EXPERIMENTAL INVESTIGATION OF DENDRITIC CATALYSTS FOR ALKENE METATHESIS

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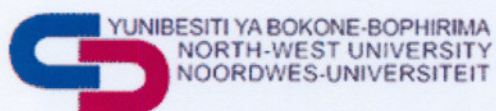
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IR	Infrared
NMR	nuclear magnetic resonance
GC	Gas chromatography
GC/MS	Gas chromatography-mass spectrometry
TOF-MS	Time-of-flight mass spectrometer
PMP	Primary metathesis product
SMP	Secondary metathesis product
C_n	Alkenes (n = 1, 2, 3,...)
C_8	Octene
C_{11}	Undecene
Pr	Propyl
G0-W	W-alkylidene dendrimer
G0	Tetraallylsilane
DAB	Polypropylene imine dendrimer
SRNF	Solvent resistant nanofiltration
$EtAlCl_2$	Ethyl aluminium dichloride
Et_2O	Diethyl ether
EtOH	Ethanol
PhCl	Chlorobenzene
Bu_4Sn	Tetrabutyltin
Bu_3SnCl	Tributyltin chloride
WCl_6	Tungsten hexachloride
$W(OAr)_2Cl_4$	Tungsten aryloxide complex

Homogeneous catalysts offer high catalytic selectivity and activity, but are very expensive. The problem with these catalysts is separation after a catalytic reaction. The synthesis of a catalytic system that has the catalytic advantages of homogeneous catalysts that can be recovered from the reaction mixture after the reaction could benefit most industries. Dendritic catalysts can address this challenge.

Various tungsten aryloxide complexes, $W(O-2,6-C_6H_3X_2)_2Cl_4$ (X = Cl, Br, Ph), were synthesised and tested for the metathesis reaction of 1-octene. Infrared spectra were used to verify that the syntheses were successful. The colour of the synthesised tungsten aryloxide complexes were the same as those synthesised previously, with $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ as black microcrystals with green luster, $W(O-2,6-C_6H_3Br_2)_2Cl_4$ as a brown powder, and $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ as black microcrystals.

The metathesis reaction was followed by GC. It was found that the substituent on the aryloxide ligand has an effect on the catalytic activity. The more electronegative the substituent, the higher the catalytic activity. The catalyst selectivity of these complexes towards the primary metathesis product (PMP), tetradecene, is high.

GC-MS was used to identify the products of the metathesis reaction of 1-octene. In reactions where Bu_4Sn was used as a co-catalyst, Bu_3SnCl was observed in the reaction mixture. This showed that a carbene formed within the catalytic system.

$$W(O-2,6-C_6H_3Cl_2)_2Cl_4 + 3\ Bu_4Sn \xrightarrow{PhCl} W(=CHPr)(C_4H_9)(O-2,6-C_6H_3Cl_2)_2Cl + 3\ Bu_3SnCl + C_4H_{10}$$
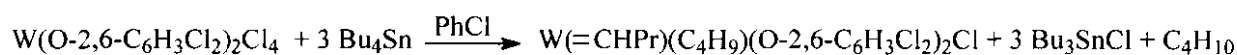
These complexes exhibited higher catalytic activity when compared to the Grubbs catalyst.

Dendritic catalysts based on $W(OAr)_2Cl_4$ were synthesised and tested for the metathesis of 1-octene. Periphery functionalised carbosilane dendrimers were synthesised and the tungsten aryloxide complex incorporated at the periphery of the dendrimer. Previously periphery functionalised dendrimers of $W(OAr)_2Cl_4$ were synthesised and used in the ring-opening metathesis polymerisation (ROMP) of norbonene. This early system had the periphery functionalised carbene located towards the inside of the dendritic catalyst, i.e. between the

SUMMARY

dendrimer and the catalytic complex. In ROMP the active carbene is part of the growing polymer chain, while in alkene metathesis the catalytically active carbene will be separated from the dendrimer thus hindering the recovery of the catalyst.

Carbosilane dendrimers with the carbene placed on the outside of the dendritic catalyst were synthesised in this study. In this manner the dendritic catalysts could be recovered after the reaction by nanofiltration. These carbosilane dendritic catalysts were tested for catalytic activity and selectivity on the metathesis of 1-octene. The W-alkylidene with the carbene on the outside showed higher catalytic activity than the W-alkylidene with the carbene on the inside.

Homogene katalisator bied hoë katalitiese selektiwiteit en aktiwiteit, maar is baie duur. Die probleme met hierdie katalisatore is die skeiding na 'n katalitiese reaksie. Die sintese van 'n katalitiese sisteem wat die voordele van homogene katalisatore het en wat herwin kan word van die reaksiemengsel na die reaksie, sal meeste industrieë bevoordeel. Dendritiese katalisatore kan hierdie uitdaging aanspreek.

Verskeie wolframarieloksiedkomplekse, $W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$ (X = Cl, Br, Ph), is gesintetiseer en getoets vir die metatese van 1-okteen. Infrarooispektra is gebruik om te verifieer dat die sintese suksesvol was. Die kleur van die gesintetiseerde wolframarieloksiedkomplekse vergelyk goed met die wat voorheen gesintetiseer is, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ as swart mikrokristalle met 'n groen skynsel, $W(O\text{-}2,6\text{-}C_6H_3Br_2)_2Cl_4$ as 'n bruin poeier, en $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ as swart mikrokristalle.

Die metatese reaksie is met behulp van GC gemonitor. Daar is gevind dat die substituente op die arieloksiedligande 'n invloed op die katalitiese aktiwiteit het. Hoe meer elektronegatief die substituent, hoe hoër die katalitiese aktiwiteit. Die katalitiese selektiwiteit van die komplekse met betrekking tot die primêre metatese produk (PMP), tetradekeen, is hoog.

GC-MS is gebruik om die produkte van die metatese reaksie van 1-okteen te identifiseer. In reaksies waar Bu_4Sn as ko-katalisator gebruik is, is Bu_3SnCl in die reaksiemengsel waargeneem. Dit toon aan dat 'n karbeen in die katalitiese sisteem gevorm het.

$$W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 + 3\ Bu_4Sn \xrightarrow{\text{PhCl}} W(=CHPr)(C_4H_9)(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl + 3\ Bu_3SnCl + C_4H_{10}$$

Hierdie komplekse toon hoër katalitiese aktiwiteit as hulle met die Grubbs katalisatore vergelyk word.

Dendritiese katalisatore gebaseer op $W(OAr)_2Cl_4$ is berei en getoets vir die metatese van 1-okteen. Periferie-gefunksionaliseerde karbosilaandendrimere is gesintetiseer deurdat wolframarieloksiedkomplekse op die periferie van die dendrimere geïnkorporeer is. Vroeër is periferie-gefunksionaliseerde dendrimere van $W(OAr)_2Cl_4$ gesintetiseer en in die ringopeningsmetatesepolimerisasie (ROMP) van norboneen gebruik. In die vorige sisteem was die perifirie-gefunksionaliseerde karbeen aan die binnekant van die dendritiese katalisator, tussen

OPSOMMING

die dendrimeer en die katalitiese kompleks geleë. Gedurende ROMP word die aktiewe karbeen deel van die groeiende polimeerketting, terwyl dit in alkeenmetatese van die dendrimeer geskei word, en herwinning van die katalisator verhinder.

Karbosilaandendrimere met die karbeen aan die buitekant van die dendritiese katalisator is in hierdie studie gesintetiseer. Sodoende kan die dendritiese katalisator deur middel van nanofiltrasie herwin word na die reaksie. Hierdie karbosilaandendritiese katalisatore is vir katalitiese aktiwiteit en selektiwiteit van die metatese van 1-okteen getoets. Die W-alkielideen met die karbeen aan die buitekant toon hoër katalitiese aktiwiteit as die W-alkielideen met die karbeen aan die buitekant.

INTRODUCTION AND AIM OF STUDY

1.1   Introduction

The importance of the metathesis reaction is increasing as more and more applications come forth. Some examples of applications of the metathesis reactions have already been proved like the Phillips triolefin process[1,2,3,4,5] whereby propene was changed to ethene and butene, the Shell-higher olefin process (SHOP)[1,2,3,4,5] whereby it uses metathesis for the making of plastics. Metathesis reactions are also used for the making of insect pheromones and the synthesis of complex organic molecules.[1,2,3,4,5]

Metal-catalysed alkene metathesis has had a huge impact on organic synthesis, and is one of the most often used chemical transformations.[6] The outstanding contribution of metathesis reactions in our society is still evident. Yves Chauvin, Robert H. Grubbs and Richard R. Schrock were awarded the Nobel Prize for Chemistry in 2005 for their ingenious work in the field of alkene metathesis.[7]

The metathesis reaction is a reversible transalkylidation process in which alkenes are converted into new products *via* the break and reformation of carbon-carbon double bonds:

$$2RHC{=}CHR' \rightleftharpoons RHC{=}CHR + R'HC{=}CHR'$$

The catalytic metathesis of alkenes was first reported in the open literature by Banks and Bailey.[8] A few years later Calderon *et al.*[8] found that the same reaction by Banks and Bailey could be performed homogeneously using the catalyst system $WCl_6/EtAlCl_2/EtOH$. This demonstrated that alkene metathesis can take place in the presence of heterogeneous as well as homogeneous catalysts.[8] A wide variety of homogeneous and heterogeneous catalytic systems active for the metathesis of alkenes are reported in literature.[2,8] Metathesis catalytic systems can be quite selective although they are inhibited in many cases by side reactions such as double bond isomerisation, oligomerisation and the alkylation of the solvent.[5]

The most active metathesis catalytic systems are normally based on the transition metals molybdenum, tungsten, rhenium, and ruthenium.[2,8] In this study the emphasis will fall on tungsten based catalysts.

Heterogeneous catalysts generally consist of a transition metal oxide or an organometallic precursor deposited on a high-surface-area support, while homogeneous catalysts mainly consist of a combination of a transition metal compound and an organometallic compound as co-catalyst. The transition metal compound being a well-defined carbene complex.[2]

1.2   Homogeneous catalysis

Homogeneous catalysts offer high catalytic activity and selectivity. In homogeneous catalysis the catalytic groups are more available to the substrates when the catalyst is completely soluble in the reaction media, however recovery is generally more difficult.[9,10,11,12,13,14] The best known homogeneous catalysts are the Grubbs and Schrock catalysts. Grubbs catalysts are based on ruthenium complexes, while Schrock catalysts are based on tungsten and molybdenum complexes. In general, Schrock catalysts are more active than Grubbs catalysts. However, Schrock catalysts are extremely sensitive to moisture and oxygen.[15] On the other hand, it has been reported that Grubbs catalysts have a remarkable stability towards a wide variety of functional groups.[3,4,15-,16,17] In this study the emphasis will fall on tungsten based catalysts.

Research on tungsten catalysts is popular and there are already more known tungsten based catalysts for the alkene metathesis than any other transition metal catalysts. The classical tungsten based catalyst system for metathesis is $WCl_6/EtAlCl_2$.[3-5] Furthermore, if the Cl-ligands of the WCl_6-catalyst are substituted with oxyaryl or alkoxy groups the activity of the metathesis catalyst can be drastically influenced.[3-5] The use of ethanol as an activator for the $WCl_6/EtAlCl_2$ catalyst system is well known.[3-5] It was found that if ethanol was added to a tungsten catalyst, the tungsten ethoxy complexes formed. These complexes formed active metathesis catalysts. It appeared as if the presence of an oxygen ligand on the tungsten core activated the catalyst.[3-5]

During the last decade different tungsten (VI) aryloxides, for example $W(OAr)_nCl_{6-n}$, $WOCl_{4-n}(OAr)_n$ and $W(=NAr)Cl_{4-n}(OAr)_n$ (OAr = unsubstituted or substituted phenoxides), have been developed which revealed a high activity and selectivity with respect to terminal alkene metathesis.[3,4,18-,19,20] The high activities were obtained in the presence of co-catalysts like R_nAlCl_{3-n}, R_4M (R=methyl or butyl, M=Sn or Pb) or alkyltinhydrides.[3,4,18,19] These catalysts are active with respect to acyclic and cyclic alkenes.[3,4,18,19]

The presence of the aromatic ring in the aryloxide ligand enhance the possibility to change the substituents on the ring, and thus to influence the electronic as well as the steric properties of the ligands on the tungsten core.[3,4] Complexes with electron-withdrawing substituents on positions

2 and 6 of the aryloxide ligand were found to be superior for metathesis of alkenes, compared to the other aryloxide ligands.[5,18-20] Besides the electronic and steric properties, the phenoxide groups of these tungsten catalysts also increase the solubility and stability of the complexes.[18,19] Ligands thus form an integral part of the active metathesis catalyst.[3,4]

Homogeneous transition metal catalysts with complex ligands have become very expensive, and this leads to an increasing need for recycling. The problematic separation of homogeneous catalysts from reaction products in solution has hampered the commercialisation of many excellent homogeneous catalysts. Dendrimers offer an alternative and viable approach to address some of the issues about heterogenising homogeneous catalysts.[9,11,12,19]

1.3   Dendrimers and dendritic catalysts

Dendrimers are highly branched macromolecules, which are constructed in a generation wise manner starting from a central initiator core molecule,[11,21] have compelling molecular structures that are reminiscent of patterns often observed in nature and particularly those found in trees and in coral. A new development is the use of dendrimers as ligands in catalysis.[9,22-24] When dendrimers contain metal element(s) in their framework they are called dendritic catalysts.[9,23,25]

Catalytic dendrimers (also called dendritic catalysts or metallodendrimers) show kinetic behaviour, activity and selectivity of a homogeneous catalyst, with the advantage of the heterogeneous catalyst, that they can be removed from the reaction mixture by the nanofiltration membrane techniques (Figure 1.1) and therefore can be recycled.[9,22-24]
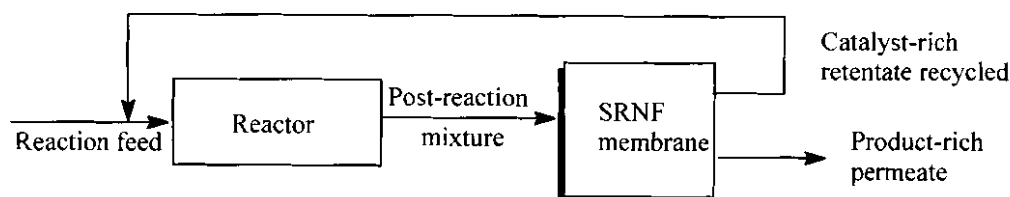

Figure 1.1   Schematic presentation of coupled reaction-separation system.

One disadvantage of the metallic dendrimers is that they have a flexible skeleton. This means that they change in size and shape in solution and this may cause the metallic dendrimers to escape through the nanofiltration membrane. This drawback can be overcome by the incorporation of aromatic molecules, which will help maintain the dendrimer shape in solution.[25]

1.4   Aims and Objectives

The aim of this study was to investigate the fundamental and applied aspects of the metathesis of linear terminal alkenes with tungsten dendritic catalysts.

To reach the aim the following objectives were stated:

1.   Investigate the Basset catalyst, $W(OAr)_2Cl_4$, and compare it with the analogue dendritic catalysts thereof for alkene metathesis.

2.   Synthesise a model dendrimer(s) and dendritic catalyst(s).

3.   Investigate the metathesis activity and selectivity of the dendritic catalyst(s) in octene metathesis under different experimental conditions (Vary the reaction conditions like temperature, solvent, *etc.* to determine the optimum conditions).

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LITERATURE REVIEW

2.1 Introduction

At the beginning of the 19th century, it was noticed that a number of chemical reactions were affected by trace amounts of substances that were not consumed in the reaction.[1] For example, traces of acid can bring about the hydrolysis of starch, and low concentrations of metal can influence the decomposition of hydrogen peroxide. Some of the most dramatic effects were, however, shown by the noble metals, platinum and palladium. In experiments carried out by Faraday, a platinum sponge was able to sustain the oxidation of ethanol vapour, the heat being released making it white-hot. Döbereiner also discovered that platinum could bring about the oxidation of hydrogen. Based on this effect he developed the lamp-lighter. In 1831, Phillips patented the effect of platinum on the oxidation of sulphur dioxide, and this later became the basis for the manufacturing of sulphuric acid.[1]

This phenomenon in which a relatively small amount of foreign material, called a catalyst, augments the rate of a chemical reaction without itself being changed[1-,2,3] or consumed is called catalysis.[4] A catalyst accelerates the chemical reaction by providing a lower energy pathway between the reactants and the products. During the reaction the catalyst may undergo changes to become a different entity, but after the completion of the catalytic cycle, it is in the same form as it had been at the start. The entity mentioned above is an intermediate, which cannot be formed without the catalyst. The formation of this intermediate and subsequent reaction generally has a much lower activation energy barrier than is required for the direct reaction of reactants to form the products. When a catalyst is in a chemical reaction its performance, called catalytic activity, is determined by the conversion of the substrate into products over time.[5,6] In most catalytic reactions, a given set of reactants could react in two or more ways to form a range of products. The degree to which only one of the possible reactions is favoured over the other, is called selectivity. Together with activity, selectivity is a key property that is vital in any practical application of the catalyst.[4]

Catalysts are conventionally divided into three categories, namely, heterogeneous (e.g. $Al_2O_3.CoMo$), homogeneous (e.g. $(Ph_3P)_3RhCl$), or biological catalysts (e.g. an enzyme) as

shown in Figure 2.1.[2-3,4] Attention will be focused on the homogeneous and heterogeneous catalysts, since they are generally of greater interest to chemists than biological catalysts.
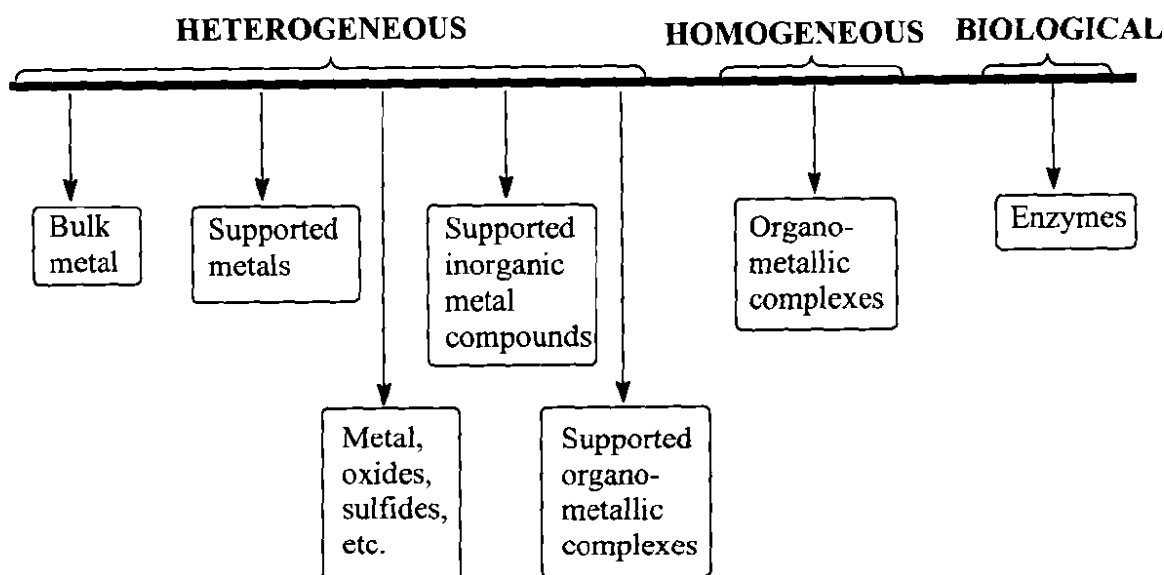
HETEROGENEOUS   **HOMOGENEOUS   BIOLOGICAL**

| Bulk metal | Supported metals | Supported inorganic metal compounds | Organo- metallic complexes | Enzymes |

| Metal, oxides, sulfides, etc. | Supported organo- metallic complexes |

Figure 2.1   General classification of catalysts.[2]

Sabatier[7] gave a first rough classification of catalytic reactions into homogeneous and heterogeneous systems. According to his classification homogeneous systems are those, where all the compounds present, or at least one of them, are miscible with the catalysts; and heterogeneous systems are based upon a solid catalyst which is in contact with a reactive liquid or gaseous phase.[4,7] In heterogeneous catalysis the reaction takes place either on the surface of the catalyst, if it is compact, or in its entire mass if it is porous.

Before 1938, homogeneous catalysis had received little attention.[7] At that time, the term catalysis in its general usage was inseparably linked to large-volume industrial chemical syntheses, like the syntheses of ammonia, coal hydrogenation, fat hardening, the Fischer-Tropsch synthesis and mineral oil processing. Catalysis was thus synonymous with heterogeneously catalysed reactions. Except for a few applications, organometallic compounds were not accorded any technical nor commercial importance. Only since the 1950s has homogeneous catalysis been an established field of organometallic chemistry becoming a central feature within the chemical sciences scenario.[7] The strengths and weaknesses of homogeneous and heterogeneous catalysis could be summarised as shown in Table 2.1.

Table 2.1   Homogeneous versus heterogeneous catalysis[7]

	Homogeneous catalysis	Heterogeneous catalysis
Activity (relative to metal content)	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Harsh
Service life of catalyst	Variable	Long
Sensitivity toward catalyst poisons	Low	High
Diffusion problems	None	May be important
Catalyst recycling	Expensive	Not necessary
Variability of steric and electronic properties of catalysts	Possible	Not possible
Mechanistic understanding	Plausible under random conditions	More or less impossible

Homogeneous catalysts offer attractive properties as depicted in Table 2.1. These properties led us to taking much interest in homogeneous catalysis. The most important homogeneous catalyst systems are derived from transition metal complexes. Transition metal complexes have a central metal atom, with either ions or groups of atoms called ligands bonded to it. When there are metal-carbon bonds, the complexes are classified as organometallic. The ligands surround the metal atom and form a polyhedron with the metal in the centre. The most frequently observed geometries are octahedral, tetragonal pyramidal, trigonal pyramidal, tetrahedral and square planar.[8] The range of effective transition metal compounds is continually being extended by manipulation of the ligands.[9]

2.1.1   Transition metals

The transition metals (Table 2.2) are elements that have partially filled **d** orbitals. These metals exhibit multiple oxidation states and bond to a variable number of ligands. The metal uses its partially filled **d** orbitals and the higher **s**- and **p**-orbitals for the formation of the metal-ligand bonds in the complex. The **(n)d** level of a transition metal cation is usually lower in energy than the **(n+1)s** level, which is lower in energy than the **(n+1)p** level where **n** is the principal quantum number.

Table 2.2 The transition metals and their numbers of d electrons in various oxidation states[8]

Group Number		4	5	6	7	8	9	10	11
First row	3d	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Second row	4d	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Third row	5d	Hf	Ta	W	Re	Os	Ir	Pt	Au
Oxidation State	d^n, **Number of d Electrons**								
Zero		4	5	6	7	8	9	10	-
I		3	4	5	6	7	8	9	10
II		2	3	4	5	6	7	8	9
III		1	2	3	4	5	6	7	8
IV		0	1	2	3	4	5	6	7

As the **d**-orbitals usually have the highest energies, electrons can easily be added or removed from them. The **d**-orbitals are primarily associated with the metal atom and because it is the **d** orbital to which electrons are added or from which they are removed, the number of these **d** electrons, d^n, is related to the oxidation state of the metal. The formal oxidation state of a metal in a complex is defined as the charge remaining on the metal when the ligands are removed in their normal closed-shell configuration.

There is usually a maximum number of ligands allowed for each d^n, provided that the complex is mononuclear, i.e has one metal atom, and diamagnetic (n is an even number, with all electrons paired):

$$n + 2(CN)_{max} = 18$$

Here n is the number of **d** electrons and CN is the metal coordination number, defined as the number of σ bonds formed between a metal and its ligands. The above equation is called the 18-electron rule. This rule can be used to predict the stoichiometries of most metal complexes.[3,8,10]

The 18-electron rule is almost always obeyed. When there is fewer than the maximum number of ligands in a metal complex, the complex is then referred to as being coordinatively unsaturated. Coordinatively unsaturated 14- and 16-electron complexes are reactive and important in catalysis.

2.1.2 Ligands and ligand effect

The study of ligand effects is one of the main themes in homogeneous catalysis.[11] The key to successful development of homogeneous catalysts has undoubtedly been the exploitation of the effects that ligands exert on the properties of metal complexes: by adjusting the electronic and steric properties of a catalytically active complex, selectivities and rates can be dramatically altered. The rate and selectivity of a given process can be optimised to the desired level through proper control of the ligand environment.[11]

If the Cl-ligands of the WCl_6-catalyst are substituted with oxyaryl or alkoxy groups the activity of the metathesis catalyst can be drastically influenced. The presence of the aromatic ring in the aryloxide ligand enhances the possibility to change the substituents on the ring, and thus to influence the electronic as well as the steric properties of the ligands on the tungsten core.[12,13]

Halide and phosphine ligands are usually used in Schrock and Grubbs metathesis catalysts. Catalytic activity increases from I < Br < Cl with halide ligands. Large halogens disfavour alkene binding due to steric crowding. When using phosphine ligands catalytic activity increases as cone angle and electron donating ability increase. As cone angle increases, dissociation of phosphine becomes more easy for steric reasons. High electron donating ligand stabilises vacant orbital in 14 e^- intermediate.[14,15]

Ligands such as NH_3 and H_2O, which have a lone pair for interaction with the metal, form classical coordination complexes with metal atoms. They are formed only by interaction of the ligand electrons with empty **d**, **s**, or **p** orbitals of the metal. These ligands react as Lewis bases, and the metal as a Lewis acid. The bond formed is rationally symmetric about the metal-ligand axis and is therefore designated as a σ bond. The ligands are unidentate, that is, they are bonded to the metal through single sigma bonds. The classical unidentate oxygen donors include H_2O, CH_3OH, and tetrahydrofuran. These ligands are hard (small and weakly polarisable), weakly basic and are only weakly bonded to transition metals in low oxidation states.

Ligands including Cl^-, Br^-, I^-, and OH^- have two or more filled orbitals which can interact with two empty metal orbitals, Figure 2.2. One of the ligand orbitals (p_x) forms a σ bond, but the second (p_y), which must be oriented perpendicular to the metal-ligand axis, can only form a bond

having no rotational symmetry; it is therefore called a π bond. For both the σ and π bonds, the electrons are donated by the ligands.

Metal   Ligand (Cl⁻)

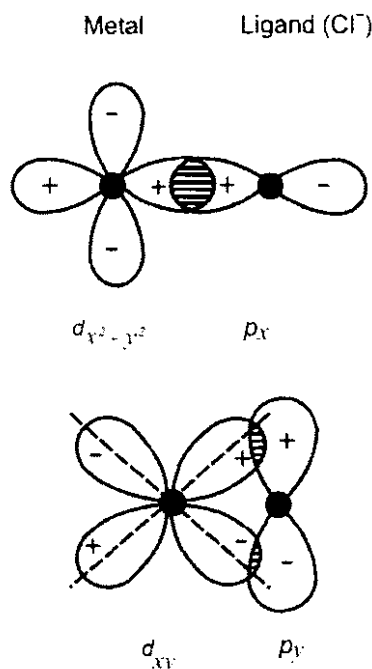$d_{x^2-y^2}$ p_x

d_{xy} p_y

Figure 2.2   Back-bonding involving two filled ligand orbitals and two empty metal orbitals.[8]

The halide ligands readily form bridges, which are easily broken in reactions with other ligands. The iodide ligand is especially important in catalysis as it is a large, polarisable "soft" ligand, that is a strong nucleophile and a weak proton acceptor. It forms strong bonds with transition metals in low oxidation state.

2.2 Homogeneous catalytic systems

The most popular homogeneous catalysts are the Grubbs and Schrock catalysts. Grubbs catalysts are based on ruthenium complexes, while Schrock catalysts are based on tungsten and molybdenum complexes. The Grubbs and Schrock catalysts are now extensively used in various kinds of metathesis reactions, such as acyclic diene metathesis (ADMET), cross-metathesis, *etc.* using various kinds of reactants. In general, Schrock catalysts are more active than Grubbs catalysts. However, Schrock catalysts are extremely sensitive to moisture and oxygen.[16] On the other hand, it has been reported that Grubbs catalysts have a remarkable stability towards a wide variety of functional groups.[12,16-17,18]

2.2.1 Tungsten (VI) complexes

As mentioned earlier tungsten (VI) aryloxide complexes of the type $W(OAr)_nCl_{6-n}$ (OAr = unsubstituted or substituted phenoxides) which are easily synthesised from WCl_6 and phenol derivates, are known to provide very active metathesis catalysts in the presence of a cocatalyst like $EtAlCl_2$, $Et_3Al_2Cl_3$ or R_4M (R=methyl or butyl, M=Sn or Pb).[11,19-20,21,22,23] The phenoxide groups present in these tungsten catalysts increase the solubility and activity of complexes,[23] and more importantly, they can be used to influence the steric and electronic properties of the reaction site.[11,22] The presence of the aromatic ring in the phenoxides affords the possibility of making systematic changes in the steric and electronic properties of the ligands on the tungsten by incorporation of different substituents on the phenol.[24] Wide variations in activity are associated with the changing of the 4-substituents on the phenoxide ligand, and electron-withdrawing groups on the phenoxide greatly increase the activity whereas electron-donating groups reduce it.[24] If the electron-withdrawing properties of the aryloxo ligand are increased, an increase in the metathesis activity is observed. Another factor influencing metathesis reactions is the position of the substituent on the aryloxide ligands. Complexes with substituents on positions 2 and 6 of the aryloxide ligands were found to be the more active catalysts for the metathesis of α-alkenes.[11,19-22]

Alkoxo and phenoxo groups in $(RO)_nWCl_{6-n}$ catalysts act as π-donors to the tungsten atom. Dodd and Rutt[23] using the system $W(OAr)_4Cl_2/EtAlCl_2$, showed that the rate of metathesis is enhanced by factors that can reduce the back-bonding from ligand to tungsten. They concluded that the carbene species, i.e., catalytic active centres, are electrophilic in nature.[23]

The substitution of Cl atom in WCl_6 by a less electronegative ligand must lead to a decrease in the tungsten reduction rate. This decrease is expected to become larger with increasing electron-donation from ligand to tungsten. If the electrophilicity of carbene species is correct, then for $(RO)_nWCl_{6-n}$ system used by Balcar et al.,[23] the nature of the OR ligand influences both the rate of formation of carbenes and their activities.

Thorn-Csányi et al.[23] found that for molybdenum and tungsten carbene catalysts (Figure 2.3), three distinguishable reaction phases exist. Firstly an induction period, then metathesis followed by the occurrence of side reactions coupled with metathesis. During the second phase metathesis takes place and equilibrium is established.[25] Considering the metathesis activity of the catalysts

investigated by Thorn-Csányi *et al.*[25], it is noted that the catalyst with the highest activity towards the side reactions also shows the highest metathesis activity and vice versa.
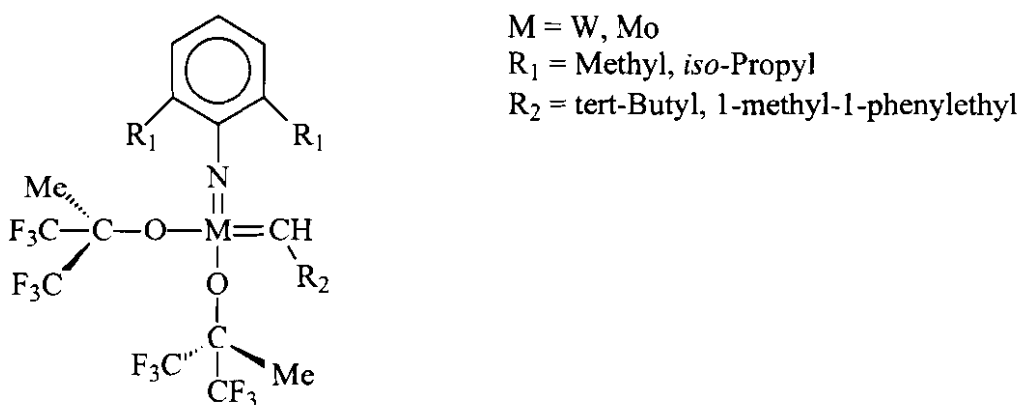
M = W, Mo
R_1 = Methyl, *iso*-Propyl
R_2 = tert-Butyl, 1-methyl-1-phenylethyl

Figure 2.3   Shrock-type carbene complexes.

2.2.2 *Grubbs catalysts*

Several studies have shown that, the air-stable well-defined carbene ruthenium catalysts,[18,26] can also induce non-metathetical transformations, such as the Kharasch addition, alkene isomerisations, or hydrogenations.[26] It was not until the 1990s that ruthenium catalysts were developed with the ability to metathesise acyclic as well as cyclic alkenes.[27] The popular complex (Figure 2.4a), known as first generation Grubbs catalysts, was followed by the development of *N*-heterocyclic carbene (NHC) ligated complexes (Figure 2.4b), known as the second generation Grubbs catalysts.[27-28,29] Grubbs second generation catalyst is more active than Grubbs first generation catalyst for all alkene metathesis reactions, however, alkene isomerisation has been reported as a side reaction with Grubbs second generation catalysts.[28] The ligand exchange (IMes vs. PCy_3) must increase the catalyst susceptibility towards isomerisation.[30] Alkene isomerisation can be a useful commercial process, as in the Shell higher olefin process (SHOP), but is most often an undesired side reaction in metal-catalysed reactions.[28]

(a)   (b)
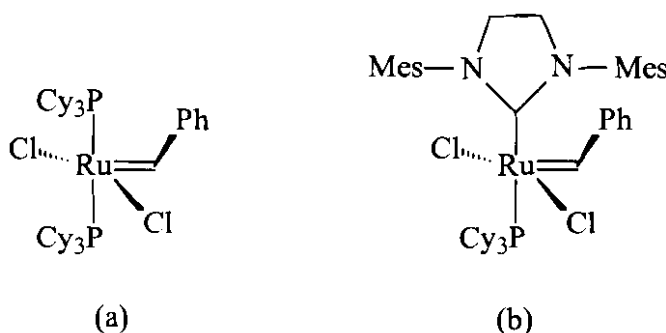
Figure 2.4   Grubbs (a) first generation and (b) second generation catalysts.

Nguyen *et al.*[31] reported the synthesis of ruthenium-based alkene metathesis catalyst, $(Ph_3P)_2Cl_2Ru=CH-CH=CPh_2$ (Figure 2.5), and its activity in the ROMP of norbornene. Making the metal centre more electrophilic by replacing the Cl in (Figure 2.5) with a variety of electron-withdrawing anionic ligands - as in examples in early-transition-metal metathesis chemistry - does lead to changes in the relative propagation rate of the ruthenium carbene centre in the polymerisation of norbornene.[31] In contrast to the catalysts developed from d^0 early-transition-metal centres, where increasing the electron-withdrawing ability of the ancillary ligands leads to increased turn over numbers, it appears that the d^6 Ru^{II} metal centre requires electron-rich ancillary ligands for increased metathesis activity.[31] The resulting anionic derivatives of the ruthenium catalyst (Figure 2.5) do not show activity for the metathesis of *cis*-cyclooctene or *cis*-2-pentene. Substitution of the triphenylphosphine ligands with better σ-donating alkylphosphines proved to be more fruitful and led to new catalysts with high metathesis activity.[31]
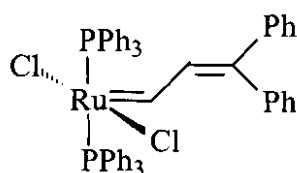
Figure 2.5   Ruthenium-based alkene metathesis catalyst.

