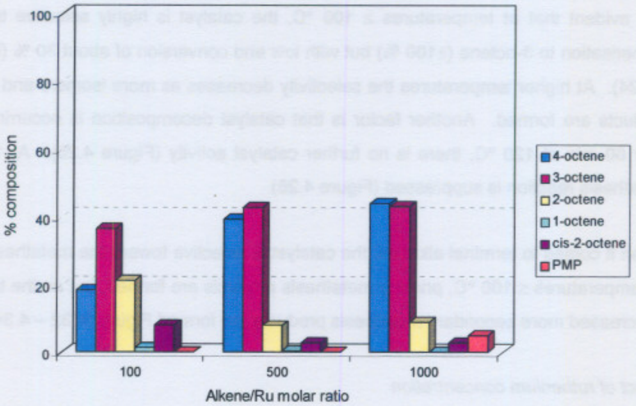


Figure 5.5 The influence of the alkene/Ru molar ratio on the reactions of 4-octene in the presence of $RuCl_2(=CHPh)(PCy_3)(IMes)$ (T = 150 °C; t = 120 min; PhCl).

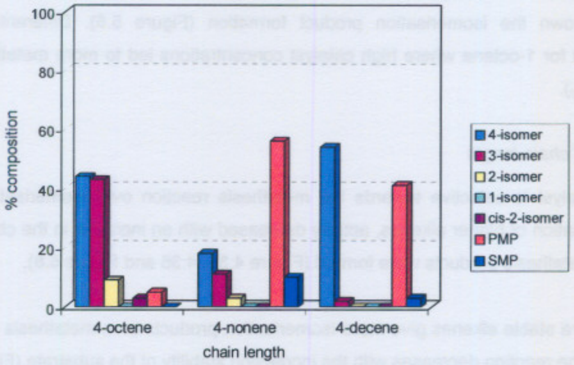


Figure 5.6 The influence of the chain length on the reactions of the internal alkenes in the presence of $RuCl_2(=CHPh)(PCy_3)(IMes)$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

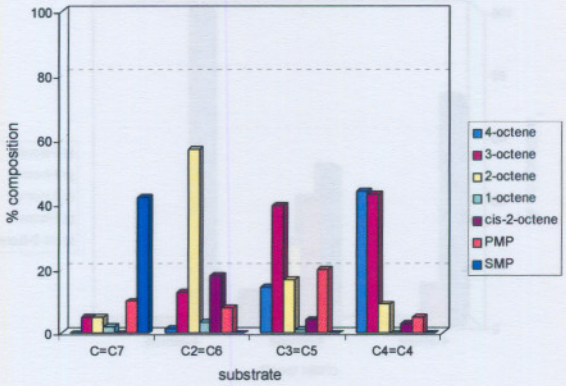


Figure 5.7 The influence of the double bond position on the reactions of octene in the presence of $RuCl_2(=CHPh)(PCy_3)(IMes)$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

5.1.3 $(Ph_3P)_3Ru(CO)(Cl)H/PhCl$ catalytic system

a. Effect of temperature

The $(Ph_3P)_3Ru(CO)(Cl)H/PhCl$ catalytic system is not active for the isomerisation of internal alkenes at low temperatures. Interestingly, at high temperatures, especially after prolonged reaction times, isomerisation products were detected (Figure 4.47). The catalyst showed high selectivity towards isomerisation to 3-octene but low conversion. The run at 150 °C shows no real indication of catalyst deactivation.

$(Ph_3P)_3Ru(CO)(Cl)H/PhCl$ is catalytically active for the isomerisation of terminal alkenes even at room temperature (Figure 4.46). It is evident that an increase in temperature result in an increase in initial reaction rates. After 1 h at 150 °C, there is no further activity and end of run conversion is around 95 % (Figure 4.49). This catalyst is clearly not active for the metathesis of both terminal and internal alkenes.

b. Effect of chain length

It is evident that an increase in chain length from (C_8 –C_9) results in an increase in the initial reaction rate, but from C_9 – C_{10} there is a decrease in the initial reaction rate (Figure 5.8).

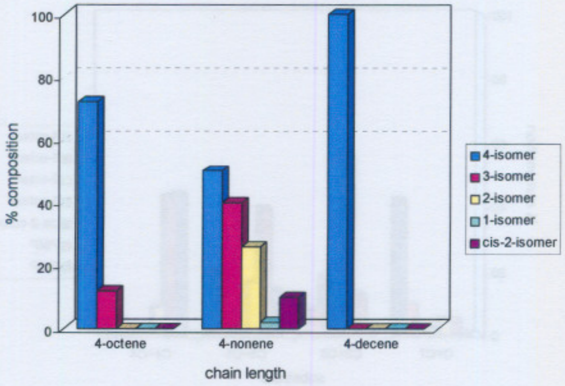


Figure 5.8 The influence of chain length on the reactions of the internal alkenes in the presence of $RuCl(H)(PPh_3)_3(CO)$ (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

5.1.4 Rhodium/PhCl catalytic systems

The rhodium carbene and dimer are catalytically active and selective for the isomerisation of both internal and terminal alkenes (Figure 4.53 – 4.55). Metathesis reactions have never been observed in reactions involving these two catalysts.

5.1.5 Metal chlorides catalytic systems

$RhCl_3{\cdot}3H_2O$ and $RuCl_3$ cannot isomerise alkenes rapidly. Longer reaction hours and high temperatures are required to get the isomerisation products. These compounds are not catalytically active for the metathesis of internal alkenes (Figure 4.56 and 4.57)

5.1.6 Turnover numbers and turnover frequencies of Grubbs catalysts

Effective turnover numbers (TON) and turnover frequencies (TOF) have been obtained for the isomerisation of various substrates in the presence of ruthenium-based catalysts.[5]

Dinger and Mol[15] found that the total turnover number 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 yet 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.

Isomerisation experiments that ranged from room temperature to 150 °C were carried out to determine the effect of temperature on TON's for $RuCl_2(=CHPh)(PCy_3)_2$ and $RuCl_2(=CHPh)(PCy_3)(IMes)$. $RuCl_2(=CHPh)(PCy_3)_2$ performed better than $RuCl_2(=CHPh)(PCy_3)(IMes)$ displaying much higher TON after 24 h (Figure 5.9), fast initiation rates should give rise to higher TON's.

$RuCl_2(=CHPh)(PCy_3)_2$ shows a clear drop-off in activity on going from terminal alkenes to internal ones whilst $RuCl_2(=CHPh)(PCy_3)(IMes)$ gives TON's higher than those measured for 1-octene (Figure 5.10).

The efficiency of the catalyst is expressed by TOF = (d[P]/dt)/[B].[6] This is the ratio of the moles of product to moles of catalyst over time. If several isomerisations occur in rapid sequence it becomes difficult to obtain an accurate TOF.

The rates of the isomerisation reaction of 1-octene using Grubbs 1 were followed at 100 to 150 °C. 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 solution, be it catalytically active, decomposed or dormant. The TOF increases with the increase in the reaction temperature.

Table 5.1 Effective TOF after 3 h at different reaction temperatures for the isomerisation of 1-octene using $RuCl_2(=CHPh)(PCy_3)_2$ as the catalyst.

Temp/°C	100	120	150
TOF/s^{-1}	6960	13020	18720

In consideration of the fact that 2-octene, 3-octene and 4-octene were isomerised after a reaction time of 1 h, to isomerise internal alkenes a very long reaction time is not required but a high temperature. High temperature and extended reaction times are necessary to overcome the high energy of activation.

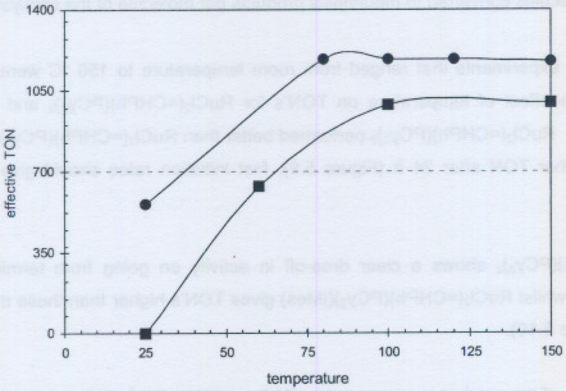


Figure 5.9 Effective TON as function of temperature for the isomerisation of 1-octene (alkene/Ru molar ratio = 1000; t = 24 h; PhCl). [● $RuCl_2(=CHPh)(PCy_3)_2$, ■ $RuCl_2(=CHPh)(PCy_3)(IMes)$]

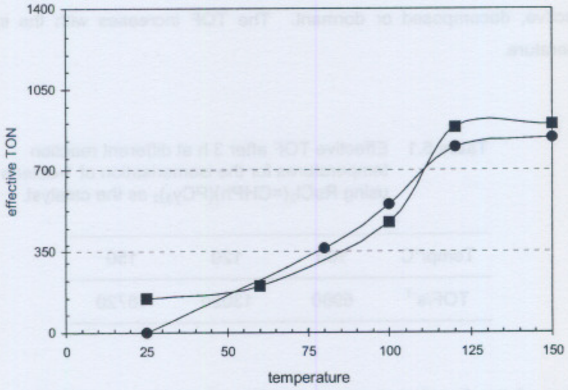


Figure 5.10 Effective TON as function of temperature for the isomerisation of 4-octene (alkene/Ru molar ratio = 1000; t = 24 h; PhCl). [● $RuCl_2(=CHPh)(PCy_3)_2$, ■ $RuCl_2(=CHPh)(PCy_3)(IMes)$]

5.2 NMR analysis

^{1}H NMR spectroscopy showed complete conversion of the starting benzylidene to a new alkylidene, which is in agreement with previous studies that showed that when the benzylidene initiator, $RuCl_2(=CHPh)(PCy_3)_2$, reacted with terminal acyclic alkenes, the initial organometallic product is the alkene.[14]

The loss of Grubbs catalyst becomes a significant problem at extended reaction times. Decomposition is evident as the intensity of the carbene proton peak at 20.0 ppm on the ^{1}H NMR spectra slowly declines. $RuCl_2(=CHPh)(PCy_3)(IMes)$ 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 $RuCl_2(=CHPh)(PCy_3)_2$.

At present, wherever possible, the best technique for hydride detection is proton NMR. In a majority of cases the hydride resonance occurs in the range 0 to -40 ppm with reference to Me_3Si. The M-H bond is of medium stability : thus its dissociation enrergy varies between 37 and 65 kcal/mol.[15] From our studies we also observed a broad resonace at -18 ppm (Spectrum 4.7), which might be responsible for the isomerisation when the catalyst has decomposed

5.3 Reaction mechanism

The mechanism of double bond migration is generally believed to involve the formation of an alkyl complex from a hydridometal species and an alkene. When a secondary alkyl complex undergoes β-hydride abstraction, a C-H bond of lower energy may be broken and an isomerised alkene formed. Dissociation of this ligand forms the isomerised alkene[8].