Homogeneous catalysts offer greater specificity and higher catalytic activity because the catalytic groups are more available to the substrates when the catalyst is completely soluble in the reaction media; however recovery is generally more difficult.[32-,33,34,35,36,37] Homogeneous transition metal catalysts with complex ligands are very expensive, and this leads to an increasing need for recycling. The problematic separation of homogeneous catalysts from reaction products in solution has hampered the commercialisation of many excellent homogeneous catalysts. For industrial catalytic processes, there is a need for the development of systems that function like homogeneous catalysts (i.e. high reactivity) and are also easy to separate from the reaction mixture.[35,36] For this reason considerable attention has been directed toward the attachment of homogeneous catalysts to insoluble supports in an attempt to combine the practical advantages of heterogeneous catalysis with the efficiency of homogeneous systems.[32,33,35]

Heterogenisation allows for the easy separation and recycling of the catalyst from the reaction mixture. However, due to the heterogeneous nature of these catalysts, there can be problems with the accessibility of the catalytic sites by the reagents in solution. To date, most of research

in this area has focused on polymer-supported catalysts and in most instances, the immobilisation of a catalytic species on a polymer support is accompanied by a significant loss in catalytic activity and/or selectivity. Polymer based catalysts are often ineffective, due to leaching of the catalytic groups, or the unavailability of catalytic sites, owing to uncontrollable polymer conformations, and indefinable incorporation of catalysts within the polymer chain.[35] Dendrimers offer an alternative and viable approach to address some of the issues about heterogenising homogeneous catalysts.[11,32,34,35] They allow the accurate control of the number and structure of the active sites, show the kinetic behaviour (activity and selectivity) of homogeneous catalysts, and can be removed from a product containing solution using ultra- and nanofiltration membrane techniques (Figure 1.1) and therefore can be recycled.[32,33,36,38-,39,40,41]

2.3 Dendrimers

The term dendrimer is derived from the Greek word *dendra*, meaning tree. These highly branched macromolecules, which are constructed in a generation-wise manner starting from a central initiator core molecule,[42,43] have compelling molecular structures that are reminiscent of patterns often observed in nature and particularly those found in trees and in coral. Dendrimers – also called arborals or cascade molecules – exhibit controlled patterns of branching and ideally are monodisperse, i.e., all the molecules should have exactly the same molecular masses, constitutions and average dimensions.[37-,38,39] Their unique architecture and monodisperse structure has been shown to result in improved physical and chemical properties (Table 2.3) when compared to traditional linear polymers.[44,45]

Dendrimers are chemically inert, compatible with most organometallic reagents[40,46] and easy to prepare. Silicon chemistry offers several quantitative reactions suitable for the construction of perfect dendrimers, such as transformation of chlorosilanes with organometallic reagents, e.g. Grignard reagents, as well as Pt-catalysed hydrosilylation. To date carbosilane, carbosiloxane, and small silane dendrimers, have been described.[38] At present, carbosilane dendrimers (Scheme 2.1) represent the most important class of Si-based dendrimers. They are kinetically and thermodynamically very stable molecules. This is due to the dissociation energy of the Si-C bond (306 kJ/mol), which is comparable to that of C-C bonds (345 kJ/mol), and the low polarity of the Si-C bond, which is an important prerequisite for further functionalisation.[38]

Table 2.3 Physical and chemical properties of dendrimers and linear polymers[45]

| Property	Linear polymer	Dendrimer
Shape	Random coil	Spherical
Viscosity	High	Low
Solubility	Low	High
Crystallinity	High	Amorphous
Reactivity	Low	High
Compatibility	Low	High
Compressibility	High	Low
Structural control	Low	Very high
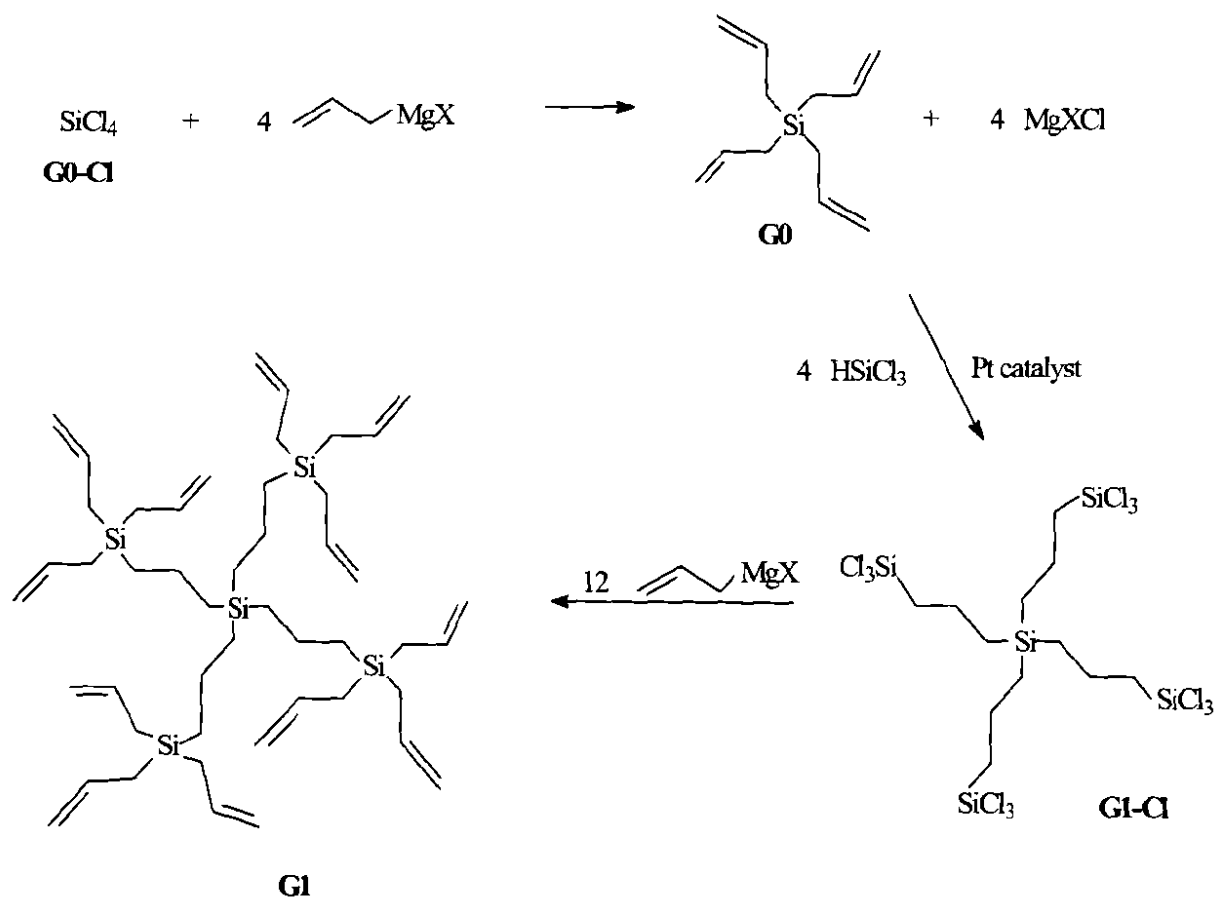
Scheme 2.1 Synthesis of carbosilane dendrimers.[47]

There are two main approaches to dendrimer synthesis, namely the divergent approach (Scheme 2.2), which involves assembling repeat units around a core through successive chemical reactions at the periphery of the growing macromolecule, and the convergent strategy (Scheme 2.3), whereby dendron wedges are built up separately and then anchored to the core in a final step.[35] To date, all reported carbosilane dendrimers have been synthesised via the divergent approach (Scheme 2.2).

Starting from the central core (G0) possessing alkenyl groups (Scheme 2.1), the dendrimer is constructed using repeating sequences of alternating hydrosilylations with chlorosilanes and ω-alkenylations with Grignard reagents. The most popular core molecules are tetraallylsilane and tetravinylsilane, which lead to dendrimers of spherosymmetrical topology.[38] The dendrimer scaffold can be subdivided into three regions: (i) the core from which the branching units emanate, (ii) the region of the inner repeat units, and (iii) the outer region with the end groups. The individual layers around the core are designated as generations.[38]

Fetters et al.[38] reported the use of a G1 carbosilane dendrimer with 12 end groups for the synthesis of a star polymer as early as 1978. However, Van der Made et al.,[38] and Muzafarov et al.,[38] independently reported the first synthesis aiming at carbosilane dendrimers of various generations. One of the most promising applications of carbosilane dendrimers is the use as scaffolds or ligands for catalytically active metal complexes.[3,38,48] Carbosilane dendrimers' inertness allows the use of a range of organometallic reagents in synthetic procedures.[45,49]

Core
molecule

First-generation
dendrimer

Second-generation
dendrimer
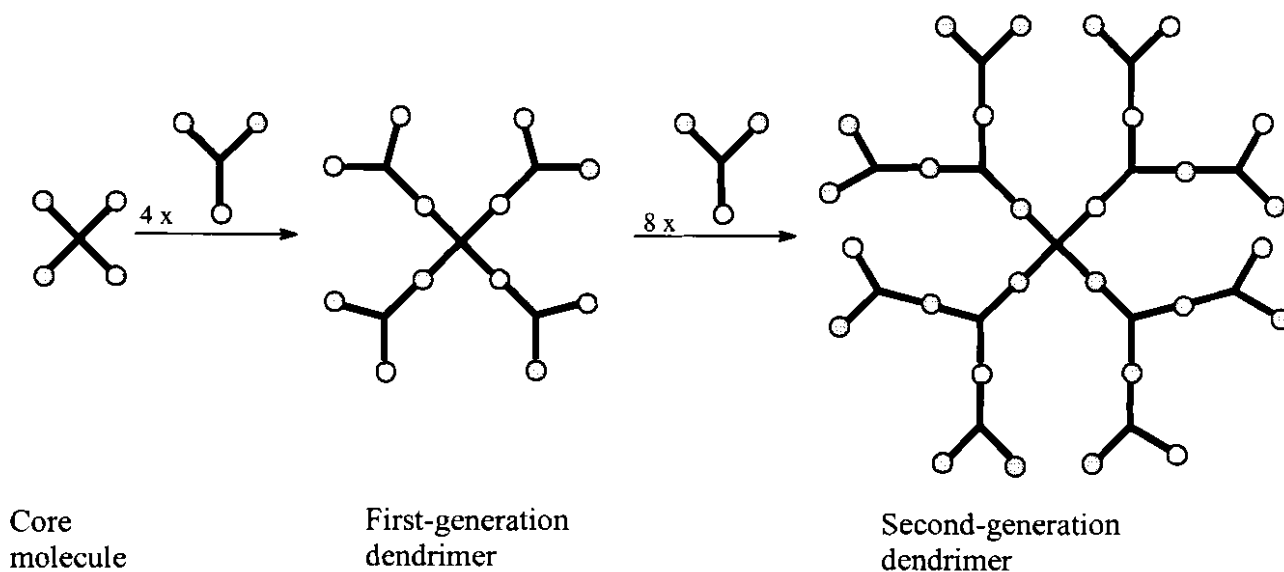
Scheme 2.2   Schematic representation of the divergent synthesis of dendrimers.[50]

18
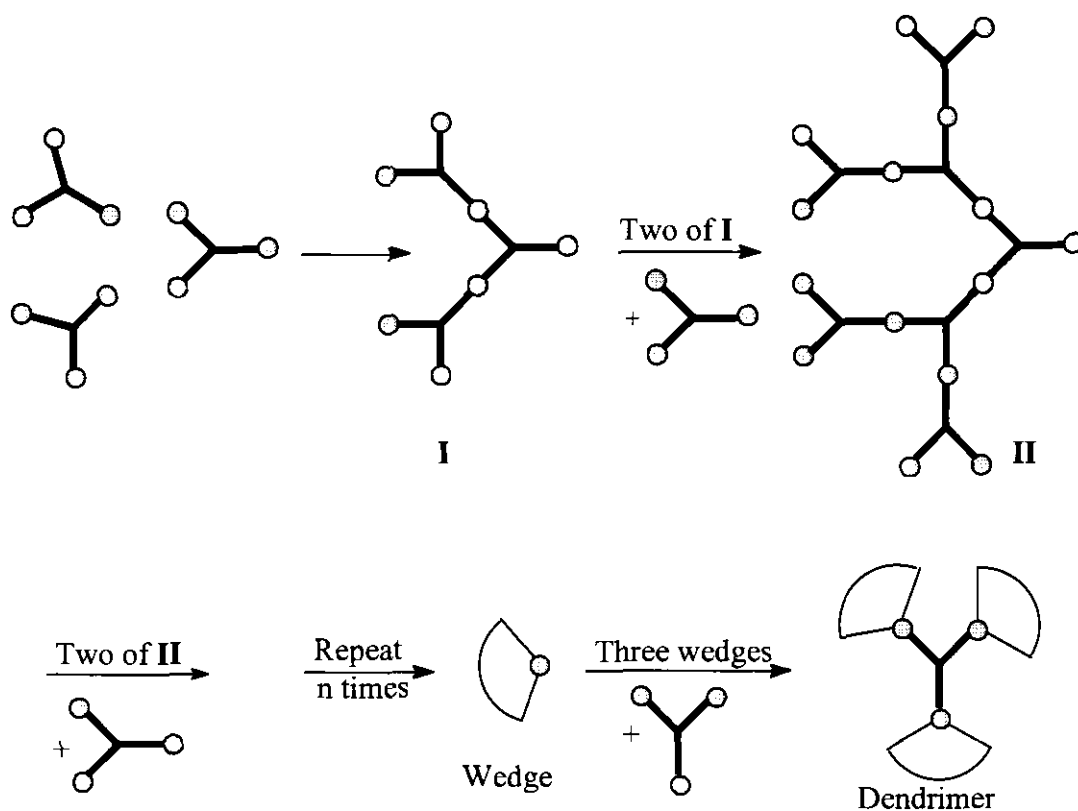
Scheme 2.3   Schematic representation of the convergent synthesis of dendrimers.[50]

2.4   Dendritic catalysts

Dendritic catalysts, also called metallodendrimers or catalytic dendrimers, are dendrimers containing metal element(s) in their framework.[32,42,51] The metal complexes or organometallic moieties can be located either at the periphery of the dendrimer or within a dendrimer matrix.[33,34,52] The incorporation of metal complexes in dendritic materials is done either by surface modification in which the mode of attachment is at the periphery of the dendrimer, or by incorporation of the transition metals within the dendritic infrastructure, normally as the core (Figure 2.6).[32]

The modification of properties (more active, selective, or more stable than homogeneous monomeric analogues dendritic catalysts) induced by the dendritic framework, obviously depends on the location of the functional group within the structure. Large differences can be expected from periphery functionalised dendrimer and core-functionalised systems.[33,41]

= transition metal

(a)   (b)
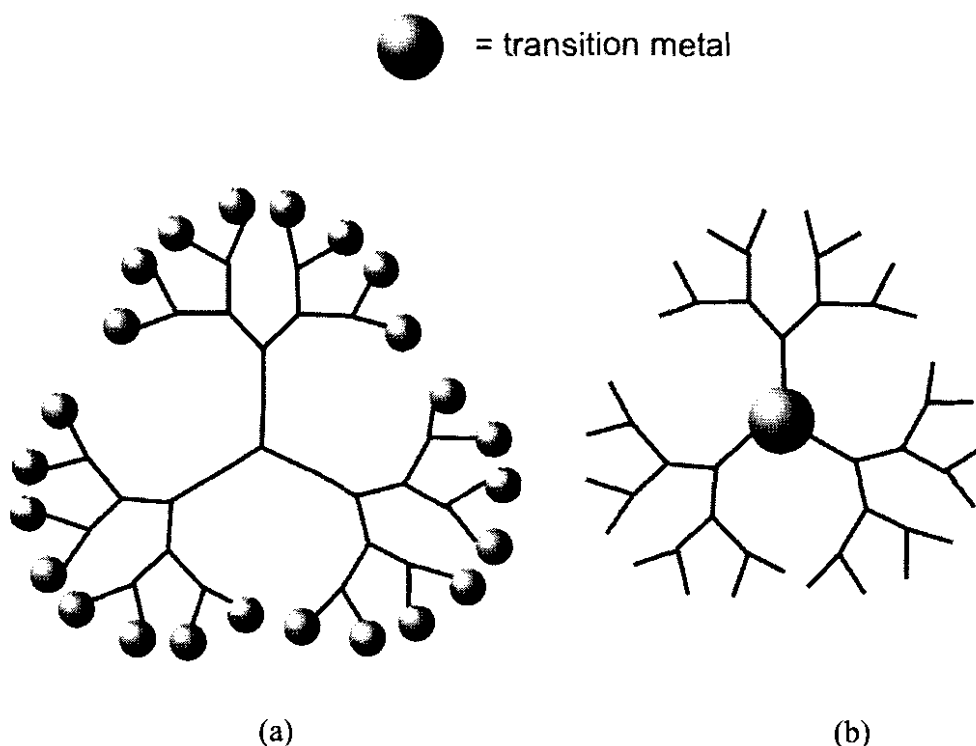
Figure 2.6   Periphery (a) and core (b) functionalised dendritic catalysts.[33,41]

Periphery functionalised dendrimers have their ligand system, thus the metal complexes, at the surface of the dendrimer. The transition metals will be directly available for the substrate, in contrast to core-functionalised systems in which the substrate has to penetrate the dendrimer prior to reaction.

The accessibility of periphery functionalised dendrimers allow reaction rates that are comparable with those of homogeneous systems. The periphery functionalised systems contain multiple reaction sites and ligands, which result in extremely high local concentrations of the catalyst and ligand. High catalyst loading is an important economical aspect. The loading on these systems is extremely high due to the inherent nature of dendritic structures and dendrimer synthesis.[35] This high local concentration greatly affects the catalytic performance in either a positive or a negative sense.[35,41]

Steric crowding was reported in organometallic dendrimers with high catalytic loading.[32,44] Peripheral congestion could lead to incomplete reaction profiles (catalyst deactivation) and unwanted side reactions. An investigation of the catalytic activity of the organometallic dendrimers by several groups[32,44] has generally led to a conclusion that performance of these systems decreases with an increase in surface congestion due to extensive branching of the dendritic structure. The interactions between neighbouring metal centres in these congested

molecules contribute significantly to the lower rates of catalysis with an increasing number of generations.[33,44] For example, Van Koten *et al.*[32,36] in their study with periphery functionalised silicon dendrimers with aryl nickel(II) centres capable of catalysing the Kharasch addition of perhaloalkanes to olefins, reported that the local concentration of nickel centres resulted in an interaction between neighbouring Ni(II) and Ni(III) sites formed during the catalytic reaction.[32]

In one of the studies on W-carbosilane dendrimers, it was found that by increasing the reaction time, more W-carbenes undergo dismutation (Scheme 2.4), resulting in high molecular weight branched starpolymers. The dismutation was attributed to the high activity of the W-alkylidene dendrimer system. This was in contrast with the corresponding Ru-alkylidene dendrimer catalysts, where no dismutation was observed.[11]

In core-functionalised dendrimers the catalyst could especially benefit from the site isolation effect or the specific micro-environment created by the dendritic structure. For reactions that are deactivated by excess ligand or *via* a bimetallic (or multimetallic) mechanism, the shielding effect of dendrimers might result in relatively stable catalysts. Core-functionalised dendrimers may also benefit from the local polarity around the catalyst created by the dendrimer.[41]

One disadvantage of metallic dendrimers is that they have a flexible skeleton. This means that they change size and shape in solution, and this may cause the first and second generation (**G1** and **G2**) dendrimers to leak through the nanofiltration membrane. Even higher generation dendrimers are still not fully retained by nanofiltration membranes. Going up in generation does not necessarily result in a significant increase in size of the dendrimers, but rather a back-folding of the dendritic branches concomitant with denser molecules is encountered.[36] This drawback can be overcome by the incorporation of aromatic molecules in the skeleton of the dendrimer, which will help maintain the dendrimer's shape in solution.[36,53]

$$W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 \ + \ 3 \ Bu_4Sn \xrightarrow{\ PhCl\ } W(=CHPr)(C_4H_9)(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl \ + \ 3 \ Bu_3SnCl \ + \ C_4H_{10}$$

I

G0-W₁

NBE = norbornene

Dismutation

[W] = W(C₄H₉)(O-2.6-C₆H₃Cl₂)₂Cl

G1D

unit dendrimer core
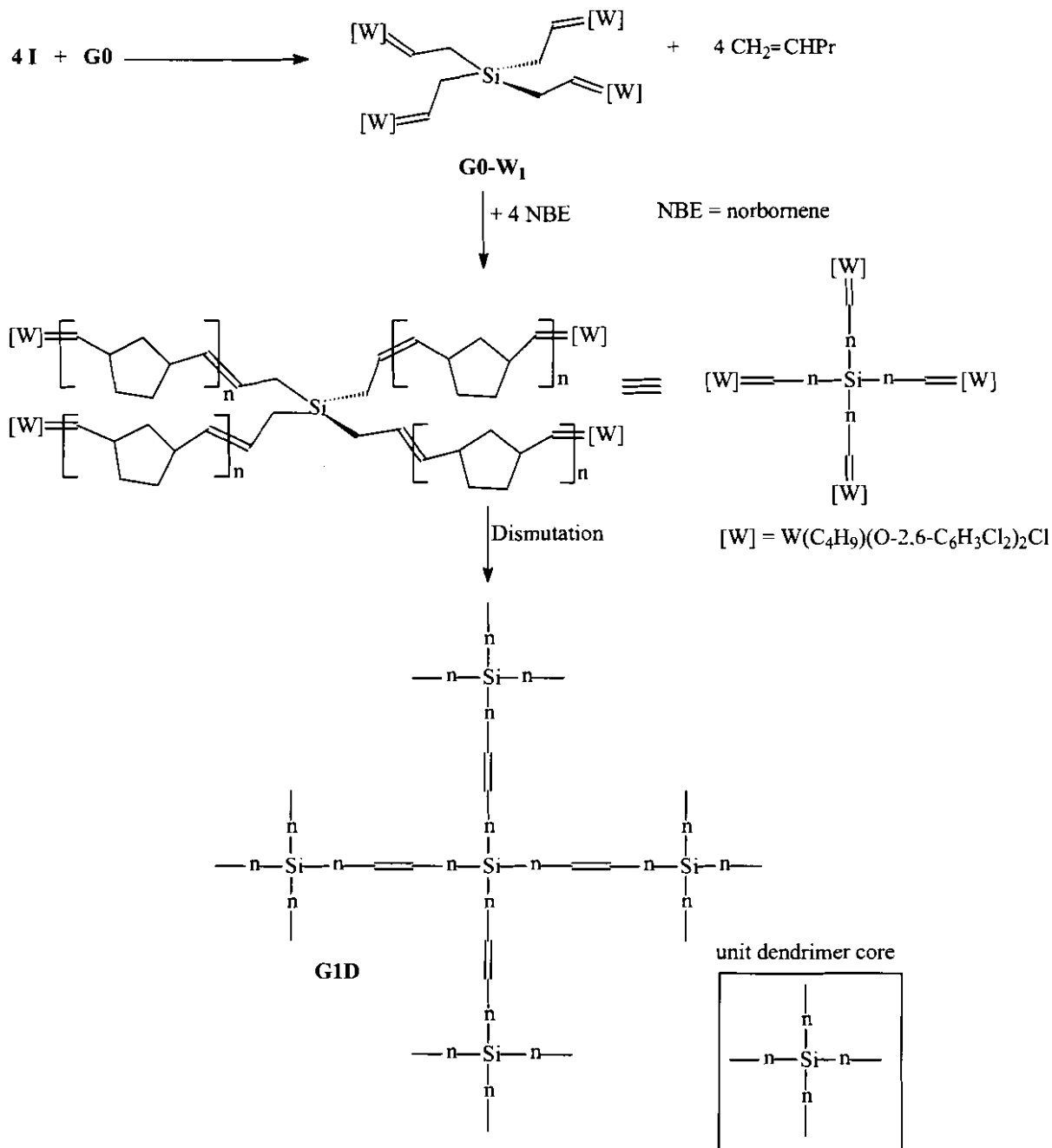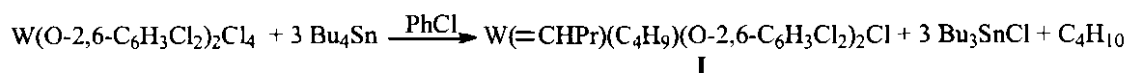
Scheme 2.4   Synthesis of starpolymers by dismutation.[11]

Much work has been done on dendritic catalysts, for example, Van Leeuwen[54] reported a star shaped hexaphosphine-palladium catalyst with a benzene core for polyketone formation from alternating CO/alkene polymerisation.   Mizugaki *et al*.[54] used DAB-dendrimer-[N(CH₂PPh₂)₂PdCl₂]₁₆ to study the selective hydrogenation of conjugated dienes to monoenes.

Diphenylphosphine-functionalised carbosilane dendrimers were synthesised by the Reek and Van Leeuwen group,[54] these ligands were then used for rhodium-catalysed hydroformylation of 1-octene. Hoveyda's group synthesised two dendritic Ru-based metathesis catalysts and applied them in catalytical ring closing, ring opening and cross metathesis.[54] Garber et al.[55] also reported the synthesis and catalytic activity of dendritic Ru-based metathesis catalysts, which can catalyse the ring closing metathesis of dienes that contain terminal alkenes. Dijkstra et al.[56] used nickelated carbosilane dendrimers in a regioselective Kharasch addition of polyhalogenoalkanes to carbon-carbon double bonds. Dendritic catalysts have been synthesised and used in hydrogenation, hydroformylation, metathesis, Kharasch addition, and could be retained by nanofiltration or ultrafiltration membrane technology. Athough these recoverable catalysts have been used in metathesis before, they have been used mostly in ROMP.[14] In this study the dendritic catalysts were applied to metathesis of terminal alkenes.

2.5   Alkene metathesis

The metathesis of alkenes has been a widely studied process due to its academic and industrial interest. It offers unique paths for petrochemical and polymer synthesis.[57] It is one of the many mentioned catalytic reactions, and was first reported in open literature by Banks and Bailey.[7] They observed that in the presence of a supported molybdenum catalyst, linear alkenes were transformed into homologs of shorter and longer carbon chains. A few years later Calderon et al.[7] found that the same reaction could be performed homogeneously using the catalyst system WCl$_6$/EtAlCl$_2$/EtOH (1:4:1). This demonstrated that alkene metathesis can take place in the presence of both heterogeneous and homogeneous catalysts.[7] During this catalytic reaction two alkene molecules react so that their double bonds are broken and reformed in such a way to give product molecules containing parts from each of the reactants. Once formed, the product alkenes are free to react with each other and reverse the process, or with other alkenes in the system to form new products.[7,9,58,59] The process occurs by transalkylidenation.[59,60]

$$R_1—CH=CH—R_2 \quad + \quad R_3—CH=CH—R_4 \rightleftharpoons \quad \begin{matrix} R_1—CH \\ \| \\ R_3—CH \end{matrix} \quad + \quad \begin{matrix} HC—R_2 \\ \| \\ HC—R_4 \end{matrix}$$
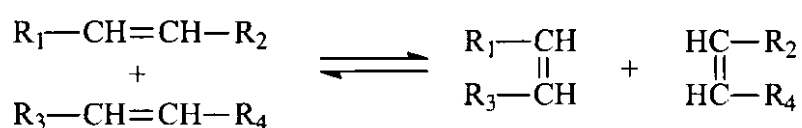
There are various broad groups into which alkene metathesis reactions fall (Scheme 2.5).[9,61]

Both terminal and internal alkenes can undergo metathesis. Metathesis of α-alkenes yields ethylene and a symmetrical internal alkene. In these cases the reaction can generally be driven to

completion by removal of the volatile ethylene. The reverse reaction, cross-metathesis with ethylene, called ethenolysis, makes it possible to prepare linear α-alkenes from internal alkenes.[7]

(a) $CH_3CH{=}CHCH_3$ $\rightleftharpoons$ $\underset{\underset{CH_2}{\parallel}}{CH_3CH}$ + $\underset{\underset{CH_2}{\parallel}}{CHCH_3}$
    +
    $CH_2{=}CH_2$

(b)
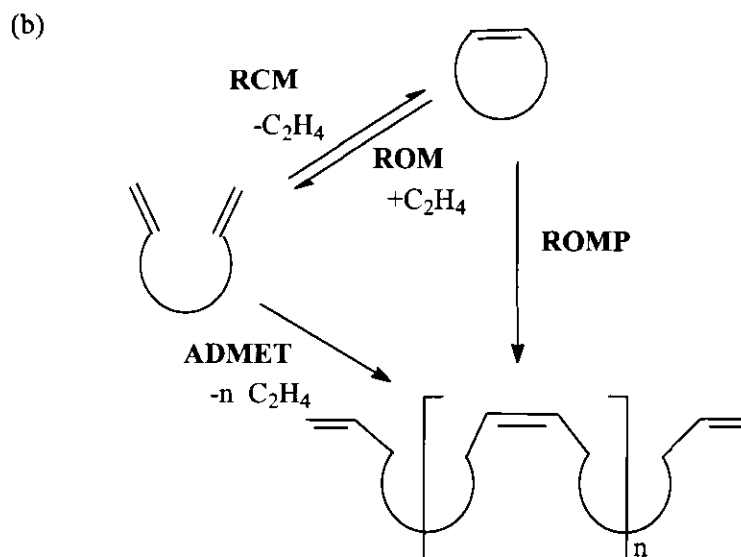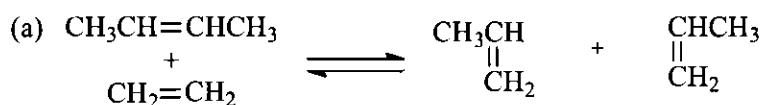
Scheme 2.5   The broad classes of metathesis reactions: (a) Cross metathesis reaction, (b) Ring-opening metathesis polymerisation (ROMP), Ring-closing metathesis (RCM), Ring-opening metathesis (ROM) and Acyclic diene metathesis (ADMET).[61]

Metathesis, isomerisation, cyclopropanation and polymerisation reactions are closely related alkene transformations. Isomerisation of the terminal alkenes occurs in parallel with metathesis, and cross-metathesis takes place between the terminal and internal alkenes (produced by isomerisation).[24]

The distribution in Table 2.4 is generally observed with 1-octene reactions:

Table 2.4   Formation of the different metathesis products during the metathesis of 1-octene.[62]

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 $(CH_3)_6CH=CH_2$

Various kinds of heterogeneous and homogeneous catalysts based on transition metals have been used for metathesis of a broad range of alkenes.

The catalysts based on metals like tungsten, molybdenum, and ruthenium are so far the most preferred. These catalysts were developed due to the extensive research mainly by Schrock, on tungsten and molybdenum, and Grubbs on ruthenium.[63] J-M Basset and J Osborn have also made important contributions on tungsten complexes.[64] Mo- and W-alkylidene complexes at present are the most active of the alkene metathesis catalysts known. Grubbs' Ru-based catalysts are more tolerant to water and a broad range of functionalities.[63,64]

2.6   Mechanism of alkene metathesis

The understanding of the reaction mechanism in metathesis reactions, is directly related to the role of the catalyst, i.e. the transition metal complex. Three transition states were proposed by as

many research groups[59] to explain the mechanism of alkene metathesis. The first of these involve a quasi-cyclobutane state as shown below:[59]

$$R_2C \overset{\|}{\underset{R_2C}{}} -M- \overset{CR'_2}{\underset{CR'_2}{\|}} \quad \Longleftrightarrow \quad R_2C \overset{\|}{\underset{R_2C}{}} \overset{CR'_2}{\underset{}{}} M \overset{CR'_2}{\underset{}{}}$$

$$R_2C \overset{\|}{\underset{}{}} CR'_2 \qquad R_2C \overset{}{\underset{}{}} CR'_2$$

$$\begin{array}{c} R_2C\overline{\mathrm{T}}CR'_2 \\ M \\ R_2C\overline{\perp}CR'_2 \end{array} \quad \Longleftrightarrow \quad \begin{array}{c} R_2C \text{---} CR'_2 \\ |\ M\ | \\ R_2C \text{---} CR'_2 \end{array}$$
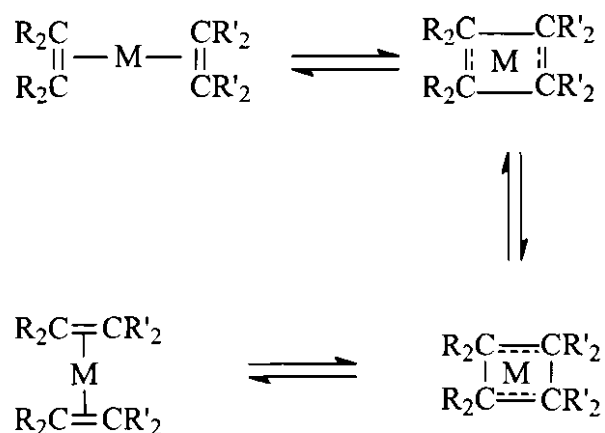
This transition state posed some problems, as no stable cyclobutanes were ever recovered from the reactions. Furthermore, cyclobutanes could not undergo metathesis reaction to form alkenes. This problem prompted two proposals which bypassed the quasi-cyclobutane transition state. One of these invoked a stereochemically non-rigid (fluxional) 5-member metallocycle. Hence the metal could exist between carbon-carbon bonds, the breakdown led to the starting materials or products.[59]

$$\begin{array}{c} R_2C\overline{\mathrm{T}}CR'_2 \\ M \\ R_2C\overline{\perp}CR'_2 \end{array} \quad \Longleftrightarrow \quad \begin{array}{c} R_2C\text{---}CR'_2 \\ / \qquad \backslash \\ R_2C \qquad CR'_2 \\ \backslash \qquad / \\ M \end{array} \quad \Longleftrightarrow \quad \begin{array}{c} R_2C\text{---}CR'_2 \\ / \qquad \backslash \\ R_2C \qquad M \\ \backslash \quad / \\ C \\ R'_2 \end{array}$$

$$\begin{array}{c} R_2C \\ \|\text{---}M\text{---}\| \\ R_2C \qquad CR'_2 \\ CR'_2 \end{array}$$
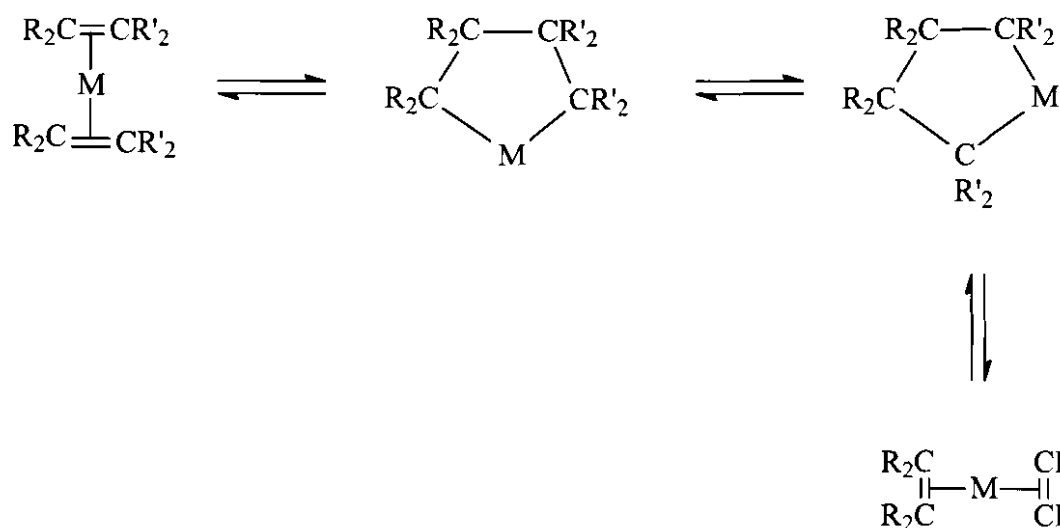
Currently it is universally accepted that alkene metathesis proceeds *via* the so-called metalcarbene chain mechanism, first proposed by Hérisson and Chauvin in 1971.[7,10,59] Hérisson and Chauvin proposed that metathesis could also be explained in terms of a stepwise process.[7,59]

$$
\begin{array}{ccc}
\underset{M}{\overset{CR_2}{\|}} + \underset{CR'_2}{\overset{CR'_2}{\|}} \rightleftharpoons & \underset{M-\underset{CR'_2}{\overset{CR'_2}{\|}}}{\overset{CR_2}{\|}} \rightleftharpoons & \underset{M-CR'_2}{\overset{R_2C-CR'_2}{|\quad\;|}} \rightleftharpoons \underset{M=CR'_2}{R_2C{=}CR'_2}
\end{array}
$$

$$
\begin{array}{c}
\Updownarrow \\
R_2C{=}CR'_2 \\
+ \\
M{=}CR'_2
\end{array}
$$
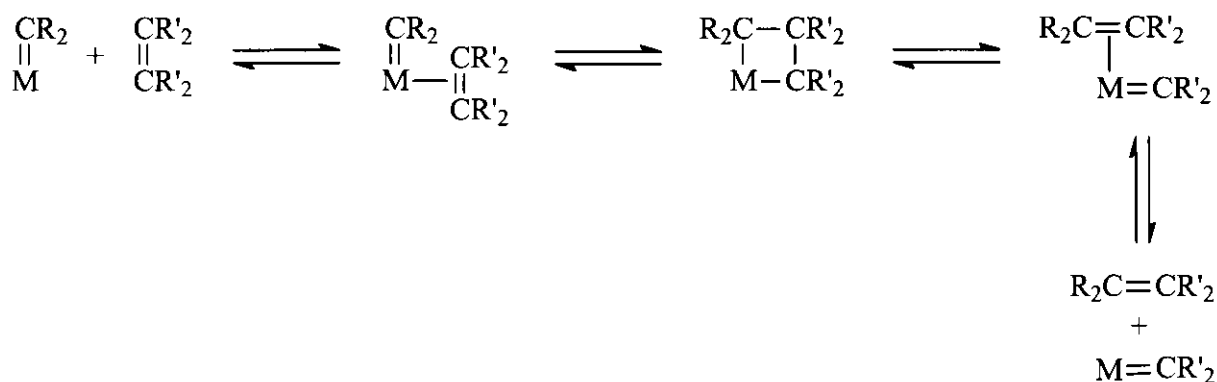
This propagation reaction involves a transition metal carbene as an active species with a vacant coordination site at the transition metal. The alkene coordinates at this vacant site and subsequently a metallacyclobutane intermediate is formed. The metallacycle is unstable and cleaves to form a new metal carbene complex and a new alkene.[7,59]