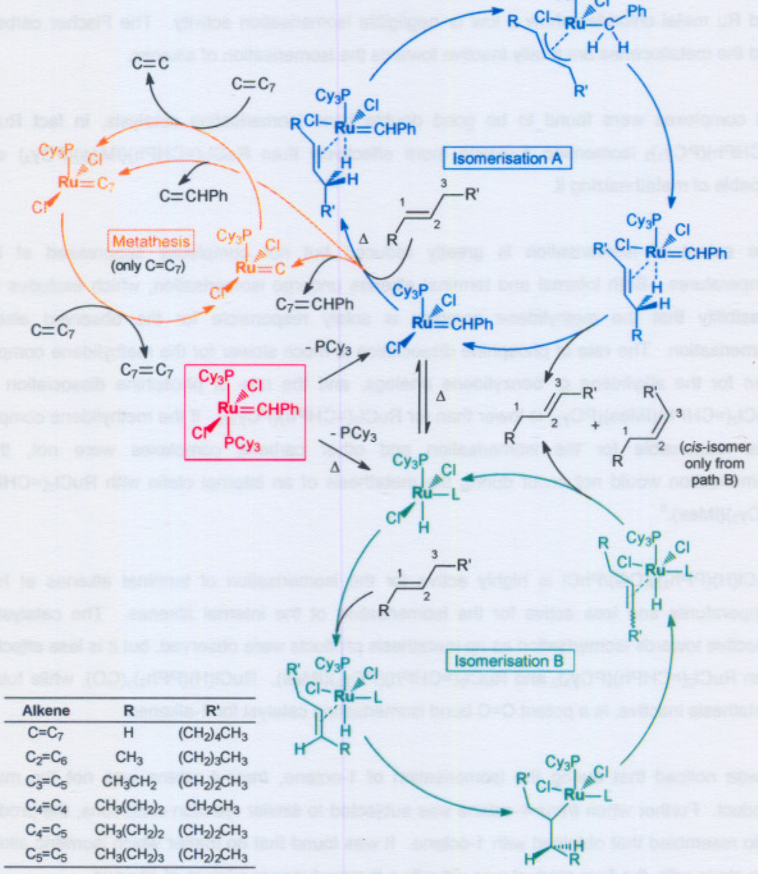
A number of reaction mechanisms have been proposed for the isomerisation of alkenes. Mechanistic studies have shown that ruthenium assisted isomerisations proceed through an intermolecular 1,3-migration of the allylic C-H, analogous to a π-allyl metal type mechanism.[9]

From our studies we found that the isomerisation reaction proceeded with first order kinetics in both catalyst and 4-octene, which provides strong support for an overall dissociative reaction mechanism in which the metallacyclobutane is generated from a 16-electron monophosphine/ alkene intermediate.[16] The mechanisms in Scheme 5.2 is proposed to explain the occurrence of the isomerisation and metathesis reactions in this study. The first step, which is the active catalyst initiation step, involves the dissociation of a PCy_3 ligand to form a monophosphine intermediate which can react along two possible pathways depending on *inter alia* the reaction temperature. At high temperatures, the reaction probably follows the **Isomerisation A** path, where the intermediate reacts with the alkene to form a metallacyclobutane, the deprotonation at the allylic position leads to a π-allyl complex, responsible for the double bond migration. The metallacycle then breaks down to form a new alkene and a new alkylidene product. At lower temperatures the **Metathesis** pathway is followed.

It is envisaged that the carbene carbon traps the allylic proton, considering that the high oxidation state of the ruthenium in Grubbs 2 will not favour the formation of a hydride complex. Furthermore, the IMes ligand, a strong σ-donor, will increase the basicity of the carbene. Since the isomerisation reactions were performed with or without solvent present and isomerisation still occurs in the absence of a credible proton source, it is likely that a π-allyl type or similar mechanism proposed by Grubbs and Trost is in effect.[10,11] To observe isomerisation via allylic intermediates, the solvent must be inert, cocatalysts avoided, and complexes chosen should not contain substituted phosphines as ligands.[13]

According to the NMR decomposition kinetic studies the carbene decomposes to a metal hydride (see Spectrum 4.1 and others). The ^{1}H NMR study of $RuCl_2(=CHPh)(PCy_3)_2$ showed the disappearance of the carbene peak and the appearance of a metal hydride at 90 °C in less than 10 min. The metal hydride formed in the absence of the alkene and could also be responsible for the isomerisation. From literature it was found that isomerisation via alkyl intermediates can be expected to occur whenever reactive hydrido-complexes are formed in solution. It is not necessary for the original complex itself to be a hydride. Complexes without hydrogen ligands may be converted to hydrido-complexes by reaction with a wide variety of reagents (e.g. amine bases, alcohols, protonic acids) that may be present as the solvent, or a cocatalyst. If such reagents are absent, a hydrido complex may form spontaneously by intramolecular reaction of a PPh_3 ligand with the transition metal.[13] In this study the metal hydride might be from the C-H activation by the Ru center biting into one of the cyclohexyl rings of the PCy_3 ligand. This could cause the shift in these protons forming a rigid 4- or 5-membered ring structure.

The second mechanism is along the **Isomerisation B** pathway. The first step, which is catalyst initiation, involves the simultaneous dissociation of one PCy_3 ligand and formation of an active monophosphine hydride intermediate at high temperatures. The Ru-H coordinates with an alkene giving an π-alkene metal complex, γ-H elimination leads to a metal σ-alkyl followed by an α-H migration along a Markovnikov insertion to form a π-alkene metal complex. The complex breaks down to form a new alkene and the metal hydride.



Alkene	R	R'
$C=C_7$	H	$(CH_2)_4CH_3$
$C_2=C_6$	CH_3	$(CH_2)_3CH_3$
$C_3=C_5$	CH_3CH_2	$(CH_2)_2CH_3$
$C_4=C_4$	$CH_3(CH_2)_2$	CH_2CH_3
$C_4=C_5$	$CH_3(CH_2)_2$	$(CH_2)_2CH_3$
$C_5=C_5$	$CH_3(CH_2)_3$	$(CH_2)_2CH_3$

Scheme 5.2 Proposed mechanism of the reactions of alkenes in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ (L = ligand).

5.4 Conclusions

$RuCl_2(=CHPh)(PCy_3)_2$, $RuCl_2(=CHPh)(IMes)(PCy_3)$, $RuCl(H)(PPh_3)_3(CO)$, rhodium carbene and dimer, are catalytically active in the isomerisation of 1-octene and 4-octene, whereas the Rh and Ru metal chlorides show a low or negligible isomerisation activity. The Fischer carbene and the metallocenes are totally inactive towards the isomerisation of alkenes.

Ru complexes were found to be good double bond isomerisation catalysts, in fact $RuCl_2(=CHPh)(PCy_3)_2$ isomerised 4-octene more effectively than $RuCl_2(=CHPh)(IMes)(PCy_3)$ was capable of metathesizing it.

The extent of isomerisation is greatly reduced but not completely suppressed at low temperatures. Both internal and terminal alkenes undergo isomerisation, which excludes the possibility that the methylidene complex is solely responsible for the observed alkene isomerisation. The rate of phosphine dissociation is much slower for the methylidene complex than for the alkylidene or benzylidene analogs, and the rate of phosphine dissociation for $RuCl_2(=CHPh)(IMes)(PCy_3)$ is lower than for $RuCl_2(=CHPh)(PCy_3)_2$. If the methylidene complex was responsible for the isomerisation and other carbene complexes were not, then isomerisation would not occur during the metathesis of an internal olefin with $RuCl_2(=CHPh)(PCy_3)(IMes)$.[6]

$RuCl(H)(PPh_3)_3(CO)/PhCl$ is highly active for the isomerisation of terminal alkenes at high temperatures and less active for the isomerisation ot the internal alkenes. The catalyst is selective towards isomerisation as no metathesis products were observed, but it is less effective than $RuCl_2(=CHPh)(PCy_3)_2$ and $RuCl_2(=CHPh)(PCy_3)(IMes)$. $RuCl(H)(PPh_3)_3(CO)$, while totally metathesis inactive, is a potent C=C bond isomerisation catalyst for 1-alkenes.

It was noticed that during the isomerisation of 1-octene, *trans*-4-octene was not the major product. Further when *trans*-4-octene was subjected to similar reaction conditions, the product ratio resembled that obtained with 1-octene. It was found that no matter which isomeric alkene one starts with, the final product was virtually a thermodynamic mixture of alkenes.

A delay in the productive metathesis of $RuCl_2(=CHPh)(IMes)(PCy_3)$ was observed at all reaction temperatures. This behaviour is consistent with the observation that catalyst initiation for $RuCl_2(=CHPh)(IMes)(PCy_3)$ is slower than for $RuCl_2(=CHPh)(PCy_3)_2$. We interpret the slower catalyst initiation to be a consequence of the rates of phosphine dissociation for the two complexes.

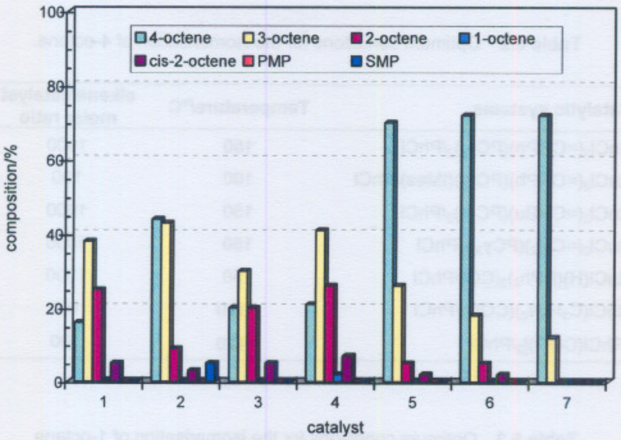


Figure 5.12 The influence of the catalyst on the reactions of 4-octene (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

1 $RuCl_2(=CHPh)(PCy_3)_2$ **2** $RuCl_2(=CHPh)(PCy_3)(IMes)$
3 $RuCl_2(=CH_2)(PCy_3)_2$ **4** $RuCl_2(=CHBu)(PCy_3)_2$ **5** $[RhCl(COD)]_2$
6 $RhCl(C_3H_5N_2)(COD)$ **7** $RuCl(H)(PPh_3)_3(CO)/PhCl$

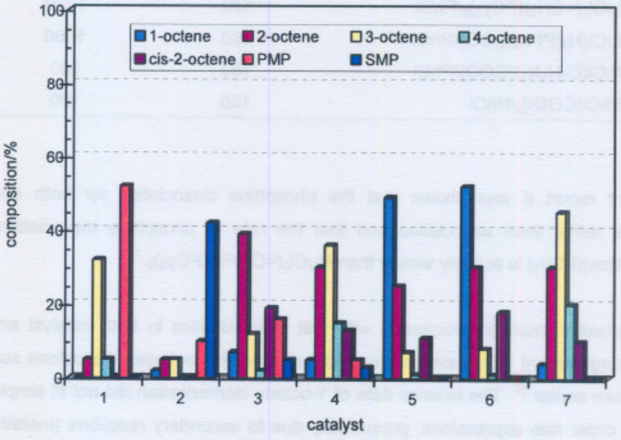


Figure 5.13 The influence of the catalyst on the reactions of 1-octene (T = 150 °C; alkene/Ru molar ratio = 1000; t = 120 min; PhCl).

Table 5.2 Optimum conditions for the isomerisation of 4-octene.

Catalytic systems	Temperature/°C	alkene/catalyst molar ratio
$RuCl_2(=CHPh)(PCy_3)_2/PhCl$	150	1000
$RuCl_2(=CHPh)(PCy_3)(IMes)/PhCl$	100	100
$RuCl_2(=CHBu)(PCy_3)_2/PhCl$	150	1000
$RuCl_2(=CH_2)(PCy_3)_2/PhCl$	150	1000
$RuCl(H)(PPh_3)_3(CO)/PhCl$	150	1000
$RhCl(C_3H_5N_2)(COD)/PhCl$	≤120	100
$[RhCl(COD)]_2/PhCl$	≤120	100

Table 5.3 Optimum conditions for the isomerisation of 1-octene

Catalytic systems	Temperature/°C	alkene/catalyst molar ratio
$RuCl_2(=CHPh)(PCy_3)_2/PhCl$	100	1000
$RuCl_2(=CHPh)(PCy_3)(IMes)/PhCl$	100	1000
$RuCl_2(=CHBu)(PCy_3)_2/PhCl$	150	1000
$RuCl_2(=CH_2)(PCy_3)_2/PhCl$	150	1000
$RuCl(H)(PPh_3)_3(CO)/PhCl$	150	1000
$RhCl(C_3H_5N_2)(COD)/PhCl$	150	100
$[RhCl(COD)]_2/PhCl$	150	100

In a recent report it was shown that the phosphine dissociation for both complexes is dissociative rather than associative and that the rate of phosphine dissociation for $RuCl_2(=CHPh)(IMes)(PCy_3)$ is actually slower than $RuCl_2(=CHPh)(PCy_3)_2$.[7]

The isomerisation reaction proceeded with first order kinetics in both catalyst and 4-octene which is in agreement with a simple bimolecular interaction between the octene substrate and the ruthenium center.[16] The kinetics data of 1-octene isomerisation did not fit simple first order or second order rate expressions, presumably due to secondary reactions (metathesis). The data showed a reasonably linear second order fit at the initial stages.

The catalytic activity of Grubbs catalyst in the isomerisation of octenes increase by more than an order of magnitude upon substitution of the olefin.[16] For example , replacing the internal alkene with the terminal alkene, lead to an in increase in tunover rates.

5.5 References

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SUMMARY

Different transition metal complexes such as $RuCl_2(=CHPh)(PCy_3)_2$, $RuCl_2(=CHPh)(PCy_3)$(IMes), $RuCl_2(=CH_2)(PCy_3)_2$, $RuCl_2(=CHBu)(PCy_3)_2$, $RuCl(H)(PPh_3)_3(CO)$, $RuCl_3$, $RhCl_3{\cdot}3H_2O$, were used to isomerise alkenes. For the majority of experiments, reactions were performed on 1-octene and 4-octene, gas chromatography was used to monitor the consumption of the starting alkenes and the formation of isomers.

The variation of the reaction temperature on the different catalytic systems, the variation of the alkene/catalyst molar ratio and the variation of the solvents on the isomerisation activity of the different catalytic systems were investigated. The results showed that the best conversion and selectivity are obtained with ruthenium carbenes. Isomerisation was observed at high temperatures $\geq$ 100 °C and at lower temperatures more metathesis products were observed.

Short chain alkenes achieved higher isomerisation activity than long chain alkenes: 4-octene > 4-nonene > 4-decene. Isomerisation favoured more stable internal alkenes with the order of activity being *trans*-4-octene > *trans*-3-octene > *trans*-2-octene > *cis*-2-octene > 1-octene.

From the study it is clear that $RuCl_2(=CHPh)(PCy_3)_2$ is a capable double bond isomerisation catalyst for internal alkenes because metathesis products were not detected in any of the reactions using it. But when it comes to terminal alkenes, the complex gives a mixture of isomerisation and metathesis products. $RuCl_2(=CHPh)(PCy_3)$(IMes) is catalytically active for the isomerisation and metathesis of both the internal and terminal alkenes at high temperatures, at room temperature it is selective towards the isomerisation of internal alkenes and metathesis of terminal alkenes.

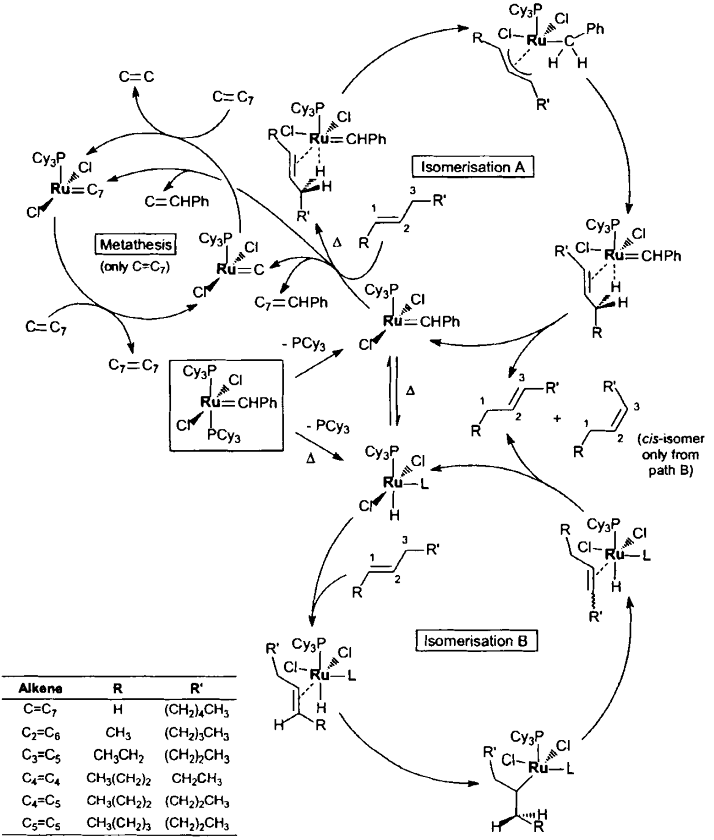
Although $RuCl(H)(PPh_3)_3(CO)/PhCl$ is catalytically active for the isomerisation of terminal alkenes at room temperature, it does not isomerise internal alkenes at lower temperatures. Interestingly, at high temperatures, especially after prolonged reaction times, isomerisation products were detected.

The rhodium carbene and dimer are also catalytically active and selective for the isomerisation of internal and terminal alkenes, metathesis reactions were not observed in reactions involving these two catalysts. $RhCl_3{\cdot}3H_2O$ and $RuCl_3$ cannot isomerise alkenes rapidly; longer reaction

hours and high temperatures are required to get the isomerisation products.

The isomerisation reaction proceeded with first order kinetics in both catalyst and 4-octene which is in agreement with a simple bimolecular interaction between the octene substrate and the ruthenium center. The kinetics data of 1-octene isomerisation did not fit simple first order or second order rate expressions, presumably due to secondary reactions (metathesis). The data showed a reasonably linear second order fit at the initial stages.

The reaction mechanisms can be illustrated by the catalytic cycles:



Alkene	R	R'
$C=C_7$	H	$(CH_2)_4CH_3$
$C_2=C_6$	CH_3	$(CH_2)_3CH_3$
$C_3=C_5$	CH_3CH_2	$(CH_2)_2CH_3$
$C_4=C_4$	$CH_3(CH_2)_2$	CH_2CH_3
$C_4=C_5$	$CH_3(CH_2)_2$	$(CH_2)_2CH_3$
$C_5=C_5$	$CH_3(CH_2)_3$	$(CH_2)_2CH_3$

OPSOMMING

Isomerisasie van alkene deur van metaalkarbene en verwante oorgangsmetaalkomplekse gebruik te maak

Verskillende oorgangsmetale soos $RuCl_2(=CHPh)(PCy_3)_2$, $RuCl_2(=CHPh)(PCy_3)(IMes)$, $RuCl_2(=CH_2)(PCy_3)_2$, $RuCl_2(=CHBu)(PCy_3)_2$, $RuCl(H)(PPh_3)_3(CO)$, $RuCl_3$, $RhCl_3{\cdot}3H_2O$, is gebruik om alkene te isomeriseer. In die meeste eksperimente is reaksies met 1-okteen en 4-okteen uitgevoer, gas chromatografie is gebruik om die verbruik van die beginalkene en die vorming van isomere te monitor.

Die invloed van die verandering van die reaksietemperatuur, alkeen/katalisatormolverhouding en oplosmiddels op die isomerisasieaktiwiteit van die verskillende katalisatorsisteme is ondersoek. Die resultate toon dat die beste omskakeling en selektiwiteit met die rutenium-karbene verkry is. Isomerisasie is by hoë temperature $\geq$ 100 °C waargeneem en by laer temperature is meer metatese waargeneem.

Kortketting alkene het hoër isomerisasieaktiwiteit as langketting alkene vertoon: 4-okteen > 4-noneen > 4-dekeen. Isomerisasie het ook by voorkeur met die meer stabiele interne alkene plaasgevind met die aktiwiteitsorde: *trans*-4-okteen > *trans*-3- okteen > *trans*-2- okteen > *cis*-2-okteen > 1- okteen.

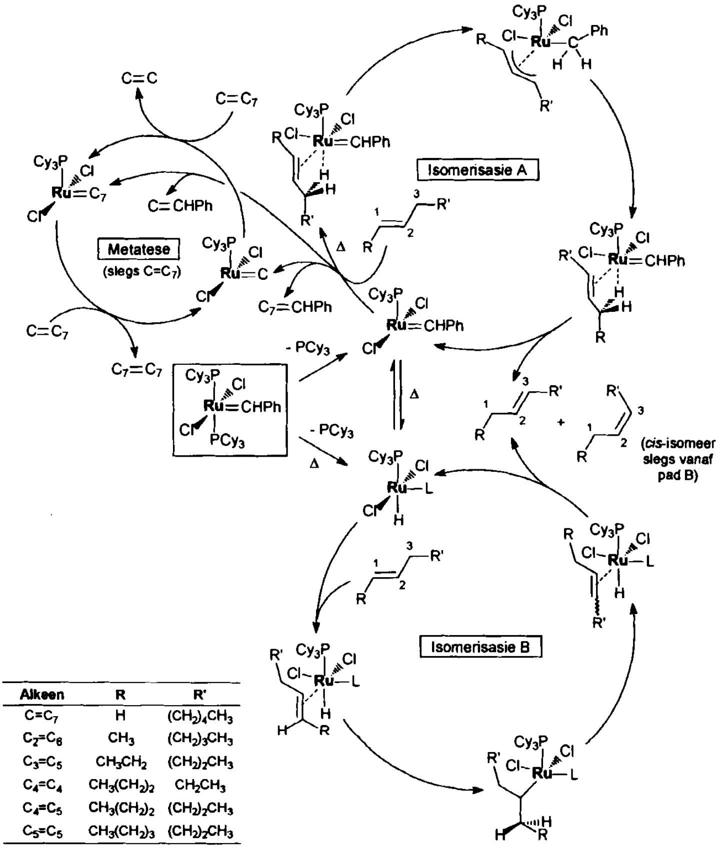
Uit hierdie studie is dit duidelik dat $RuCl_2(=CHPh)(PCy_3)_2$ is 'n aktiewe dubbelbindingisomerisasiekatalisator vir interne alkene omdat metateseprodukte nie tydens hierdie reaksies waargeneem is nie. In die geval van terminale alkene het die kompleks 'n mengsel isomerisasie- en metateseprodukte gelewer. $RuCl_2(=CHPh)(PCy_3)(IMes)$ is katalities aktief vir die isomerisasie en metatese van beide interne en terminal alkene by hoë temperature, by kamertemperatuur is dit selektief ten opsigte van die isomerisasie van interne alkene en die metatese van terminale alkene.

Alhoewel $RuCl(H)(PPh_3)_3(CO)/PhCl$ katalities aktief vir die isomerisasie van terminale alkene by kamertemperatuur is, isomeriseer dit nie interne alkene by laer temperature nie. Interresantheidshalwe is isomerisasie wel by hoë temperature met verlengde reaksietye waargeneem. Die rodiumkarbeen en –dimeer is ook katalities aktief en selektief vir die isomerisasie van interne en terminale alkene. Metatesereaksies is nie waargeneem nie. $RhCl_3{\cdot}3H_2O$ en $RuCl_3$ kon nie alkene vinnig isomeriseer nie; langer reaksietye en hoër temperature was nodig om isomeri-

sasieprodukte te verkry.