2.6.1 Carbene generation

Metal alkyl complexes of the early transition metals appear to be excellent sources of metal carbene complexes. Cooper and Green[65] suggested that an α-hydrogen abstraction might be a general and important transformation. In the case of the catalyst/co-catalyst combination, for example, the combination WCl_6/Me_4Sn, a transition metal alkyl species could be readily formed by alkylation of the transition metal. α-Hydrogen abstraction from the methyltungsten species would give the metal carbene species.[7,59]

$$
WCl_6 + 2\ Me_4Sn \xrightarrow[-2\ Me_3SnCl]{} Cl_4W\underset{CH_3}{\overset{CH_3}{<}} \longrightarrow Cl_4W{=}CH_2 + CH_4
$$
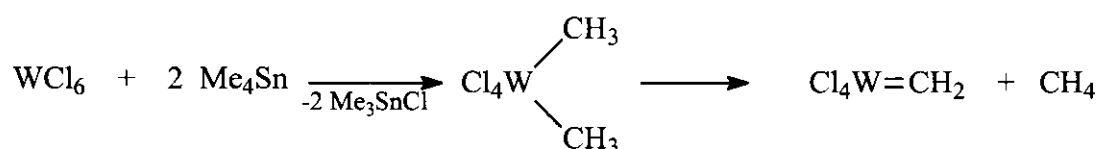
Methane evolution can be observed when the catalyst components are brought together. Shrock[65] found that transition metal alkyls could be converted to carbene (alkylidene) complexes on treatment with alkyllithium reagents. Green and coworkers have provided an excellent route to metallacycles from π-allyl complexes.[65] They found that tungsten and related molybdenum π-allyl complexes would undergo reduction with metal hydrides or lithium alkyls to produce metallacyclobutanes. Metallacyclobutanes can also be produced by the addition of cyclopropanes to transition metals. Metallacyclopentanes are easily formed from alkenes and reduced transition metals.[65] These systems can produce metallacyclobutanes either by ring

2.7   References

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contraction or possibly by α-C-C bond cleavage.[65] Although there are no clear examples of the cleavage route to carbenes, related reactions suggest its possibility.[65]

Most homogeneous systems contain alkylating agents. The generally used catalysts are prepared from soluble components such as $WCl_6/EtOH/EtAlCl_2$, $WCl_6/BuLi$, $Me_4Sn/WOCl_4$, $MoCl_2(NO)_2L_2/Al_2Me_3Cl_3$ (L = phosphine or amine) and $Re(CO)_5Cl/EtAlCl_2$.[65] Recent reports suggest that some heterogeneous systems can be activated by alkylating agents.[7,60]

The presence of an oxo ligand is favourable for tungsten catalysts and may be generated by the addition of an alcohol, traces of oxygen, or by the use of $WOCl_4$ instead of WCl_6.[7,65]

$$
\begin{array}{ccccc}
\underset{W}{\overset{O}{\underset{\diagdown CH_3}{\overset{\|}{\diagup}}}}CH_3 & \longrightarrow & \underset{W}{\overset{OH}{\underset{\diagdown CH_3}{\overset{|}{\diagup}}}}CH_2 & \longrightarrow & \underset{W}{\overset{O}{\overset{\|}{}}}{=}CH_2 + CH_4
\end{array}
$$
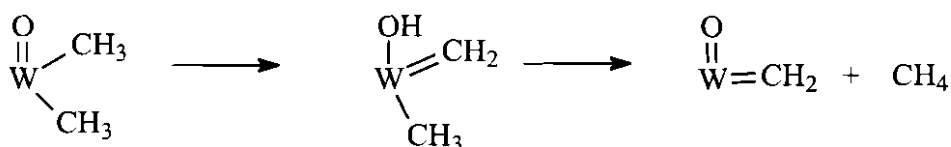
An oxo group significantly increases the driving force for the formation of a metallacyclic intermediate. When using metal carbene complexes as catalysts, a metal carbene initiation step is not necessary. The demonstration that the discrete metal carbene complexes could serve as highly active catalysts for alkene metathesis, supported the proposal of Hérisson and Chauvin that the reaction proceeds via metal carbene intermediates.[7] Chauvin suggested the following scheme for catalyst initiation:[65]

$$W{-}Cl + M'{-}CH_3 \longrightarrow W{-}CH_3 + M'{-}Cl$$

$$W{-}CH_3 \xrightarrow{-H^+} W{=}CH_2 \xrightarrow{} \diagup\!\diagdown + W{=}CHC_2H_5$$

M' = Li, Mg, or Sn
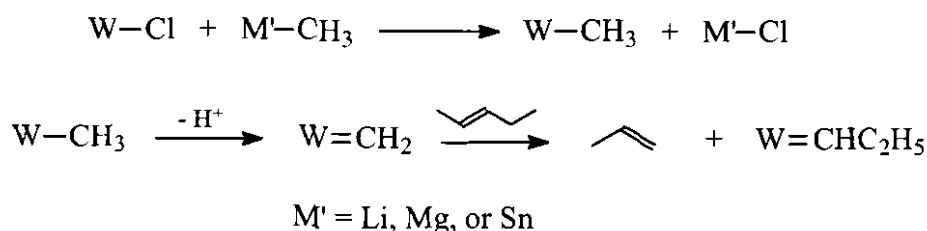
He reported that fragments from the co-catalyst appeared in the resulting alkene mixture and that methane was a by-product. The preparation of a tantalum carbene and a hydrocarbon fragment from a metal halide and two equivalents of an alkyllithium provides an excellent model for the general route of carbene formation in these systems. Consistent with this suggestion was the observation that unlabelled methane was produced from WCl_6 and dimethylzinc, even in deuterated solvents. This led to proposals similar to that of Chauvin.[65]

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EXPERIMENTAL

3.1   Materials

3.1.1   Reagents

2,6-Dichloro-, 2,6-dibromo-, 2,6-diphenylphenol (Aldrich), dichloromethane (Merck), ethanol (Labchem), hexane (Labchem) were used as received. Tungsten hexachloride, WCl_6, (Merck) was purified (see section 3.2.1) before use.

Grubbs first generation catalyst, $RuCl_2(PCy_3)_2(=CHPh)$, (Fluka) and tetrabutyltin, Bu_4Sn, (Aldrich) were used as received. Chlorobenzene (Merck) was dried under reflux over CaH_2 for 3 h followed by distillation, before use. 1-Octene (Aldrich) was passed through a neutral alumina column for purification. The purification and drying of solvents were performed under nitrogen.

Allylmagnesium bromide (Aldrich), diethylether (Labchem), silicon tetrachloride (Aldrich), magnesium sulphate (Merck) were used as received. Tetraallylsilane (Merck) for the synthesis of G0-W was also used as received.

3.1.2   Apparatus

All metathesis reactions were done in 5 ml Supelco Mininert® mini-reactors equipped with a screw cap and a septum. An aluminium heating block was used to heat the mini-reactors. An experimental set up (Figure 3.1) with an addition funnel equipped with pressure equalisation arm was used for the synthesis of the 2,6-disubstituted aryloxide tungsten (VI) complexes and tetraallylsilane. Solvents were transferred using Hamilton gastight syringes.

3.2   Experimental Procedure

3.2.1   Purification of WCl_6

WCl_6 was transferred into a round bottom flask under nitrogen. It was then heated below 275 °C, and tungsten oxide compounds (yellowish-red) which have a sublimation temperature lower than that of WCl_6 were removed by a constant nitrogen flow. WCl_6 was heated under

nitrogen until all tungsten oxide had been removed. Dark-purple crystals (WCl₆) remained in the flask. WCl₆ was stored under nitrogen to avoid oxidation indicated by colour change from purple-red to yellow. The crystals were used in the preparation of tungsten complexes.
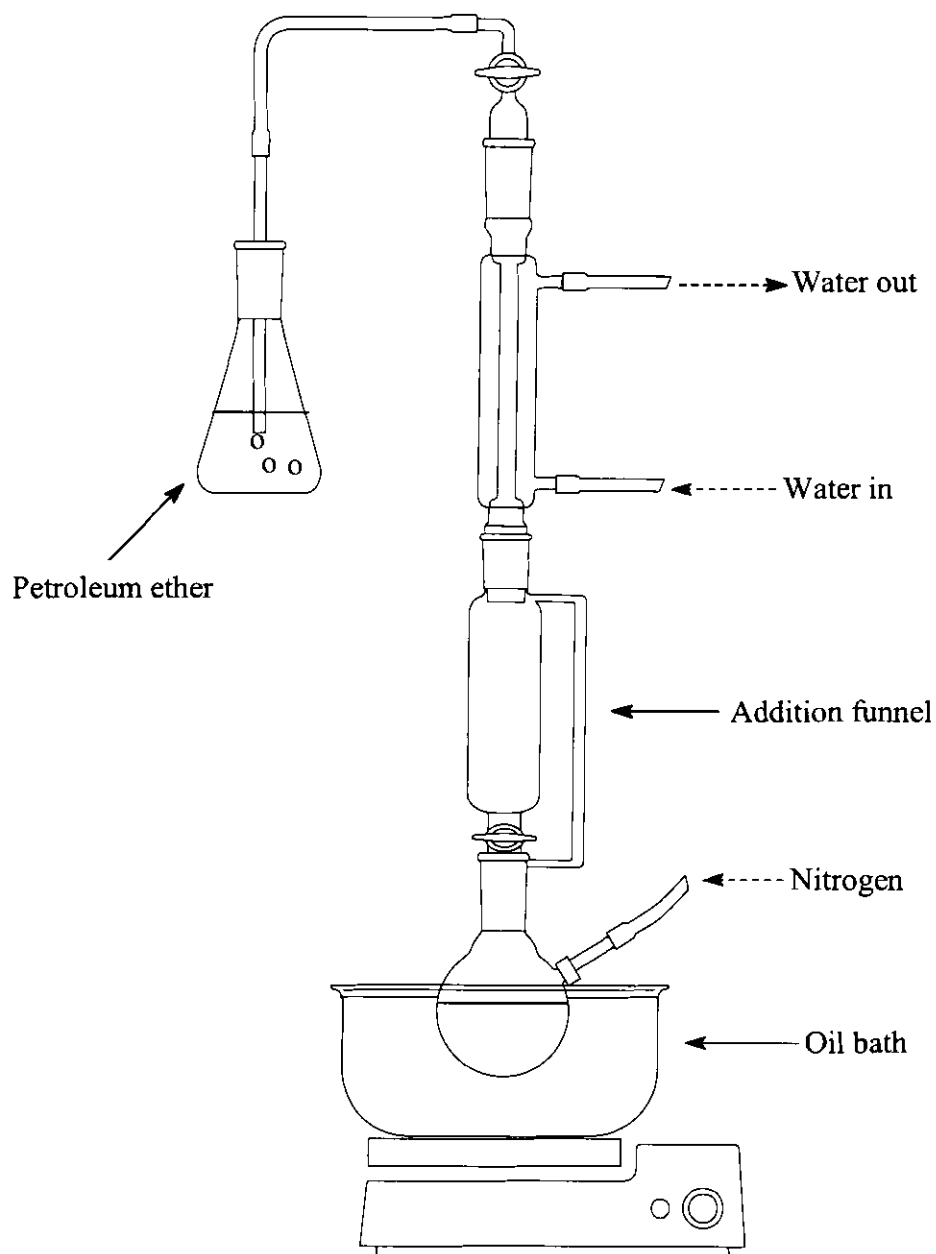
Figure 3.1 Experimental set up for the synthesis of the W-complexes[2] and tetraallysilane.

3.2.2 Synthesis of 2,6-disubstituted aryloxide tungsten (VI) complexes

Tungsten (VI) aryloxide complexes of the type $W(OAr)_nCl_{6-n}$ (OAr = unsubstituted or substituted phenoxides) could easily be synthesised according to the method of Quignard et al.[1-3] from WCl_6 and phenol derivatives (Scheme 3.1).
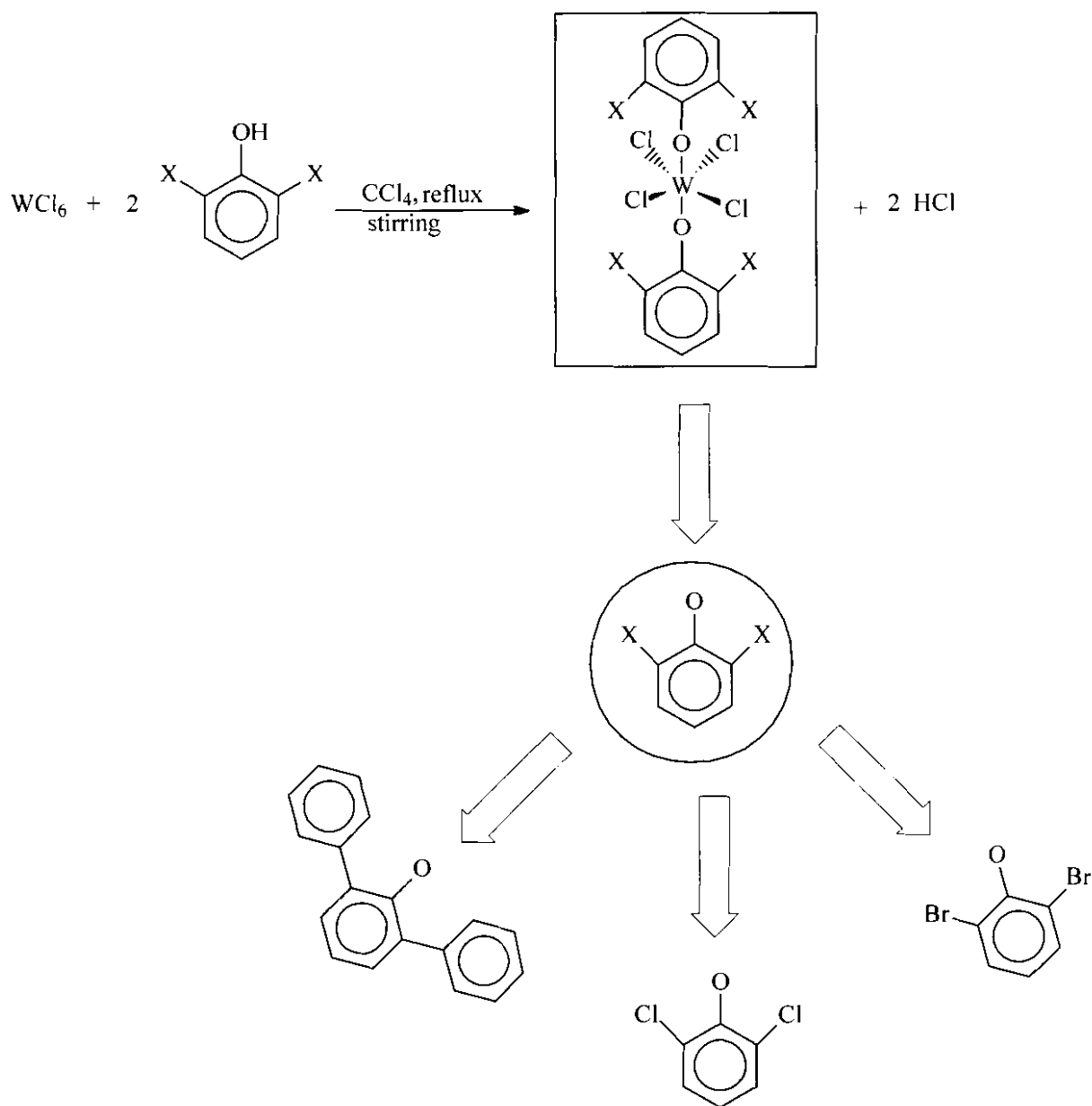
Scheme 3.1 Preparation of the $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes (X = Cl, Br, Ph).

Synthesis of $W(O-2,6-C_6H_3Cl_2)_2Cl_4$

A solution of $HO-2,6-C_6H_3Cl_2$ (0.839 g; 5.1 mmol) in 20 ml CCl_4 was added to WCl_6 (1.02 g; 2.56 mmol) suspended in 20 ml of carbon tetrachloride (CCl_4) in a round bottom flask. The

reaction mixture was stirred under reflux for 4 h. During the reaction, the reaction mixture turned from red to dark red. Filtration of the mixture followed by recrystallisation from ethanol gave $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ as black microcrystals with a green luster. The reaction was performed under nitrogen atmosphere.

Synthesis of $W(O-2,6-C_6H_3Br_2)_2Cl_4$

A solution of $HO-2,6-C_6H_3Br_2$ (3.045 g; 12.0 mmol) in 20 ml CCl_4 was added to WCl_6 (2.39 g; 6.00 mmol) suspended in 20 ml of carbon tetrachloride (CCl_4) in a round bottom flask. The reaction mixture was stirred under reflux for 4 h. During the reaction, the reaction mixture turned from red to deep red. Filtration of the mixture, followed by washing with hexane, gave $W(O-2,6-C_6H_3Br_2)_2Cl_4$ as a brown-black powder, which slowly decomposes in air. The reaction was performed under nitrogen atmosphere.

Synthesis of $W(O-2,6-C_6H_3Ph_2)_2Cl_4$

A solution of $HO-2,6-C_6H_3Ph_2$ (4.27 g; 17.3 mmol) in 10 ml CCl_4 was added to WCl_6 (3.44 g; 8.63 mmol) suspended in 20 ml of carbon tetrachloride (CCl_4) in a round bottom flask. The reaction mixture was stirred under reflux for 5 h. During the reaction the colour changed from deep-red to deep-purple. Filtration of the mixture, followed by recrystallisation from dichloromethane/ethanol (1:1), gave $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ as black microcrystals. The reaction was performed under nitrogen atmosphere.

3.2.3 Synthesis of Tetraallylsilane (G0)

The Van der Made *et al.* method[4] *(alkenylation)* was used for the synthesis of tetraallylsilane (Scheme 3.2). Silicon tetrachloride (4.0 ml; 0.035 mol) in 50 ml of diethylether was slowly added under nitrogen to 1.0 mol dm^{-3} allylmagnesium bromide (147 ml; 0.0147 mol) in diethylether using a pressure equalising funnel. The mixture was refluxed for 4 h, cooled to 0 °C and hydrolysed with 10 % NH_4Cl. A white gel formed. Three portions of 50 ml diethylether were used to extract tetraallylsilane from the suspension. Diethylether was removed by distillation, and tetraallylsilane, a clear liquid, remained. The organic layer was washed with water and dried over $MgSO_4$.

$$SiCl_4 \; + \; 4 \; \diagdown\diagup\diagdown\diagup MgBr \xrightarrow{Et_2O}$$

G0 (Tetraallylsilane)
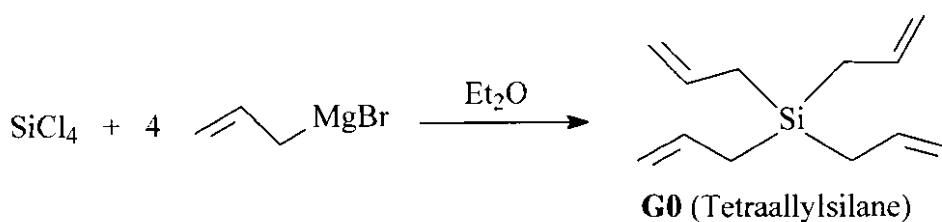
Scheme 3.2 The synthesis of tetraallylsilane.[5]

3.2.4 Synthesis of tungsten (VI) alkylidene dendrimer (G0-W)

Two methods were followed to synthesise W-alkylidene dendrimers from G0. The Beerens *et al.*[3] (Scheme 3.3) and a new proposed method (Scheme 3.4). With the Beerens *et al.* method[3] the recovery of the catalyst will be impossible since the carbene is placed between the dendrimer and the catalyst and with metathesis the catalyst will be detached from the dendrimer. So we proposed a method with the hope that the carbene would be placed on the outside of the tungsten catalyst so that the W-alkylidene dendrimer could be recovered after metathesis by nanofiltration.

Beerens et al. method[3]

$W(O-2,6-C_6H_3Cl_2)_2Cl_4$ (0.016 g; 2.5 x 10^{-5} mol) was added into a reaction flask under nitrogen. Chlorobenzene (0.3 ml) was added. The reaction mixture was heated at various temperatures for 10 minutes. Bu_4Sn (0.025 ml; 0.75 x 10^{-4} mol) was added as a co-catalyst. The mixture was heated and stirred at desired temperature for 20 minutes, after which (0.00145 ml; 6.25 x 10^{-6} mol) tetraallylsilane was added. The solution was stirred for another 90 minutes under nitrogen. The W-alkylidene dendrimer (G0-W$_1$) was characterised by IR, NMR, GC-MS and GC, and tested for the metathesis of 1-octene.

Proposed method

$W(O-2,6-C_6H_3Cl_2)_2Cl_4$ (0.016 g; 2.5 x 10^{-5} mol) was added into a reaction flask under nitrogen. Chlorobenzene (0.3 ml) was added. The reaction mixture was heated at various temperatures for 10 minutes. Tetraallylsilane (0.00145 ml; 6.25 x 10^{-6} mol) was added to the mixture. The solution was heated and stirred for 90 minutes under nitrogen. Bu_4Sn (0.025 ml; 0.75 x 10^{-4} mol) was added as a co-catalyst and the mixture was stirred and heated for a further 20 minutes. The W-alkylidene dendrimer (G0-W$_2$) was characterised by IR, NMR, GC-MS and GC, and tested for the metathesis of 1-octene.

$$W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 \ + 3 \ Bu_4Sn \xrightarrow{\text{PhCl}} W(=CHPr)(C_4H_9)(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl + 3 \ Bu_3SnCl + C_4H_{10}$$

I

$$4 \ I \ + \ G0 \longrightarrow$$ G0-W$_1$ $$+ \quad 4 \ CH_2=CHPr$$

[W] = W(C$_4$H$_9$)(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl
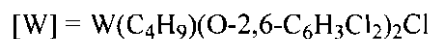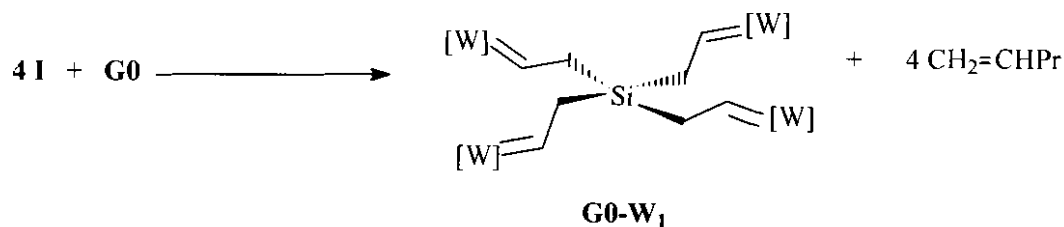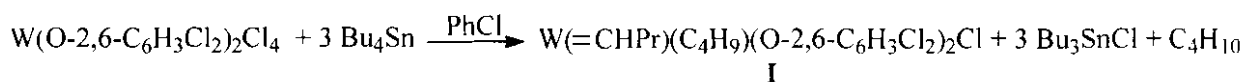
Scheme 3.3 The synthesis of G0-W$_1$ according to Beerens *et al.*[3]

$$4 \ W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 \ + \quad G0 \xrightarrow{\text{PhCl}}$$

[W] = W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_3$

12 Bu$_4$Sn

G0-W$_2$ $$+ \quad 12 \ Bu_3SnCl \ + \ 4 \ C_4H_{10}$$

(OAr = O-2,6-C$_6$H$_3$Cl$_2$)
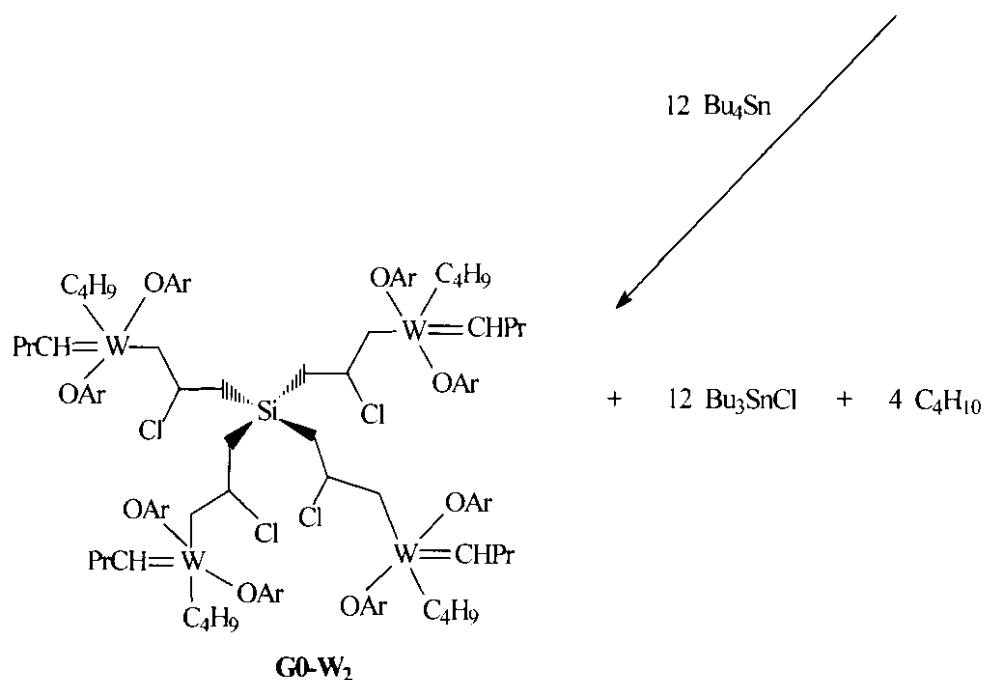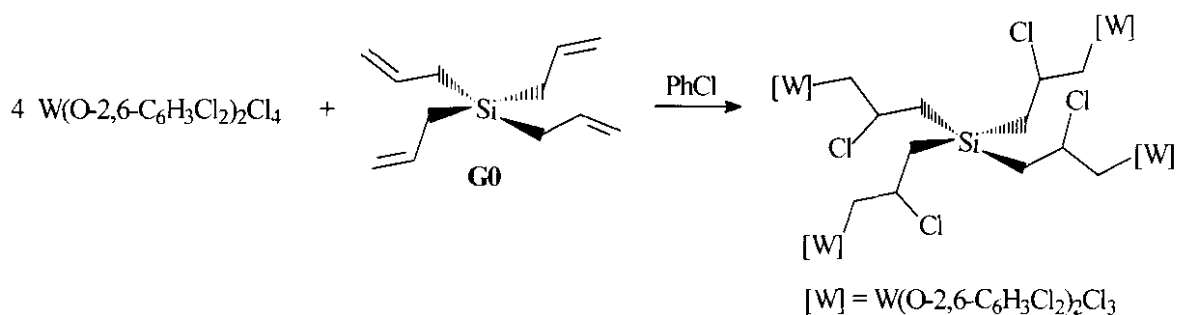
Scheme 3.4 The synthesis of G0-W$_2$ according to new proposed method.

38

3.2.5   Metathesis reactions

In this study only homogeneous metathesis reactions with tungsten and Grubbs first generation catalysts were investigated. The activity and selectivity of the above mentioned catalysts were studied. W-alkylidene dendrimers prepared as discussed above were also tested for metathesis activity.
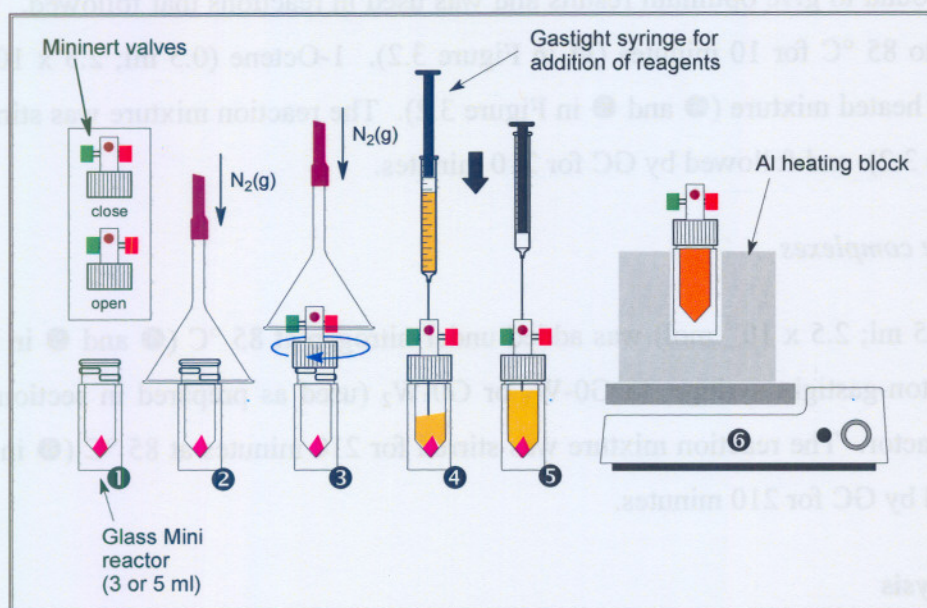
Figure 3.2   An illustration of catalytic reaction procedure followed for all metathesis reactions.

$W(O-2,6-C_6H_3X_2)_2Cl_4$ *complexes*

The tungsten (VI) complexes (0.016 g; 2.5×10^{-5} mol) were transferred under nitrogen into 5 ml mini reactors (❶,❷ and ❸ in Figure 3.2). Chlorobenzene was added as a solvent to the complexes, using a Hamilton-gastight syringe (❹ and ❺ in Figure 3.2). To determine the optimum concentration for the reaction the amount of chlorobenzene was varied from 0.3 to 2.5 ml. An amount of 0.3 ml was found to give optimum results and was used in the reactions that followed. The mixture was heated to 85 °C for 10 minutes (❻ in Figure 3.2), it was found that chlorobenzene takes about 10 minutes to reach the surrounding temperature (Appendix 2). Bu$_4$Sn, the co-catalyst, (0.025 ml; 0.75×10^{-5} mol) was added (❹ and ❺ in Figure 3.2) to the heated mixture. The reaction mixture was heated at 85 °C for 20 minutes (❻ in Figure 3.2). After 20 minutes activation time, 1-octene (0.5 ml; 2.5×10^{-3} mol) was added (❹ and ❺ in Figure 3.2). The reaction mixture was stirred at 85 °C (❻ in Figure 3.2) and followed with GC for 210 minutes.

RuCl₂(PCy₃)₂(=CHPh) complex

The Grubbs complex (0.021 g; 2.5 x 10⁻⁵ mol) was transferred under nitrogen into 5 ml mini reactor (❶,❷ and ❸ in Figure 3.2). Chlorobenzene was added as a solvent to the complex using a Hamilton-gastight syringe (❹ and ❺ in Figure 3.2). To determine the optimum concentration for the reaction the amount of chlorobenzene was varied from 0.3 to 2.5 ml. An amount of 0.3 ml was found to give optimum results and was used in reactions that followed. The mixture was heated to 85 °C for 10 minutes (❻ in Figure 3.2). 1-Octene (0.5 ml; 2.5 x 10⁻³ mol) was added to the heated mixture (❹ and ❺ in Figure 3.2). The reaction mixture was stirred at 85 °C (❻ in Figure 3.2) and followed by GC for 210 minutes.

W-alkylidene complexes

1-Octene (0.5 ml; 2.5 x 10⁻³ mol) was added under nitrogen at 85 °C (❹ and ❺ in Figure 3.2), using Hamilton-gastight syringe, to G0-W₁ or G0-W₂ (used as prepared in section 3.2.4) in a 5 ml mini reactor. The reaction mixture was stirred for 210 minutes at 85 °C (❻ in Figure 3.2) and followed by GC for 210 minutes.

3.3 Analysis

3.3.1 Gas Chromatography (GC)

GC analysis was performed on an HP 6850 gas chromatography equipped with an HP-5 column (30 m x 0.32 mm x 1.00 μm, 100% Methyl siloxane) and flame ionisation detector (FID). The following temperature programme and analytical conditions were used:

Oven programme:

250 °C for 10 min

10 °C min⁻¹

70 °C for 3 min
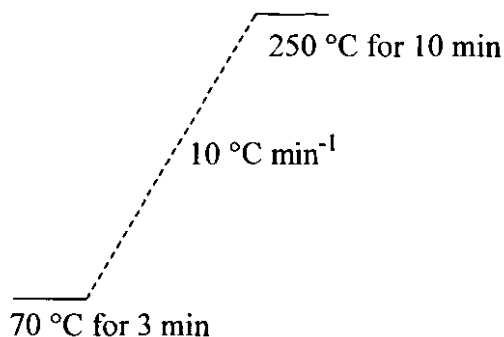
Inlet temperature	250 °C
Detector temperature	250 °C
N₂ carrier gas flow rate	0.8 ml min⁻¹ at room temperature

Fuel gas flow

H_2 flow rate	40.0 ml min^{-1}
Air flow rate	450 ml min^{-1}

Injection volume   0.2 μL

The percentage yield was calculated using Ackman's method:[5]

$$\% \text{ conversion} = 1 - \frac{C_s}{\Sigma C_i}$$

where:

i = $1, 2, ..., n$

C_s =   corrected peak area for the substrate

C_i =   corrected peak area for the component i in the product mixture with n components

Corrected peak areas (C_i) were calculated from molecular response factors:

$$C_i = \frac{R_x}{R_i} \times A_i$$

where:

R_x =   the molecular response factor for the reference component, normally the substrate

R_i =   the molecular response factor for any component i

A_i =   the peak area for the component i

Molecular response factors (MRF) were estimated based on the effective carbon response (ECR) values (Table 3.1).[5]

Table 3.1   Effective carbon response values for carbon based functional groups

Functional Group	ECR
-C-	100
-C-C-	200
-C=C-	178
-COO	0
-CN	0

3.3.2 Gas Chromatography-Mass Spectrometry (GC/MS)

Samples prepared for GC analyses were also injected on a GC-MS. MS analyses were performed on an HP 6890 GC-MS equipped with a PE-001 capillary column (60 m x 0.32 mm x 1.00 μm, Elite Methyl Siloxane) connected to an Autospec Micromass Time-of-Flight mass spectrometer. The NIST database of the OPUS v 3.6 X software was used for characterisation of the products identified during analyses. Temperature programme and analytical conditions used were the same as those used in paragraph 3.3.1.