Die isomerisasiereaksie het met eerste-orde kinetika in beide katalisator en 4-okteen verloop. Dit is in ooreenstemming met 'n eenvoudige bimolekulêre interaksie tussen die okteensubstraat en die rutheniumsentrum. Die kinetiese data van die 1-okteenisomerisasie het nie eenvoudige eerste-orde en tweede-orde tempo uitdrukkings gepas nie, moontlik as gevolg van sekondêre reaksies (metatese). Die data toon 'n redelike lineêre tweede-orde passing in die beginstadium.

Die meganismes van die verskillende reaksies word deur die katalitiese siklusse geïllustreer:



Alkeen	R	R'
$C=C_7$	H	$(CH_2)_4CH_3$
$C_2=C_6$	CH_3	$(CH_2)_3CH_3$
$C_3=C_5$	CH_3CH_2	$(CH_2)_2CH_3$
$C_4=C_4$	$CH_3(CH_2)_2$	CH_2CH_3
$C_4=C_5$	$CH_3(CH_2)_2$	$(CH_2)_2CH_3$
$C_5=C_5$	$CH_3(CH_2)_3$	$(CH_2)_2CH_3$

ACKNOWLEDGEMENTS

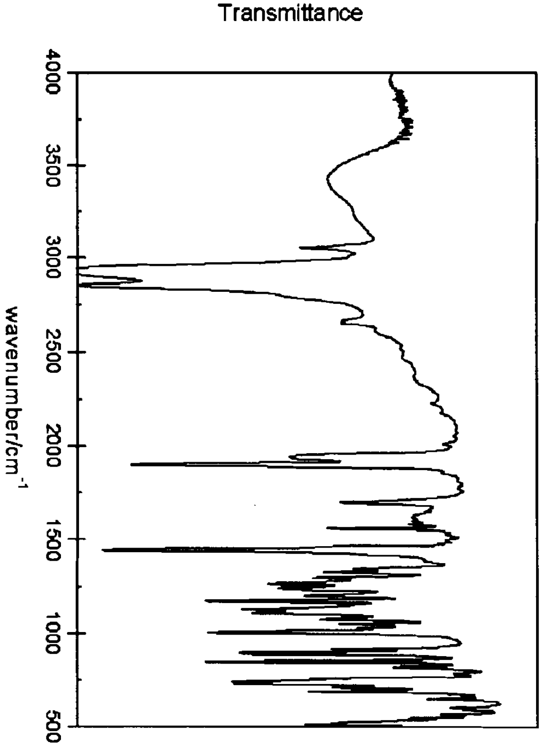
On completion of this study I would like to express my sincerest appreciation and gratitude to the many people who have assisted me in various ways.

- Prof Manie Vosloo, my promoter, for his guidance and knowledge of the subject, his understanding and willingness to help through the stressful times.
- Mr Andre Joubert, for his expertise with NMR.
- Dr Gerhard Lachmann, for his patience in helping me with the kinetic studies.
- Lynette and Andrew, for the ordering of chemicals.
- The Catalysis and Synthesis group, for their friendship and lending a hand.
- Megan Kirk and Cathy Dwyer (Sasol), for their help with the NMR studies.
- Hendrine Krieg for the language editing.
- My entire family, for their love and support through my studies.
- Eric, for being by my side
- PU vir CHO and Sasol for their financial assistance.

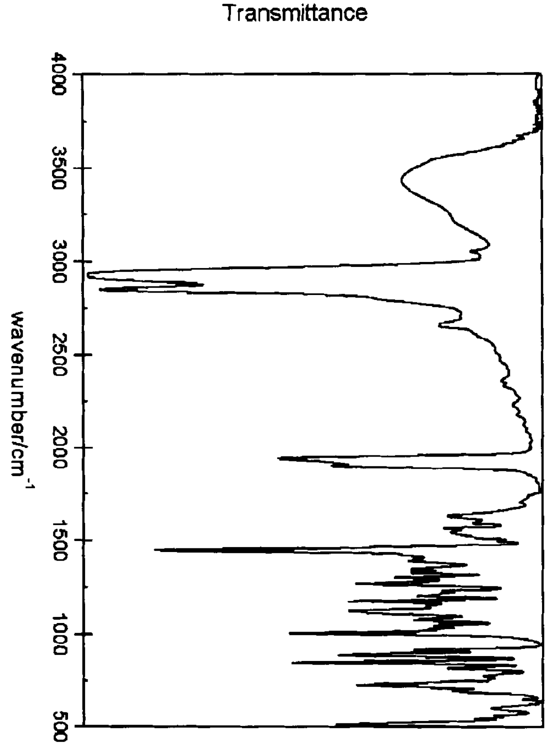
I am eternally grateful to our Heavenly Father for His grace
to have allowed me to complete this work.

APPENDIX

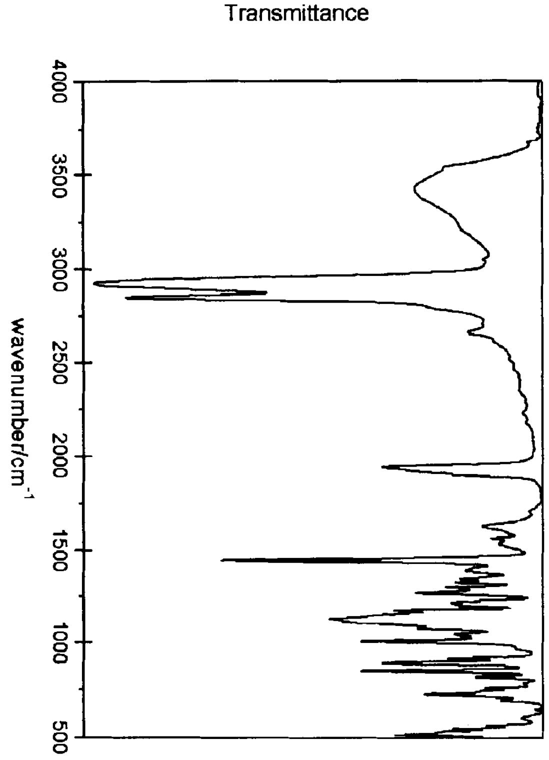
A.1 FTIR analysis of complexes



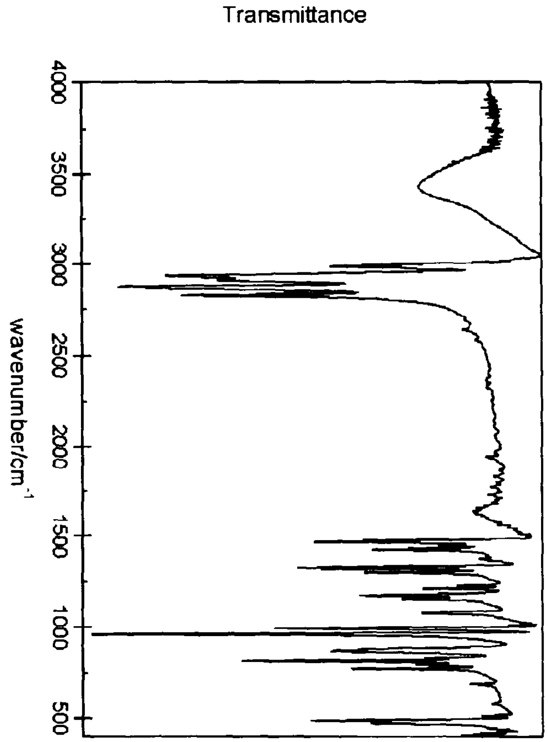
Spectrum A.1.1 IR spectrum of the $RuCl_2(=CHPh)(PCy_3)_2$ complex.



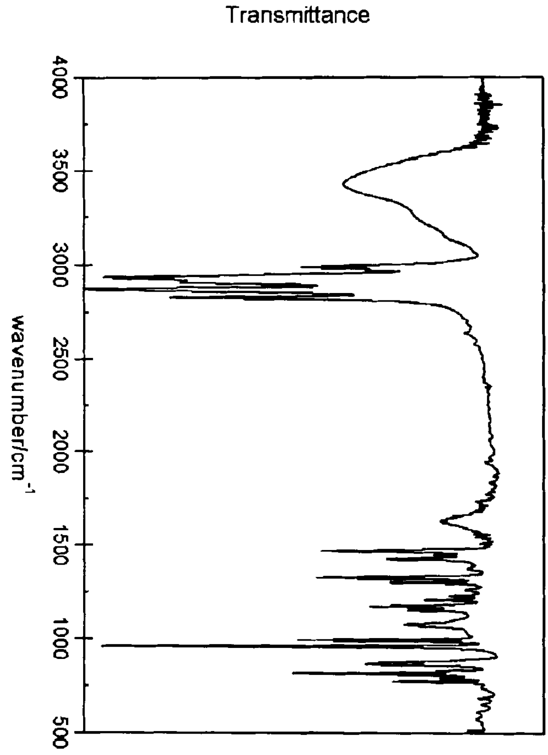
Spectrum A.1.2 IR spectrum of the RuCl$_2$(=CH$_2$)(PCy$_3$)$_2$ complex.



Spectrum A.1.3 IR spectrum of the $RuCl_2(=CHBu)(PCy_3)_2$ complex.

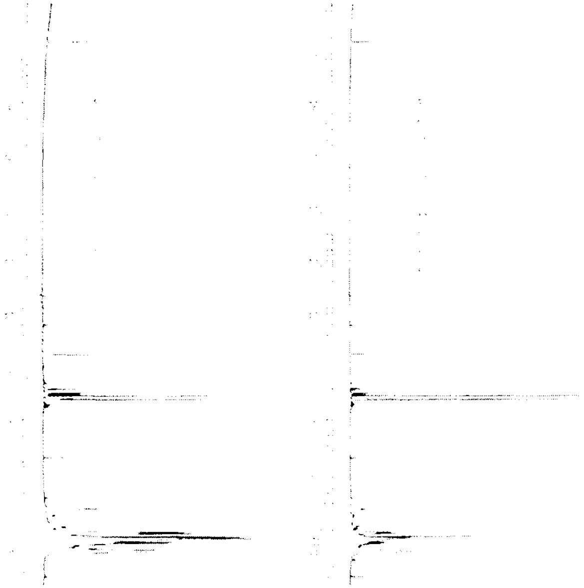


Spectrum A.1.4 IR spectrum of the [RhCl(COD)]$_2$ complex.

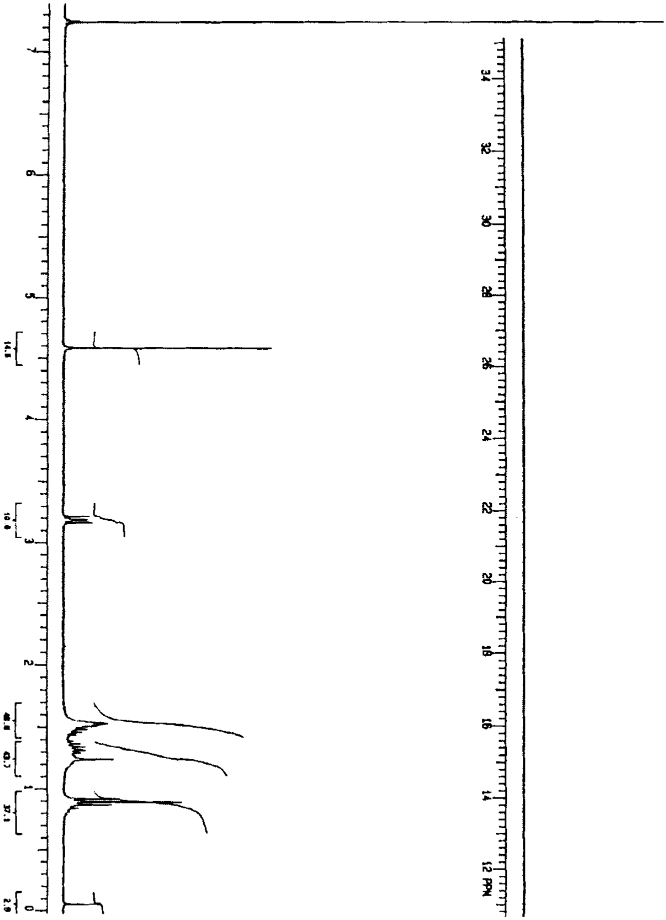


Spectrum A.1.5 IR spectrum of the RhCl($C_3H_5N_2$)(COD) complex.

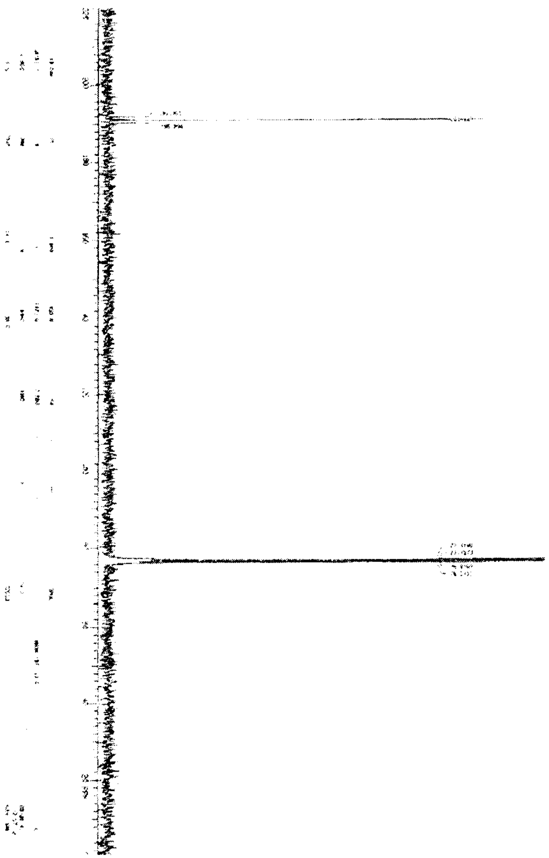
A.2 NMR analysis of complexes



Spectrum A.2.1 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl.

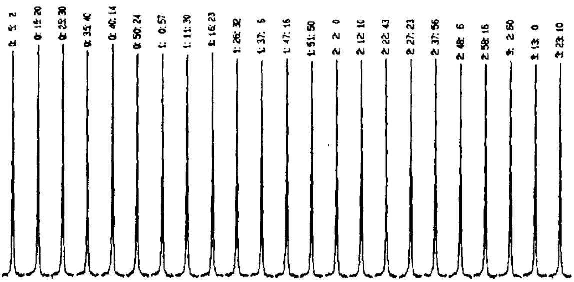


Spectrum A.2.2 ^{1}H NMR spectrum of $W(=C(OMe)Bu)(CO)_5$ in C_6D_5Cl.

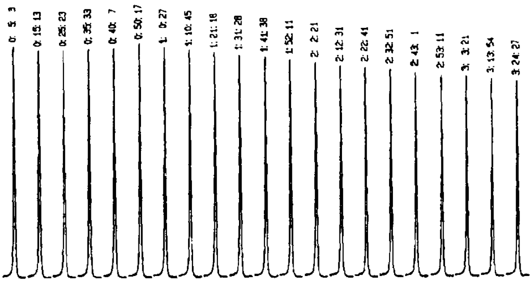


Spectrum A.2.3 ^{13}C NMR spectrum of $W(=C(OMe)Bu)(CO)_5$ in C_6D_5Cl.

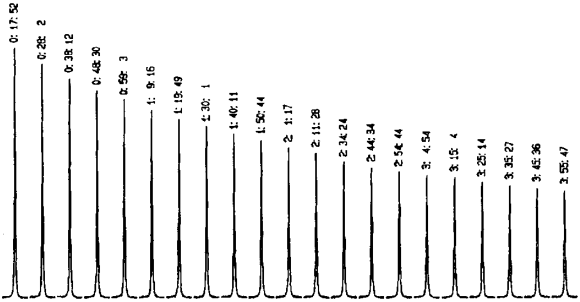
B.1 Decomposition of $RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_5Cl



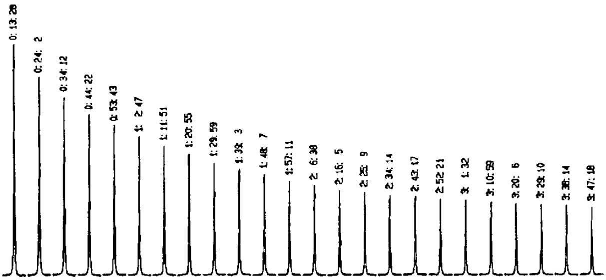
Spectrum B.1.1 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 20 °C.



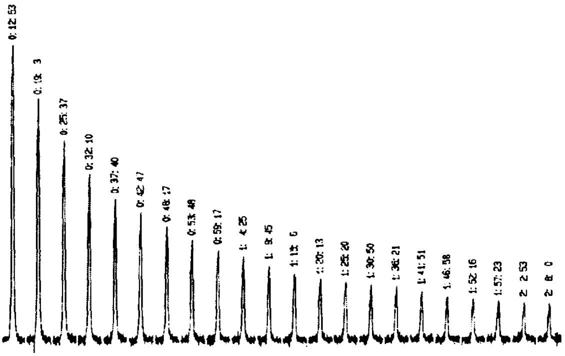
Spectrum B.1.2 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 40 °C.



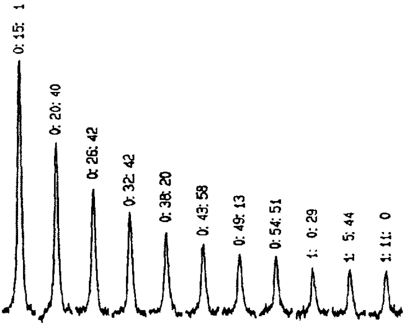
Spectrum B.1.3 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 60 °C.



Spectrum B.1.4 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 80 °C.

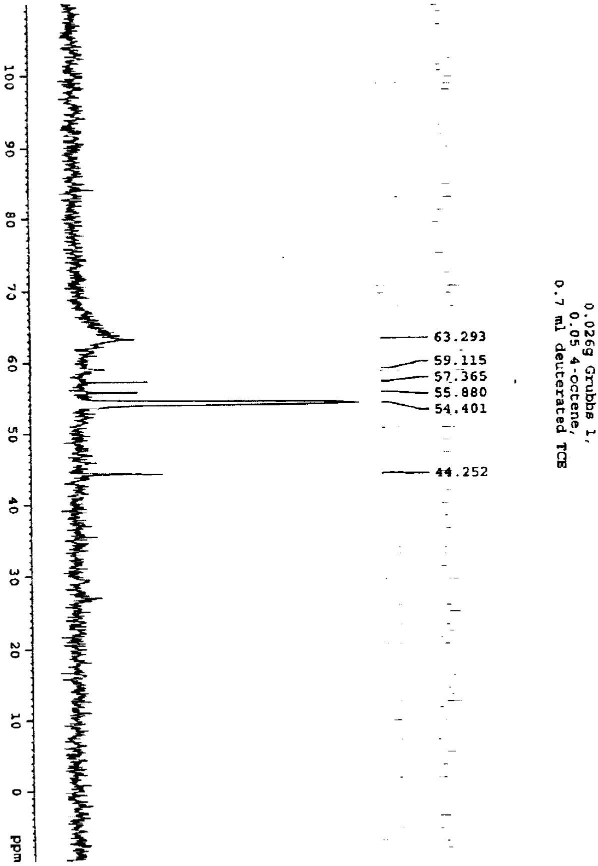


Spectrum B.1.5 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 100 °C.

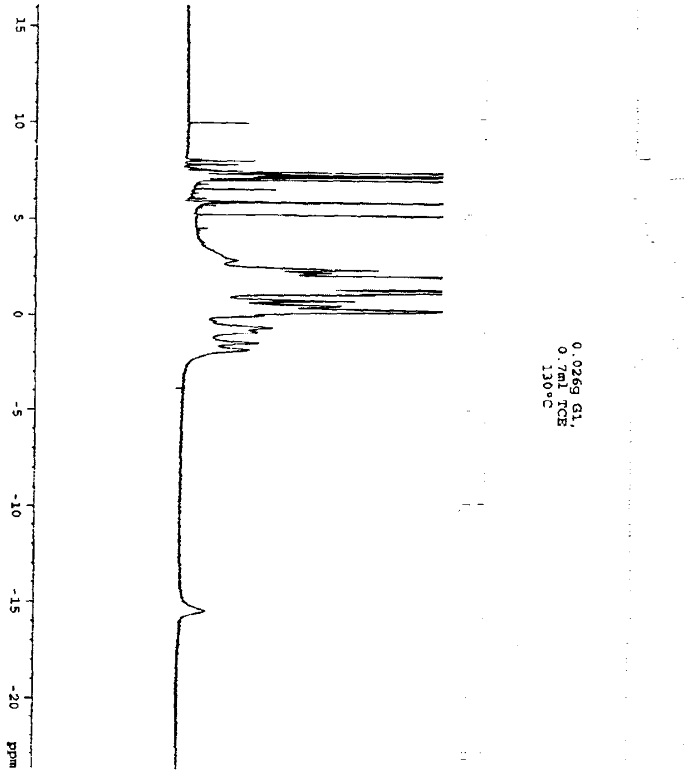


Spectrum B.1.6 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2/C_6D_5Cl$ 120 °C.