3.3.3 Two Dimensional Gas Chromatograph Time-of-Flight Mass Spectrometry (GCXGC-TOFMS)

GCXGC-TOFMS analysis were performed on an HP 6890N gas chromatograph with a high pressure electronic pressure control (EPC) module. The GC is equipped with two columns, namely, a VF-5MS column (30 m x 0.32 mm ID, 1 μm film thickness) and a DB column (17.2 m x 0.1 mm ID, 0.1 μm film thickness) connected to LECO Pegasus 4D Time-of-Flight mass spectrometer. The following temperature programmes and analytical conditions were used:

Oven programme (Column 1 (VF-5MS):

250 °C for 2 min

10 °C min^{-1}

70 °C for 3 min

Oven programme (Column 2 (DB)):

255 °C for 2 min

10 °C min^{-1}

75 °C for 3 min
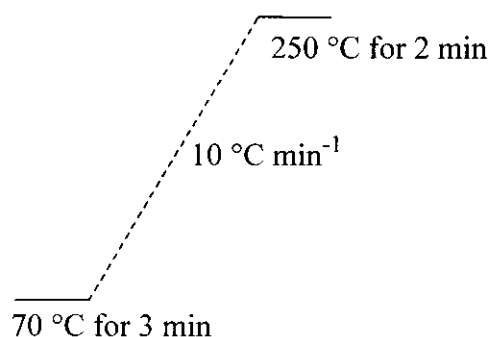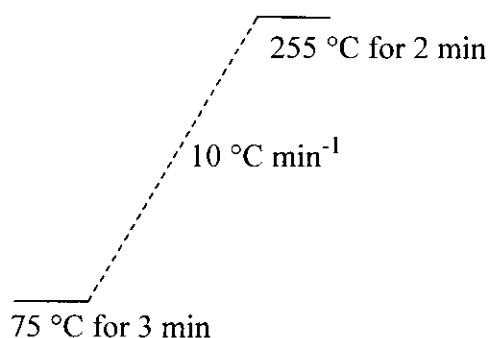
Acquisition rate   150 spectra sec^{-1}

Transfer line temperature:	250 °C
Source temperature	200 °C
Detector voltage	-1750 V
Second dimension Separation Time	3 sec
Inlet temperature	200 °C
Injection volume	0.1 μL
Helium carrier gas flow rate	1.0 mL min^{-1}, constant flow

Once data acquisition was complete, the sample file for the 1-octene reaction products was processed with automated peak finding and spectral deconvolution software, followed by library searching of the NIST (National Institutes of Standards and Technology) library. A second dimension column peak width of 0.15 seconds and a signal-to-noise cut off of 250:1 were used for peak finding. The threshold values were set in order to simplify the results, by reducing the number of located peaks to a level which could be easily assimilated and to locate the major components in the sample.

3.3.4 Infrared spectroscopy (IR)

IR analyses were carried out on a Nicolet Magna-FTIR 550 spectrophotometer, at a resolution of 8 cm^{-1}, a scan range of 4 000 – 500 cm^{-1}, and a total of 200 scans. Samples were prepared as KBr pellets. For liquid samples, a drop of a sample was placed on a clear prepared KBr pellet and analysed. For solid samples about 2 mg of the sample was mixed with approximately 300 mg of dried KBr and pressed into a pellet.

3.3.5 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra (^{1}H, ^{13}C) at 300 and 75 mHz respectively were obtained using a Varian Gemini 300 spectrometer. Approximately 40 mg of the sample was dissolved in 0.7 ml of $CDCl_3$ in an NMR tube.

3.4   References

[1]   Quignard F, Leconte M, Basset JM, Hsu LY, Alexander JJ & Shore SG, *Inorg. Chem.*, 1987, **26**, 4272

[2]   Van Schalkwyk C, Vosloo HCM & Du Plessis JAK, *J. Mol. Catal. A: Chem.*, 1998, **133**, 167

[3]   Beerens H, Verpoot F & Verdonck L, *J. Mol. Catal. A: Chem.*, 2000, **159**, 197

[4]   Marvey BB, *Metathesis of unsaturated esters*, PhD-thesis, PU vir CHO, 2001

[5]   Van der Made AW & Van Leeuwen PWNM, *J. Chem. Soc., Chem. Commun.*, 1400

RESULTS AND DISCUSSIONS

4.1 Introduction

Beerens *et al.*[1] found the activity of W-alkylidene dendrimer catalysts to be higher than that of Ru-alkylidene dendrimer catalysts in the polymerisation of norbornene *via* ring-opening metathesis. In this study the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system was investigated for alkene metathesis. This system was compared to other $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes and Grubbs first generation catalyst. The tungsten complexes with the chlorine substituted aryloxide ligand, were incorporated in the periphery of the carbosilane dendrimer for the synthesis of dendritic catalysts and their metathesis activity and selectivity were studied.

The activity and selectivity of a catalyst in a reaction are influenced by various factors. In this study only the catalyst concentration, the temperature of the reaction mixture and the substituent on the pre-catalyst were investigated.

4.2 Metathesis reactions

As mentioned in Chapter 3, the conversion of 1-octene was followed using GC. Gas chromatographic analyses of the reaction mixtures indicated the formation of a number of products, as shown in Gas chromatogram 4.1.

The products were identified using GC-MS (Appendix 1). The major product being 7-tetradecene which is the desired primary metathesis product. By-products included C_6-C_{13} alkenes formed due to double bond isomerisation of 1-octene followed by metathesis. Dimerisation was also observed by the appearance of C_{16} on the chromatogram. It was more observed with bromine and phenyl substituted aryloxide tungsten complexes than with the chlorine substituted one. The formation of by-products above C_{16} were also observed. This is due to cross metathesis with the dimers. Apart from the primary and secondary metathesis products, Bu_3SnCl and Bu_4Sn were also identified (Gas chromatogram 4.1 and Appendix 1).
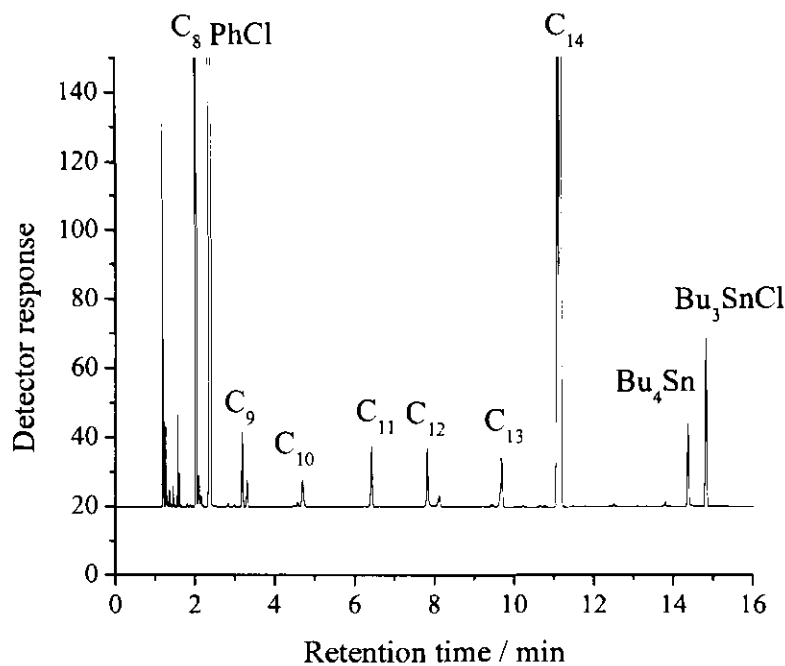
Gas chromatogram 4.1 Typical gas chromatogram of the reaction products of 1-octene in the presence of $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic system (X = Cl, Br, Ph).
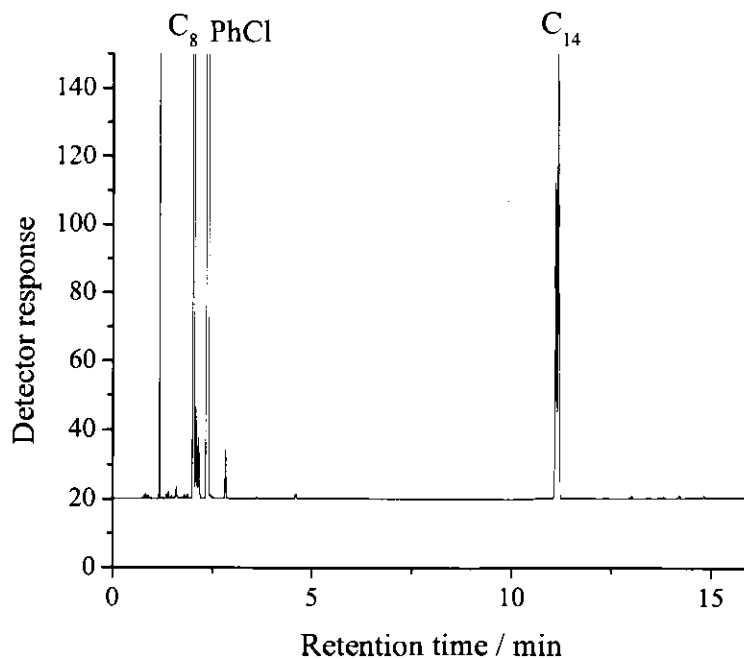
Gas chromatogram 4.2 Typical gas chromatogram of the reaction products of 1-octene in the presence of $RuCl_2(PCy_3)_2(=CHPh)$.

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A typical gas chromatogram of the products formed during the reaction of 1-octene in the presence of Grubbs first generation catalyst is shown above (Gas chromatogram 4.2). Gas chromatographic analyses of the reaction mixtures, as with tungsten complexes, indicated the formation of a number of products. The major product being 7-tetradecene which is the desired metathesis product. The Bu_3SnCl and Bu_4Sn peaks observed around 15 minutes on the gas chromatogram of tungsten systems are not observed in ruthenium systems chromatogram since no co-catalyst was used.

To further identify the products of 1-octene metathesis reaction, GCXGC-TOF MS was used. Unique software features, *viz.* the *Peak Find* and *Spectral Deconvolution* algorithms, were used to locate and identify individual components present in the sample. The Contour Plot and the Surface Plot, showing the Total Ion Chromatograms (TIC) for the analysis are illustrated in Figures 4.1 and 4.2. Peak intensity is colour scaled in the figures from blue to red, with red representing the highest intensity. The x-axis shows the separation on the VF-5 MS column, which is on the basis of boiling point. The y-axis shows the separation on the DB-17 column, which is on the basis of polarity. The positions of compounds in the Contour Plot are indicated by black dots.
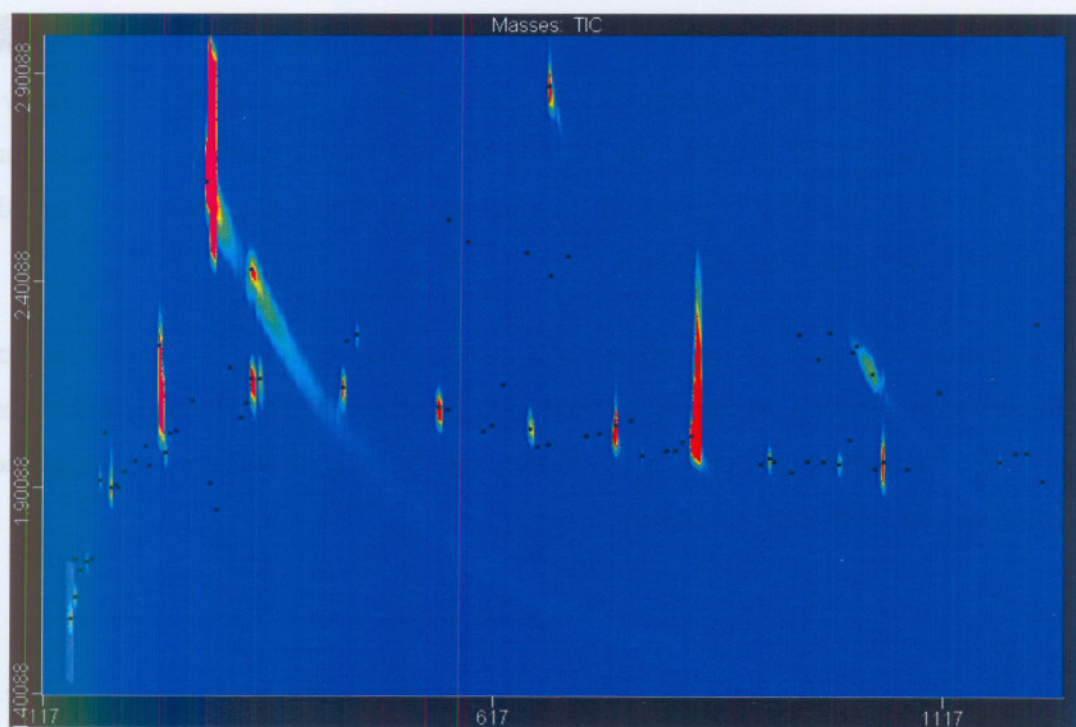
Figure 4.1   Contour Plot, showing the Total Ion Chromatogram (TIC), of the 1-octene reaction products.
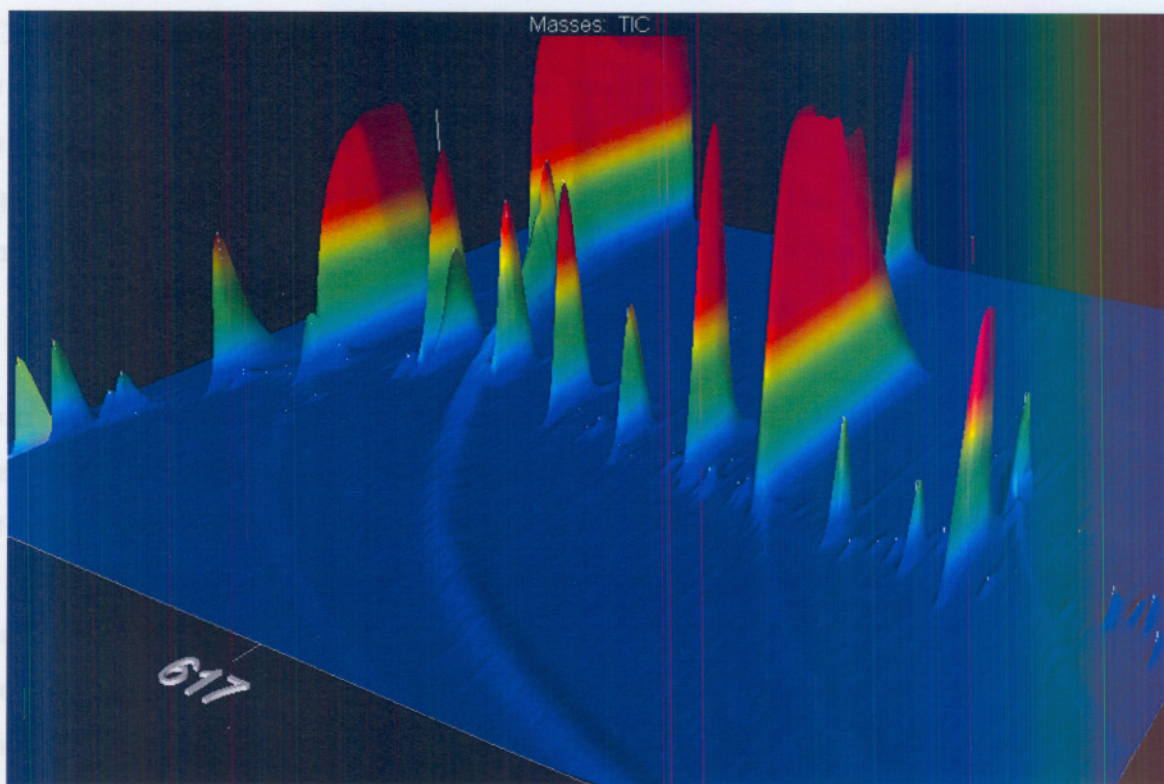
Figure 4.2   Surface Plot, showing the Total Ion Chromatogram (TIC), of the 1-octene reaction products.

The angle from which the surface plot is observed (this is fully rotatable) nicely shows the low level peaks between the major components. The large ridge at the bottom is caused by carry over of the large amount of solvent. In 1D GC-MS this would interfere with the analysis. However, in 2D GCXGC-MS it is removed from the area in which the peaks occur and thus in no way interferes with peak identification.

Table 4.1 contains retention times for each located peak in addition to the first library hit from the library search results (the data processing method used found the 10 best library matches for each peak identified in the sample, but in the case of this sample, which contains numerous components, it is not practical to print more than one match).

Table 4.1   Peak table for the 1-octene metathesis reaction mixture

Peak #	Name	R.T. (s)	Peak #	Name	R.T. (s)
1	2-Butene	146.896 , 1.584	40	Benzeneacetaldehyde, 4-chloro-à-methyl-	653.287 , 2.468
2	Cyclopropane, ethyl-	152.888 , 1.637	41	6-Dodecene, (E)-	656.284 , 2.046
3	Acetone	152.888 , 1.729	42	4-Decene, 2,2-dimethyl-, (E)-	665.273 , 2.000
4	Propane, 2-chloro-2-methyl-	158.881 , 1.703	43	2-Dodecene, (E)-	677.258 , 2.006
5	1-Hexene	164.874 , 1.723	44	Phenol, 2,6-dichloro-	677.258 , 2.871
6	1-Pentene, 4,4-dimethyl-	170.867 , 1.729	45	Benzeneacetaldehyde, 4-chloro-à-methyl-	680.255 , 2.416
7	Butane, 1-chloro-	179.856 , 1.921	46	p-(Chlorophenyl)acetone	698.233 , 2.462
8	Benzene	185.849 , 2.033	47	5-Tridecene, (E)-	719.208 , 2.026
9	1-Heptene	191.842 , 1.901	48	6-Tridecene, (Z)-	734.190 , 2.033
10	2-Hexene, 2-methyl-	197.834 , 1.907	49	3-Tridecene, (E)-	752.168 , 2.053
11	2-Hexene, 5,5-dimethyl-, (Z)-	200.831 , 1.901	50	1-Tridecene	770.147 , 2.066
12	trans-3,4,4-Trimethyl-2-pentene	206.824 , 1.940	51	2-Butyl-1-decene	782.132 , 1.980
13	1-Heptene, 3-methyl-	218.809 , 1.967	52	5-Tetradecene, (E)-	809.100 , 1.993
14	1-Heptene, 4-methyl-	230.795 , 2.000	53	Tridecane, 3-methylene-	818.089 , 1.993
15	Heptane, 3-methyl-	233.791 , 1.954	54	7-Tetradecene, (E)-	827.078 , 2.013
16	1-Octene	245.777 , 2.244	55	6-Tetradecene, (E)-	836.068 , 2.026
17	Octane	251.770 , 1.987	56	Cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	913.974 , 1.960
18	3-Octene, (E)-	257.762 , 2.033	57	1-Pentadecene	922.963 , 1.973
19	2-Octene, (Z)-	263.755 , 2.039	58	7-Hexadecene, (Z)-	928.956 , 1.967
20	1,4-Dimethyl-1-cyclohexene	281.734 , 2.112	59	Stannane, tributylethyl-	946.934 , 1.940
21	Benzene, chloro-	296.716 , 2.640	60	2-(p-Chlorophenyl)-2-methylpropionic acid	955.924 , 2.270
22	Cyclooctane	302.708 , 1.914	61	3-Hexadecene, (Z)-	964.913 , 1.967
23	cis-1-Methyl-2-ethylcyclopentane	308.701 , 1.848	62	Benzene, chloro(2-chloroethyl)-	976.898 , 2.211
24	n-Butyl ether	323.683 , 2.191	63	Pentadecane, 8-methylene-	982.891 , 1.967
25	1-Nonene	335.669 , 2.072	64	Benzeneethanol, 4-chloro-á-methyl-	988.884 , 2.277
26	3-Heptene, 2,6-dimethyl-	341.662 , 2.105	65	1-Hexadecene	1000.87 , 1.960
27	cis-2-Nonene	347.654 , 2.165	66	Cyclotetradecane	1012.86 , 2.020
28	Benzene, chloro-	347.654 , 2.429	67	Benzeneacetaldehyde, 4-chloro-à-methyl-	1015.85 , 2.231
29	3-Nonene	356.644 , 2.165	68	Stannane, tributylchloro-	1018.85 , 2.244
30	trans-3-Decene	449.532 , 2.145	69	Stannane, tributylchloro-	1036.83 , 2.178
31	Octane, 4-chloro-	452.528 , 2.257	70	1,7-Dimethyl-4-(1-methylethyl)cyclodecane	1039.82 , 1.947
32	Octane, 2-chloro-	464.514 , 2.270	71	Stannane, tetrabutyl-	1048.81 , 1.968
33	5-Undecene, (E)-	554.406 , 2.099	72	8-Heptadecene	1075.78 , 1.947
34	4-Decene, 8-methyl-, (E)-	566.392 , 2.092	73	1-Decyn-4-ol	1111.74 , 2.132
35	Benzene, 1-chloro-2-(1-methylethyl)-	566.392 , 2.548	74	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	1177.66 , 1.969
36	Benzene, 1-chloro-4-(1-methylethyl)-	587.366 , 2.495	75	3-Eicosyne	1195.64 , 1.987
37	2-Undecene, 3-methyl-, (E)-	605.345 , 2.039	76	9-Eicosyne	1207.62 , 1.987
38	3-Decene, 2,2-dimethyl-, (E)-	614.334 , 2.053	77	n-Hexadecanoic acid	1219.61 , 2.297
39	2-Chloro-2-methylnonane	626.320 , 2.152	78	tri-n-Butyltin hydride	1225.60 , 1.920

If the analyte name in Table 4.1 is incorrect, the true analyte identification may be further down the library hit list, or the compound may not be present in the mass spectral databases used to search the spectrum. It may occur that the same analyte is a match for more than one peak in Table 4.1. This can occur when two or more analytes in the sample are structurally similar which results in similar mass

spectra. This is a particular problem with this sample, where many hydrocarbons are present with double bonds in differing positions. Mass spectrometry can be an unreliable tool for differentiating isomers of this type, and final structural assignment is best done by using reliable retention time data.

Editing of the Table 4.1 should be done to produce a table in which multiple assignments of the same compound and nonsensical assignments have been eliminated. No editing has been attempted on these results.

4.3   Tungsten (VI) aryloxide complexes

The 2,6-disubstituted aryloxide complexes of W(VI), $W(O-2,6-C_6H_3X_2)_2Cl_4$ (X = Cl, Br, Ph), were prepared and the structure determined using IR. These complexes were then tested for metathesis activity and selectivity.

4.3.1   Structure of tungsten complexes

Figure 4.3 shows the infrared spectra of $W(O-2,6-C_6H_3Cl_2)_2Cl_4$, $W(O-2,6-C_6H_3Br_2)_2Cl_4$, $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ respectively. A comparative analysis of the infrared spectra of $W(O-2,6-C_6H_3X_2)_2Cl_4$ (X = Cl, Br, Ph) is shown in Table 4.2.

Table 4.2   Analysis of infrared spectrum of the $W(O-2,6-C_6H_3X_2)_2Cl_4$-complexes (X = Cl, Br, Ph)

Complex	IR peak / cm^{-1} (Experimental)	IR peak / cm^{-1} (Literature)[2,3]	Functional groups
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$	1560	1590	Ph-O
	1450	1450	Ph
	780	780	2,6-disubstituted
	700	700	C-Cl
$W(O-2,6-C_6H_3Br_2)_2Cl_4$	1560	1550	Ph-O
	1440	1400	Ph
	760	760	2,6-disubstituted
	740	700	C-Br
$W(O-2,6-C_6H_3Ph_2)_2Cl_4$	3010	3050	Aromatic
	1560	1580	Ph-O
	1490	1450	Ph
	750	770	2,6-disubstituted
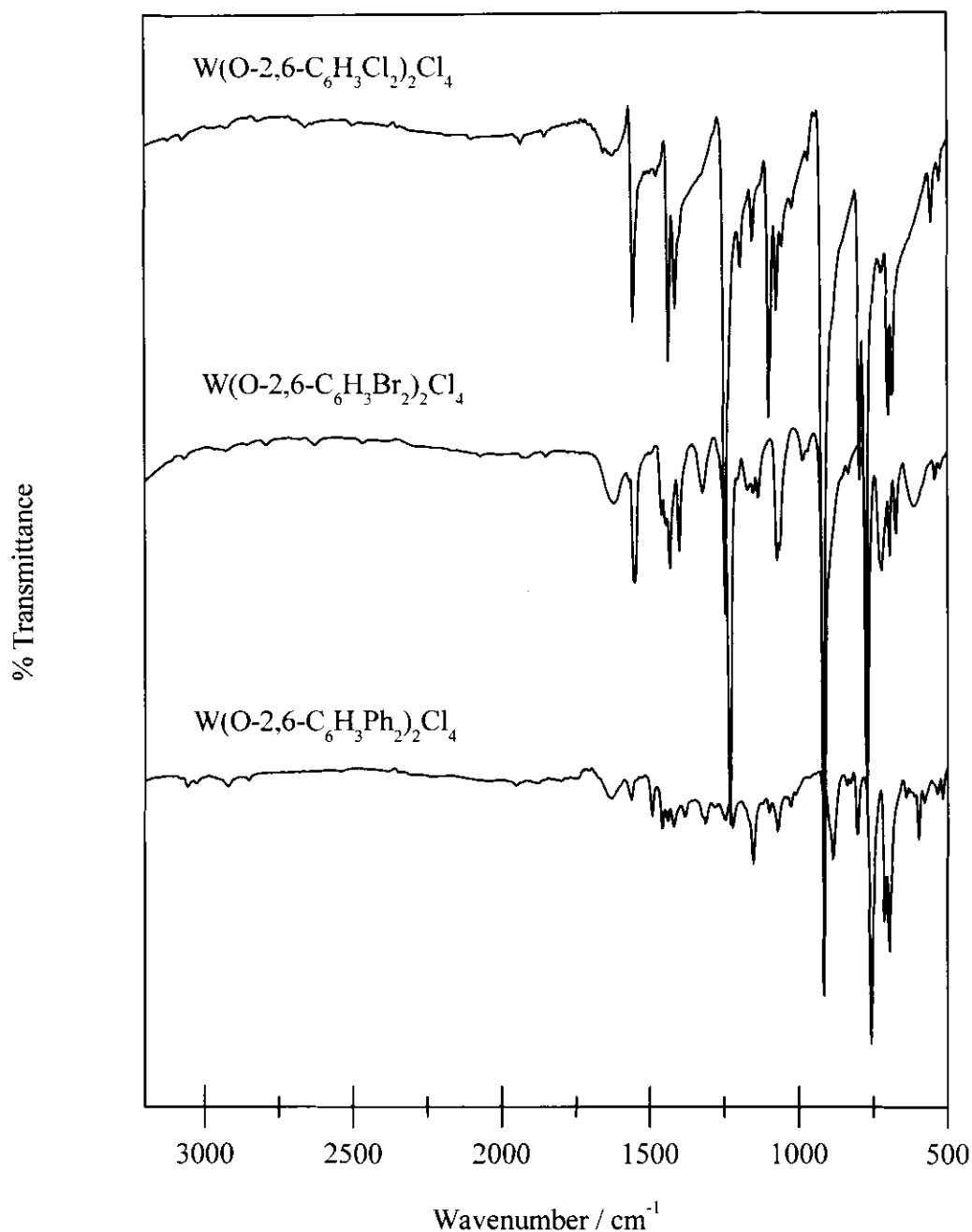
Figure 4.3   FTIR spectra of the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$-complexes (X = Cl, Br, Ph).

IR spectra of the complexes synthesised are in agreement with literature findings.[2]

4.3.2   Metathesis activity and selectivity

Van Schalkwyk *et al.*[3] found that the optimum reaction conditions for the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn (X = Cl, Br, Ph) catalytic systems, include a reaction temperature of 85 °C, Sn/W molar ratio = 3 and an activation time of 20 min.

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Influence of catalyst concentration

The concentration at which $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system has the highest activity was determined by using different volumes of chlorobenzene in the metathesis reaction of 1-octene. The volume of chlorobenzene was reduced gradually from 2.5 to 0.3 ml. Figures 4.4 to 4.7 show the conversion of 1-octene into PMP and SMP.
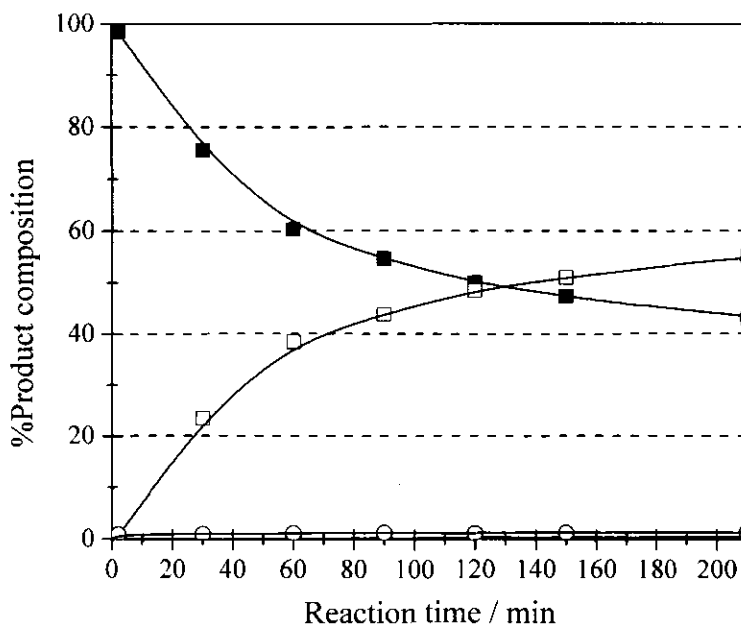
Figure 4.4 Conversion of 1-octene in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl; catalyst concentration = 0.9852×10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

Figure 4.4 shows the percentage yield of PMP and SMP and the consumption of 1-octene over a period of 210 minutes. The primary metathesis reaction reaches 40% in 60 minutes. The % PMP obtained after 210 minutes is about 55%. The catalyst concentration used in this reaction $(0.9852 \times 10^{-8}$ mol dm$^{-3})$ is the lowest used concentration in these reactions.
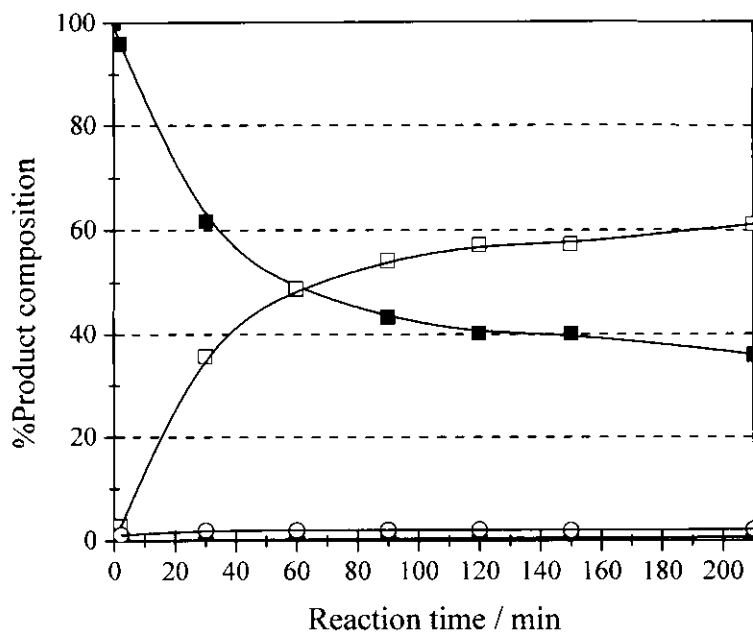
Figure 4.5   Conversion of 1-octene in the presence of the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85 °C;   Sn/W molar ratio = 3;   alkene/W molar ratio = 100; activation time = 20 min;   solvent = PhCl;   catalyst concentration = 1.970 x 10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].
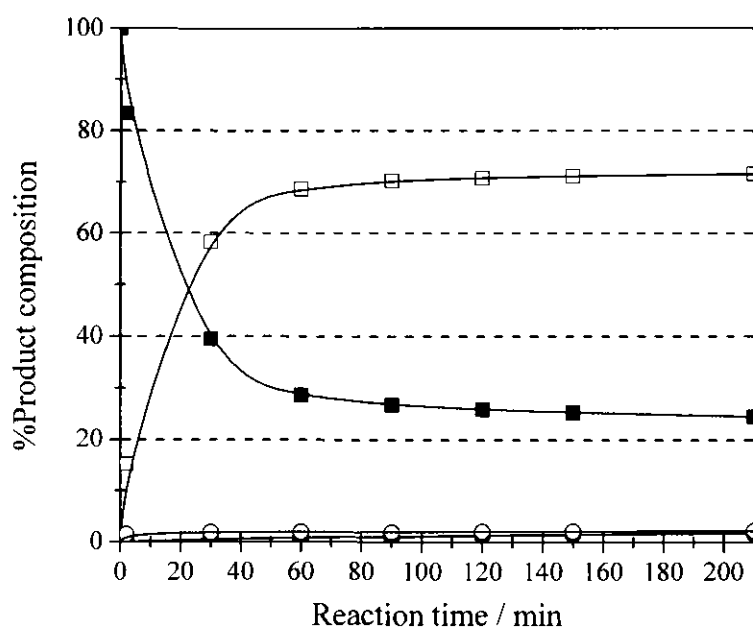
Figure 4.6   Conversion of 1-octene in the presence of the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85 °C;   Sn/W molar ratio = 3;   alkene/W molar ratio = 100; activation time = 20 min;   solvent = PhCl;   catalyst concentration = 4.105 x 10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].
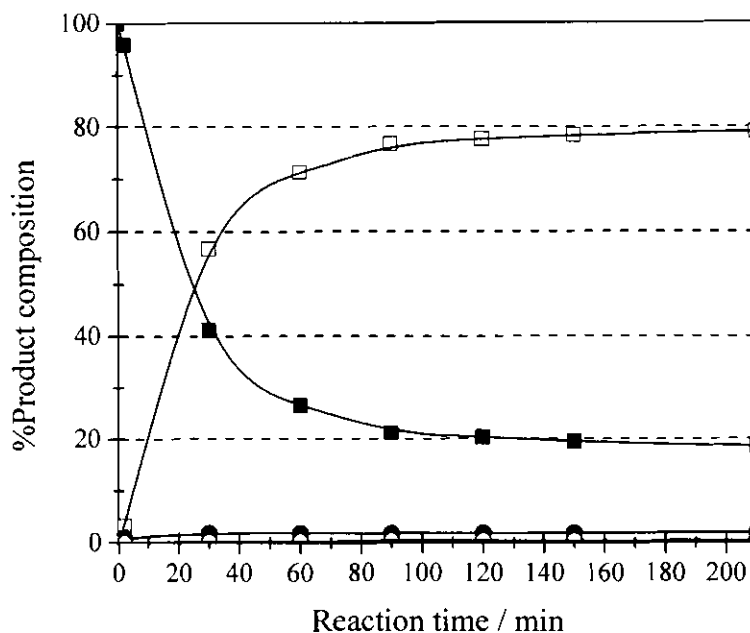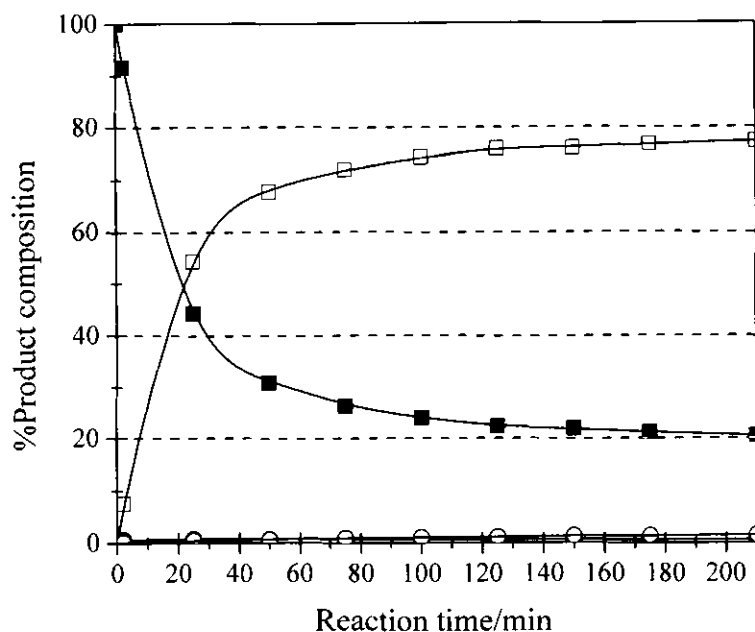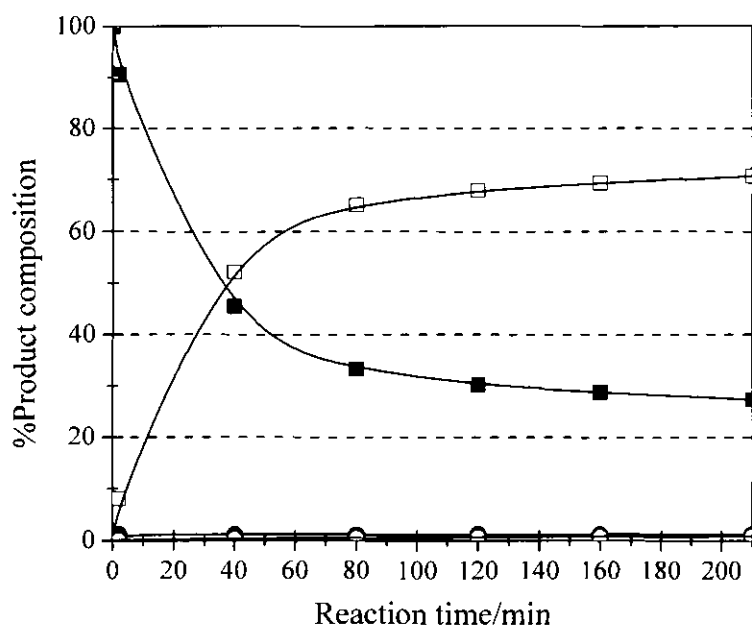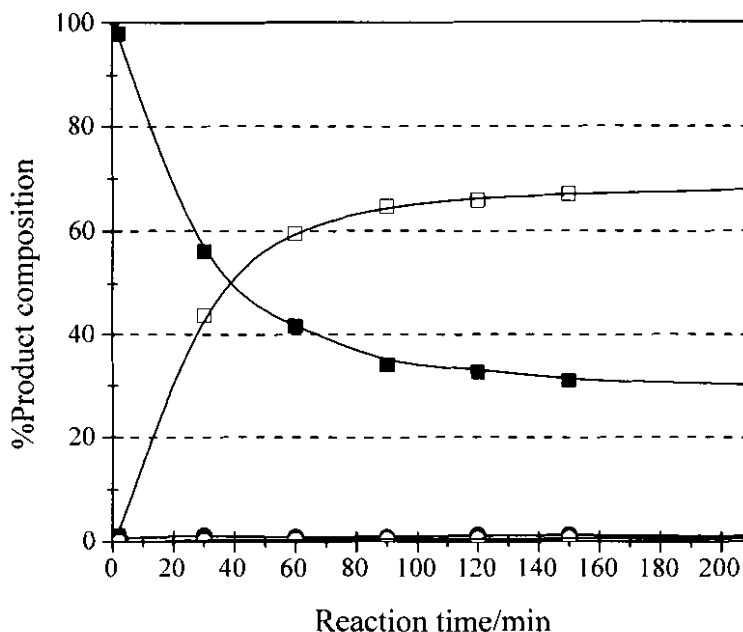
Figure 4.7 Conversion of 1-octene in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$/Bu$_4$Sn catalytic system (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl; catalyst concentration = 8.210×10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

The catalyst concentration used to obtain the results in Figure 4.5 is twice that in Figure 4.4. Over a period of 210 minutes there is a 6% increase in the formation of PMP and a slight increase in the formation of SMP in comparison with the previous catalyst concentration in Figure 4.4. The primary metathesis reaction doubles reaching 40% in 30 minutes. In Figure 4.6, 4.105×10^{-8} mol dm^{-3} of $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ complex, which is four times that used in Figure 4.4, was used. Over a period of 210 minutes the PMP formation increases by 17% in comparison with the initially used concentration. The primary metathesis reaction is three times faster reaching 40% in 20 minutes.

Figure 4.7 shows the results obtained using catalyst concentration that is eight times that used in Figure 4.4. A 24% increase in the formation of PMP and a slight increase in the formation of SMP in comparison with the previous catalyst concentrations were observed. The rate of the primary metathesis reaction remained at 40% in 20 minutes.

Table 4.3   Conversion of 1-octene at different concentrations of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system in 210 minutes (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl)

$[W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4]/(10^{-8}\ mol\ dm^{-3})$	PMP (%)	SMP (%)	Selectivity (%)
0.9852	55.1	0.51	99.1
1.970	61.2	0.66	99.0
4.105	71.6	1.72	97.7
8.210	79.0	1.95	98.1

Table 4.3 summarises the influence of the concentration of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalyst on the activity and selectivity of the catalyst. The conversion of 1-octene to PMP and SMP, which is the catalyst activity, was found to increase with an increase in catalyst concentration. The selectivity slightly decreased with an increase in activity. In their study with Schrock-type carbene complexes Thorn-Csányi et al.[4] also found that catalysts with the highest metathesis activity showed the highest activity towards side reactions. At the catalyst concentration 8.210×10^{-8} mol dm^{-3}, the catalytic activity and PMP yield were the highest. This concentration was used for further investigation

Influence of temperature

$W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ was used in the metathesis reactions of 1-octene at different temperatures to determine the optimum reaction temperature. This was done by comparing the activity and selectivity of the catalyst at different temperatures.

Figure 4.8 shows the % PMP at different temperatures over 210 minutes. The conversion of 1-octene into 7-tetradecene (PMP) increases with an increase in temperature.

%PMP

Reaction time/min
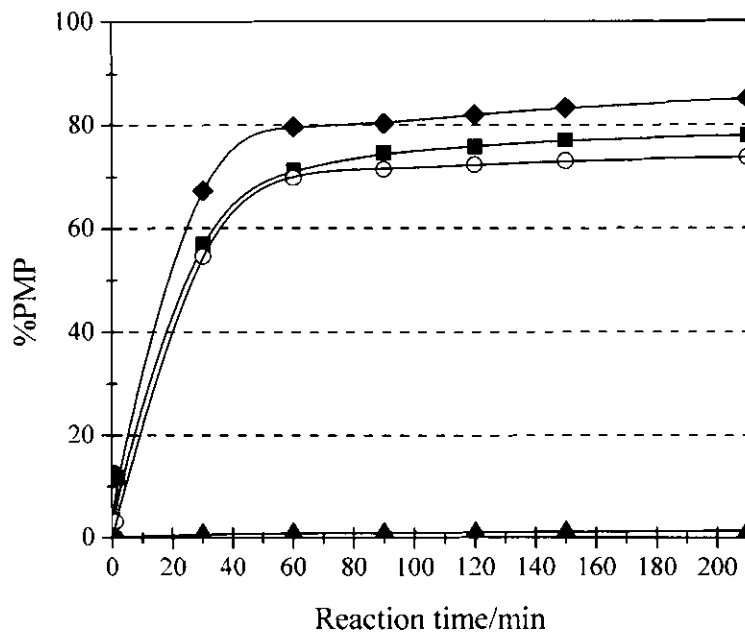
Figure 4.8 The metathesis activity of W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system with 1-octene at different temperatures (Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl; catalyst concentration = 8.210 x 10^{-8} mol dm^{-3}) [♦ 120 °C; ■ 100 °C; ○ 85 °C; ▲ 45 °C; ● 25 °C].

%SMP
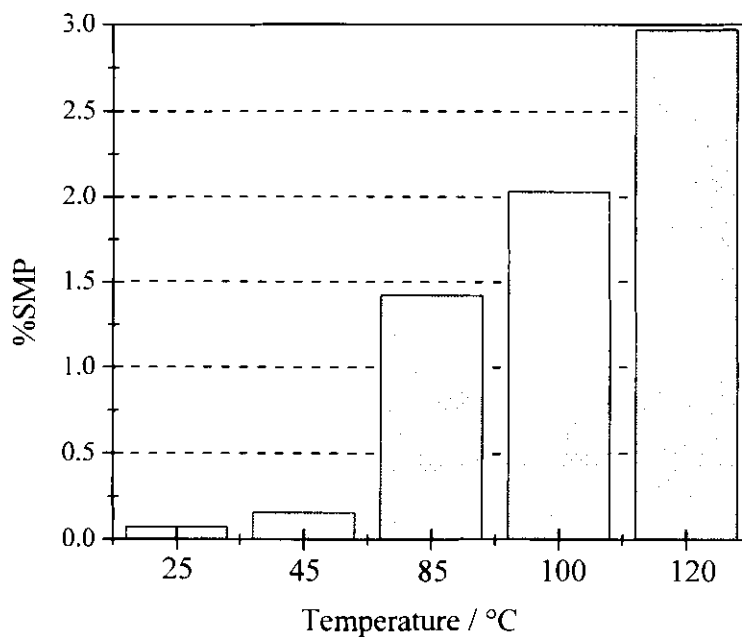
Temperature / °C

Figure 4.9 Percentage secondary metathesis product (SMP) of the metathesis reaction of 1-octene with W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system at different temperatures after 210 minutes.

Figure 4.9 shows that the percentage secondary metathesis product (SMP) increases with an increase in temperature in 210 minutes.
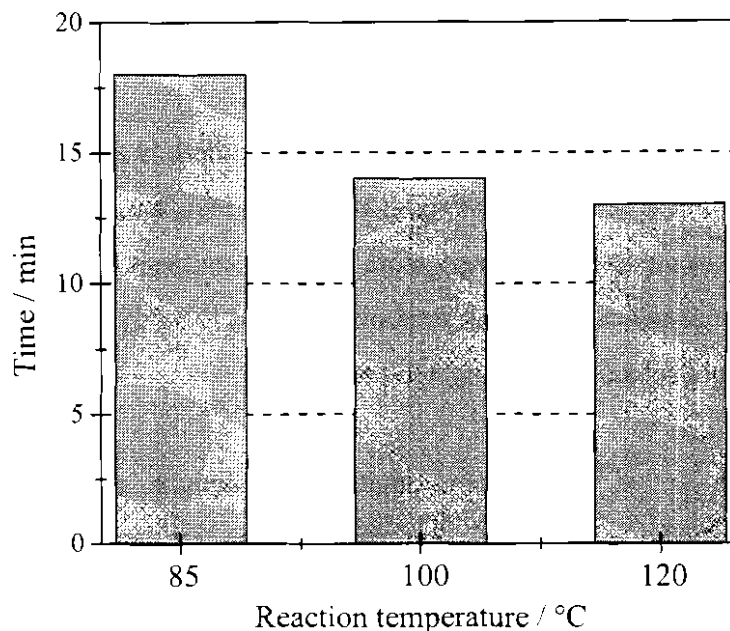
Figure 4.10   Time taken to reach 40% PMP at different reaction temperatures.

The time taken by a metathesis reaction to reach 40% PMP at different reaction temperatures is shown in Figure 4.10. At low temperatures (25 and 45 °C) 40% PMP was never reached. The time taken by a metathesis reaction to reach 40% PMP, is found to decreases with an increase in temperature.

Table 4.4   Conversion of 1-octene at different temperatures with $W(O-2,6-C_6H_3Cl_2)_2Cl_4/$ Bu$_4$Sn catalytic system in 210 minutes (Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl)

Temperature (°C)	PMP (%)	SMP (%)	Selectivity (%)
25	0.00	0.08	0.00
45	1.40	0.16	89.9
85	73.8	1.42	98.1
100	77.9	2.03	97.5
120	85.1	2.97	96.6

The conversion of 1-octene to PMPs and SMPs increases with an increase in temperature. This means that as the temperature of the reaction increases, the activity of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalyst also increases, while the selectivity decreases with an increase in temperature. At lower temperatures (< 85 °C) the metathesis activity is very low.

As mentioned earlier with an increase in metathesis activity there is also an increase in activity towards side reactions. Since at 85 °C the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalyst has the highest selectivity, it was taken as an optimum temperature for the metathesis of 1-octene with the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ complex. This temperature was used to study the influence of aryloxide ligands on the activity and selectivity of tungsten complexes.

Like Van Schalkwyk *et al.*[3] we found that the optimum reaction temperature for $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ to be 85 °C, but the optimum activation time was found to be reached in 10 min see (Appendix 2). However, the activation time of 20 minutes was used to allow the reaction to stabilise.

Influence of the substituent on the aryloxide ligand

The electronic effect of the substituents on the aryloxide ligand of tungsten complexes was investigated by looking at the conversion of 1-octene to 7-tetradecene. The kinetic profiles of the reactions of 1-octene in the presence of $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ complexes, where X = Cl, Br, Ph are illustrated in Figures 4.11-13.

Figures 4.11 - 4.13, show consumption of 1-octene and its conversion to PMP and SMP over 210 minutes. In the presence of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system (Figure 4.11) the conversion is about 77% PMP and 2% SMP in 210 minutes. The primary metathesis reaction is initially very rapid reaching 40% PMP in 17 minutes. In the presence of $W(O-2,6-C_6H_3Br_2)_2Cl_4/Bu_4Sn$ catalytic system (Figure 4.12) the conversion of 1-octene into PMP is about 71% and SMP is about 1% in 210 minutes, which is 6% less PMP than that of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system. The primary metathesis reaction is initially still rapid, but less than that of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalyst, reaching 40% PMP in 28 minutes.

Figure 4.11   Conversion of 1-octene in the presence of the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

Figure 4.12   Conversion of 1-octene in the presence of the W(O-2,6-C$_6$H$_3$Br$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

Figure 4.13   Conversion of 1-octene in the presence of the W(O-2,6-C$_6$H$_3$Ph$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

In the presence of W(O-2,6-C$_6$H$_3$Ph$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (Figure 4.13) the conversion is about 68% PMP and 1% SMP in 210 minutes, which is 9% less PMP than that of the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system. The primary metathesis reaction is the same as that of W(O-2,6-C$_6$H$_3$Br$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system, reaching 40% PMP in about 28 minutes. These results indicate that an increase in the electron-withdrawing properties of substituents on the oxyaryl ligand causes an increase in the metathesis activity. The chlorine substituted aryloxide ligand, having the most electronegative substituent, shows higher activity than the bromine and phenyl substituted ligands.

Results obtained in the presence of the W(O-2,6-C$_6$H$_3$X$_2$)$_2$Cl$_4$/Bu$_4$Sn (X = Cl, Br, Ph) catalytic systems are summarised in Table 4.5. The catalytic system containing phenyl substituted ligand, has a higher selectivity than the ones containing the bromine and chlorine substituted ligands.

Table 4.5 Influence of W(O-2,6-C$_6$H$_3$X$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic systems (X = Cl, Br, Ph; temperature = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20; solvent = PhCl) on the selectivity and activity in the metathesis reactions of 1-octene after 210 minute

Catalyst	PMP (%)	SMP (%)	Selectivity (%)
W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$	77.3	1.52	98.1
W(O-2,6-C$_6$H$_3$Br$_2$)$_2$Cl$_4$	70.7	0.83	98.8
W(O-2,6-C$_6$H$_3$Ph$_2$)$_2$Cl$_4$	68.0	0.67	99.0

4.4 Grubbs catalyst

For comparison purposes the well-defined Grubbs first generation catalyst [RuCl$_2$(PCy$_3$)$_2$(=CHPh)] was used in the metathesis of 1-octene in different concentrations. This catalytic system, (RuCl$_2$(PCy$_3$)$_2$(=CHPh)), like tungsten, is well known for the metathesis of terminal alkenes and is stable in air. The reaction conditions used were the same as for the tungsten catalytic systems except that no co-catalyst was added.

4.4.1 Influence of catalyst concentration

The kinetic profiles of reactions of 1-octene in the presence of different concentrations of RuCl$_2$(PCy$_3$)$_2$(=CHPh) complex are shown in Figure 4.14-17. The concentration was varied as with W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$ catalytic system.

Figure 4.14 illustrates the percentage yield of PMP and the consumption of 1-octene in 210 minutes. The %PMP formed was about 32%. The primary metathesis reaction was very slow and did not reach 40% PMP.
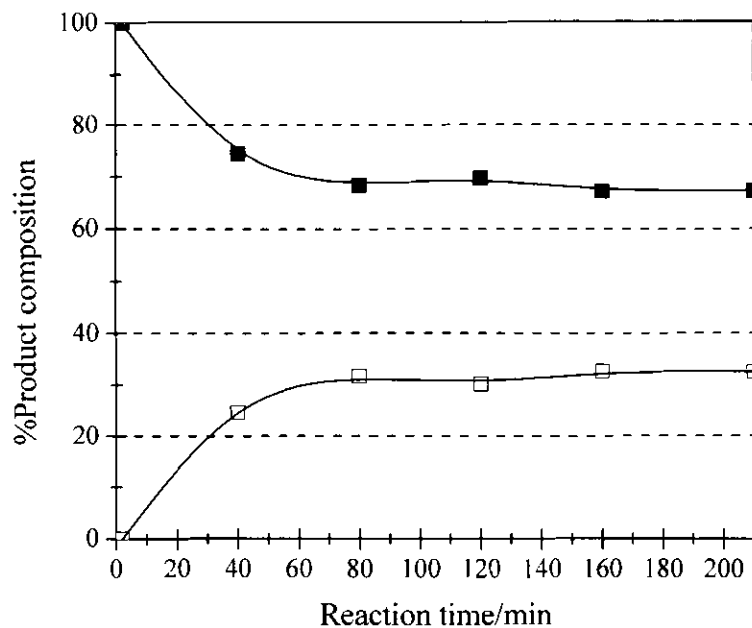
Figure 4.14 Conversion of 1-octene in the presence of the $RuCl_2(PCy_3)_2(=CHPh)$ catalytic system (temperature = 85 °C; alkene/Ru molar ratio = 100; solvent = PhCl; catalyst concentration = 1.021 x 10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP].
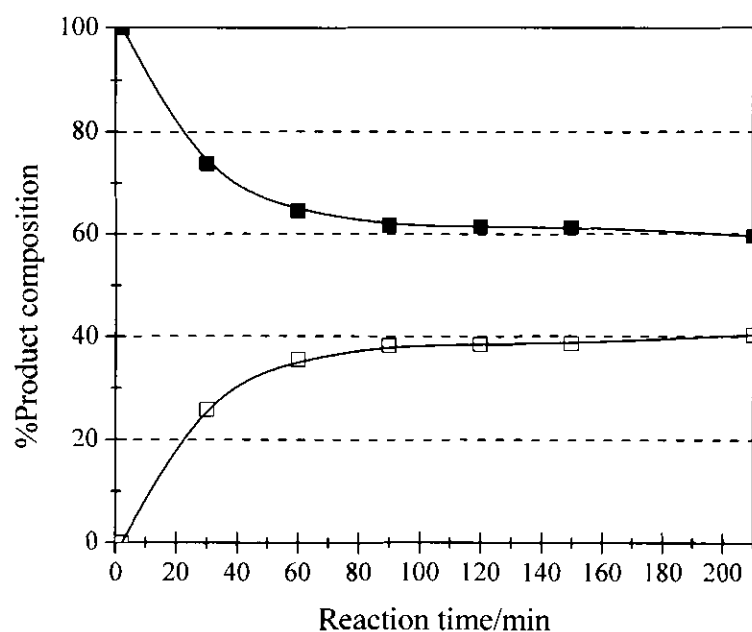
Figure 4.15 Conversion of 1-octene in the presence of the $RuCl_2(PCy_3)_2(=CHPh)$ catalytic system (temperature = 85 °C; alkene/Ru molar ratio = 100; solvent = PhCl; catalyst concentration = 2.041 x 10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP].
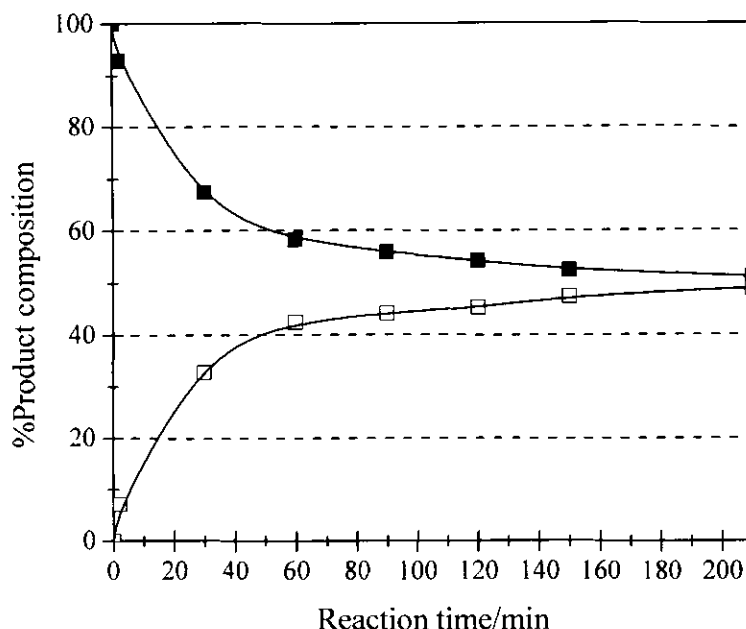
Figure 4.16 Conversion of 1-octene in the presence of the $RuCl_2(PCy_3)_2(=CHPh)$ catalytic system (temperature = 85 °C; alkene/Ru molar ratio = 100; solvent = PhCl; catalyst concentration = 4.253×10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP].

The catalyst concentration in this reaction, Figure 4.15, was twice that of the reaction depicted in Figure 4.14. The PMP yield increased by 8% from that in Figure 4.14. The primary metathesis reaction rate increased slightly, reaching 40% in 210 minutes.

A catalyst concentration four times that used in the reaction depicted in Figure 4.14 was used for the reaction in Figure 4.16. The PMP yield increased by 17% compared to the PMP yield at the lowest used catalyst concentration (Figure 4.14). The rate of the primary metathesis reaction increased rapidly, reaching 40% in 52 minutes.

The catalyst concentration used in the reaction illustrated in Figure 4.17 was eight times the concentration used in the reaction depicted in Figure 4.14. The PMP yield increased by 30% from the lowest used concentration in Figure 4.14. The primary metathesis reaction was very rapid compared to the three reactions above, reaching 40% in 35 minutes.
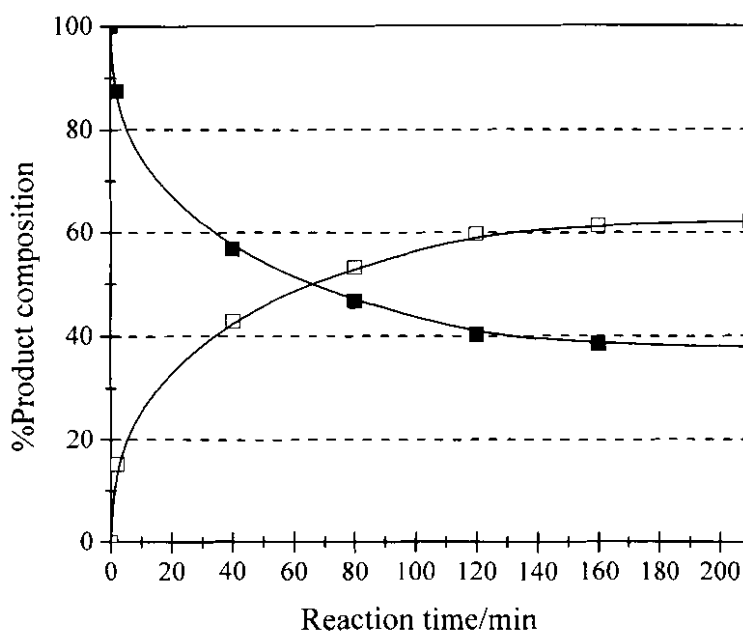
Figure 4.17 Conversion of 1-octene in the presence of the RuCl$_2$(PCy$_3$)$_2$(=CHPh) catalytic system (temperature = 85 °C; alkene/Ru molar ratio = 100; solvent = PhCl; catalyst concentration = 8.506 x 10^{-8} mol dm^{-3}) [■ 1-octene; □ PMP].

Table 4.6 shows that as the concentration of Grubbs first generation catalyst (Grubbs1) increases, the %PMP formed increases, *i.e.* the catalytic activity increases as the catalyst concentration increases. The fact that no significant amount of SMP formed, is an indication that Grubbs1 has a very high selectivity.

Table 4.6 Conversion of 1-octene with different concentrations of RuCl$_2$(PCy$_3$)$_2$(=CHPh) catalytic system in 210 minutes (temperature = 85 °C; alkene/Ru molar ratio = 100; activation time = 20; solvent = PhCl)

[RuCl$_2$(PCy$_3$)$_2$(=CHPh)]/(10^{-8} mol dm^{-3})	1-Octene (%)	PMP (%)
1.021	67.4	32.6
2.041	59.6	40.4
4.253	51.1	48.9
8.506	37.9	62.1

The catalyst concentration 8.506 x 10^{-8} mol dm^{-3} was considered optimum. This optimum concentration (8.506 x 10^{-8} mol dm^{-3}) was used to study the influence of temperature on the activity of Grubbs1.

4.4.2 Influence of temperature

$RuCl_2(PCy_3)_2(=CHPh)$ was used in the metathesis reactions of 1-octene at different temperatures to determine the optimum reaction temperature. This was done by comparing the activity and selectivity of the catalyst at different temperatures.
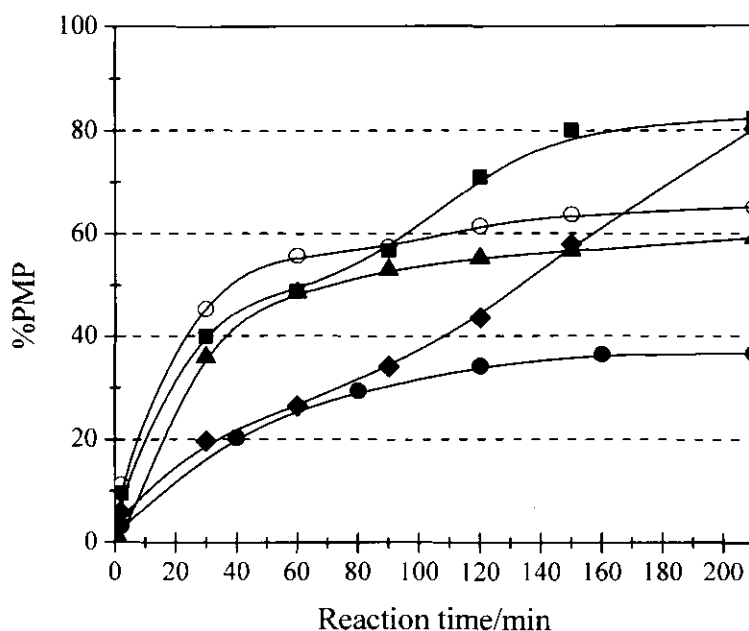
Figure 4.18 The conversion of 1-octene in the presence of $RuCl_2(PCy_3)_2(=CHPh)$ catalytic system at different temperatures (alkene/Ru molar ratio = 100; solvent = PhCl; catalyst concentration = 8.506 x 10^{-8} mol dm^{-3}) [♦ 120 °C; ■ 100 °C; o 85 °C; ▲ 45 °C; ● 25 °C].

Figure 4.18 illustrates the %PMP obtained with $RuCl_2(PCy_3)_2(=CHPh)$ catalytic system at different reaction temperatures. The activity of the catalyst increased with an increase in temperature to an optimum of 85 °C. Above 85 °C there was a delay in the formation of the PMP, due to the fact that the 1-octene started to turn into vapour and leaked from the reactor because of the pressure that built up.

Figure 4.19 shows the time taken by a metathesis reaction to reach 40% PMP at different reaction temperatures. At 25 °C the metathesis reaction had not reached 40% PMP in 210 minutes. The shortest time taken to reach 40% PMP was at 85 °C. Above 85 °C the time

taken to reach 40% started to increase. However the results above 85 °C is not reliable due to leaking reactor.
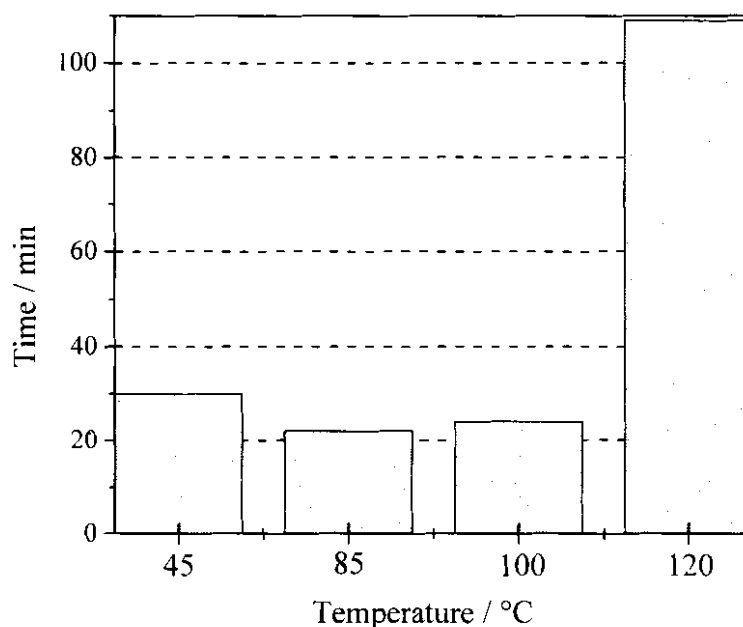
Figure 4.19   Time taken to reach 40% PMP at different reaction temperatures in the metathesis of 1-octene with RuCl$_2$(PCy$_3$)$_2$(=CHPh) catalytic system (alkene/Ru molar ratio = 100; solvent = PhCl).

Table 4.7   Conversion of 1-octene at different temperatures with RuCl$_2$(PCy$_3$)$_2$(=CHPh) catalytic system in 210 minutes (alkene/Ru molar ratio = 100; solvent = PhCl)

Temperature (°C)	PMP (%)
25	36.6
45	59.1
85	65.1

The conversion of 1-octene into PMP increased with an increase in temperature (Table 4.7). High %PMPs were observed after 210 minutes. The consumption of 1-octene seemed to have increased, because less 1-octene was found after 210 minutes. SMP and selectivity of Grubbs 1 are not shown in Table 4.7 because SMP were insignificant. Due to the leaking of 1-octene the primary metathesis reaction rate above 85 °C could not be determined.

W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$/Bu$_4$Sn system offered a great specificity (selectivity > 98%) and high catalytic activity (> 70%). RuCl$_2$(PCy$_3$)$_2$(=CHPh) catalytic system also showed high selectivity but its activity, although high above 60%, was lower than that of W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$/Bu$_4$Sn complex. Tungsten aryloxide complex [W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$/Bu$_4$Sn] was studied further with carbosilane dendrimers as ligands.

4.5 W-alkylidene dendrimers (G0-W)

Two methods were employed for the incorporation of W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$/Bu$_4$Sn complex on the periphery of the tetraallylsilane dendrimer, namely, Beerens et al.[1] method and a new proposed method. The W-alkylidene dendrimers were synthesised, characterised and tested for activity of the metathesis of 1-octene.

4.5.1 Structure of Tetraallysilane (G0)

FTIR and GC-MS were used to determine the structure of the synthesised tetraallysilane, to determine whether the synthesis had been successful. The infrared spectra of the commercial and synthesised tetraallylsilane were found to be the same as shown in Figure 4.20. At 3090 cm^{-1} a =C-H stretching vibration for terminal methylene group in vinyl (-C=CH$_2$) alkenes was observed. The absorption bands of -CH asymmetric and symmetric vibration could be seen at 3000 and 2920 cm^{-1} respectively[5], and the CH$_2$ asymmetrical and symmetrical vibrations at 2990 and 2890 cm^{-1} respectively. At 1630 cm^{-1} C=C stretching vibration for simple vinyl alkenes could also be observed. The C-H out-of-plane bending or wagging vibrations of hydrogens attached to unsaturated carbons could be observed at 940 and 900 cm^{-1}. In-plane bending of the unsaturated C-H bond absorption occurred at 1440 and 1390 cm^{-1}, symmetric and asymmetric vibrations respectively.[5]

The GC analyses showed that the synthesised tetraallylsilane was not as pure as commercial tetraallylsilane, see Gas chromatograms 4.3 and 4.4.
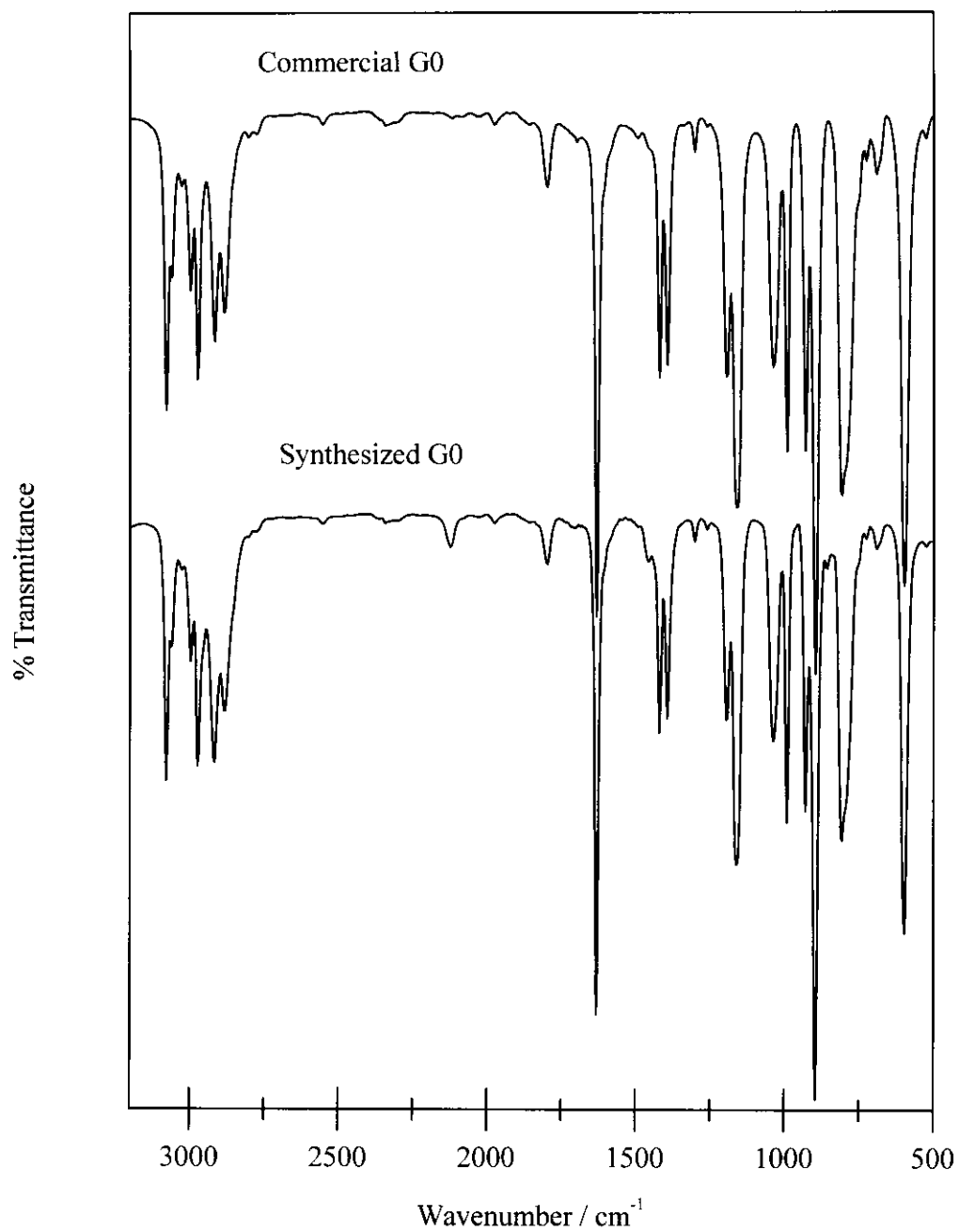
Figure 4.20 FTIR spectra of commercial tetraallylsilane and synthesised tetraallylsilane.
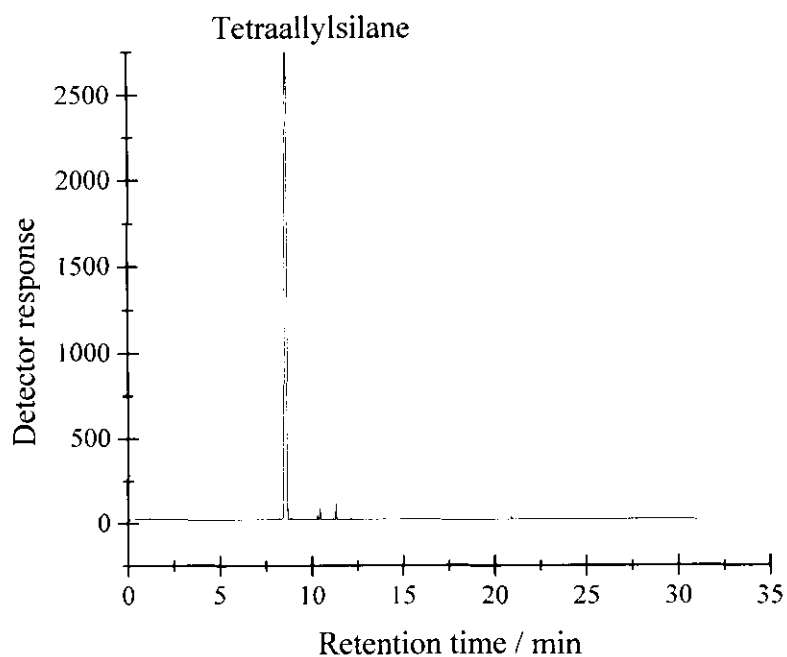
Gas chromatogram 4.3   Gas chromatogram of commercial tetraallylsilane (G0).
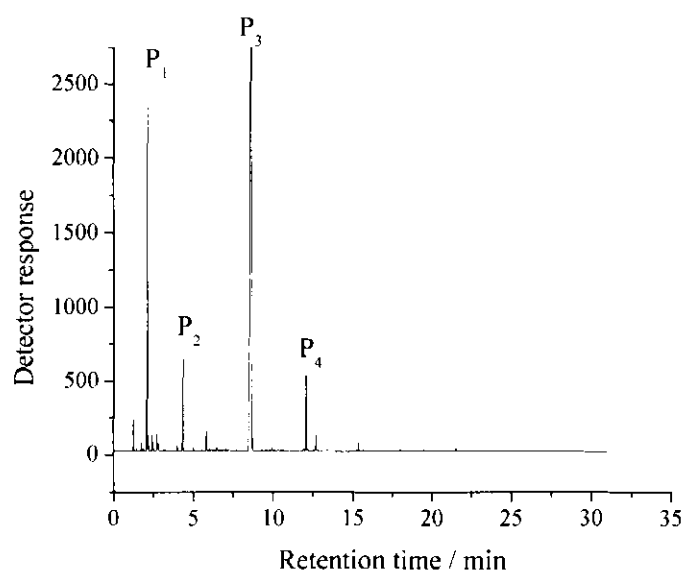
Gas Chromatogram 4.4   Gas chromatogram of synthesised tetraallylsilane (G0) [P$_1$ = triallylsilane; P$_2$ = 4-methyl-1,3-pentadiene; P$_3$ = tetraallylsilane; P$_4$ = 7-isopropenyl-4,5-dimethyloctahydroinden-4-yl)methanol].