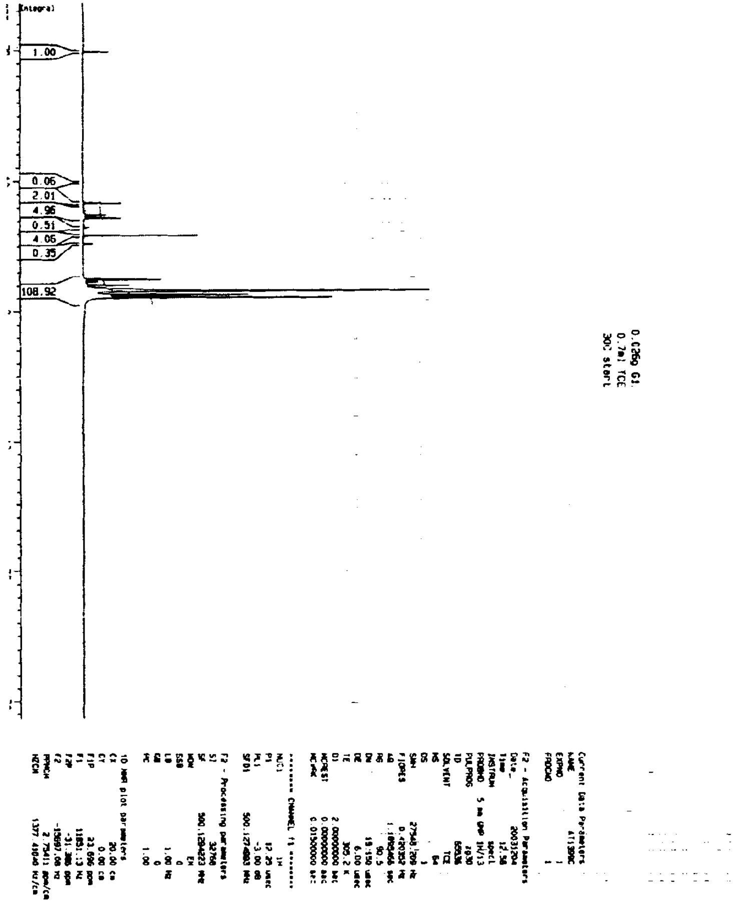
B.2 NMR spectra of $RuCl_2(=CHPh)(PCy_3)_2$ in TCE



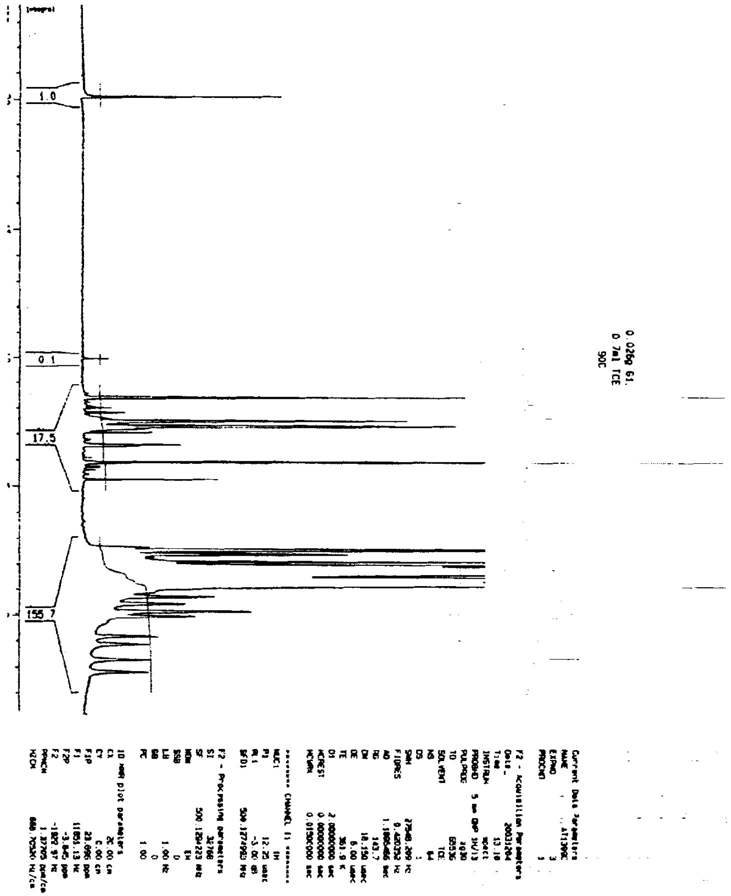
Spectrum B.2.1 ^{31}P NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 90 °C.



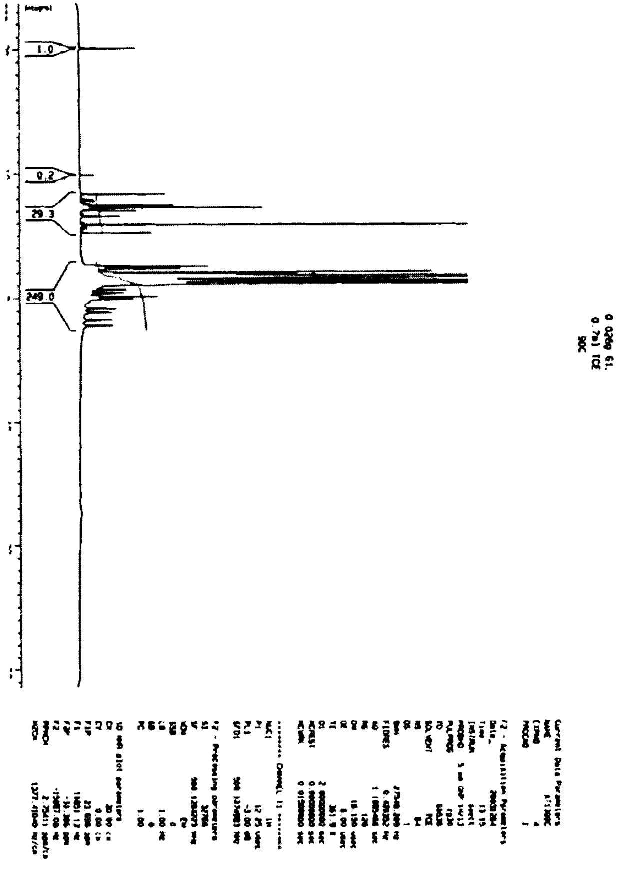
Spectrum B.2.2 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 130 °C.



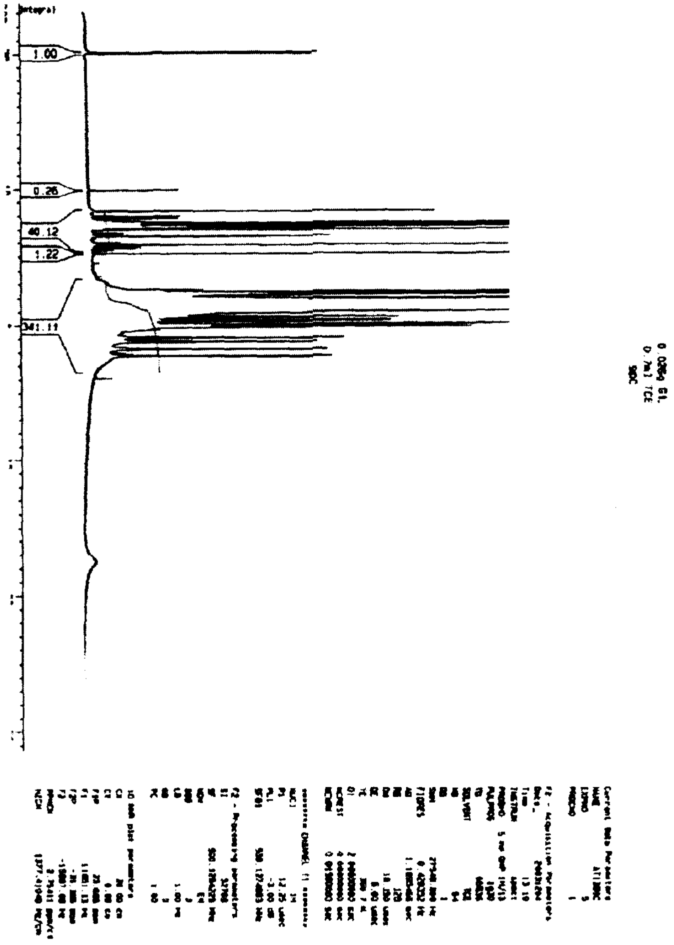
Spectrum B.2.3 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 30 °C.



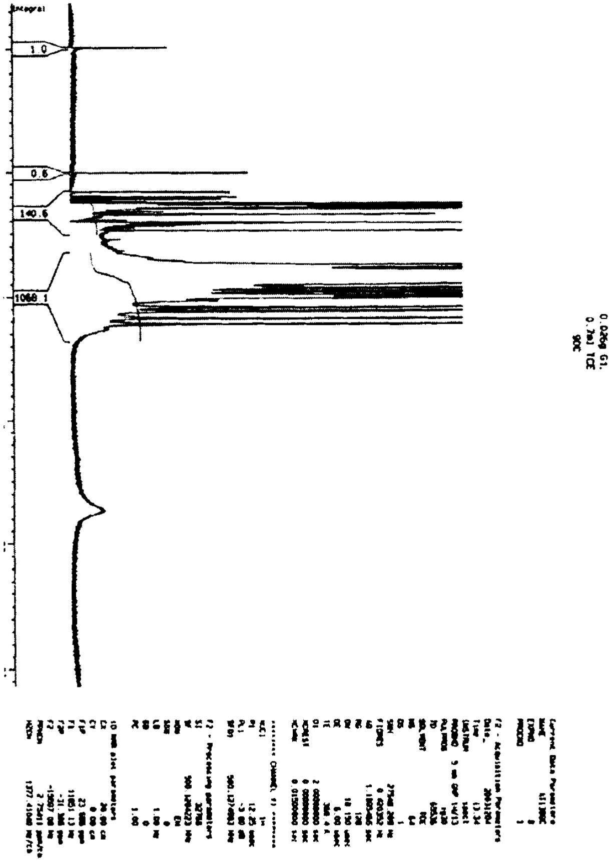
Spectrum B.2.4 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 12 min.



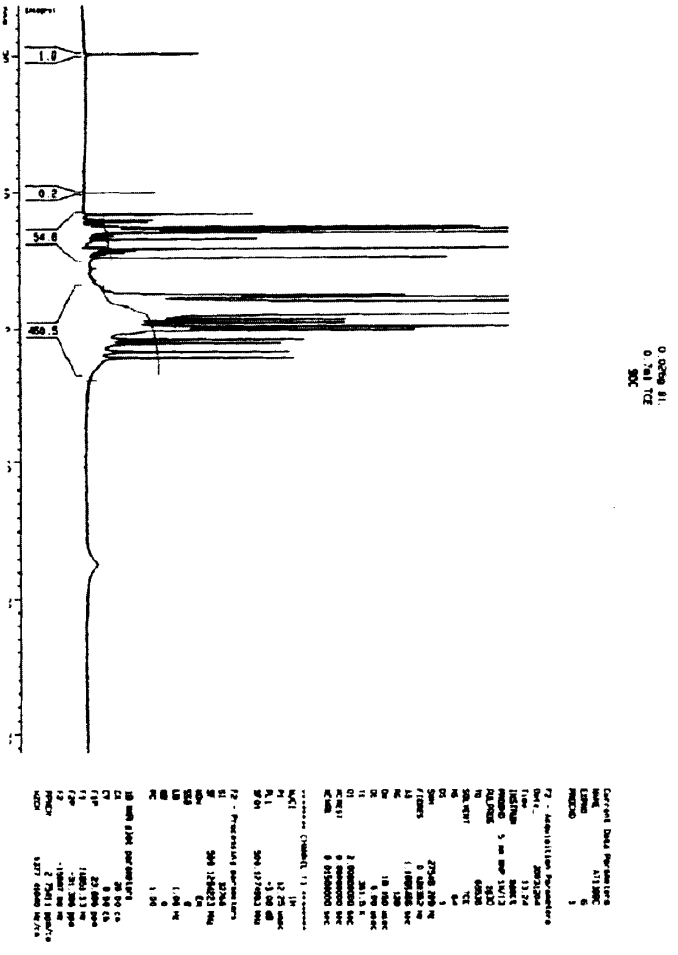
Spectrum B.2.5 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 17 min.



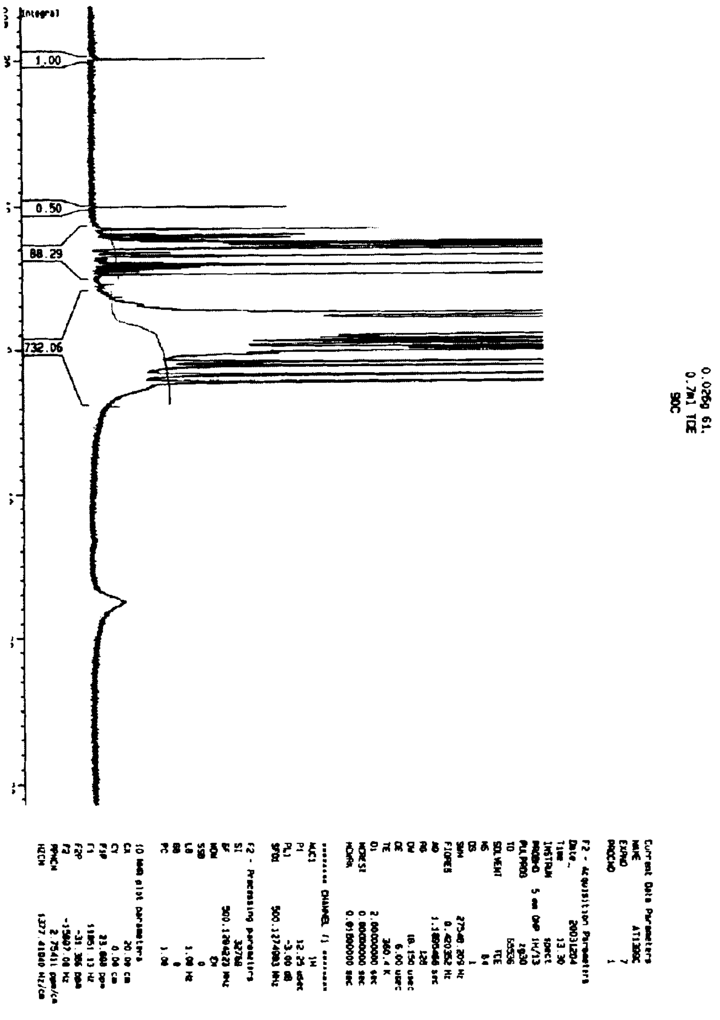
Spectrum B.2.6 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 21 min.



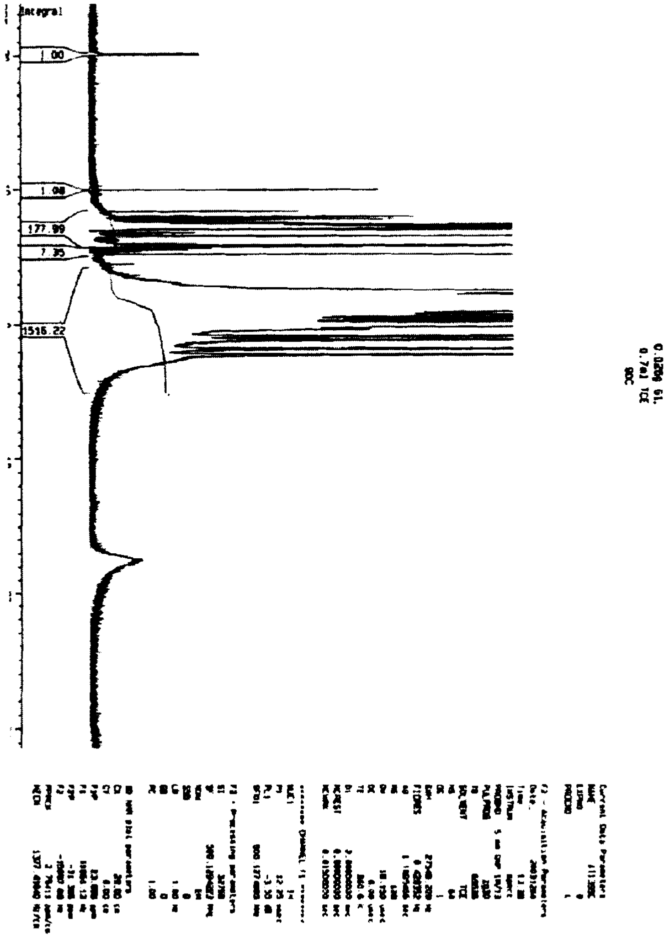
Spectrum B.2.7 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 36 min.



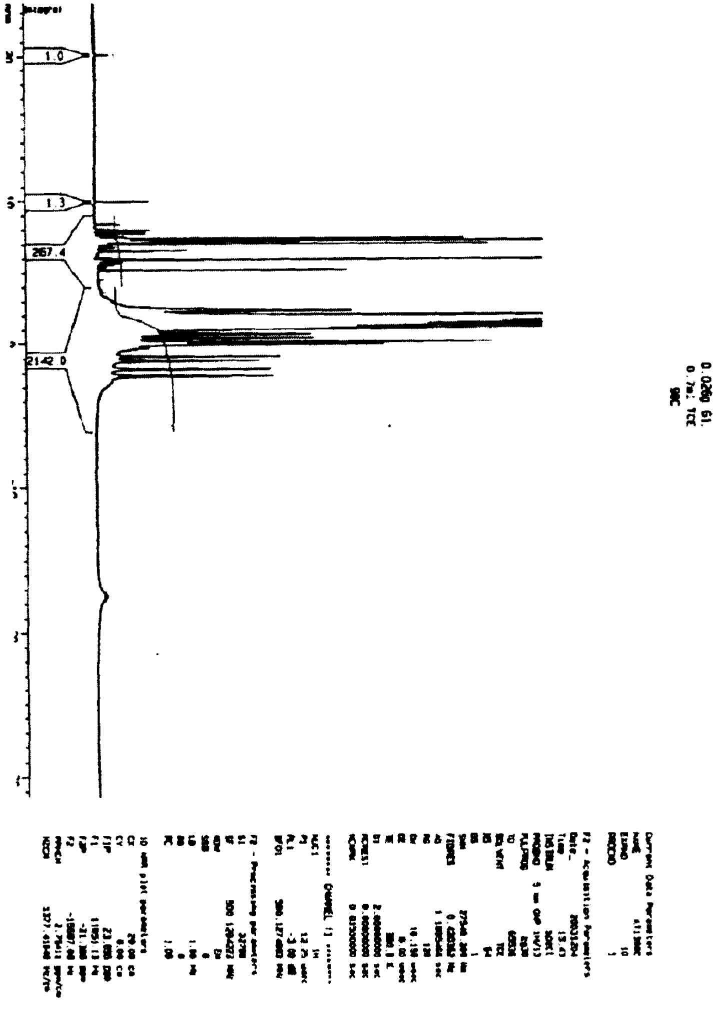
Spectrum B.2.8 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 26 min.



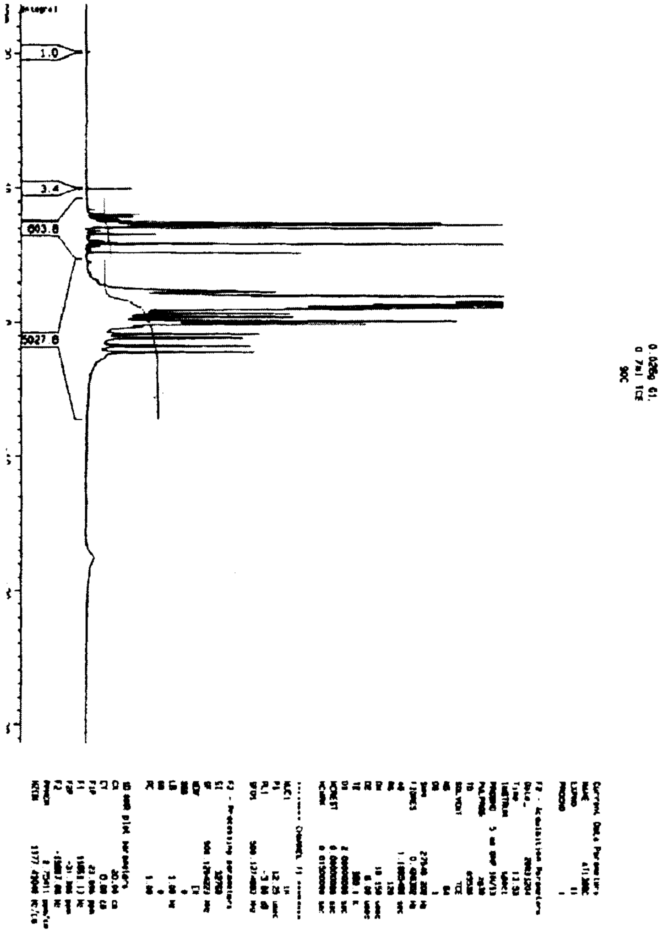
Spectrum B.2.9 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 32 min.



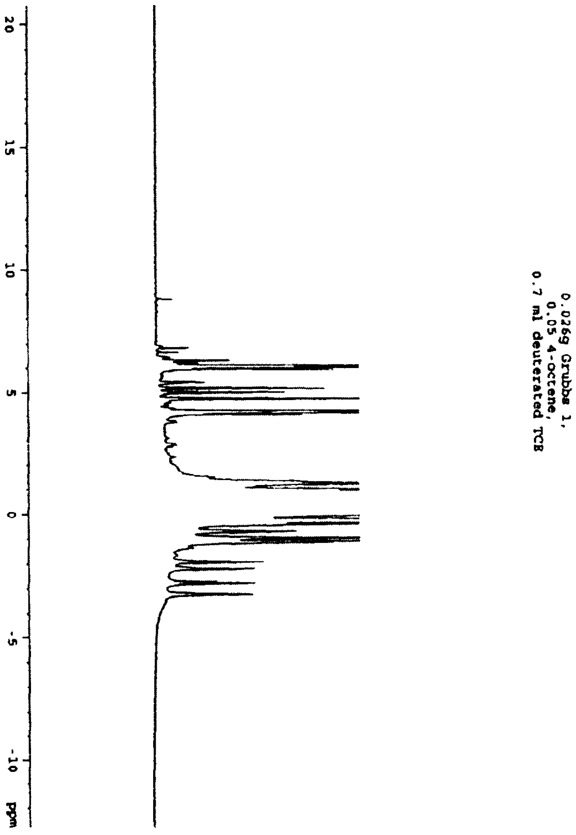
Spectrum B.2.10 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 40 min.



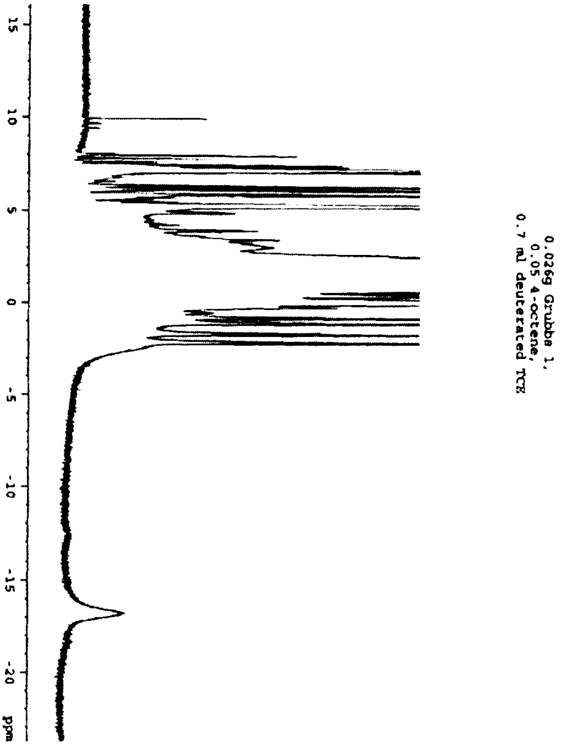
Spectrum B.2.11 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C after 45 min.