The mass spectra of both commercial and synthesised tetraallylsilane, was found to be the same and can be seen in Figures 4.21.

Abundance

(9.642 min): commercial

m/z-->

Abundance

(9.642 min): synthesized

m/z-->
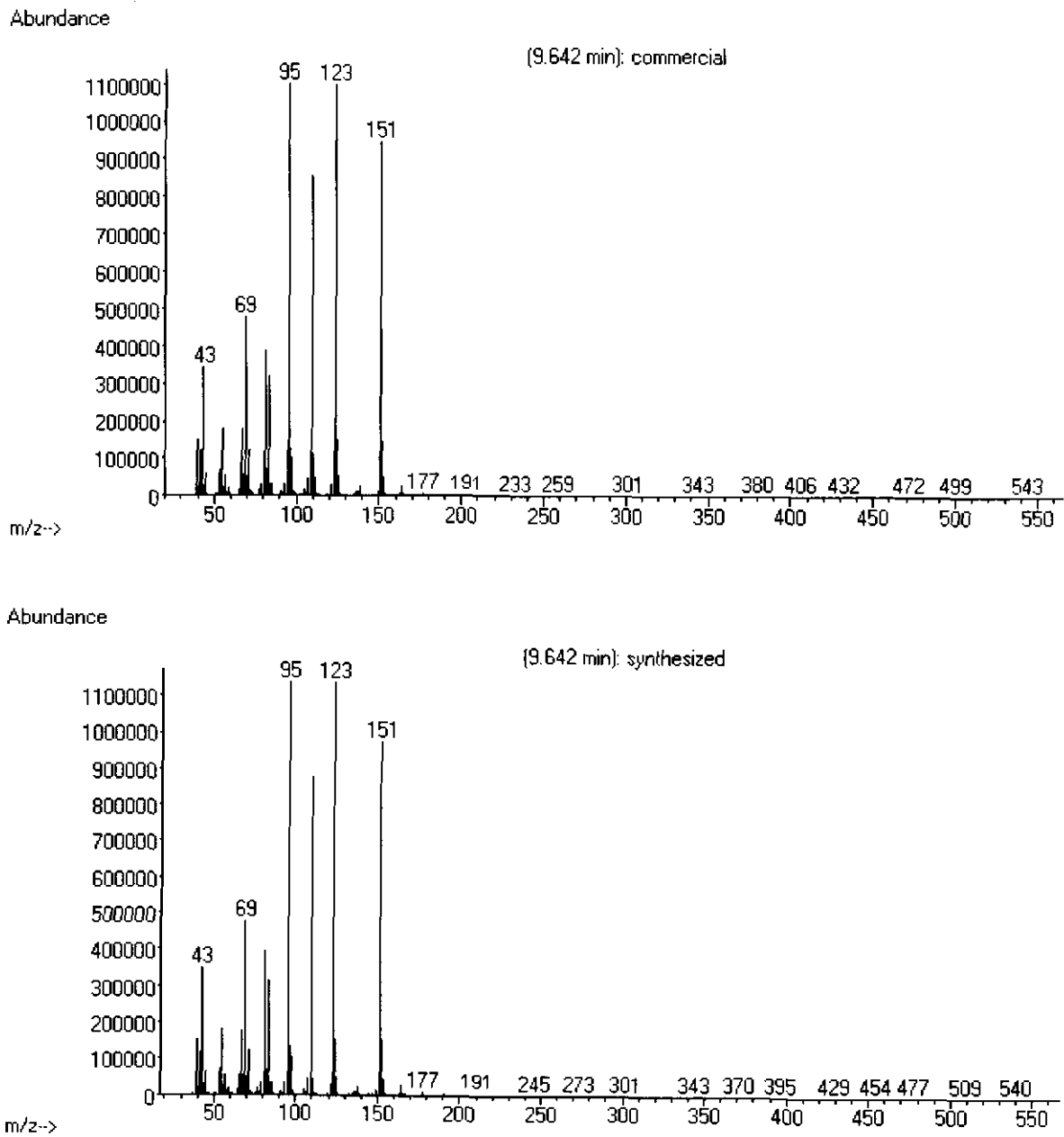
Figure 4.21   MS spectra of tetraallylsilane.
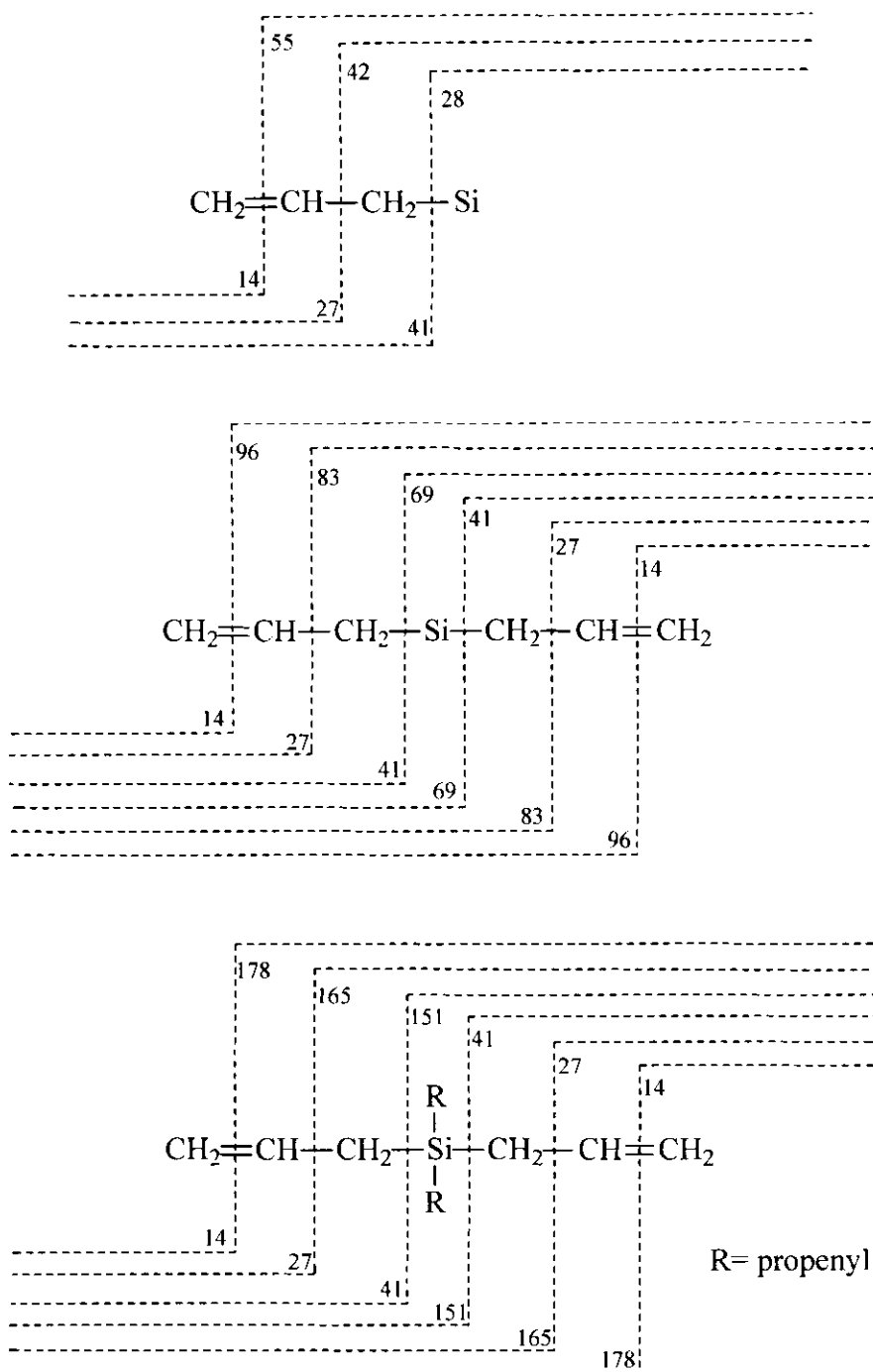
Figure 4.22   Analysis of MS spectra of tetraallylsilane.

The molecular masses of synthesised and commercial tetraallylsilane are shown to be 191. This molecular mass is in agreement with the molecular mass of tetraallylsilane (Figure 4.22).

Since it was more expensive to synthesise and purify G0 than to buy it, commercial tetraallysilane was used for further synthesis.

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4.5.2 Structure of W-alkylidene dendrimers (G0-W₁ and G0-W₂)

FTIR and NMR were used to analyse the G0-W structures. IR spectra of both G0-W$_1$ and G0-W$_2$ are shown in Figure 4.23. The terminal alkene stretching absorption peak for G0-W was observed, but at a lower frequency 3080 cm^{-1} than for G0 (Figure 4.20) due to substitution on the C=C. A new peak, which was not present in the tetraallylsilane spectrum, was observed at 3010 cm^{-1}. This is due to aromatic Ar-H (=C-H) stretching vibration. The C-H stretching of the CH$_2$ and -C-H were now observed at lower frequency. The C=C stretching vibration, which was observed at 1630 cm^{-1} was replaced by Ar-H stretching with a shoulder on the side at the same frequency. The C-H out-of-plane bending vibration was observed as a single band at 900 cm^{-1}, in the tetraallylsilane spectrum. Two strong bands were observed instead at 940 and 900 cm^{-1}. The single band signify a disubstituted alkene.[5]

Table 4.8   Analysis of infrared spectrum of G0 and G0-W

Compound	IR peak / cm^{-1}	Functional groups
Tetraallylsilane (commercial & synthesized)	3090	=C-H
(G0)	3000 & 2920	$\geqslant$C−H
	2990 & 2890	CH$_2$
	1630	C=C
	1390 & 1440	C-H unsaturated
	940 & 900	C-H
	810	Si-C
G0-W$_1$ and G0-W$_2$	3080	=C-H
	3010	=C-H aromatic
	1630	Ar-H
	900	C-H

The disappearance of the allylic double bond at 1630 cm^{-1} and the formation of the new signals at 3080 and 3010 cm^{-1} (Table 4.8) for the W-alkylidene bond were a clear indication of the link between the dendrimer and the W-complexes. This is in line with findings by Beerens et al.[1]. The small peak observed around 1630 cm^{-1} in the W-alkylidene complexes is due to the aromatic H of the aryloxide ligand, which was not present in the tetraallysilane spectum. This peak is not as sharp and intense as the C=C peak observed with tetraallyllsilane.
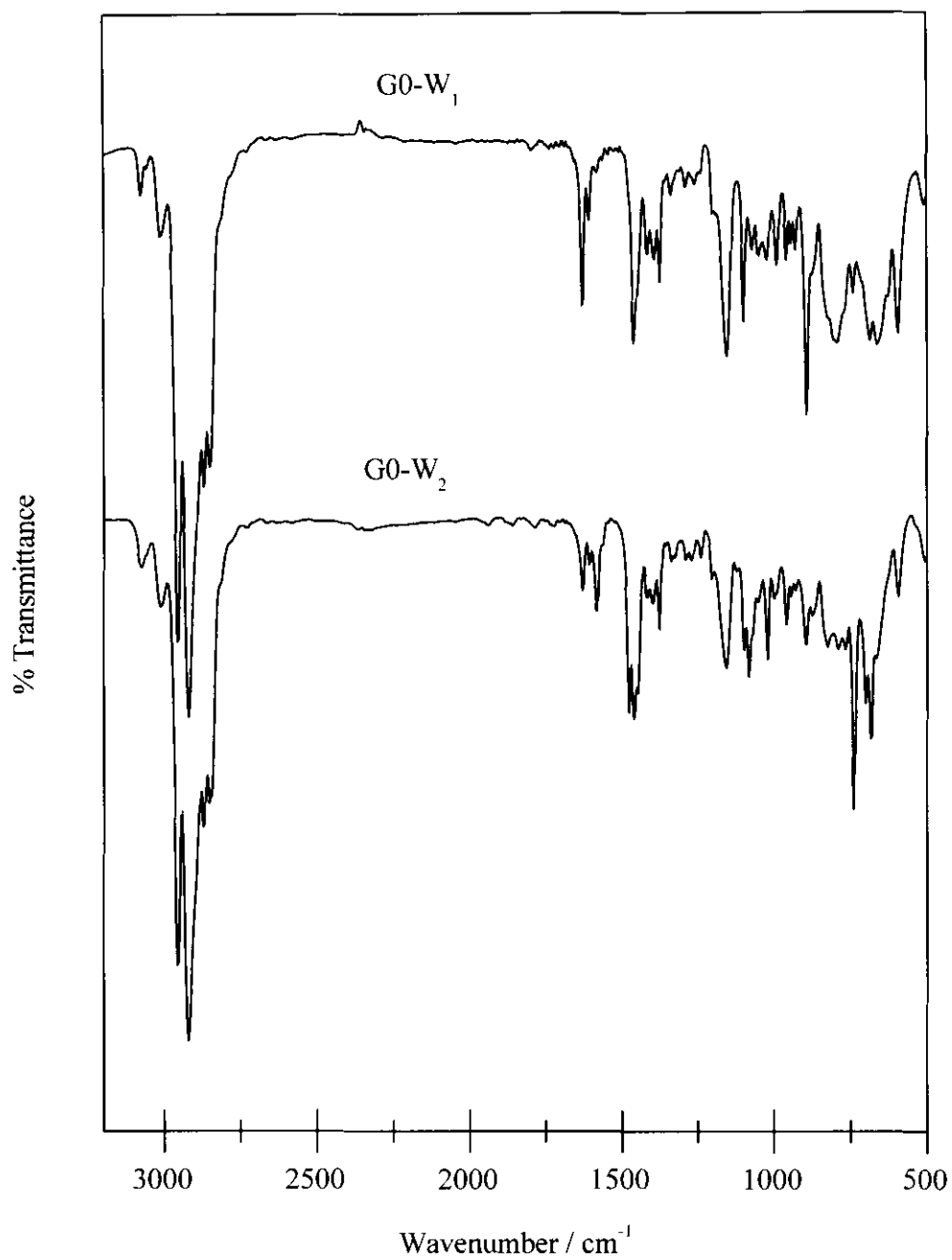
Figure 4.23 FTIR spectra of G0-W$_1$ and G0-W$_2$.

NMR spectra of G0-W$_1$ and G0-W$_2$, before activation with Bu$_4$Sn, and G0-W$_2$ are given below, Figures 4.24-29.
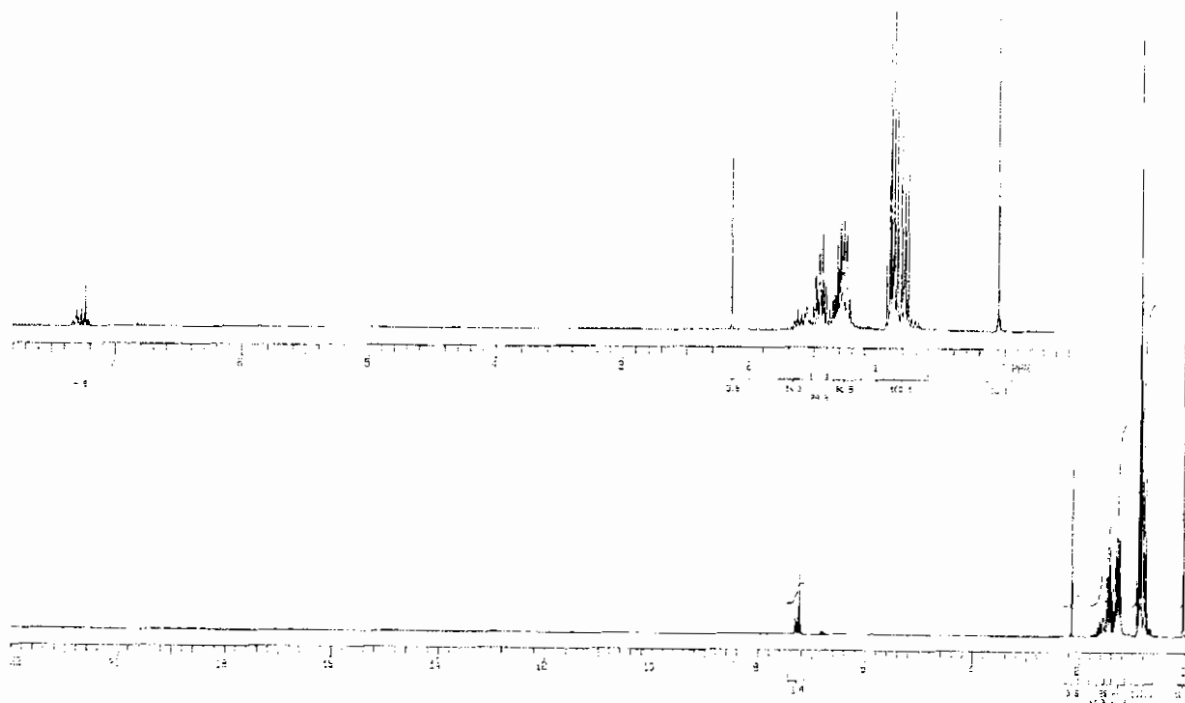
Figure 4.24 ^{1}H-NMR of G0-W$_1$.
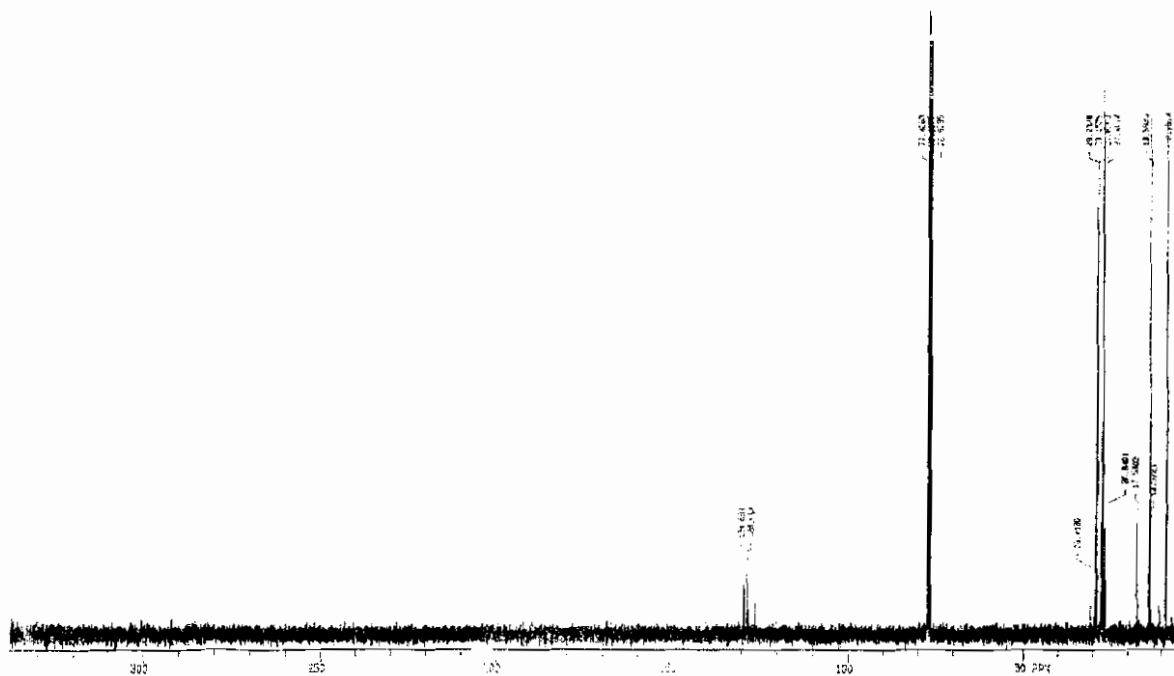
Figure 4.25 ^{13}C-NMR of G0-W$_1$.
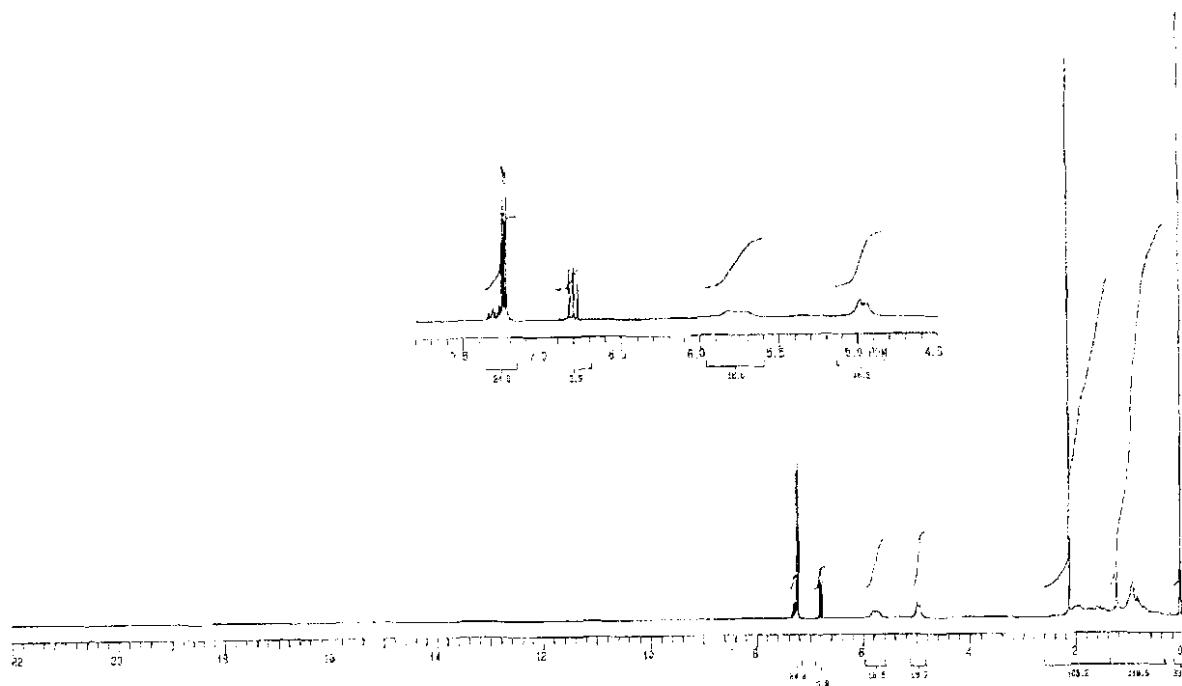
Figure 4.26　^{1}H-NMR of G0-W$_2$ without Bu$_4$Sn.
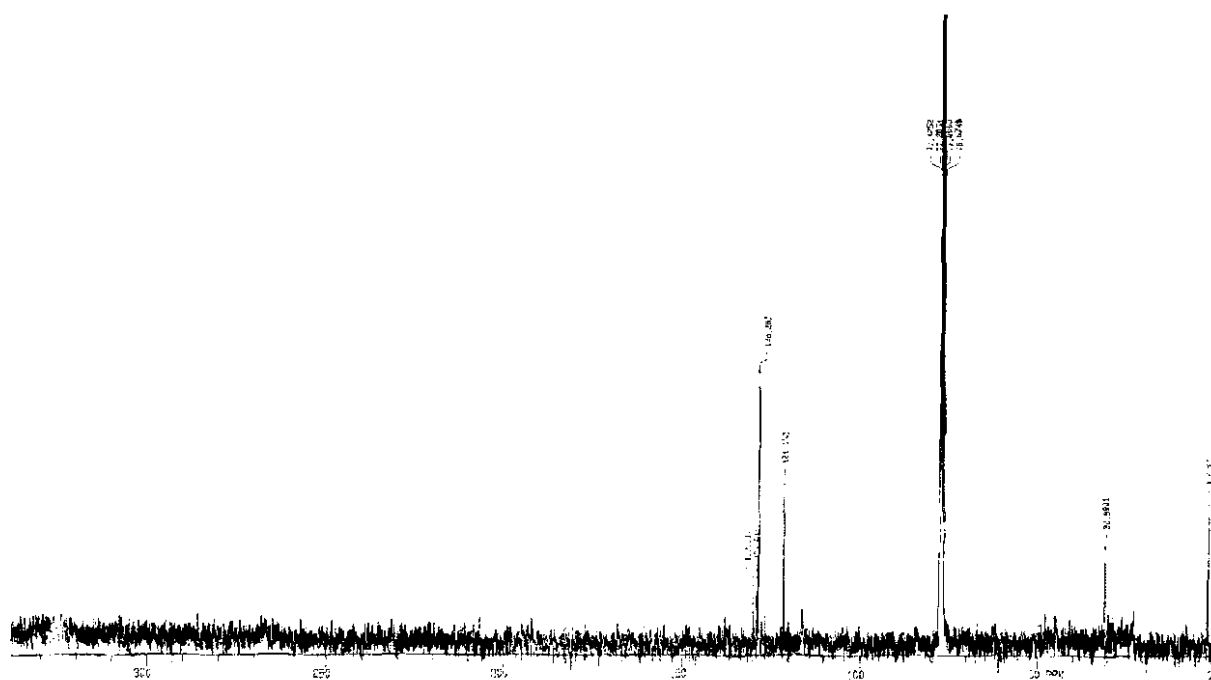
Figure 4.27　^{13}C-NMR of G0-W$_2$ without Bu$_4$Sn.
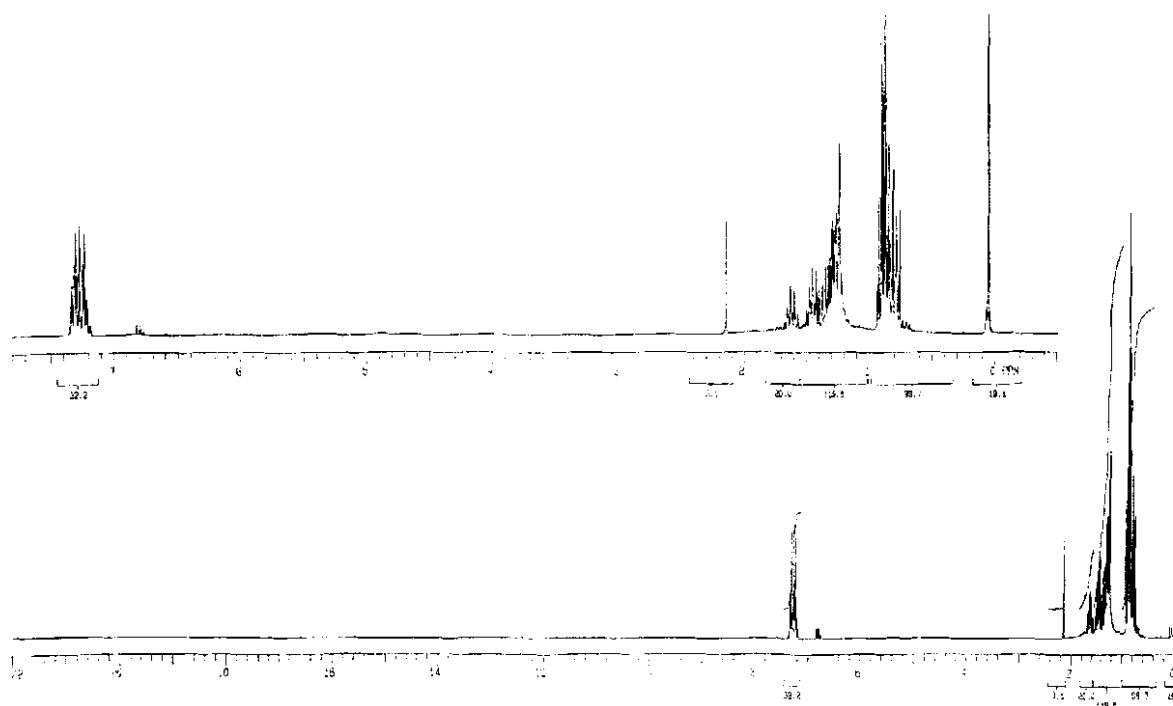
Figure 4.28 ^{1}H-NMR of G0-W$_2$.
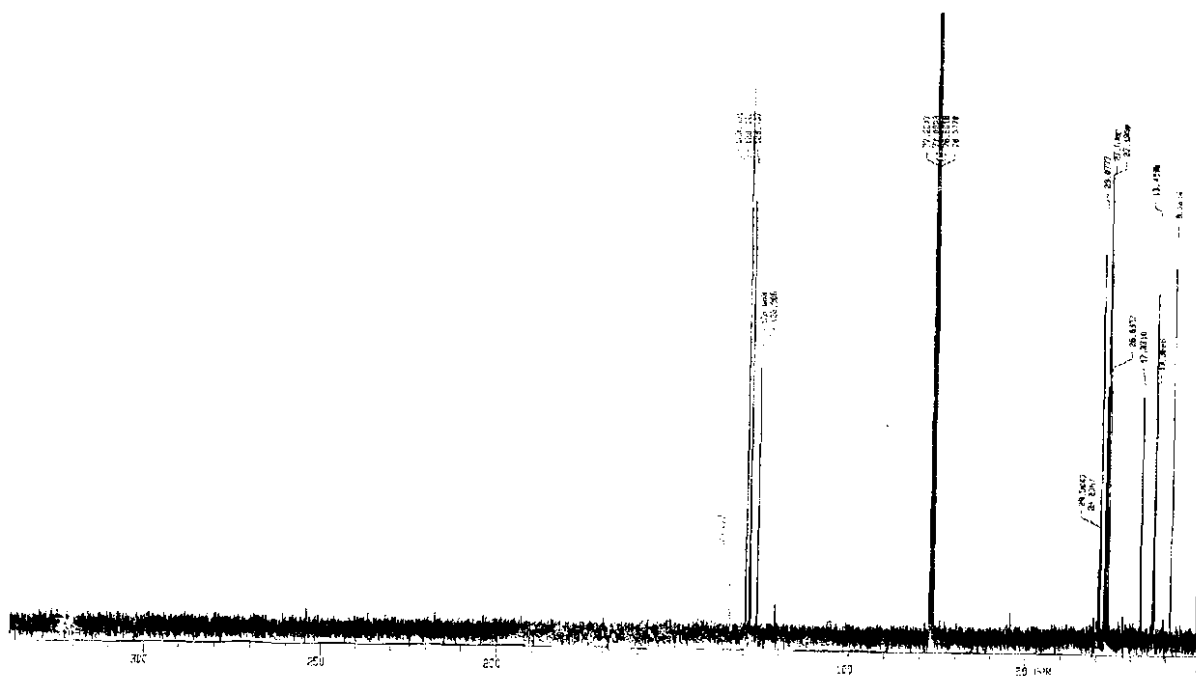
Figure 4.29 ^{13}C-NMR of G0-W$_2$.

A carbene singlet in ^{1}H NMR and a double bond character of the W=C_α linkage in ^{13}C-NMR were expected to reflect in low-field chemical shifts. Double bond peak for C_α carbons usually appears in the region 220-300 ppm.[6] NMR could not give us conclusive results because W-alkylidene dendrimers were characterised in the solution in which they were prepared, and their concentrations were too low for NMR analysis.

4.5.3 Metathesis reactions

The conversion of 1-octene to PMP and SMP, with G0-W_1 and G0-W_2, was followed by GC. The optimum conditions found earlier for the tungsten complex, W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$ were used in this investigation.
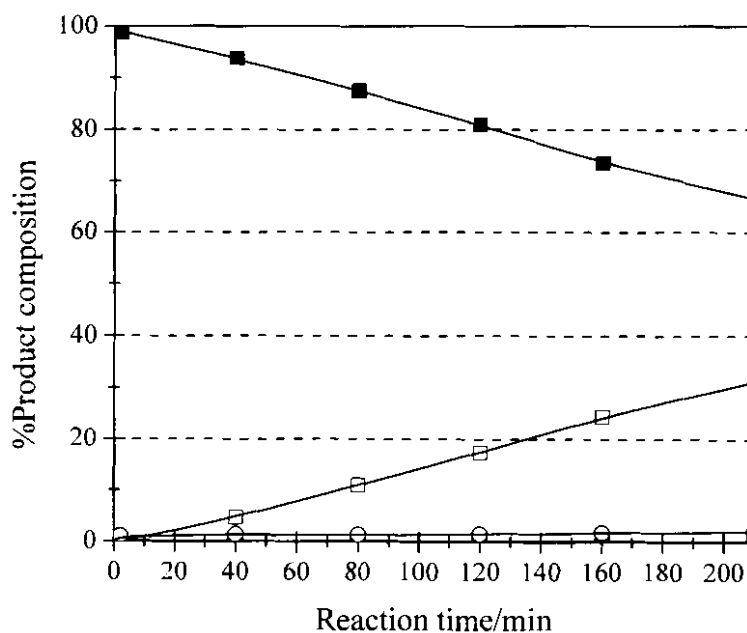
Figure 4.30 Conversion of 1-octene in the presence of the W(O-2,6-$C_6H_3Cl_2$)$_2Cl_4$/Bu$_4$Sn/G0 (G0-W_1) catalytic system (temperature = 85 °C; G0/W molar ratio = 4; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20; solvent = PhCl) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].
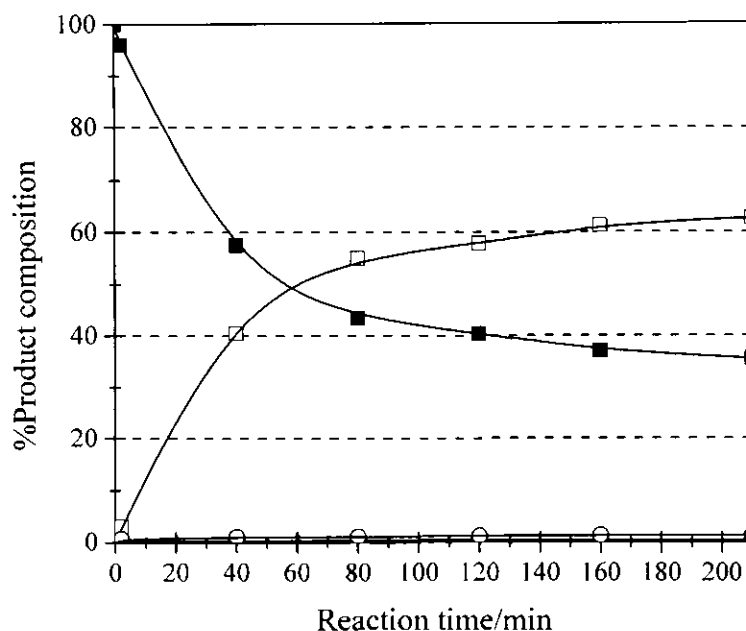
Figure 4.31   Conversion of 1-octene in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/G0/Bu_4Sn$ (G0-W_2) catalytic system (temperature = 85 °C; G0/W molar ratio = 4; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20; solvent = PhCl) [■ 1-octene; □ PMP; ● SMP; ○ Bu$_3$SnCl].

Figures 4.30 and 4.31 show conversion of 1-octene into PMP and SMP over a period of 210 minutes. The primary metathesis reaction in the presence of G0-W_1 was initially slow, not reaching 40% in 210 minutes. The %PMP was about 31.2%.

The conversion of 1-octene in the presence of G0-W_2 into PMP and SMP over a period of 210 minutes is depicted in Figure 4.31. The % PMP was 62.7% and % SMP was 0.41%. After 210 minutes there was 32% more PMP in the presence of G0-W_2 compared to G0-W_1. The primary metathesis reaction was very rapid compared to that of G0-W_1 reaching 40% in 39 minutes.

Table 4.9   Conversion of 1-octene with W-alkylidene dendrimers after 210 minutes

W-alkylidene dendrimers	1-Octene (%)	PMP (%)	SMP (%)	Selectivity (%)
G0-W_1	66.6	31.2	0.23	99.3
G0-W_2	35.6	62.7	0.41	99.4

G0-W$_2$ show higher activity than G0-W$_1$ (Table 4.9), in the conversion of 1-octene to PMP and SMP. The selectivity of both systems was found to be high. The primary metathesis reaction of G0-W$_2$ was double that of G0-W$_1$. The fact that, with G0-W$_1$ 40% PMP was not reached within 210 minutes, implies that the carbene in this catalytical system was hindered.

Influence of temperature on the activity and selectivity of G0-W

W-alkylidene dendrimers were tested for activity and selectivity in the metathesis reactions of 1-octene at different temperatures.
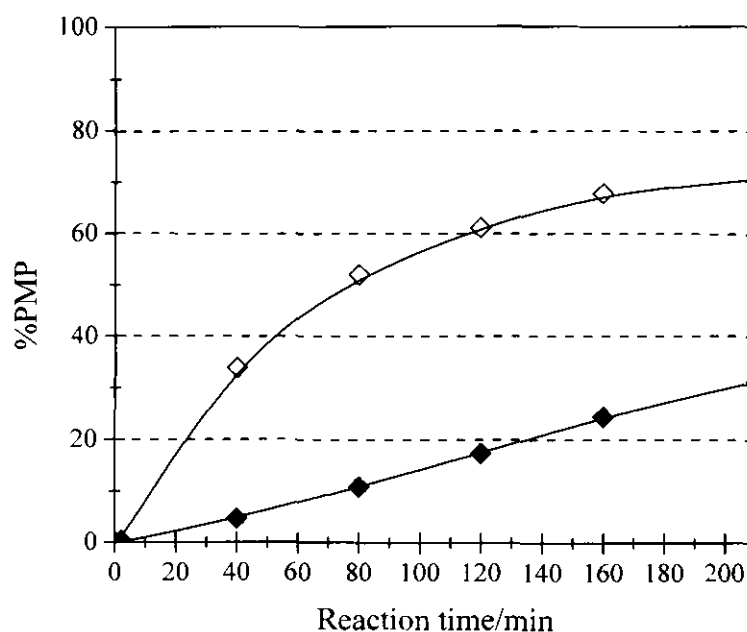
Figure 4.32 The metathesis activity of W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn/G0 (G0-W$_1$) catalytic system with 1-octene at different temperatures (G0/W molar ratio = 4; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20; solvent = PhCl) [◆ 85 °C; ◇ 100 °C].

The activity of W-alkylidene dendrimer (G0-W$_1$) at different temperatures can be observed from Figure 4.32 over a period of 210 minutes. The % PMP (which indicates activity) increased with an increase in temperature. The PMP at 85 °C was 31.2%, and at 100 °C it was 70.7%, increasing by 39.5%. Below 85 °C no metathesis activity was observed for the G0-W$_1$ system. The primary metathesis reaction was very slow for G0-W$_1$ at 85 °C, and 40% PMP was not reached within 210 minutes. At 100 °C the primary metathesis reaction increased, reaching 40% PMP in 52 minutes. The % SMP remained below 0.5%, resulting in high selectivity.
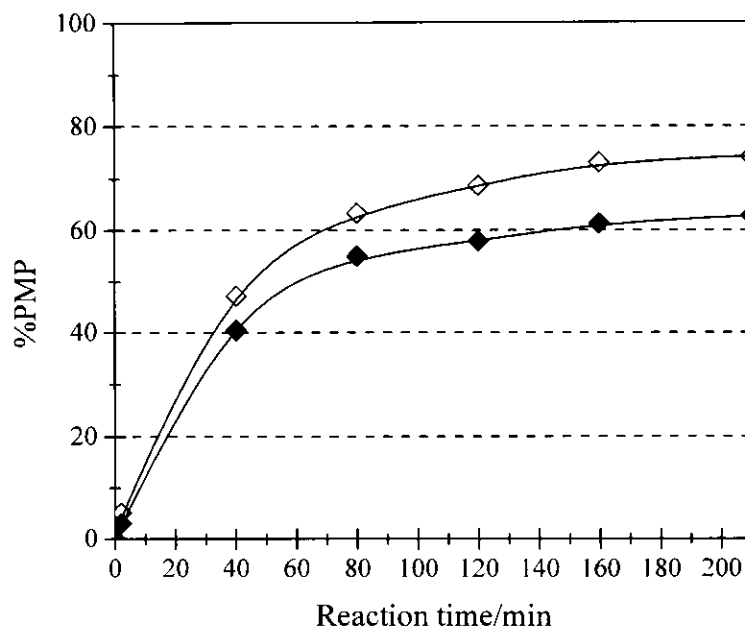
Figure 4.33 The metathesis activity of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/G0/Bu_4Sn$ ($G0\text{-}W_2$) catalytic system with 1-octene at different temperatures (G0/W molar ratio = 4; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20; solvent = PhCl) [♦ 85 °C; ◊ 100 °C].

Figure 4.33 depicts the activity of W-alkylidene dendrimer ($G0\text{-}W_2$) at different temperatures in 210 minutes. The %PMP increased with an increase in temperature. The PMP at 85 °C was 62.7%, and at 100 °C it was 74.3%, increasing by 11.6%. Below 85 °C no metathesis activity was observed. The primary metathesis reaction at 85 °C reached 40% PMP in about 40 minutes and at 100 °C the primary metathesis reaction increased, reaching 40% PMP in 33 minutes.

Table 4.10 Conversion of 1-octene at different temperatures in the presence of $G0\text{-}W_1$ and $G0\text{-}W_2$

Temperature (°C)	G0-W₁ PMP (%)	G0-W₂ PMP (%)
25	0.00	0.00
45	0.00	0.00
85	31.2	62.7
100	70.7	74.3

Table 4.10 summarises the influence of temperature on $G0\text{-}W_1$ and $G0\text{-}W_2$. The conversion of 1-octene into PMP increased with an increase in temperature for both W-alkylidene dendrimers.

As mentioned earlier no metathesis reactions were observed at lower temperatures. Because of the position of the carbene on $G0-W_2$ which was easily accessible to the substrate (Scheme 3.4), $G0-W_2$ had higher activity than $G0-W_1$ which had the carbene on the inside. The selectivity of both systems was found to be high.

The optimum temperature for tungsten aryloxide complexes was found to be 85 °C for metathesis reactions of 1-octene. Table 4.11 summarises the activity and selectivity of the W-alkylidene complexes at this temperature.

Table 4.11   Reactions of 1-octene with W-alkylidene complexes at 85 °C

Catalytic system	PMP (%)	SMP (%)	Selectivity	Time for 40% PMP formation (min)
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$	73.80	1.42	98.1	17
$G0-W_1$	31.2	0.23	99.3	Not reached
$G0-W_2$	62.7	0.41	99.4	40

When looking at the three W complexes, $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ exhibited the highest activity. Its selectivity was high, but compared to the W-alkylidene dendrimers it was low. $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ and $G0-W_2$ displayed rapid primary metathesis reaction when compared to $G0-W_1$. This was due to the fact that the carbene on the two catalytic systems was readily available for the substrate. $G0-W_2$ proved to be the better W-alkylidene complex. Its activity was comparable to that of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$, and it had a high selectivity.

4.6 References

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[3]   Van Schalkwyk C, *Ondersoek van 'n Homogene Metatesekatalisatorsisteem vir gebruik in 'n Skeidingsproses*, MSc-dissertation, PU vir CHO, 1997

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CONCLUSIONS

The study of ligand effects is one of the main themes in homogeneous catalysis.[1] The key to successful development of homogeneous catalysts has undoubtedly been the exploitation of the effects that ligands exert on the properties of metal complexes. The rate and selectivity of a given process can be optimised to the desired level through proper control of the ligand environment.[1]

5.1   2,6-Disubstituted aryloxide tungsten (VI) complexes

Various tungsten (VI) aryloxide complexes of the type $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ (X=Cl, Br, Ph) were synthesised and tested for selectivity and activity in metathesis reactions.

The complex with the phenyl substituted ligand has a higher selectivity towards PMP than the complexes with bromine and chlorine substituted ligands. Looking at the structures of the three substituted ligands (Scheme 3.1), the phenyl substitute ligand has more steric hindrance due to the bulkiness of the phenyl group and the electron donating properties make it more stable. The chlorine substituted ligand is the smallest of the three and has the lowest selectivity towards PMP. Because of its high electron withdrawing properties chlorine substituted ligand gives the highest metathesis activity. Dias *et al.*[2] found in their study that the more electron-withdrawing and smaller halogens generate more active catalysts. The electron donating properties of phenyl substituted ligand makes it less reactive and hence lower metathesis activity is attained with this catalytic system.

The activity of $W(O-2,6-C_2H_3Cl_2)_2Cl_4/Bu_4Sn$ system increases with an increase in catalyst concentration and reaction temperature. The optimum catalyst concentration and reaction temperature were found to be 8.210×10^{-8} mol dm^{-3} and 85 °C respectively.

5.2   Grubbs catalyst

One advantage of the Grubbs catalyst is its high selectivity, but its activity is not as high as that of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ at 85 °C (Figure 4.8). The formation of PMP was about 63.4% for Grubbs catalyst, while that of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ system was around 73.8% at

85 °C in 210 minutes. Our study showed that tungsten complexes have a very high catalytic activity compared to Grubbs catalyst. This is supported by former studies.[3,4]

5.3   W-alkylidene dendrimers

Dendritic catalysts have been synthesised before, but their application in metathesis of 1-octene has not been reported.[5,6,7] For example, Quignard et al.[8] synthesised carbosilane W-alkylidene dendrimers and used them in ROMP of norbonene. These dendritic catalysts decomposed with time and could not be recovered at the end of the reaction by nanofiltration (Scheme 2.4). The carbene on the W-alkylidene dendrimers by Beerens et al.[8] ($GO-W_1$) was situated on the inside (between the dendrimer and the W) (Scheme 3.3).

In this study a novel method was used to attempt the synthesis of carbosilane W-alkylidene dendrimers ($GO-W_2$) with the carbene on the outside (W between dendrimer and carbene) (Scheme 3.4). This meant that the W-complex will not dissociate from the dendrimer during the reaction and that would make the recycling of the dendritic catalyst by nanomembrane technology possible.

However, NMR and IR spectra could not give conclusive results about the position of the carbene in the W-alkylidene dendrimers.

During the metathesis of 1-octene with the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ system one of the first products that form is undecene (C_{11}) (Scheme 5.1).
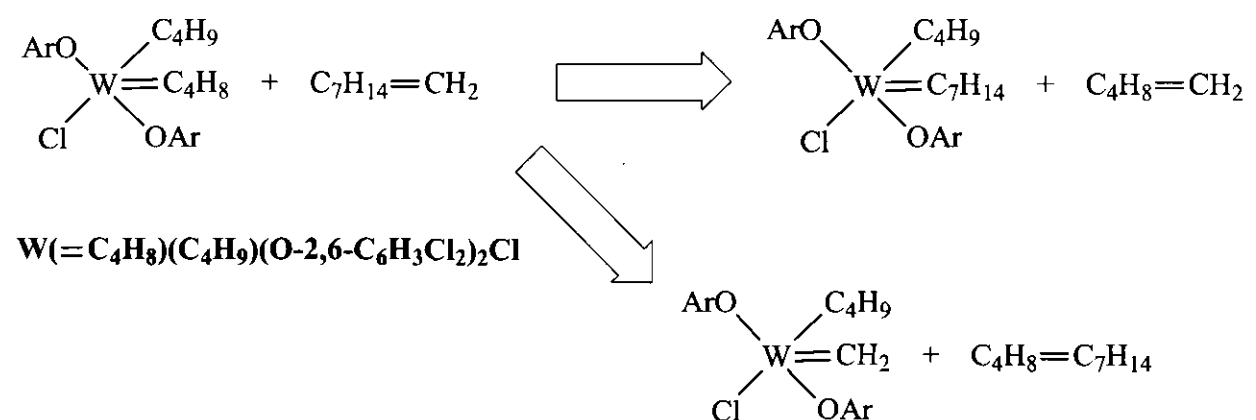
Scheme 5.1   The formation of undecene (C_{11}) during the metathesis of 1-octene with the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ system.

During the metathesis of 1-octene with the G0-W_1 system, C_{11} does not form immediately (Scheme 5.2), it forms later in the reaction due to isomerisation. Thorn-Csányi *et al.*[9] in their results showed that the double bond isomerisation occurs when the metathesis reaction has proceeded to an advanced extent. Synchronously with the decomposition of the carbene species, side reactions take place.
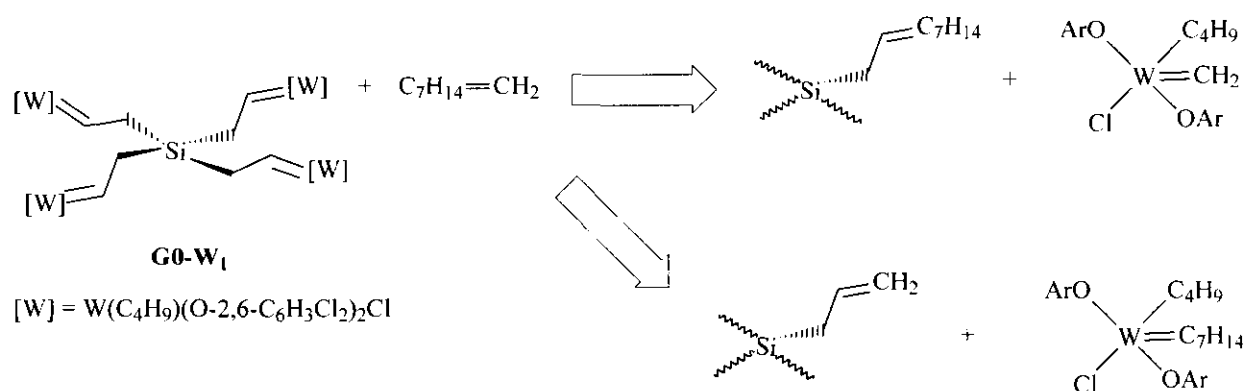
Scheme 5.2   The first step in the metathesis of 1-octene with the G0-W_1 system.

The formation of C_{11} during the metathesis reaction of 1-octene with $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$, G0-$W_1$ and G0-W_2 catalytic systems are compared in Figure 5.1.
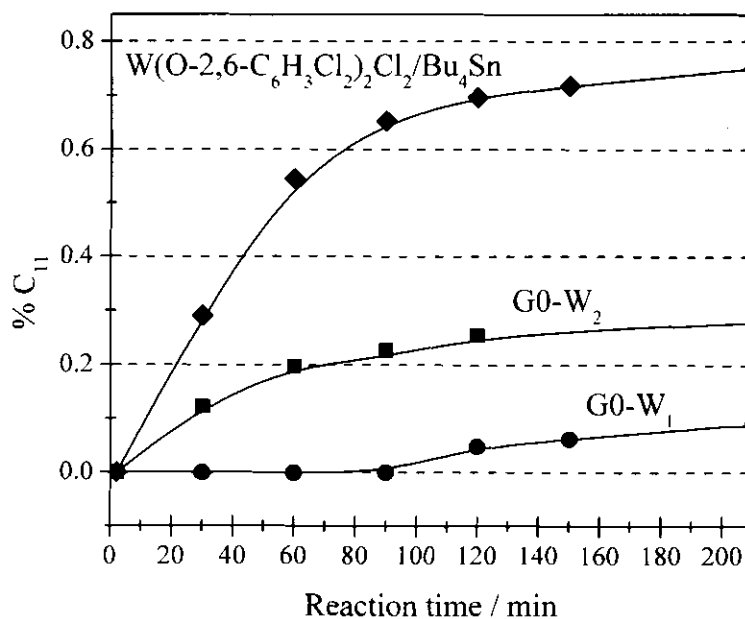
Figure 5.1   The formation of undecene (C_{11}) with the W-systems.

The formation of C_{11} at the beginning of the reaction with $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ and G0-W_2 complexes and the absence of C_{11} in the first 90 minutes of the reaction with G0-W_1 is proof that we have two W-alkylidene dendrimers with the carbene at different positions. The high catalytic activity and metathesis reaction rate of G0-W_2 compared to G0-W_1 at the beginning of the reaction is an indication that the carbene in G0-W_2 is more accessible than in G0-W_1. From this it could be concluded that the carbene in G0-W_2 is on the outside (Scheme 5.3).
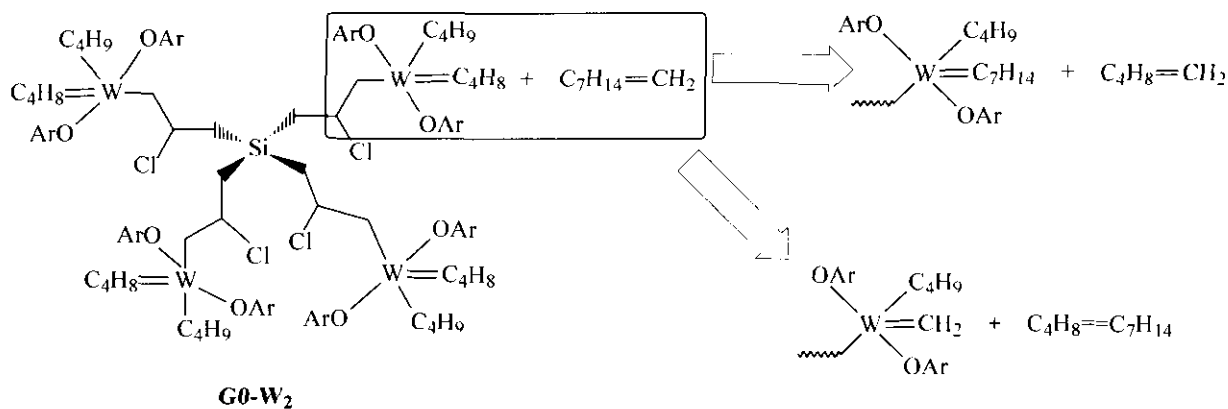
G0-W_2

Scheme 5.3 The formation of undecene (C_{11}) from 1-octene with the G0-W_2 systems.

Further work still needs to be done. W-alkylidene dendrimers still need to be tested for activity after all the 1-octene has been consumed. The G0-W_2 has to be separated from the product *via* nano- or ultrafiltration technology. Higher generations of carbosilane dendrimers and other dendrimers need to be explored in order to develop more effective catalysts for the metathesis of 1-octene.

5.4 References

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Figure A1.3 MS analysis of 2-heptene (98 g/mol).
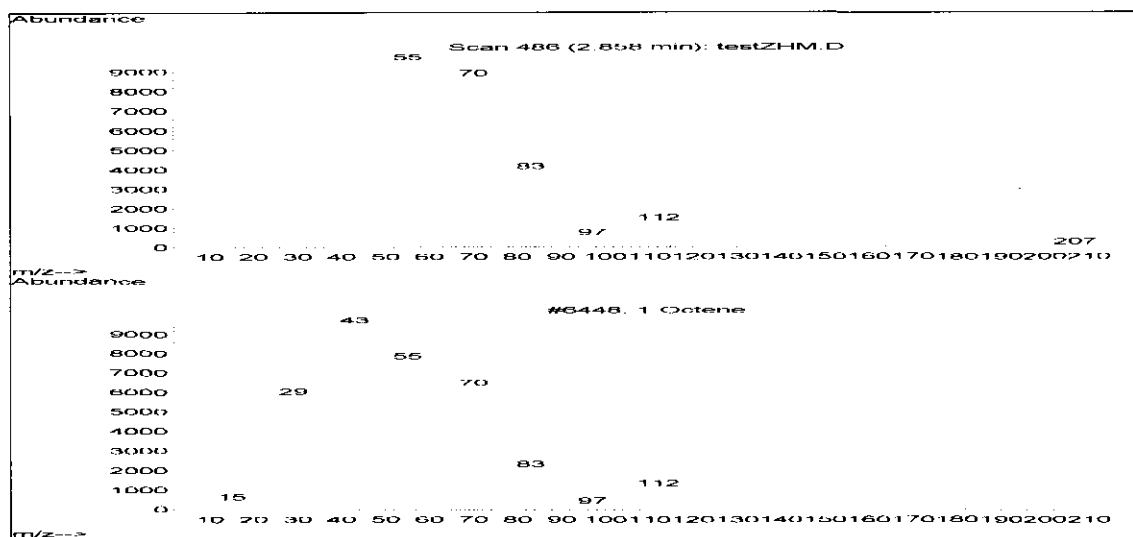
Figure A1.4 MS of 1-octene.
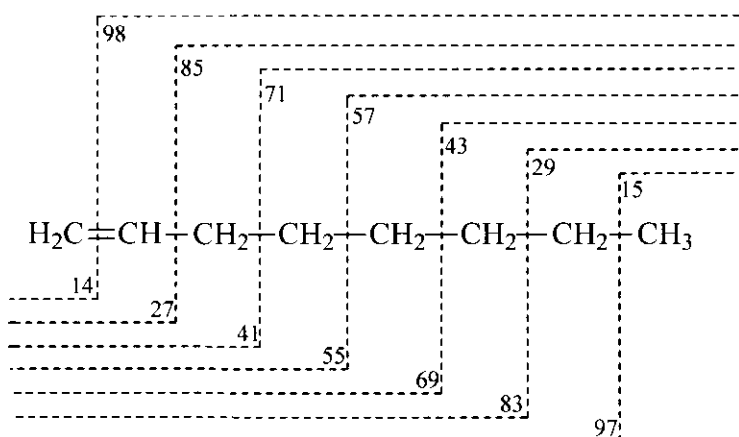
Figure A1.5 MS analysis of 1-octene (112 g/mol).
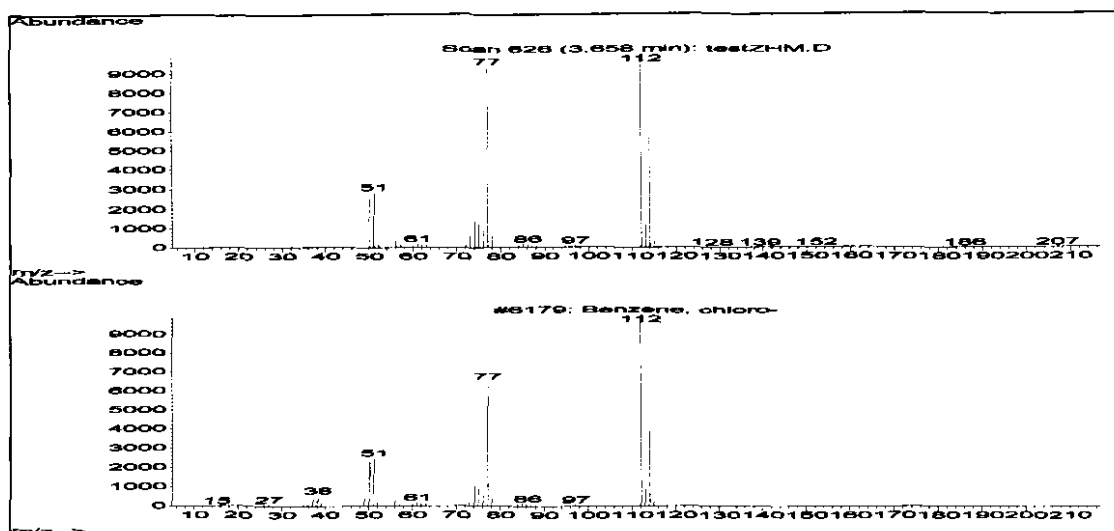
Figure A1.6   MS of chlorobenzene.
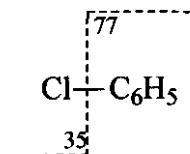
Figure A1.7   MS analysis of chlorobenzene (112 g/mol).
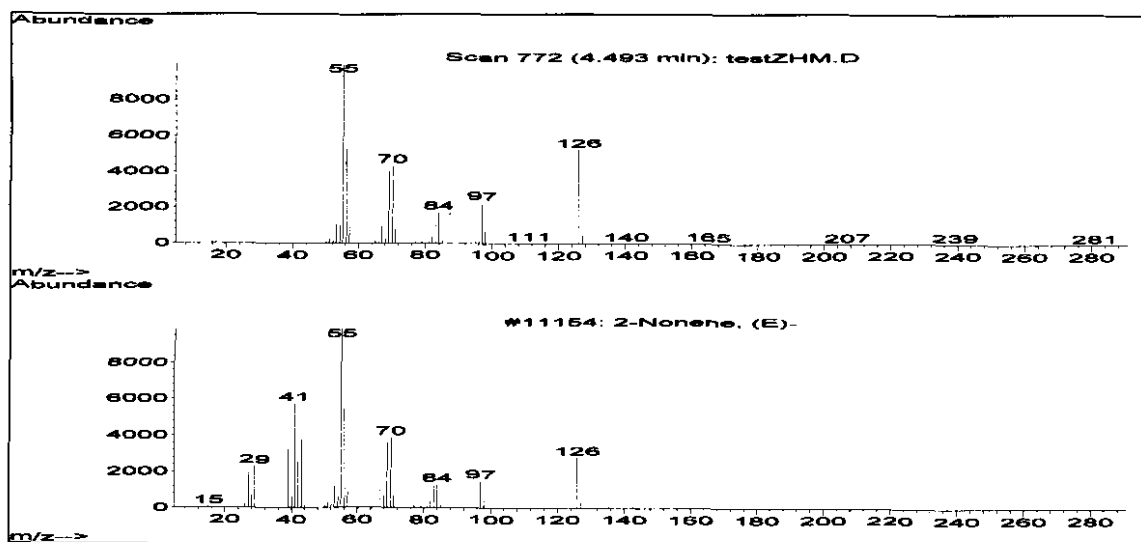
Figure A1.8   MS of 2-nonene.
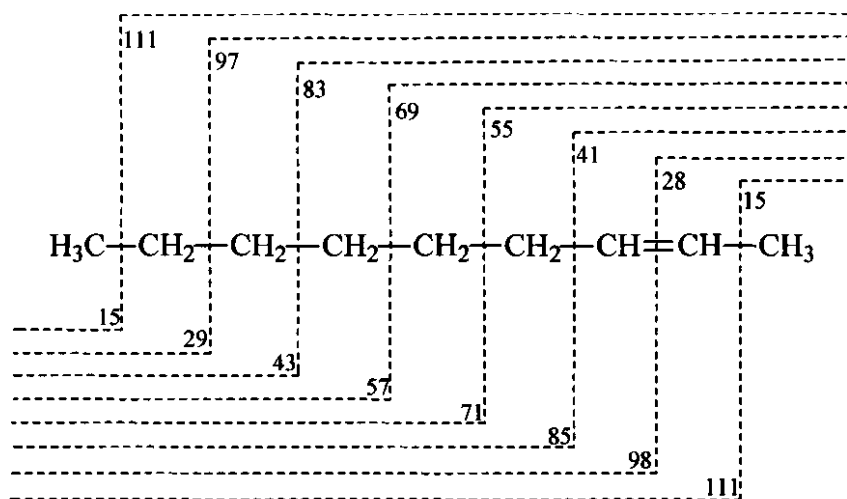
Figure A1.9 MS analysis of 2-nonene (126 g/mol).
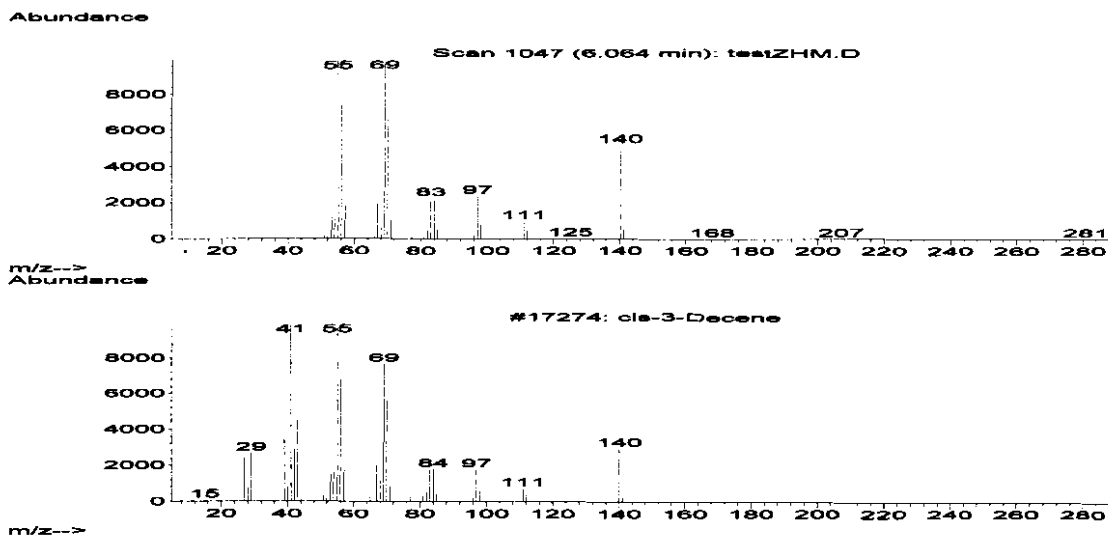
Figure A1.10 MS of 3-decene.
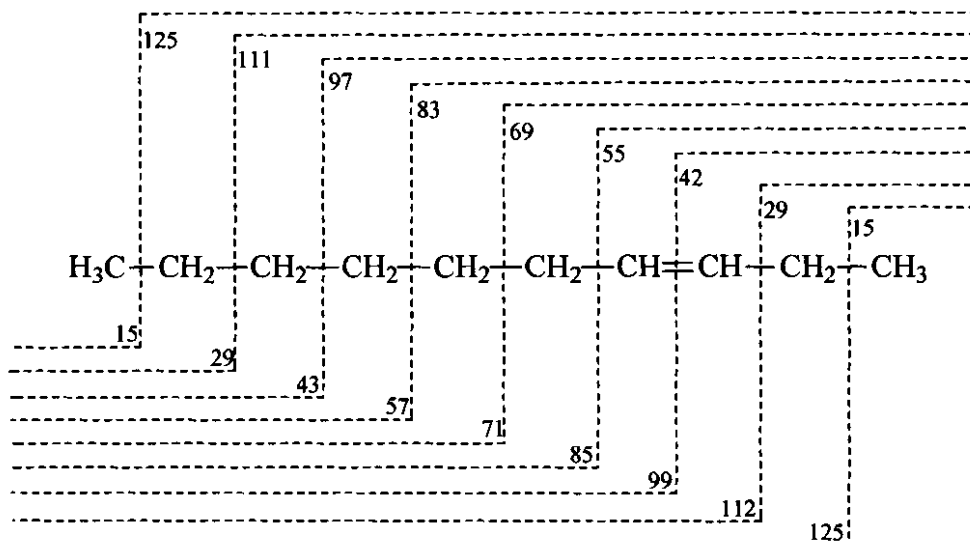
Figure A1.11 MS analysis of 3-decene (140 g/mol).
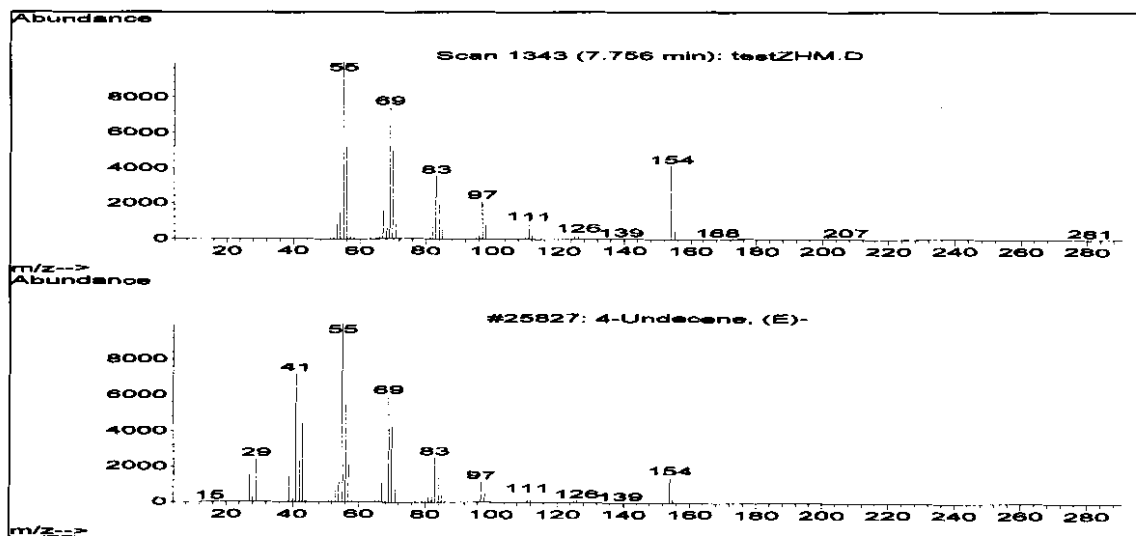
Figure A1.12 MS of 4-undecene.