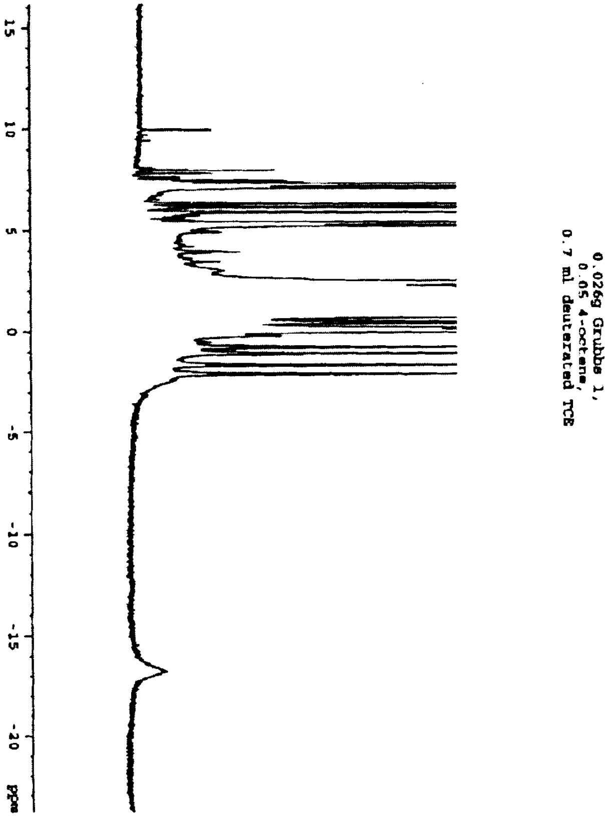
Spectrum B.2.12 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/TCE at 90 °C.



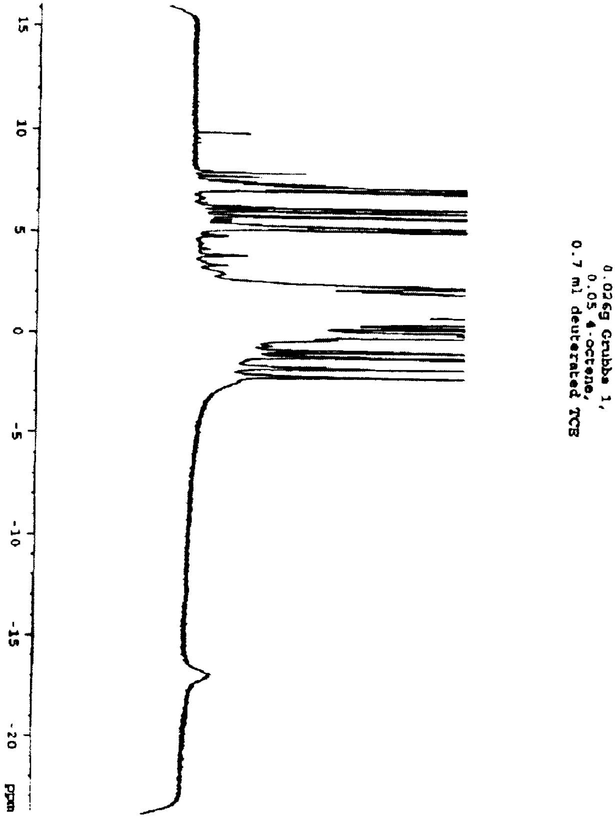
Spectrum B.2.13 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 30 °C.



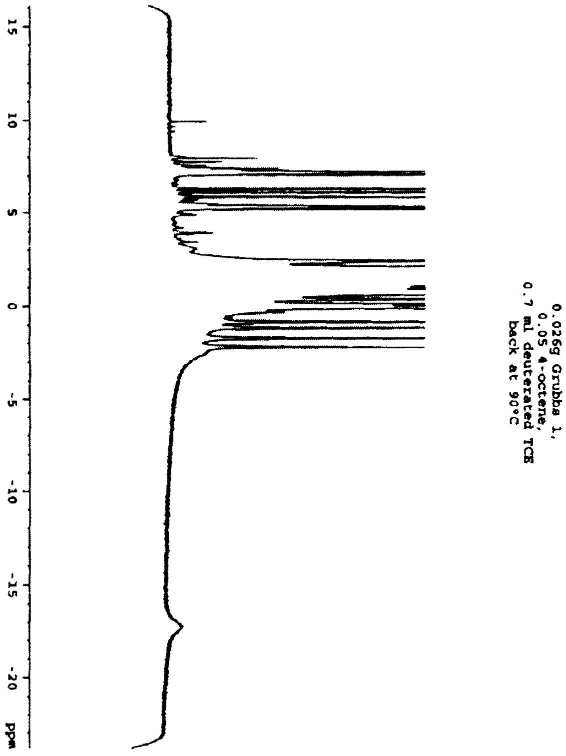
Spectrum B.2.14 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 90 °C.



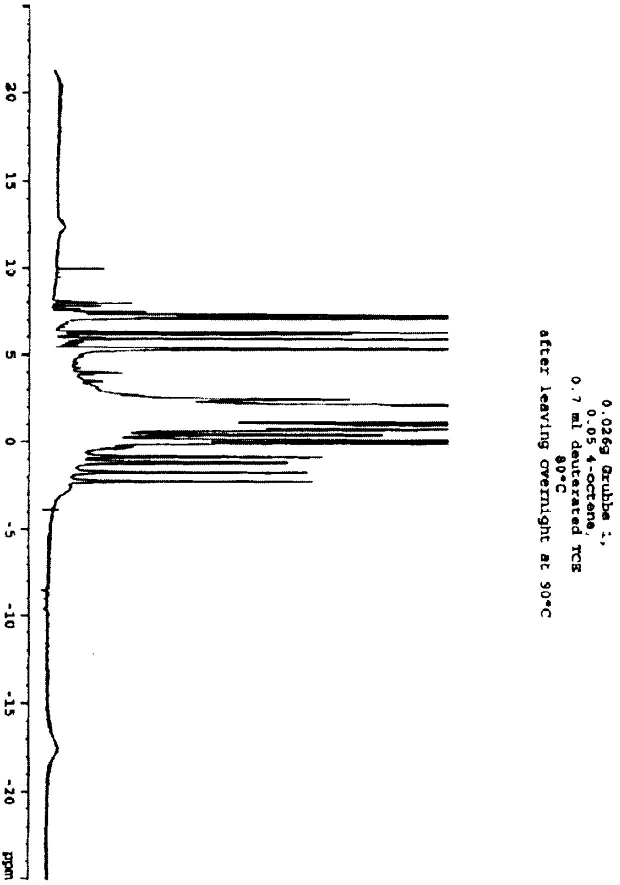
Spectrum B.2.15 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 90 °C.



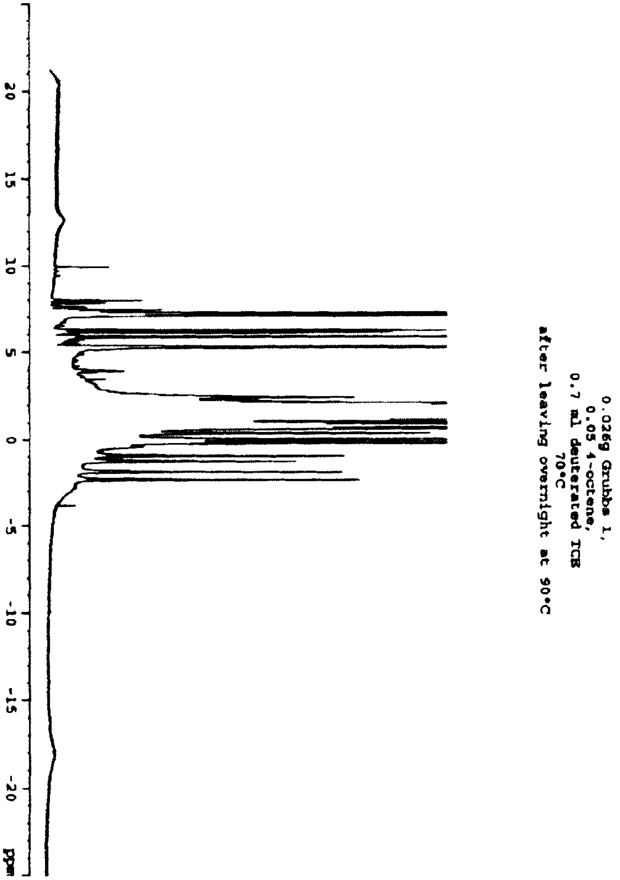
Spectrum B.2.16 ^1H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 30 °C.



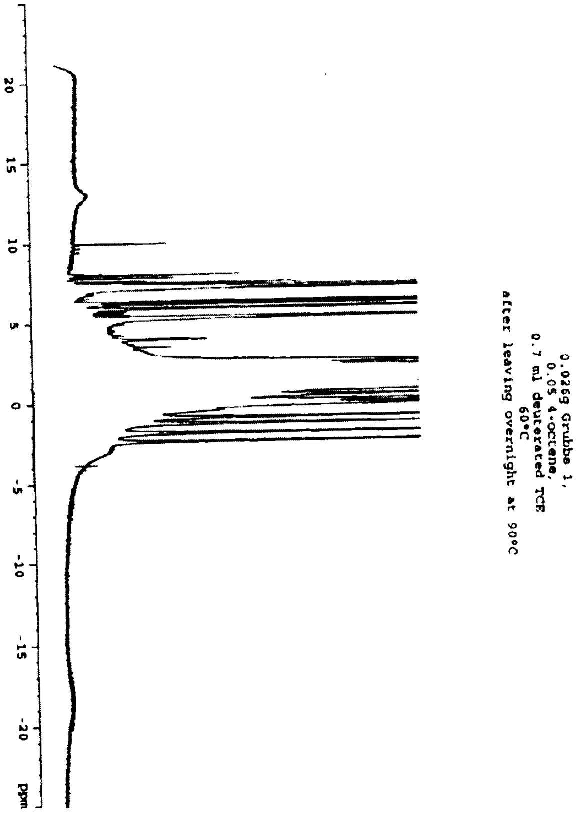
Spectrum B.2.17 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 90 °C.



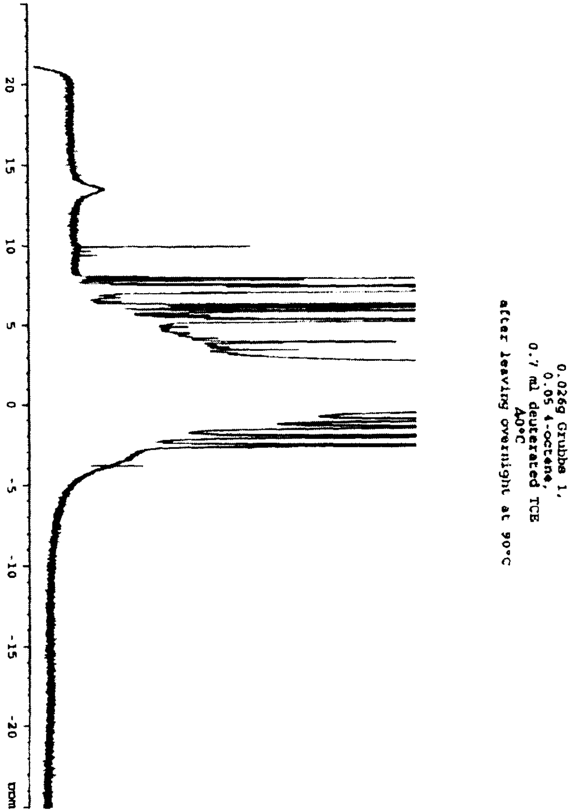
Spectrum B.2.18 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 80 °C.



Spectrum B.2.19 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 70 °C.



Spectrum B.2.20 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 60 °C.



Spectrum B.2.21 ^{1}H NMR spectrum of $RuCl_2(=CHPh)(PCy_3)_2$/4-octene/TCE at 40 °C.