95
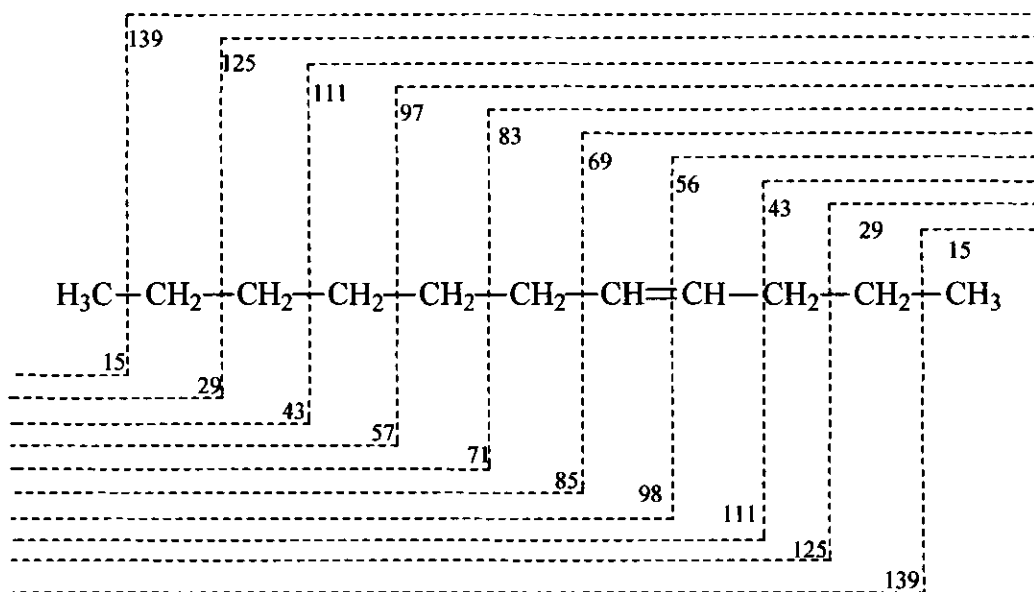
Figure A1.13 MS analysis of 4-undecene (154 g/mol).
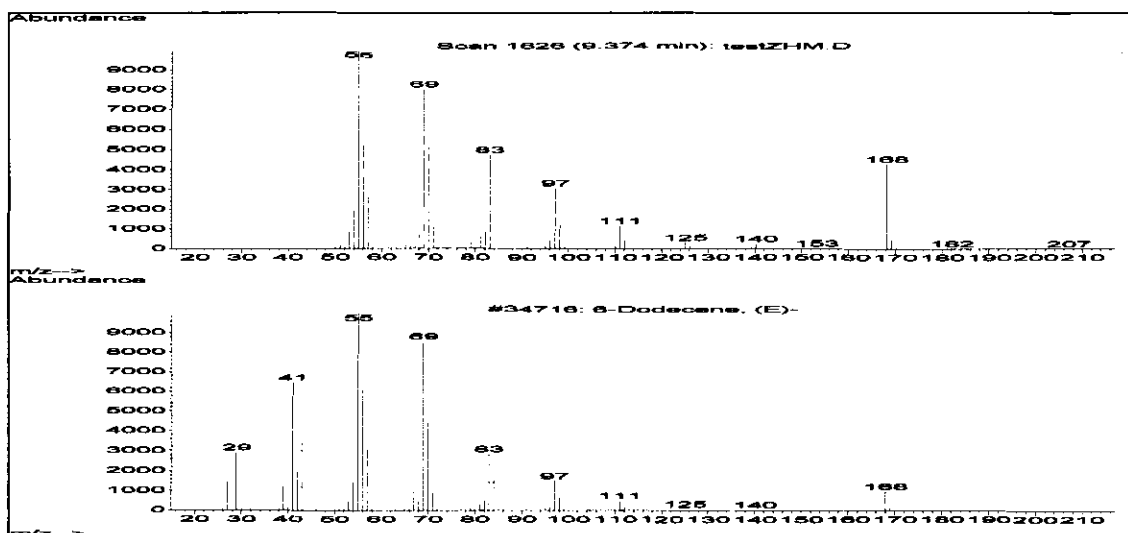
Figure A1.14 MS of 6-dodecene.

H₃C⊢CH₂⊣CH₂⊣CH₂⊢CH₂⊢CH≑CH⊢CH₂⊣CH₂⊣CH₂⊣CH₂⊢CH₃
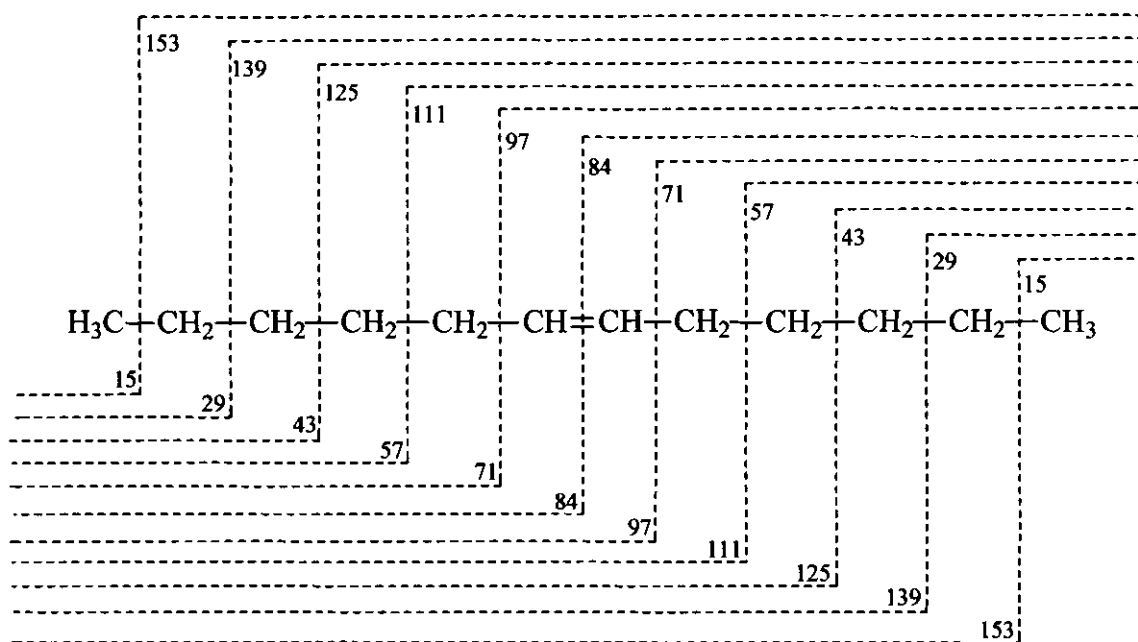
Figure A1.15 MS analysis of 6-dodecene (168 g/mol).
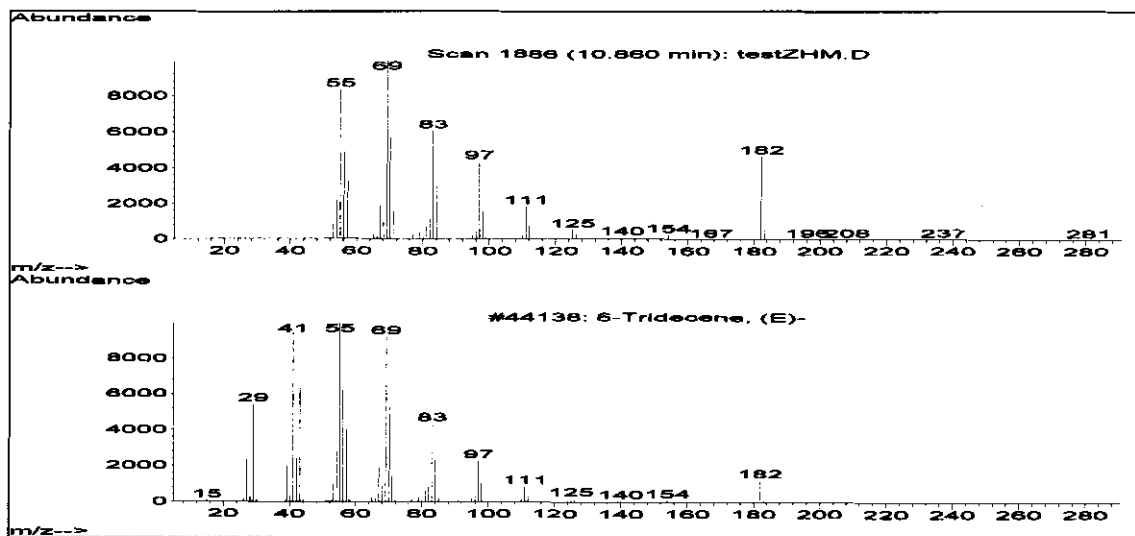
Figure A1.16 MS of tridecene.

$$H_3C-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$
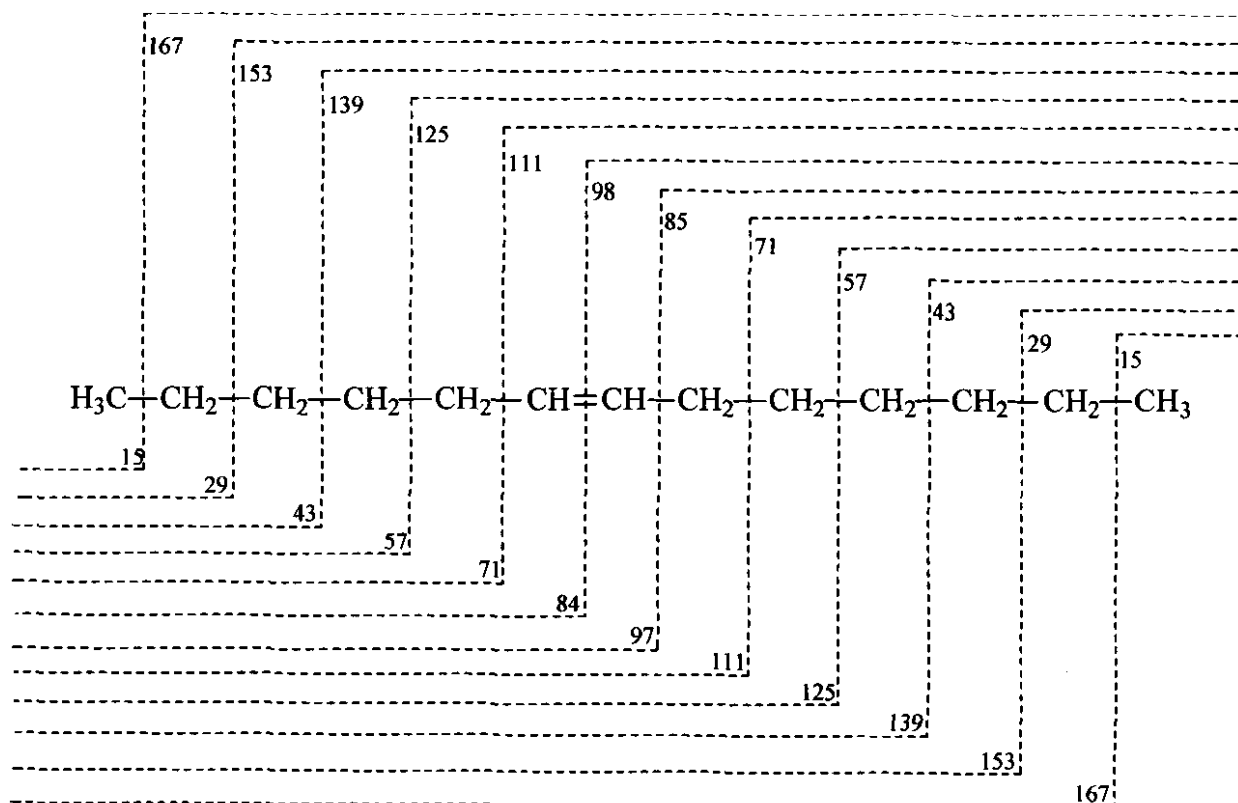
Figure A1.17 MS analysis of 6-tridecene (182 g/mol).
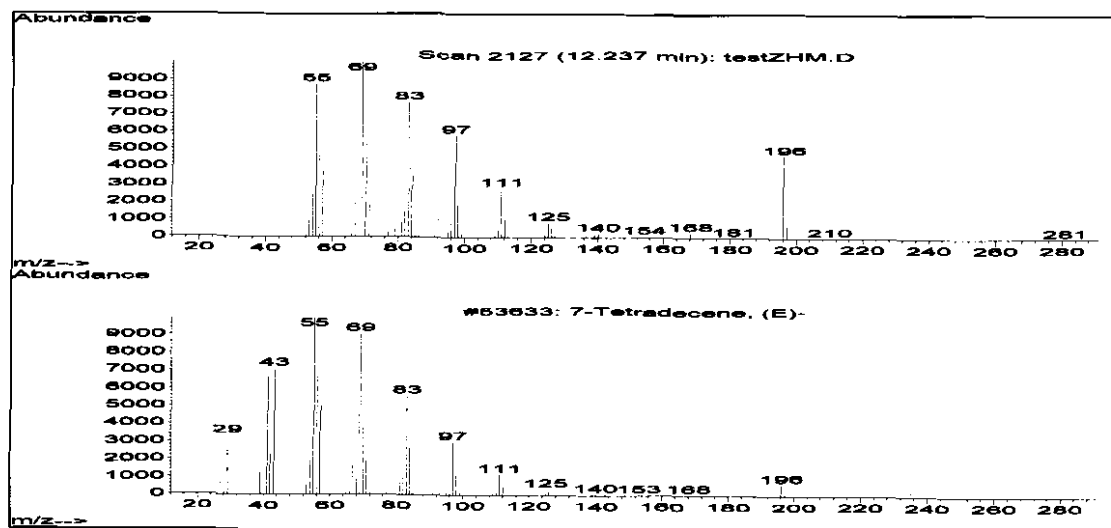
Figure A1.18 MS of 7-tetradecene.
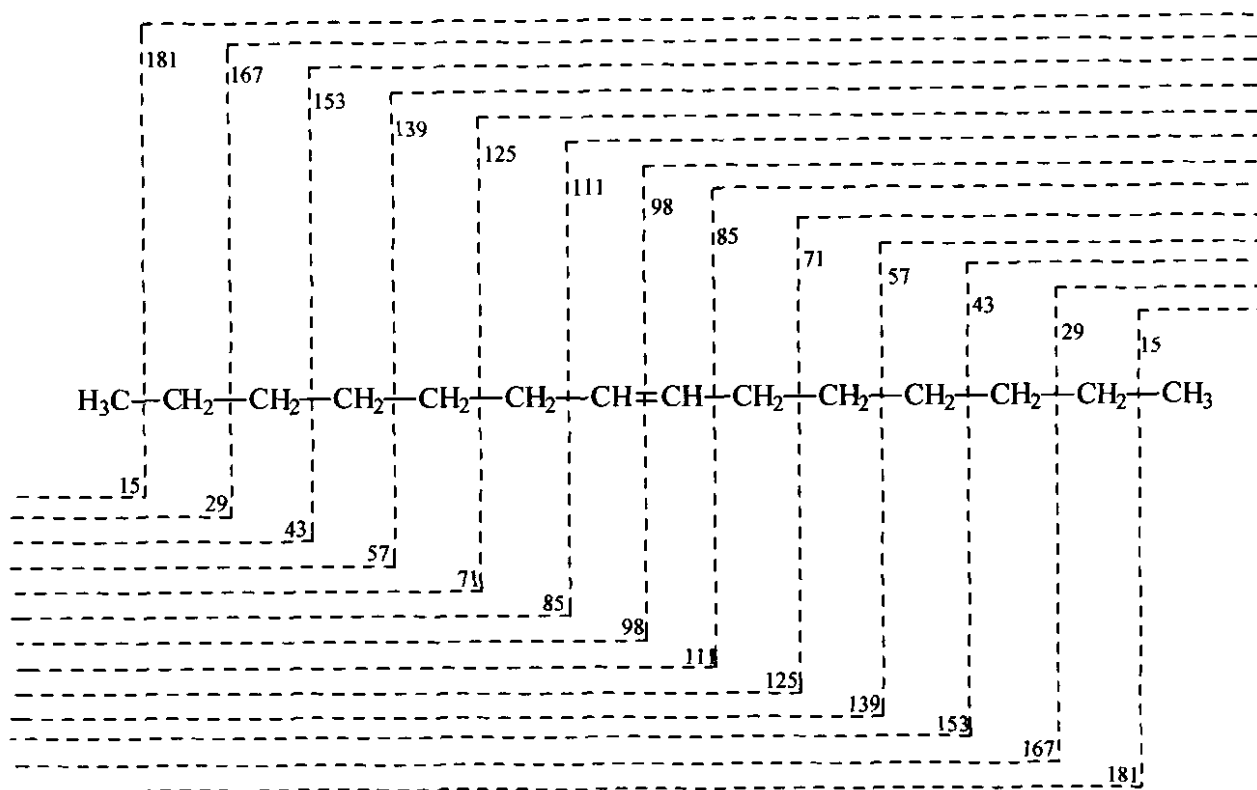
Figure A1.19 MS analysis of 7-tetradecene (196 g/mol).
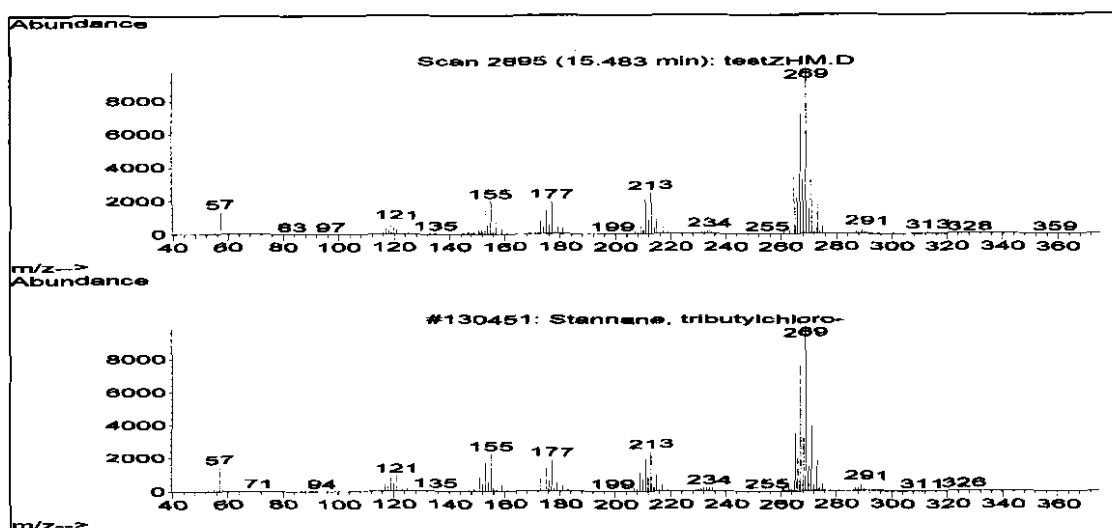
Figure A1.20 MS of tributyltinchloride.
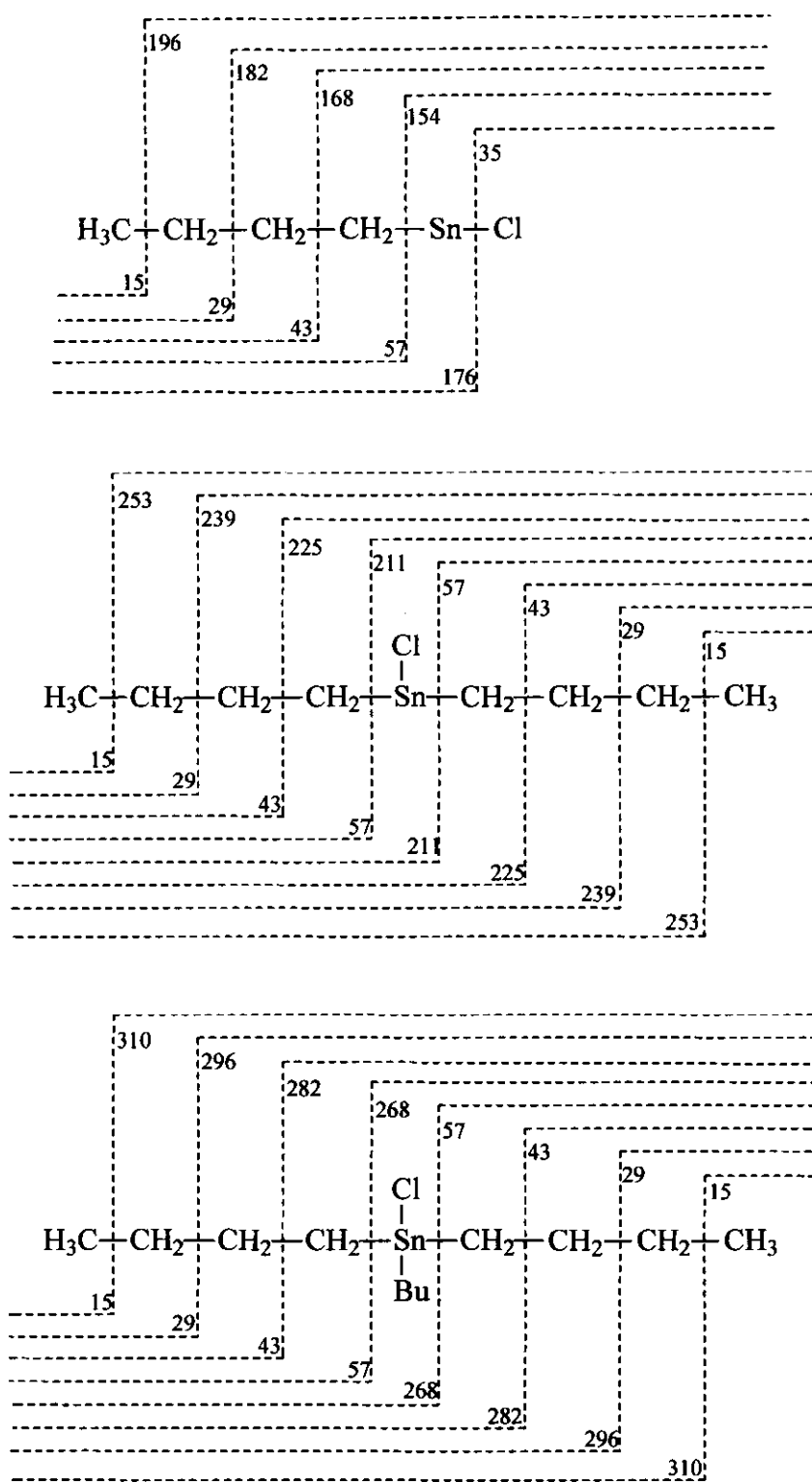
Figure A1.21 MS analysis of tributyltinchloride (325 g/mol).
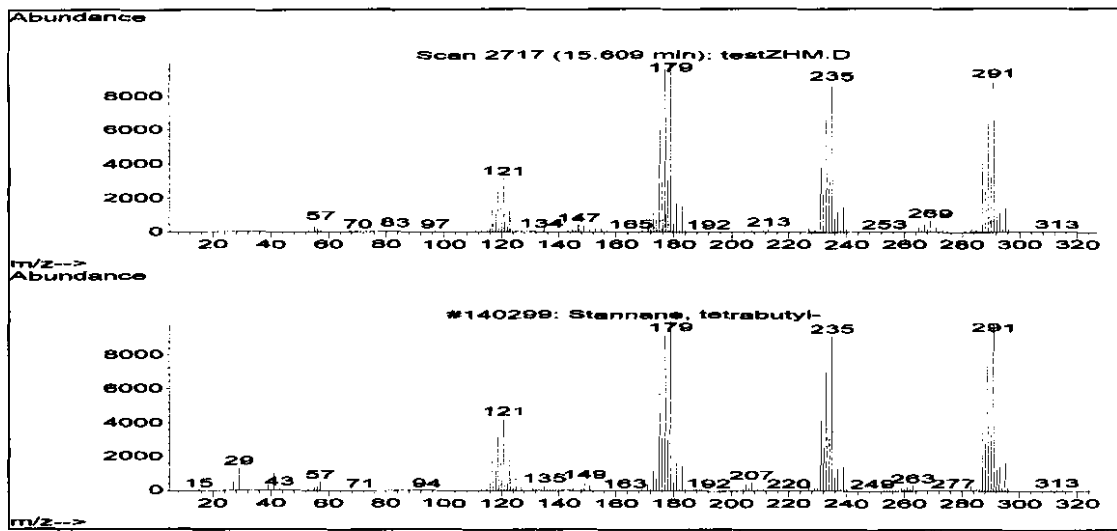
Figure A1.22 MS of tetrabutyltin.
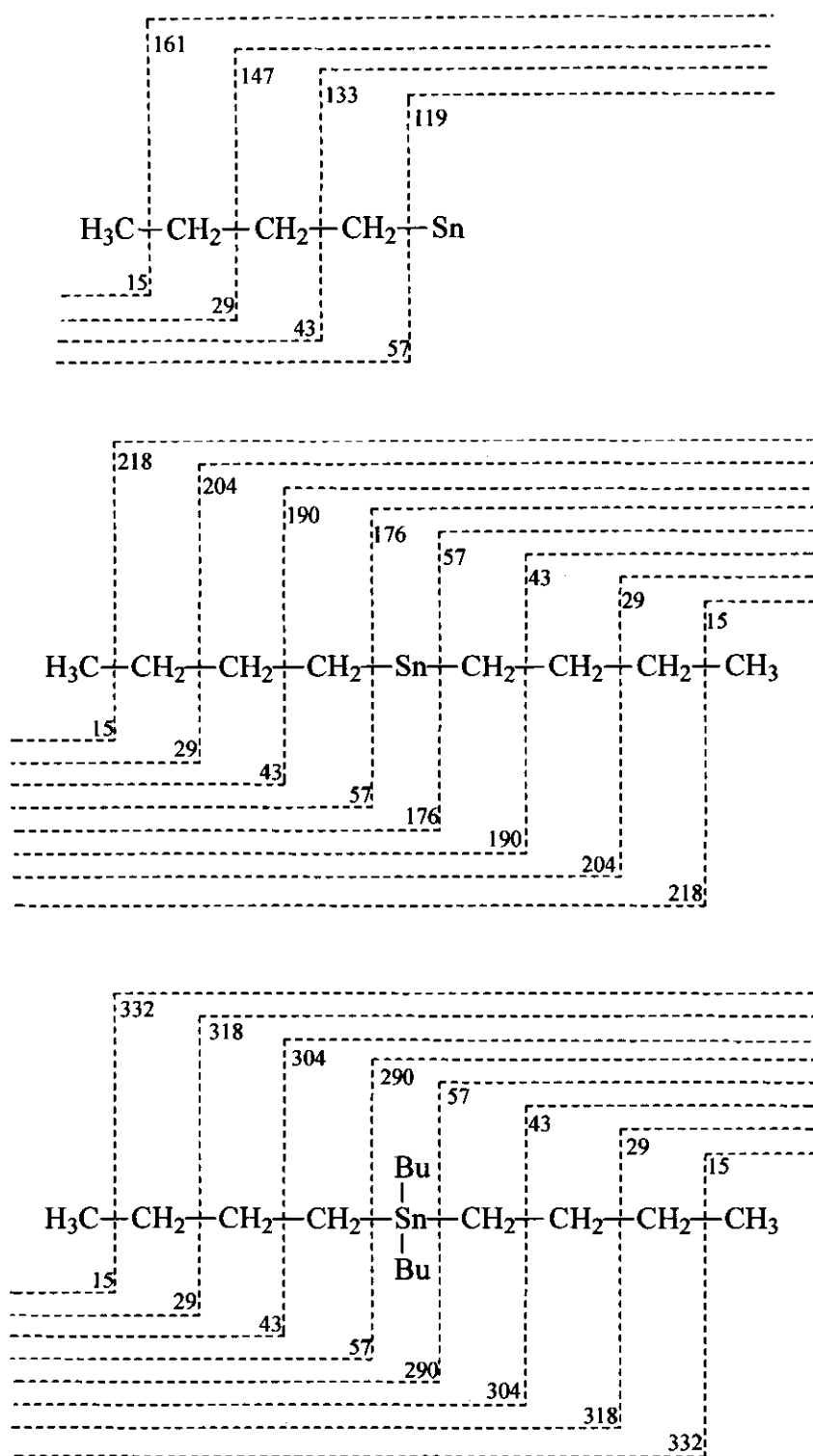
Figure A1.23 MS analysis of tetrabutyltin (347 g/mol).

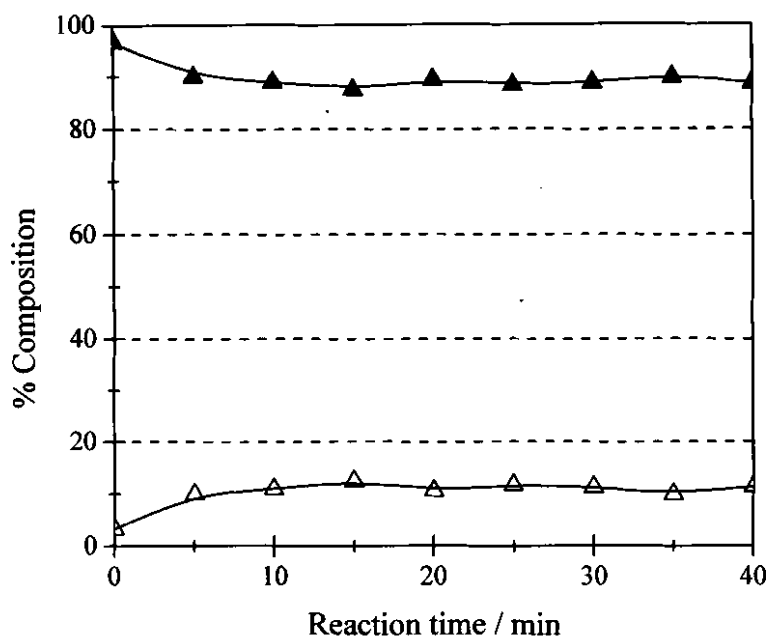# FORMATION OF Bu₃SnCl in W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn SYSTEM
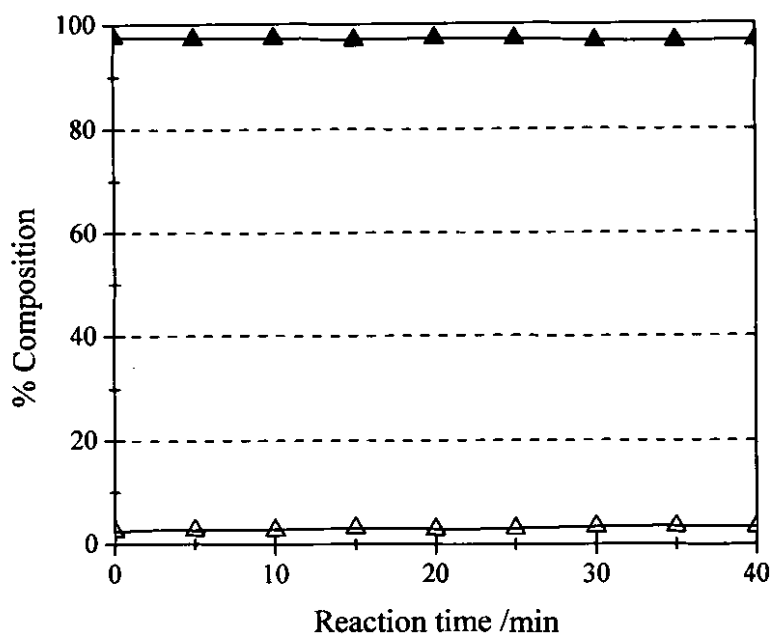
Figure A2.1 Formation of Bu₃SnCl in W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn catalytic system (temperature = 25°C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; solvent = PhCl (0.3ml)) [▲Bu₄Sn ;△ Bu₃SnCl].
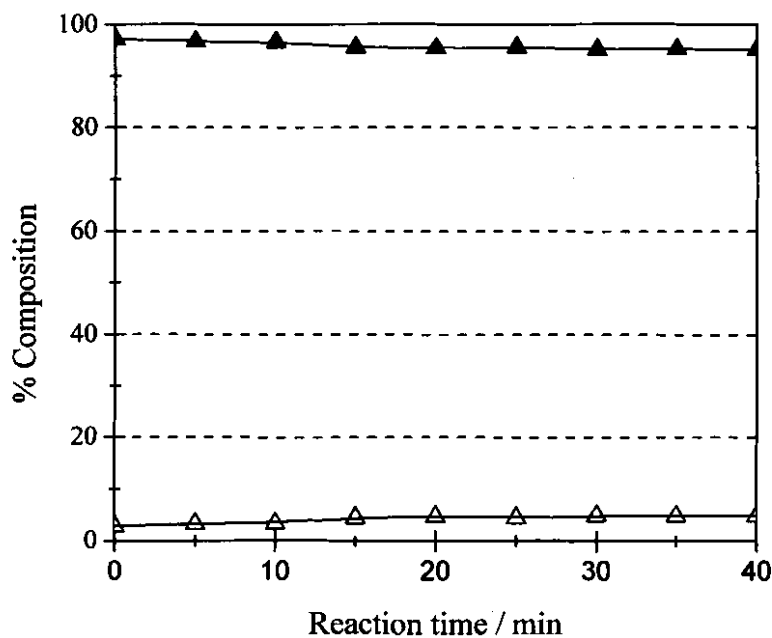
Figure A2.2 Formation of Bu₃SnCl in W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn catalytic system (temperature = 45°C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; solvent = PhCl (0.3ml)) [▲Bu₄Sn ;△ Bu₃SnCl].
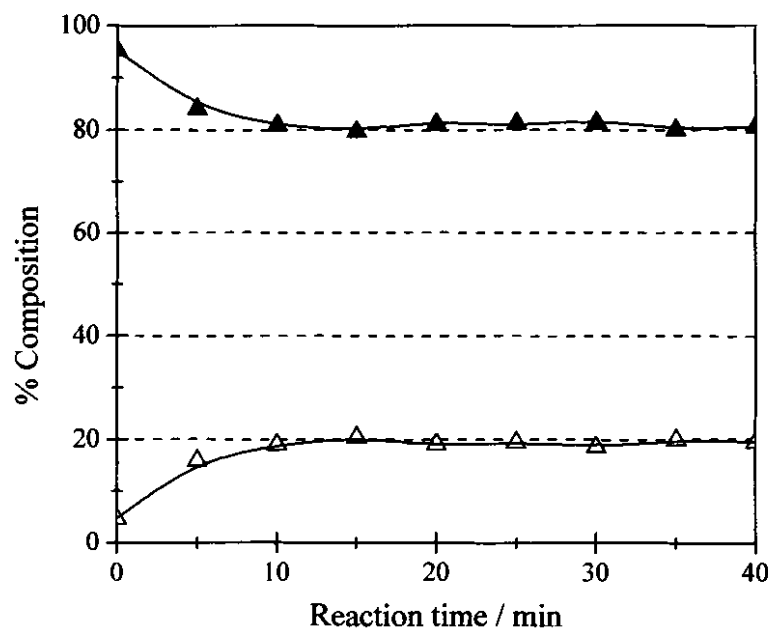
Figure A2.3: Formation of Bu₃SnCl in W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn catalytic system

(temperature = 85°C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; solvent = PhCl (0.3ml)) [▲Bu₄Sn ;Δ Bu₃SnCl].

Figure A2.4 Formation of Bu₃SnCl in W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn catalytic system

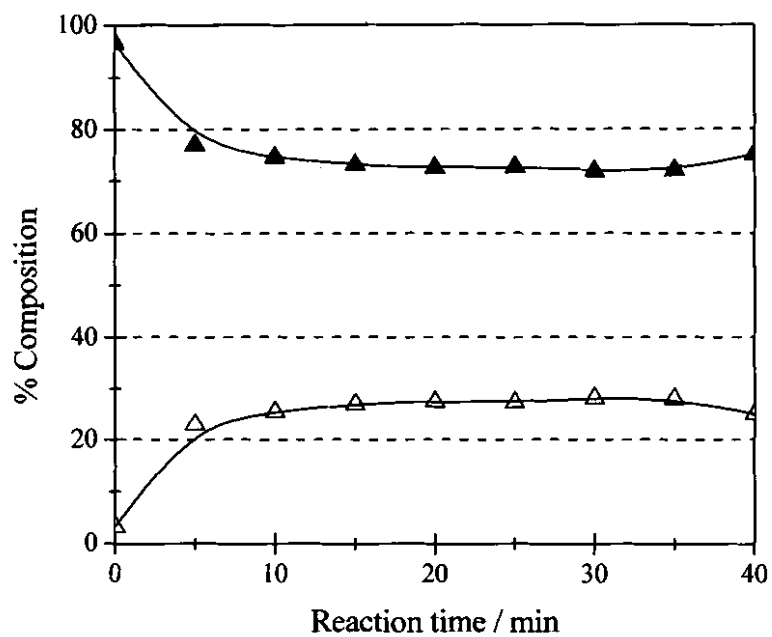(temperature = 100°C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; solvent = PhCl (0.3ml)) [▲Bu₄Sn ;Δ Bu₃SnCl].

Figure A2.5 Formation of Bu_3SnCl in $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system

(temperature = 120°C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; solvent

= PhCl (0.3ml)) [▲ Bu_4Sn ;△ Bu_3SnC].